



# A Comprehensive Review of Copper-Based Wood Preservatives

*With a focus on new  
micronized or dispersed  
copper systems*

By Mike H. Freeman\* and Craig R. McIntyre\*

## Abstract

This paper focuses on the wood preservation aspects of copper based biocides. Included in this review are the following: Above ground and ground contact efficacy, permanence in above ground and ground contact uses, soil and water contact leaching, effects on wood properties and certain fixation aspects of copper systems. Previously unpublished data on the new micronized/dispersed copper based wood preservative systems are also included. These micronized systems now dominate the U.S. residential treated wood market which in turn accounts for roughly 50 percent of global wood preservation usage.

Copper is an essential micronutrient for most living cells. In larger doses though, the copper ion demonstrates activity as an algacide, bactericide, fungicide, insecticide, and moldicide. Presently copper compounds are used for algal control, wood treatment, antifouling pigments, and crop fungicides (Richardson 1997). The fungicidal properties of copper were recognized in the 1700s, and copper-based preservatives have been widely and successfully used for more than a century. Although borates and organic biocides are gaining importance, copper remains the primary biocide component used today to protect wood used in ground contact or fully exposed to the weather (Lebow et al. 2004).

Copper is needed against this challenge since very few organic molecules (other than creosote and penta) possess activity towards soft rot fungi (Hughes 2004).

The volume of wood products treated with copper-based preservatives grew exponentially during the 1970s and 1980s and remains high today. Copper compounds also have

---

This paper was received for publication in August 2008 and has undergone the Journal's peer review process. Article No. 10523

\* Forest Products Society Member

© Forest Products Society 2008

Forest Prod. J. 58(11): 6-27

advantages: it is relatively easy to create waterborne formulations; it is easy to analyze and determine penetration in wood, and copper slows photodegradation by UV radiation and water (Archer and Preston 2006). The focus on copper-based preservatives has increased following concerns about environmental effects of chromium and arsenic and resulting restrictions on the use of chromated copper arsenate (CCA). Much of the early work on copper-based formulations forms the basis for the ammoniacal and amine copper-based systems currently in the marketplace as CCA replacements (Preston et al. 1985). These formulations include quats or azoles as co-biocides. Recently micronized copper formulations with the same co-biocides have come into use. The drawbacks on use of copper compounds include: copper tolerance exhibited in a number of fungal species, possible corrosivity to metal fasteners and aquatic toxicity (Archer and Preston 2006). This paper presents a discussion on copper issues such as the mode of action, problems of copper tolerance, replacements for CCA, the latest micronized formulations and environmental effects of copper-based preservatives.

### Mode of action of copper

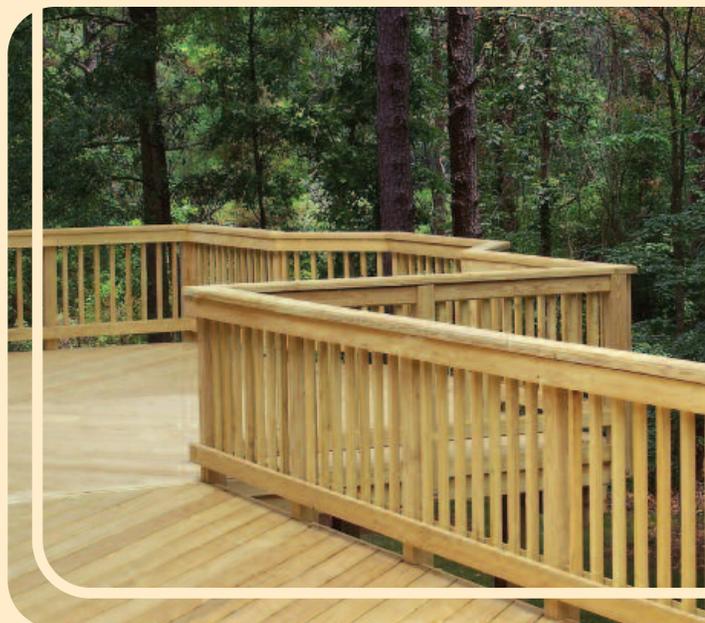
The initial uptake of copper in cells is most likely by ion-exchange followed by permeation throughout the cell (Somers 1963). Copper is accumulated passively in fungal spores by unspecific reactions with cell constituents. High levels of copper uptake are required for fungicidal action in fungi, and it is suggested that there are different sites of action for the fungistatic and fungicidal processes (Somers 1963). Increased copper uptake by spores is observed under anaerobic conditions and with temperature increase. At 35 °C, uptake is almost three times that at 4 °C. The distribution of accumulated copper in spores varies with fungal species and fungal cell walls have a varying affinity for copper. The fungicidal property of copper is dependent on its affinity to different groups on fungal proteins, particularly thiol groups. Excess copper causes damage by oxidizing proteins, enzymes, lipids and therefore interrupting enzymatic processes (Eaton and Hale 1993, Rui and Morrell 1994). Copper also inhibits intracellular enzymes responsible for destruction of lignocellulosic materials, binds to the cell wall and interrupts the transport of nutrients into and out of the cell. If enough copper enters the cell, it can lead to denaturation of proteins and enzymes leading to cell death (Archer and Preston 2006).

One specific mechanism proposed is the interaction of  $\text{Cu}^{2+}$  with hydrogen peroxide, which results in reduction to  $\text{Cu}^+$  and production of free radicals from hydrogen peroxide and oxygen. Free radicals result in an uncontrolled oxidation process via the Haber-Weiss cycle (Simpson et al. 1988, Gunther et al. 1995). In aqueous solution the  $\text{Cu}^+$  derivatives are readily oxidized to  $\text{Cu}^{2+}$ .

Copper toxicity can be suppressed by limiting its biological availability through complexation or precipitation with proteins or metal chelating agents, e.g., ethylenediamine-tetra-acetic acid (EDTA). Copper toxicity may also be reduced in some copper tolerant fungal species in presence of a nitrogen source, e.g., increased ammonia in alkaline copper quaternary (ACQ), and this is attributed to stimulation of oxalic acid production (Ruddick and Xie 1994, Humar et al. 2005).

### Tolerance and copper induced fungal secretions

The ability of some fungi to decay wood is stimulated by low levels of copper in the wood. Compared with other microbes, fungi can be extremely tolerant of toxic metals at high concentrations. Several brown-rot wood decay fungi in the genera *Serpula* and some species that were once included within the genus *Poria* are tolerant of copper (De Groot and Woodward 1999). Since copper is the



Copper-treated wood is widely used in residential applications.

most frequently used biocide for wood preservation, a major requirement of any formulation of copper-based wood preservative is efficacy against copper-tolerant fungi (Nicholas and Schultz 1997). Renewed interest and concern about the capability of certain fungi to decay wood treated with copper preservatives stemmed from the voluntary 2004 withdrawal from residential applications of wood treated with CCA. The arsenic in CCA effectively controlled copper tolerant fungi (Steenkjær Hastrup et al. 2005).

Microbes possess a range of tolerance mechanisms, most featuring some kind of detoxification. Copper tolerance has been ascribed to diverse mechanisms involving trapping of the metal by cell-wall components, altered uptake of copper when the plasma membrane of mycelium is less permeable to copper, extracellular chelation or precipitation by secreted metabolites and intracellular complexing by metallothioneins and phytochelatin (Cervantes and Gutierrez-Corona 1994). If a substance which binds and detoxifies a metal has a significant presence, the metal content of the mycelium may be high even if permeability to the metal is not.

Considerable work has been done regarding fungal ability to immobilize copper by precipitating copper oxalate crystals around the hyphae (Sutter et al. 1983, Murphy and

Levy 1983). Copper tolerance has been linked to oxalic acid producing species such as *Wolfiporia cocos* and *Poria placenta* (Sutter et al. 1983, Clausen et al. 2000, Woodward and De Groot 1999). A reduction of the toxicity of copper with increased acidity has been observed in several fungi. The presence of copper in waterborne preservatives ACQ, copper citrate (CC), and CCA has been shown to stimulate production of 66 to 93 percent more oxalic acid compared to untreated controls within 2 weeks of exposure of blocks to test fungi (Clausen and Green 2003). Calcium oxalate and copper oxalate crystals are commonly observed in decayed wood that has been treated with copper-based preservatives. Choi et al (2002) demonstrated that copper prevents germination of the spores of copper-tolerant fungi since spores are not actively producing oxalic acid. Consequently, preservatives containing copper without an effective co-biocide can provide good performance when there is no likelihood of attack by fungus mycelium.

The relative tolerance of fungal strains to copper-containing preservatives varies with the formulation of the preservative. Oxine copper offers excellent protection against decay fungi including copper-tolerant fungi. In contrast to the stimulated production of oxalic acid by ACQ, CC, and CCA, oxine copper has been shown to prevent oxalic acid production and weight loss by *P. placenta*, *W. cocos*, *Meruliporia incrassata*, and *Anrodia vaillantii*.

(Clausen and Green 2003). Studies using copper naphthenate did not give a similar performance as oxine copper (Sutter et al. 1983). Similarly, the same strains of *S. lacrymans* used in agar plate assays against CCA and in agar block tests against copper naphthenate (CuNap) showed a difference in relative tolerance of the isolates against the two preservatives (De Groot and Woodward 1999). Sutter et al. (1983) postulated that the oil component in CuNap and oxine copper physically prevents movement of precipitated copper oxalate to the exterior of the wood surface. Morrell (1991) commented that copper naphthenate would perform well in temperate regions since attack has only been noted in Florida even though copper-tolerant fungi are seemingly widespread. Variation with CC was also observed in that 11 of 12 isolates of *S. lacrymans* were tolerant towards CC because it induced high levels of oxalic acid early in the decay process (Sutter et al. 1983). As a result, CC is often used in laboratory studies on copper-tolerant fungi where the presence of co-biocides, such as chromium and arsenic, could confound the results (De Groot and Woodward 1999).

Fungal reactions triggered by the presence of copper include the formation of a thicker cell wall and increased proportion of extracellular mucilaginous material (ECMM). Vesentini et al. (2006a) exposed copper-treated Scots pine blocks to *Coriolus versicolor* and *Gloeophyllum trabeum* and observed an increase in *N*-acetyl glucosamine in fungal mycelium. The amount of *N*-acetyl glucosamine is correlated with the amount of chitin present (Nilsson and Bjurman

Table 1. — Summary of copper-containing formulations and AWPA retentions.

Preservative	Co-biocide	AWPA Retention kg/m <sup>3</sup>		
		Above ground (UC1-UC3B)	Ground Contact UC4A UC4B	
ACC		4.0	8.0	
ACQ-A, B, D	DDAC or DDA-Carb	4.0	6.4	9.6
ACQ- C	ADBAC	4.0	6.4	9.6
ACZA	Zinc, Arsenic	4.0	6.4	9.6
CCA-C	Arsenic	4.0	6.4	9.6
Copper Azole (CA-B)	Triazole	1.7	3.3	5.0
Copper HDO (CX-A)	HDO, boric acid	3.3	—	—
CuNap—Water Borne		1.1 <sup>a</sup>	1.8 <sup>a</sup>	—
CuNap—Oil Borne		0.6 <sup>a</sup>	1.0 – 2.4 <sup>ab</sup>	
Oxine Cu—Oil Borne		0.1 <sup>a</sup>	—	—

<sup>a</sup> Copper as metal

<sup>b</sup> Retentions vary based on species and use

Table 2. — Summary of ICC-ES retentions.

Company	System	ICC-ES Retention kg/m <sup>3</sup>		
		Above ground (UC1-UC3B)	Ground Contact UC4A UC4B	
Arch	CA-C	1.0	2.4	4.0
Arch	Micro CA <sup>a</sup>	0.8	2.2	3.6
Osmose	ACQ	3.2	6.4	9.6
Osmose	Micro CA	1.0	2.4	3.7
Osmose	Micro CQ <sup>a</sup>	2.4	5.4	9.6
PhibroWood	Micro CA	1.1	2.6	3.8
Viance	ACQ	2.4	6.4	9.6
Dr. Wolman (BASF)	CX-A	3.3	4.8	7.2

<sup>a</sup>Micronized formulations-see text for explanation

1998). The increase of chitin deposition in fungal cell wall is related to the development of a thick cell wall. Increasing the copper concentration in *Trametes versicolor* culture media results in a decrease in the length of mycelia peripheral growth unit (PGU) and to the increased proportion of ECMM (Vesentini et al. 2006b). Both decreased PGU and increased proportion of ECMM increase tolerance in fungi to copper.

### Copper-containing systems

In recent years, several preservative formulations have been standardized by the American Wood Protection Association (AWPA) for use in applications previously dominated by CCA. The alternatives all center on copper as their primary active ingredient but include inorganic or organic co-biocides instead of chromium and arsenic. The first commercial copper preservatives were based on copper solubilized as an aqueous monoethanolamine or ammoniacal complex. These copper systems include alkaline copper quaternary (ACQ), copper azole (CA-B), ammoniacal copper borate (ACB), ammoniacal copper zinc arsenate (ACZA), and copper xyligen (CX-A) (Lebow et al. 2004). Other aqueous systems include acid copper

chromate (ACC) and water-borne copper naphthenate. As well, there are copper systems used in Europe such as copper betaine, but these systems are not widely used in North America and won't be included here. The copper-based formulations may be grouped as:

- ◆ Water-borne soluble copper formulations
- ◆ Oil-borne copper complexes
- ◆ Water-borne micronized copper formulations

### Water-borne soluble copper formulations CCA —

For most of the latter half of the 20th century, the wood preservation industry was dominated by CCA. Since the voluntary restrictions in 2004 though, its use has been limited to industrial applications in structurally critical members such as poles, piling, foundations, support columns and the like. In the CCA-C formulation, chromium, copper and arsenic are present at 47.5, 18.5, and 34 percent, respectively, expressed as oxides. Copper provides protection against fungi, chromium fixes copper and arsenic in the wood, and arsenic provides supplemental protection against copper-tolerant fungi and insects. CCA was very much of a one-size-fits-all type of treatment (Lebow et al. 2004).

Table 3. — AWPA E19 fixation test results.

	Copper (mg/L) in Leachate				Percent Loss of Micro CQ Compared to ACQ				
	Days from Treatment to Sampling				Days from Treatment to Sampling				
	1	3	7	15	1	3	7	15	Average
<b>4 kg/m<sup>3</sup></b>									
Micro CQ 4 °C	2.2	1.8	1.7	1	21%	17%	21%	16%	19%
ACQ-D 4 °C	10.7	10.3	8	6.4					
Micro CQ 22 °C	1.9	1.5	1.2	0.9	21%	23%	31%	38%	28%
ACQ-D 22 °C	9.2	6.6	3.9	2.4					
Micro CQ 50 °C	1.7	1.1	1.3	1.5	53%	39%	32%	29%	38%
ACQ-D 50 °C	3.2	2.8	4.1	5.2					
<b>6.4 kg/m<sup>3</sup></b>									
Micro CQ 4 °C	4.4	2.7	2.3	2.7	19%	13%	10%	15%	14%
ACQ-D 4 °C	23.7	21.5	22.7	18.1					
Micro CQ 22 °C	2.8	2.1	2.3	1.9	14%	13%	16%	37%	20%
ACQ-D 22 °C	19.8	16.8	14.2	5.2					
Micro CQ 50 °C	1.9	1.4	1.7	2	18%	26%	24%	24%	23%
ACQ-D 50 °C	10.3	5.4	7	8.2					
<b>9.6 kg/m<sup>3</sup></b>									
Micro CQ 4 °C	8.4	3.7	3.5	3.5	17%	8%	8%	8%	10%
ACQ-D 4 °C	48.7	47.8	44.2	46.4					
Micro CQ 22 °C	4.3	2.5	2.7	2.7	10%	6%	8%	11%	9%
ACQ-D 22 °C	44.3	41.9	32.3	23.9					
Micro CQ 50 °C	2.4	2.2	2.1	2.6	8%	12%	18%	14%	13%
ACQ-D 50 °C	29.9	18.6	11.7	18.2					

Table 4. — MSU soil block test results.

Test-Institution	Formula	Condition <sup>a</sup>	Brown-rot fungi Thresholds, kg/m <sup>3</sup>				White-rot fungi Thresholds, kg/m <sup>3</sup>	
			<i>G. trabeum</i>	<i>P. placenta</i>	<i>N. lepideus</i>	<i>T. lilacino-gilva</i>	<i>T. versicolor</i>	<i>I. lacteus</i>
1-MSU-E10	Micro CA-1	L	1.6-1.8	2.2-2.6	<0.80	>3.2	1.4-1.6	<0.80
		NL	1.6-1.8	2.4-2.8	<0.80	>3.2	1.4-1.6	<0.80
1-MSU-E10	Micro CA-2	L		2.1-2.2				
		NL		2.2-2.6				
1-MSU-E10	CA-B	L	1.6-1.8	2.1-2.4	<0.80	>3.2	1.6-1.8	<0.80
		NL	1.6-1.8	<0.80	<0.80	>3.2	1.6-1.8	<0.80
2-MSU-E10	Micro CQ	L	3.5-4.2	8.3-8.6	<2.4	4.5-4.8	4.5-4.8	<2.4
		NL	3.7-4.0	8.3-8.6	<2.4	6.1-6.4	6.1-6.4	<2.4
2-MSU-E10	ACQ-D	L	4.2-4.5	7.0-7.4	<2.4	<2.4	<2.4	<2.4
		NL	4.2-4.5	<2.4	<2.4	<2.4	<2.4	<2.4
3-MSU-E22	Micro CA	NL	0.60	2.6	<0.16	1.8	1.4	<0.16
3-MSU-E22	CA-B	NL	<1.3	<3.2	1.4	>4.5	>2.0	0.64
3-MSU-E22	Micro CQ	NL	1.6	3.0	0.24		0.80	0.72
3-MSU-E22	ACQ-D	NL	1.8	<2.9	0.19		0.88	0.80
4-MSU-E22	Micro CA	NL	<0.80	1.6-2.4	<0.80		<0.80	<0.80
5-MSU-E22	ACQ-D		1.2 -2.4	1.2 -2.4	<1.2		<1.2	<1.2

<sup>a</sup>L = leached and NL = not leached

Today CCA-treated wood is often used as the reference standard in evaluating biological performance of new preservatives. It has been difficult to develop low toxicity, inexpensive replacements that can protect wood in such a broad range of applications as CCA does. Now there are more types of preservatives, and each is more closely targeted toward specific applications. In addition, there is greater emphasis on using the minimum retentions needed depending on end-use application because the replacements are more expensive. Leaching studies such as those reported here indicate that these CCA alternatives release preservative components into the environment at a rate greater than or equal to that of CCA. However these components have lower mammalian toxicity, and they are less likely to cause concern in residential applications. CCA is less corrosive to brass and steel than the other copper formulations (Zhang and Jiang 2006).

#### ACQ —

Variations of ACQ include Types A, B, C, and D (AWPA 2008), which differ in the ratio of CuO to quaternary compound, the particular type of quaternary compound used, and the solvent system used. Types A, B, and D use didydimethylammoniumchloride (DDAC) or didydimethylammoniumcarbonate (DDA-Carb) as the co-biocides. ACQ-B is an ammoniacal formulation, and ACQ-A

and D are copper amine formulations. ACQ-C uses alkylbenzyltrimethylammoniumchloride (ADBAC) as the co-biocide and can be either an ammoniacal or an amine formulation or use a mixture of the two solvents. ACQ-A has a 1:1 ratio of CuO to quaternary while the remaining three have 2:1 ratios. ACQ-B-treated wood has a dark greenish-brown color and may have a slight ammonia odor until the wood dries. Wood treated with ACQ-A or D has a light brown color and little noticeable odor, while wood treated with ACQ-C varies in appearance between that of ACQ-B and ACQ-D, depending on the formulation. The multiple formulations allow some flexibility in achieving compatibility with a specific wood species and application. The ammoniacal ACQ-B formulation is used in the western United States because it allows better penetration in difficult to treat western species while treating plants in the remainder of the country generally use amine systems (Lebow et al. 2004). Ammonia may also be added to amine formulations to improve penetration in western species.

#### Copper azole —

Copper azole is another preservative formulation that relies primarily on amine copper and a co-biocide to further protect wood from decay and insect attack. The first copper azole formulation CBA-A, included boric acid but the more recent CA-B contains just copper (96%) and tebu-

Table 5. — Additional E10 soil block test results.

Test-Institution	Formula	Condition <sup>a</sup>	Brown-rot fungi Thresholds, kg/m <sup>3</sup>			White-rot fungi Thresholds, kg/m <sup>3</sup>		
			<i>G. trabeum</i>	<i>P. placenta</i>	<i>N. lepideus</i>	<i>Pl.ostreatus</i>	<i>T. versicolor</i>	<i>I. lacteus</i>
1-MTU E10	Micro	L	<0.83	1.5	<0.83	<0.83	<0.83	<0.83
	CA	NL	<0.83	1.5	<0.83	<0.83	<0.83	<0.83
1-MTU-E10	ACQ-D	L	2.1	2.1	<1.2	<0.83	<0.83	<0.83
		NL	2.1	<1.2	<1.2	<0.83	<0.83	<0.83
			<i>G. trabeum</i>	<i>P. placenta</i>	<i>C. puteana</i>	<i>Pl.ostreatus</i>	<i>I. lacteus</i>	
2-FOR-E10	Micro	L	<0.83	0.83	0.83-1.7	<0.83		<0.83
2-FOR-E10	CA							
	Micro	L	<1.0	<1.0	5.5	<1.0		<1.0
	CQ							

<sup>a</sup>L = leached and NL = not leached

conazole (4%). Wood treated with either copper azole formulation has a brownish-green color and little or no odor. The formulations are listed in AWPA standards for treatment of a wide range of softwood species. Although listed as an amine formulation, copper azole may also be formulated as an amine-ammonia formulation with the ammonia included when the formulation is intended for refractory species (Lebow et al. 2004).

This year, a third copper azole formulation, CA-C, was proposed for AWPA listing. This formulation uses 2 percent propiconazole and 2 percent tebuconazole as the cobiocides, and this combination of azoles has been shown to be synergistic (Buschhaus and Valcke 1995).

#### Ammoniacal copper zinc arsenate —

Ammoniacal copper zinc arsenate (ACZA) was developed in the early 1980s as an improvement on ammoniacal copper arsenate (ACA) which dates back to the 1930s. Used primarily in western North America for treatment of Douglas-fir, AZCA contains copper oxide (50%), zinc oxide (25%), and arsenic pentoxide (25%). The color of the treated wood varies from olive to bluish-green. The wood may have a slight ammonia odor until it is thoroughly dry. As with other ammonia containing preservatives, ACZA penetrates difficult to treat species so treating plants using ACZA are located in western states where lumber from many of the native trees is difficult to treat with CCA (Lebow et al. 2004). ACZA reacts strongly with wood cells, and it has been well tested in both terrestrial and aquatic conditions in temperate zones. ACZA provides excellent protection, especially in marine exposures (Rhatigan et al. 2000, Zahora et al. 2000).

#### ACC —

ACC contains 32 percent copper oxide and 68 percent chromium trioxide and has been used since the 1920s mainly for wood in cooling towers. The high chromium content prevents corrosion associated with acidic copper preservatives. The treated wood has a light greenish-brown color and little odor. While ACC provides good above ground service life, wood used in ground contact may suffer occasional early failures due to copper tolerant fungi attack. ACC has limited critical structural application uses in the AWPA although some applications such as posts are listed. It may

be difficult to obtain adequate penetration in refractory wood species because ACC must be used at relatively low treating temperatures and rapid reactions of chromium in the wood can hinder further penetration during longer pressure periods (Lebow et al. 2004).

#### Copper Xyligen —

Copper Xyligen (CX-A), which is also known as copper-HDO, is a water-borne wood preservative based on Cu-HDO (bis-(N-cyclohexyl-diazoniumdioxy)-copper), copper carbonate, and boric acid as active ingredients. This system is largely used in Europe, and some treaters have begun to use the product in the United States. Currently, the AWPA lists only above ground uses for CX-A.

#### Copper borate —

Copper borate is an effective treatment for wood composites where protection against mold, decay, and termites is required. Oriented strand board containing a 10 percent copper borate formulation showed superior resistance to mold growth and also provided similar protection as that of zinc borate and boric oxide against fungal decay and Formosan termite attack. Copper borate showed a negative impact on physical properties when certain phenolic resins were used, but further research reduced this impact. With proper phenolic resin selection, or the use of MDI resin, adequate physical properties can be obtained (Smart and Wall 2006).

#### Oil-borne copper complexes

Organometallic compounds are formed by the reaction of metal ions with an organic ligand. Copper containing organometallics used in wood preservation are copper naphthenate (CuNap) and oxine copper. Advantages of organometallics include: (i) a relatively low metal content (ii) fewer metal corrosion problems than systems formulated with uncomplexed copper ions and (iii) the metal coordination sites that are not complexed with the ligand could bind to the carboxylic or phenolic groups in wood to make the formulation relatively leach-resistant (Schultz et al. 2003).

#### Copper naphthenate oil-borne —

CuNap is the reaction product of a copper salt and naphthenic acids (Barnes, et al. 2001). Oil-borne CuNap

Table 6. — *Ensis* AWPC soil block test results.

Formula	Threshold, kg/m <sup>3</sup>					
	<i>C. olivacea</i>	<i>F. lilacino-gilva</i>	<i>G. abietinum</i>	<i>S. lacrymans</i>	<i>P. tephropora</i>	<i>L. crassa</i>
<b>Test 1</b>						
Micro CQ	1.9-3.2	1.0-1.9	<1.0	1.9-3.2	<1.0	<1.0
ACQ-D	1.9-3.2	1.0-1.9	<1.0	1.9-3.2	<1.0	1.9-3.2
CCA-C	0.6-1.2	0.6-1.2	<0.60	1.2-2.0	<0.60	<0.60
<b>Test 2</b>						
	<i>C. olivacea</i>	<i>F. lilacino-gilva</i>	<i>G. abietinum</i>	<i>P. placenta</i>	<i>P. tephropora</i>	<i>L. crassa</i>
Micro CQ-1	<0.60	>1.3	<0.60	1.0-1.3	<0.60	<0.60
Micro CQ-2	<0.60	>1.3	<0.60	>1.3	<0.60	—
CA-B	<0.60	>1.3	<0.60	>1.3	<0.60	0.60-1.0
CCA-C	<0.60	1.2-2.0	<0.60	>1.3	0.60-1.2	1.2-2.0

has been used for over 50 years in wood preservation, typically in utility poles, fence posts, and lumber. Oil-borne CuNap gives equivalent performance to creosote or pentachlorophenol (penta) at appropriate comparable retentions. Grace et al. (1993) showed CuNap to be effective against *Coptotermes formosanus* for pine treated to 0.04 pcf (0.64 kg/m<sup>3</sup>) (as Cu). It has excellent potential for use as a crosstie (sleeper) preservative (Barnes et al 2001). CuNap is known to control many decay fungi, molds, mildew, dry rot, certain marine growths, termites, other wood inhabiting insects, and bacteria. One of the principal reasons that CuNap is gaining market acceptance and is being compared to other oil-borne wood preservatives is its low mammalian toxicity. Almost all former penta plants in Missouri and the western states of Montana, Wyoming, and Colorado have switched over to CuNap. CuNap is typically supplied as an 8 percent concentrate that is dilutable with a wide variety of organic solvents.

#### Copper naphthenate water-borne —

Water-borne CuNap presents some advantages such as low volatile organic compound emissions and relatively low cost by using water as the carrier (Kamdem et al. 1996, Freeman 2002). The active ingredient is dissolved in a solution of an alkanolamine and/or ammonia in water. Kamdem et al. (1996) reported that water-borne CuNap with 2 kgm<sup>-3</sup> copper retention was sufficient to protect red oak (*Quercus rubra*) and red maple (*Acer rubrum*) against some white rot and brown rot fungi. Freeman et al. (2004) reported that, after 6 to 7 years of field trials in Michigan, Florida, and Mississippi, water-borne CuNap treated southern pine (*Pinus* sp) at 0.76 kgm<sup>-3</sup> copper retention provided comparable performance to wood treated with ACQ-C at 8.4 kgm<sup>-3</sup> actives, CCA at 5.6 kgm<sup>-3</sup> actives and oil-borne CuNap at 1.86 kgm<sup>-3</sup> copper retentions.

#### Oxine copper —

Oxine copper is formed by the reaction of copper with 8-quinolinol. The AWPFA formulation consists of 10 percent copper-8-quinolinolate, 10 percent nickel-2-ethylhexanoate, and 80 percent inert ingredients. It has been used

for wood treatment since the 1950s (Myers 1989). Oil-borne oxine copper does not accelerate corrosion of metal fasteners relative to untreated wood (Lebow 2007). A water soluble form of oxine copper can be made with dodecylbenzene sulfonic acid, and this corrodes metals (Morrell 2005, Groenier and Lebow 2006). The treated wood is colorless to greenish-brown and has little or no odor (Morrell 2005). In recent years oxine copper has increasingly been used as an alternative to copper naphthenate in above ground uses. It does not present the characteristic naphthenic acid odor, is odorless and resistant to hydrolysis. Oxine copper can be dissolved in hydrocarbon solvents but provides longer protection when delivered in heavy oil (Lebow 2007). It is an excellent fungicide that is effective at very low concentrations and is also toxic to insects (Myers et al. 1989, Groenier and Lebow 2006). Its greatest advantage is high efficacy and low mammalian toxicity. It is the only EPA-registered wood preservative permitted by the U.S. Food and Drug Administration for treatment of wood used in direct contact with food. The low water solubility and low vapor pressure contribute to its stability in wood and provide the necessary longevity. Its greatest disadvantage is the high cost (Morrell, 2005).

#### Water-borne micronized copper formulations

In these formulations, small “micronized” particles of copper compounds are dispersed in the carrier instead of using dissolved copper. There are a number of patents and patent applications that specifically cover the micronized copper technology as it relates to wood preservatives, and the following provides a general review of the literature. For more details, see Leach and Zhang 2006, Richardson and Hodge 2004, Richardson and Hodge 2006, Zhang and Leach 2005, and other patent literature by these authors.

Micronized particles are produced by mechanical grinding of water- or oil-insoluble copper compounds with aid of dispersing/wetting agents in a carrier using a commercial grinding mill or by chemical means resulting in 90 percent or more of the particles being less than 1000 nm size. The commonly used carrier is water, and commonly

Table 7. — MSU E23 soil bed test results for brown rot decay.

Formula	Retention, kg/m <sup>3</sup>	Average % Strength at Month						
		3	6	9	12	18	24	30
<b>Test 1</b>								
Micro CA	1.6		107.2	102.6	96.2	80.5	65.3	46.5
	3.4		104.7	104.1	97.2	87	80.1	63.3
	5.1		107.4	102.3	95.7	88.8	84.3	69.9
CA-B	1.6		104.9	101.1	96.5	81	79.1	53.2
	3.4		103.4	100.6	95.4	89.2	84.7	70.2
	5.1		101.9	99	93.5	88.1	86.1	72.6
Controls			70.5	44.4	21.9	2.1	0	
<b>Test 2</b>								
Micro CA	1.6	97.5	a		96.5			
	3.4	99			98.5			
	5.0	98.4			97.5			
CA-B	1.6	96.6			97.4			
	3.4	96.5			96.6			
	5.0	96.4			94.7			
Micro CQ	3.2	94.1			96.3			
	6.4	94.5			97.8			
	9.6	94.4			98			
ACQ-D	3.2	93.8			95.4			
	6.4	92.3			93.6			
	9.6	92.3			91.7			
Controls	—	93.9			34.8			

<sup>a</sup>The 6 month results were deemed unreliable by the researchers.

used dispersing agents are polymeric dispersants, which attach to the surface of particles and keep the particles away from each other. Also, the presence of dispersing/wetting agents improves particle size reduction during milling and stabilizes the particles during storage and treating. The size of these particles can range from 1 to 25000 nm, and the particulate character may affect penetration of wood cell walls and reaction with wood's molecular constituents. The degree of penetration and uniformity of distribution of particles into the wood cellular structure is inversely related to the prevalence of particles with relatively large particle size. Larger particles are generally easier to prepare, but particles with long axes greater than 25000 nm may clog tracheids and inhibit the uptake of additional preservative. If the particle size of the micronized preservative is less than the diameter of the window pit (typically 10,000 nm) or membrane openings in a bordered pit (typically 400 to 600 nm) openings, complete penetration and a uniform distribution of micronized preservative in wood is expected.

Using field emission scanning electron microscopy coupled with x-ray microanalysis (EDAX), Matsunaga et al. (2007) examined the microdistribution of copper in southern pine treated with micronized copper wood preservative to determine if it differed from that of wood treated with conventional water-borne copper preservatives. Results revealed the presence of nano-sized copper and iron particles (from grinding media) ranging from 10 to 700 nm in micronized treated wood that were abundantly present in pit chambers and on tertiary wall layers adjacent to the lumens of tracheids and ray parenchyma cells. Copper and iron were mainly present as separate particles.

Copper was also found in wood cell walls where its concentration was slightly higher in the middle lamella than in the secondary wall layer. In this respect the microdistribution of copper in wood treated with dispersed copper resembles that observed in wood treated with conventional soluble copper-based wood preservatives but the amounts of copper in the cell wall components differed between the formulations. In further work, Matsunaga et al. (2008) refined their experimental techniques and indicate that they are working to compare the concentrations of metals in cell walls of wood samples treated with conventional and micronized formulations.

Stirling et al (2008) reported distributions similar to those of Matsunaga based on Environmental Scanning Electron Microscopy (ESEM) and Energy Dispersive X-Ray Spectrometry (EDS) results. X-ray analysis indicated that there was a small amount of Cu in the cell walls in both micronized copper and soluble systems. The authors suggest that copper-containing particles in the treated wood slowly release mobile copper, which may further penetrate through the cell wall.

However, the numerous particulate deposits of copper in voids within the wood have also been discussed. Archer (2007) raised concern that soft rot attack may be a problem for micronized formulations. White-rot organisms are also inhibited more by cell-wall treatment than by cell-lumen treatment and numerous studies have shown that the ability to control soft-rot in hardwoods depends on the levels of copper in the S2 layer of wood cell walls (Hale and Eaton 1986, Ryan and Drysdale 1988). Cell wall treatment also improves the effectiveness of a preservative system in resisting depletion and hence, the good performance of

many water-borne wood preservatives has been attributed, in part, to the fact that they are absorbed into the cell wall and uniformly distributed in the microstructure of wood (Arsenault 1973).

Any suitable copper source can be used to obtain micronized particles but basic copper carbonate is most commonly used. Micronized formulations are also not limited to water-borne compositions; it is believed that particles carried in organic carriers, such as oils, will effectively penetrate wood as well. Non-biocidal components added to enhance performance may include water repellants, colorants, emulsifying agents, dispersants, stabilizers, solubilizing agents, UV inhibitors and wood dimensional stabilizers. Insecticides can be mixed with micronized metal formulations and preferred co-fungicides are quats and triazoles. Micronized copper carbonate compositions generally have a pH in the range of 7 to 9, but inclusion of acids in the compositions will give a neutral or acidic pH.

Wood treated with micronized copper is only slightly more corrosive than untreated lumber and less corrosive than other water-borne copper formulations to metal fasteners. The treated wood is also lighter in color; hence lighter-colored paints and stains can be used.

Micronized formulations are not listed in the AWWA standards, which contain only the various soluble formulations. There are many reasons for this including formulation confidentiality, extent of testing, and sponsor preferences. Accordingly, **Table 1** shows a summary of required retentions for some copper containing formulations currently listed in AWWA Standards.

In contrast, the International Code Council Evaluation Services (ICC-ES) issues Evaluation Services Reports (ESR) that list preservatives at retentions that may be different from those in the AWWA. An important point though is that a product with an ESR is deemed satisfactory for building code regulated uses. Thus, the lower retentions of the ICC-ES dominate commercial use and several micronized products are listed (**Table 2**).

### Fixation and leaching of copper in treated wood

The effectiveness of fixation-chemical reactions that prevent leaching is dependent on treating factors, such as

preservative formulation, preservative retention, and processing techniques, as well as post-treatment conditioning factors, such as temperature, humidity, and air flow. CCA has been studied more extensively than the other preservatives. The most rapid leaching occurs within the first months of service and is greatest in products with high retention levels and high proportions of exposed surface area, especially end-grain. Leaching is also increased by exposing the wood to high water flow, low pH, and water-soluble organic acids. Site, wood species, and preservative type play major roles in copper leaching from treated wood. Waterlogged sites, and/or sites with low pH cause greatest loss to all treatments irrespective of wood species and preservative type. Organic acids (humic, lactic, malonic and fulvic acids) known to be associated with forest litter are important agents of depletion (Cooper et al 2001). Less efficient fixation reactions, perhaps caused by higher extractive content of some wood species and poor preservative distribution (macro- and micro-) may result in more leaching (Wakeling 2006). Movement of leached chromium and copper appears to be quite limited in soil, because the metals are tightly bound to organic soil constituents. Generally, the preservative components are least mobile in organic soils, slightly more mobile in clay soils, and most mobile in sandy soils. In aquatic applications, the leached preservative components form complexes with the organic sediment fines, and accordingly are either deposited or moved downstream with the sediments (Lebow 1996).

Both oil-borne wood preservatives oxine copper and copper naphthenate resist leaching because they are relatively insoluble in water. In CCA treatment, chromium is used to improve the fixation in wood. The reduction of the reactive and mobile Cr (VI) to Cr (III) is crucial in the formation of insoluble complexes in CCA-treated wood with the formation of chromium arsenate and chromium hydroxide, while the products formed between copper and wood carboxylate is relatively more soluble (Pizzi 1982a, b). This formulation limits copper leaching while providing continuous bio-availability of copper toward wood destroying organisms. The reactions in the fixation of CCA in wood involve a number of mechanisms. The final fixation products are dominated by chromium (III) arsenate, chromium (III) hydroxide, and copper (II)- wood carboxylate complexes. Carboxylate groups are generated in large numbers in the reduction of chromium (VI) by primary alcohol groups in lignin and carbohydrate fractions, or in the oxidative degradation of lignin (Bull 2001).

The microdistribution of copper in the cell walls of wood treated with CCA or CCB or the newer preservatives that are free of chromium or arsenic has been extensively studied using scanning or transmission electron microscopy in combination with x-ray microanalysis (Dawson-Andoh and Kamdem 1998, Petri et al. 2000, Matsunaga et al. 2007). These studies have shown that the copper concentration is higher in the middle lamella and cell corners than in the secondary wall. This is attributed to higher affinity of ionic copper for lignin, which reaches its highest concentration in the middle lamella, than for cellulose (Lebow 1996), or the increased density of the middle lamella compared to the secondary cell wall (Cao and

Table 8. — MSU E23 soil bed test results for soft rot attack.

Formula	Retention, kg/m <sup>3</sup>	Average % Strength at Month		
		3	6	12
Micro CA	1.6	97.4	78.2	60.5
	3.4	98.3	81.9	77.8
	5.0	97.6	83.4	77.5
CA-B	1.6	96.5	81.5	70.1
	3.4	96.2	82.4	84
	5.0	95.4	79.2	81.4
Micro CQ	3.2	96.4	77.2	66.9
	6.4	96.4	84.1	81.5
	9.6	95.7	85.7	88.6
ACQ-D	3.2	96.8	80	70.5
	6.4	94	80.8	81.9
	9.6	93.7	80.3	82.7
Controls	—	75.8	42.4	0

Kamdern 2005, Matsunaga et al. 2007) or to cation exchange with weak acid groups such as pectic and other uronic acids present in the cell walls (Cooper 1991). Hence within wood, various functional groups are preferential adsorption sites for transition metal ions irrespective of the carrier solvent (Petri et al. 2000).

The importance of chromium-free preservatives is increasing. Since the use of chromium in wood preservatives is significantly limited or even banned in several European countries, in order to use copper as a fungicide in the future, new techniques to improve copper fixation have been developed (Humar et al 2007). The replacement of CCA by alkaline copper compounds has heightened awareness of the potential impact of copper losses on aquatic organisms. Reducing these losses will be necessary to avoid continued regulatory actions against the use of preservatives in these environments. While post treatment processing and coatings can reduce losses, neither is completely effective. Adding chemical compounds to the alkaline system to complex or otherwise reduce copper losses, much in the same way that chromium acts in CCA, has been attempted.

Alternatively, copper leaching could be reduced by incorporating additives into the preservative formulation that block or slow copper migration. Additives should be hydrophobic and have the ability to react with the wood matrix, convey groups that can easily bond with copper, enable some of the sorbed copper to be released under wet conditions and then bind to copper again once the moisture content decreases (Roussel et al. 2000). Additives that limit metal loss may also permit the use of lower initial preservative loadings to produce equivalent protection.

A common fabric softener, di(hydrogenated tallowalkyl) dimethyl ammonium chloride (2HT), reduces copper losses from ACQ and copper azole and hence improves overall biological performance (Mitsuhashi et al. 2007). The potential mechanism by which 2HT alters copper losses from wood remains unclear,

Table 9. — No-choice E1 Formosan test results.

Test-Institution	Formula	Retention, kg/m <sup>3</sup>	Weight Loss, %	Rating	Mortality, %
1-LSU	Micro CA-1	0.80	5.2	8.2	44
		1.6	4.7	8.3	30
		2.4	7.3	8.2	37
		3.2	5.9	8.9	50
1-LSU	Micro CA-2	0.80	5.5	8.2	39
		1.6	3.8	8.4	54
		2.4	5.5	8.2	78
		3.2	3.8	8.4	77
1-LSU	Micro CA-3	0.80	1.3	9	80
		1.6	1.7	9	87
		2.4	3.9	9.1	30
		3.2	3.1	8.9	24
1-LSU	ACQ-D	1.2	3.3	8.5	53
		2.4	3.1	8.7	53
		4.0	5.1	8.5	50
		6.4	5.6	8.3	58
1-LSU	UNT	—	27.4	2	6
2-LSU	Micro CA	0.80	10.4	7.6	34
		1.6	5.0	8.5	68
		2.2	4.4	8.5	66
		3.5	2.5	9.0	83
2-LSU	CA-B	1.8	2.2	8.9	48
		3.7	1.8	10	37
2-LSU	Micro CQ	1.9	4.8	7.6	65
		4.3	2.2	9.1	90
		5.9	1.3	9.0	78
		6.4	1.7	8.6	72
2-LSU	ACQ-D	3.8	0.6	10	77
		6.1	0.3	10	64
2-LSU	CCA-C	3.8	1.8	9.4	100
		6.2	1.4	9.3	100
2-LSU	UNT	—	31.5	1.6	8
3-MSU	Micro CA-1	0.80	4.5	9	a
		1.6	1.7	9	
		2.2	2.5	9	
		3.2	2.1	9	
3-MSU	Micro CA-2	0.80	4.0	9	a
		1.6	2.9	9	
		2.2	2.4	9	
		3.2	2.7	9	
3-MSU	CA-B	0.80	2.6	9	a
		1.6	2.1	9	
		2.2	2.5	9	
		3.2	2.0	9	
3-MSU	Water Treat	—	21.9	3.2	a
3-MSU	UNT	—	21.4	4	a

<sup>a</sup> See text for mortality data

Table 10. — MSU choice E1 Formosan test results.

Formula	<i>Reticulitermes flavipes</i>				<i>Coptotermes formosanus</i>		
	Condition <sup>a</sup>	Retention, kg/m <sup>3</sup>	Weight Loss, %	Rating	Retention, kg/m <sup>3</sup>	Weight Loss,%	Rating
Micro CQ	L	2.4	0.11	9.2	2.4	0	9
	NL	2.2	1.46	9	2.3	0.37	9
	L	4.2	0.24	9.4	4.2	0.12	9
	NL	4.2	1.56	9.2	4.2	0.5	9
	L	7.0	0.37	10	6.7	0	9.2
	NL	6.6	1.43	9.6	6.7	0.86	9
Controls	Both		13-60	0.5-8		38-46	0-3.2
ACQ-D	L	2.5	0.63	9	2.6	0.35	9
	NL	2.6	2.09	9.2	2.6	0.25	9.4
	L	4.2	1.14	9	4.2	0	9
	NL	4.3	1.51	9.8	4.0	0.58	9
	L	6.7	1.13	9	6.8	0	9
	NL	6.2	1.59	8	6.4	0.79	9
Controls	Both		17-56	0.8-5.6		35-48	0.8-3.6
Water	L	—	37.92	1.4	—	32.23	1.6
Treat		—	37.24	2.4	—	11.74	4.6
Water	NL	—	32.46	1.6	—	19.11	4.6
Treat		—	19.7	3.8	—	23.65	2.4

<sup>a</sup>L = leached and NL = not leached

Table 11. — MSU E7 19 mm Gainesville, Florida stake test results.

Formula	Retention, kg/m <sup>3</sup>	12 Months		Rating at 24 Months		36 Months	
		DCY	TER	DCY	TER	DCY	TER
Micro CA	1.6	10	10	9.9	10	9.4	9.4
	3.4	10	10	10	10	10	9.8
Micro CQ	4.2	10	10	8.3	9.9	7.0	8.5
	6.7	10	10	9.9	10	9.7	9.9
ACQ-D	3.8	10	10	5.6	7.2	3.3	5.1
	6.1	10	10	9.8	10	7.8	9.4

Table 12. — MSU E7 19 mm Mississippi stake test results.

Formula	Retention, kg/m <sup>3</sup>	Rating at							
		12 Months				24 Months			
		Saucier, Mississippi				Dorman, Mississippi			
		DCY	TER	DCY	TER	DCY	TER	DCY	TER
Micro CA	1.3	10	9.9	10	9.8	9.8	10	9.8	9.8
	3.4	9.9	9.9	9.9	9.7	10	10	10	10
	4.8	10	9.9	10	9.9	10	10	10	10
CA-B	1.3	10	9.9	10	9.9	10	9.9	9.2	9.8
	3.4	10	10	10	9.9	9.9	10	9.8	10
	4.3	10	10	10	10	9.8	10	9.9	10
Controls	—	6.1	5.5	2.3	1.7	6.5	8.4	3.1	6.6

but it is possible that hydrophobic interactions may enable 2HT sorption on cellulose. While improved water repellency could slow wetting and drying cycles, thereby reducing the overall losses, other water repellants have not produced the reductions in copper losses noted with this compound. These results suggest that 2HT may have other, more subtle effects on copper mobility.

Ammonia is a very effective fixation agent but its use is limited due to emission and odor concerns. As noted,

ammonia was replaced with amines, and the copper:amine molar ratio significantly affects 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 formulations. The rates of stabilization or fixation of copper in ACQ-treated wood were compared for different post treatment conditioning temperatures (22 °C and 50 °C), solution concentrations

(0.4 to 2.3%) and wood species. Copper stabilized much faster at lower ACQ retentions and when conditioned at 50 °C compared to high retentions and stabilization at 22 °C. Species effects were minor (Ung and Cooper 2005).

The type of amine used affects the stability, polarity and solubility of the copper amine complex. Cupric ions form complexes with ethanolamine through amino and hydroxyl groups in aqueous solution due to formation of a five-member ring complex. These processes are significantly affected by pH of the impregnated wood. If the copper-amine complexes exist in wood by physical interaction, they will leach easily. For better fixation, the copper-amine complexes interact with wood through chemical reactions with lignin carboxylic and phenolic hydroxyl groups (Zhang and Kamdem 2000, Ruddick et al. 2001). In a ligand exchange reaction mechanism, copper-ethanolamine complexes exchange ligands with wood and release one or two amine molecules. In the second possible reaction mechanism, non-charged species of copper-ethanolamine complexes are transformed into charged species during impregnation. The carboxyl and phenolic groups can react with the charged species to form a stable wood-copper-ethanolamine complex (Zhang and Kamdem 2000).

A study of the interaction of copper ethanolamine and wood components using Fourier transform infrared spectroscopy (FTIR) confirmed that Cu-EA interacts with carboxylic groups, phenolic hydroxyl groups and ester groups on lignin to form copper carboxylate and phenolate complexes (Zhang and Kamdem 2000). After treatment with copper-ethanolamine, stable copper-nitrogen-lignin complexes can be formed through reaction with guaiacyl units in lignin. The fixation reaction of copper preservatives in wood was studied using the reaction between vanillin, a lignin model compound, and copper to form di(ethanolamine)-bis (vanillinato)dycopper(II); [Cu(vanillin) (ethanolamine)]<sub>2</sub> (Xie et al. 1995, Zhang and Kamdem 2000). Fixation of copper-ethanolamine based wood preservatives is not as good as fixation of copper-chromium ones, because ethanolamine causes lignin depolymerization, resulting in leachable complexes of copper-ethanolamine-lignin monomers. Lignin degradation is reflected in higher organic carbon content in leachates, mass losses after leaching and changes in mechanical properties. There was good correlation between organic carbon in leachates and copper leaching. The main source of organic carbon was wood components (Humar et al. 2007).

Copper amine based preservatives can have higher copper losses due to leaching compared to CCA. A study on the effect of temperature, relative humidity, and duration of post-treatments on accelerating copper fixation in ACQ-D in Chinese fir wood blocks revealed that relative humidity has little effect on fixation rate although moisture is required for reactions to proceed. Temperature has a

significant effect on accelerating copper fixation. The fixation rate is much higher and the predicted time needed for complete fixation is much shorter at higher temperatures (50 to 70 °C). The percentage of copper leached decreased linearly with the length of post treatment exposure (Cao and Yu 2007). Boron addition reduced copper fixation in wood impregnated with copper-ethanolamine compared to wood impregnated with copper-ethanolamine alone, but the boron improved performance against the copper tolerant fungus *A. vaillantii* (Pohleven and Humar 2006).

Thomason and Pasek (1997) postulated that copper and boron are selectively adsorbed via two distinct and separate pathways. Adsorbed copper reacted exclusively with hemicellulose carboxyl groups while boron reacted at other locations, presumably forming esters with lignin phenols. This mechanism differs from the above proposals for a copper:lignin complex. The authors suggest that this difference may be due to the heterogeneous structure of wood limiting the formation of copper:lignin complexes whereas these complexes can form under modeling conditions.

In a test on efficacy of a combination of copper-ethanolamine and boron solutions against copper tolerant fungi, Pohleven and Humar (2006) and Humar et al. (2005)

Table 13. — Second MTU E7 19 mm Hawaii stake test results\*.

Formula	Retention, kg/m <sup>3</sup>	Rating at					
		12 Months		21 Months		33 Months	
		DCY	TER	DCY	TER	DCY	TER
Micro CA	0.80	10	10	9.5	9.8	5.3	8.9
	1.6	10	10	10	10	9.8	10
	2.5	10	10	10	10	10	10
	3.2	10	10	10	10	10	10
Micro CQ	2.4	10	10	9.8	10	8.3	9.9
	4.0	10	10	9.9	10	9.9	10
	6.4	10	10	9.95	10	9.9	10
	9.6	10	10	10	10	10	10
ACQ-D	2.4	10	10	9.7	10	8.4	9.9
	4.0	10	10	9.9	10	9.5	9.8
	6.4	10	10	10	10	9.9	10
	9.6	10	10	10	10	9.8	10
UNT	—	8	10	0.9	5.6	0	7

\* Stakes originally installed at Hilo and moved to Oahu at year 1.

Table 14. — *Ensis Innisfail, Australia stake test results.*

Formula	Retention, kg/m <sup>3</sup>	Rating at 17 Months	
		Eucalyptus	Radiata
Micro CQ	3.0	9	9.9
	4.0	8.8	9.9
	5.0	9.4	10
	6.6	9.4	10
ACQ	3.0	8.1	9.9
	4.0	8.4	9.9
	5.3	8.6	9.8
	6.7	9.4	10
CCA	0.80	2	5.9
	1.6	7.3	8.4
	2.9	3.9	9.9
UNT	—	0	0

found that copper fixation is significantly improved by addition of carboxylic acids. The boron increases efficacy against fungi but decreases copper fixation. Octanoic acid improves copper fixation, and slightly decreases effectiveness against copper tolerant fungi (Humar et al. 2005). Thus there must be a balance between fixation and performance of impregnated wood. In leached specimens, resistance to the copper tolerant fungus *A. vaillantii* is significantly decreased, probably due to loss of boron. Tannins have low toxicity as wood preservatives, but they can fix biocides because of their excellent chelating properties. Co-impregnation in a two-step treatment with copper, zinc, and boron showed that good retention of copper (II) ions is achieved by first impregnating wood with commercial chestnut tannin. The treated wood meets the European standard for protection against decay. No protection against blue-staining fungi was obtained as boron retention was not achieved (Scalbert et al 1998).

### Micronized copper fixation mechanisms

In contrast to soluble copper-based wood preservative systems such as CCA, CA-B and ACQ, wherein the Cu<sup>2+</sup> ions are believed to chemically “fix” in wood after treatment, the micronized copper preservative particles with polymeric dispersant molecules attached to the particle surface are carried into wood through vacuum/pressure impregnation and physically deposited into the wood structure. After treatment, the micronized particles are believed to “fix” to wood through strong adhesion between the polymeric dispersants and wood fiber by similar mechanisms as occur in wood coating applications. The adhesion would anchor the micronized copper parti-

cles within the wood and prevent the particles from being dislodged by the normal weathering conditions that the treated wood may be subjected to in service. In addition, there is a small portion of free Cu<sup>2+</sup> present in wood after treatment as confirmed by the AWPA E11 leaching study (Stirling et al 2008) and SEM Studies (Matsunaga et al 2007, Stirling et al 2008). It is possible that the minor amounts of free Cu<sup>2+</sup> ions associated with the micronized particle formulations bind to various components of the wood by similar mechanisms as other soluble copper preservatives such as ion exchange (Cooper 1991). However, the majority of fixation in micronized systems is believed to be simple deposition as opposed to reaction.

The importance of this distinction can be seen in **Table 3** where the results of an AWPA E19 Fixation test are presented. At every sampling, the losses from the micronized copper system were significantly less than the losses from the matched soluble system. Interestingly, there was an inverse relationship between retention and copper loss in that lowest retention samples showed that the micronized formulation lost about 30 percent as much copper as ACQ-D did while the highest retention samples showed that the micronized formulation lost about 10 percent as much copper as ACQ-D did. The middle retention of the micronized system lost about 20 percent of the copper that ACQ-D lost.

### Micronized copper systems compared to amine-based systems

This section compares data from amine-solubilized copper based wood preservative systems with copper systems that have the copper-based portion of the system as sub-micron particle size dispersions. Both biological and non-biological tests are discussed. As is typical with wood preservative research, there were a number of slight variations in the formulations tested. Essentially all of the variations dealt with the co-biocides though, and therefore the micronized formulations are grouped without regard to these small changes. Therefore, “Micro CQ” is used to designate systems with quaternary co-biocides while “Micro CA” is used for systems with azole co-biocides. In some cases, two or more copper azole variations were included in the same test so the different formulations are designated with a numerical suffix. Generally speaking, the co-biocides within a test are of similar character. It should be recognized that a “Micro CA or CQ” in one test may not be exactly the same as a “Micro CA or CQ” in another test but this is unimportant. The primary emphasis is to compare the Micro and amine products in the same test. Lastly, the amine-solubilized formulations are designated simply as CA-B or ACQ-D.

Table 15. — MSU E18 ground proximity test results.

Formula	Retention, kg/m <sup>3</sup>	Hilo, Hawaii	Saucier, Miss.	Rating at	
				Hilo, Hawaii	Saucier, Miss.
<b>Test 1</b>		<b>12 months</b>			
Micro CA	1.6	10	10		
	2.4	10	10		
	0.80	10	10		
CA-B	1.6	10	10		
	2.4	10	10		
	4.8	10	10		
Micro CQ	1.6	10	10		
	4.8	10	10		
ACQ-D	1.6	10	10		
	4.0	10	10		
	4.8	10	10		
UNT	—	9.1	9.3		
<b>Test 2</b>		<b>15 months</b>		<b>27 months</b>	
Micro CA	0.80	10	10	10	10
	1.6	10	10	10	10
	2.4	10	10	10	10
CA-B	0.80	10	10	10	10
	1.6	10	10	10	10
	2.4	10	10	10	10
Controls	—	7	9.9	1.2	9.4

The testing discussed in this section, unless otherwise noted, was conducted in ISO 17025 conforming laboratories that have also received accreditation by the International Accreditation System (IAS) or an equivalent certifying agency. The tests were performed by using consensus-based, industry-ratified and adopted test methods with no significant deviations from the standardized protocol, unless otherwise noted in that section. The tests are well-known within the industry.

### Biological efficacy tests

#### Laboratory tests

##### Soil Block Test Summaries

Mississippi State University researchers conducted Soil Block tests comparing micronized and soluble formulations using both AWPA E10 and E22 protocols and common test fungi (**Table 4**). In these tests, southern pine (*Pinus spp.*) was used for brown rot fungi and beech (*Fagus spp.*), cottonwood (*Populus spp.*) or sweetgum (*Liquidambar styraciflua* L.) for the white rot fungi. It should also be mentioned that all of the untreated controls in the soil block tests discussed here showed good fungal virulence on the untreated hardwood or softwood species used.

The thresholds determined in the first E10 test for two micronized copper azole formulations and an amine based copper azole were very similar in the leached condition. Note that one micronized formulation was only tested against the copper tolerant *P. placenta*. In all, there were no meaningful differences determined for the various formulations although the unleached CA-B control “apparently” had a lower threshold with *P. placenta*. Presumably, this difference is due to soluble, unfixed components that are readily leached.

A second MSU E10 test compared a micronized copper quaternary with soluble ACQ. In this case, two brown rot fungi, *P. placenta* and *T. lilacino-gilva*, had significantly higher

Table 16. — CSIRO lunchbox termite test results.

Wood	Formula	Retention, kg/m <sup>3</sup>	Wt. loss (%)	
			<i>C. acinaciformis</i>	<i>M. darwiniensis</i>
Pine	Micro CQ	3.2	0.3	5.8
		6.2	0.2	1.4
	ACQ-D	3.4	0.4	5.1
		6.2	0.6	3.0
	CCA-C	3.5	0.6	2.0
		6.9	0.4	3.1
Water	—	91.7	94	
Gum	Micro CQ	3.2	0.9	7.6
		6.4	0.7	2.8
	ACQ-D	2.9	1.5	9.1
		6.2	1.9	3.1
	CCA-C	3.2	0.7	2.3
		5.6	1.0	2.5
Water	—	67.8	98.2	

thresholds for the micronized formula compared to the soluble one. This is somewhat anomalous in that a third MSU Soil Block test that was done by the E22 procedure had the micronized copper product with a similar threshold to the soluble formulation for *P. placenta*. As reported later in **Table 6**, testing with the synonymous *Fomitopsis lilacino-gilva* showed that the Micro CQ in that test gave the same threshold as ACQ-D. Thus, the performance in the second MSU E10 test may be anomalous or an indication of sensitivity of the quaternary portion of the formulation.

MSU researchers also conducted AWPA E22 Soil Block tests using the same four brown rot fungi and two white rot fungi. For the six fungi in the third MSU test, the thresholds for the micronized formulations were the same or better than the thresholds for the soluble products. Other E22 tests run by MSU gave the results shown as Test 4 and Test 5. It should be noted that the formulas listed were not tested at the same time but the results show similar thresholds as the other tests.

Michigan Technological University (MTU) and FPInnovations–Forintek Division (FOR) also conducted AWPA E10 Soil Block Tests (**Table 5**). MTU used southern pine for 3 brown rot fungi and birch (*Betula spp.*) for 3 white rot fungi. Again no meaningful differences in performance were seen between soluble and micronized formulations. The Forintek AWPA E10 Soil Block tests compared Micro CA and Micro CQ and *Coniophora puteana* was substituted for *N. lepideus*. The data showed relatively low thresholds in this test, however, the weight losses of the untreated controls were very high and virulence was not an issue in this test. The performances of the soluble and micronized products were generally similar in this test except for the copper tolerant *C. puteana*. In

Table 17. — Michigan State E11 leaching test results.

Formulation	Retention, kg/m <sup>3</sup>	Component loss (%)				
		Cu	Teb.	Quat	Cr	As
Micro CA-1	1.6	4.4	11.5			
	3.4	5.4	6.8			
	5.0	8.9	6.0			
Micro CA-2	1.6	4.1	5.3			
	3.4	5.4	2.6			
	5.0	7.6	4.3			
CA-B	1.6	11.5	8.4			
	3.4	16.4	5.4			
	5.0	23.0	5.7			
Micro CQ	4.0	4.1		7.7		
	6.4	5.2		7.7		
	9.6	7.5		5.4		
ACQ	4.0	8.6		7.0		
	6.4	23.5		10.0		
	9.6	26.0		5.0		
CCA - C	4.0	4.6			7.2	26.6
	6.4	9.8			10.2	35.4
	9.6	14.8			12.6	37.2

Table 18. — MSU and TPI E11 leaching test results.

Test-Institution	Formula	Retention, kg/m <sup>3</sup>	Component loss (%)			
			Copper	Quat	Chromium	Arsenic
1-MSU	Micro CQ	4.0	7.3	7.7	—	—
		6.4	6.4	8.0	—	—
1-MSU	ACQ-D	4.0	15.1	7.4	—	—
		6.4	19.3	6.4	—	—
1-MSU	CCA-C	4.0	4.4	—	6.8	30.3
		6.4	10.5	—	2.8	25.4
			Copper	Quat	Tebuconazole	
2-TPI	Micro CA	1.9	1.5	—	1.5	
		3.2	1.4	—	3.3	
2-TPI	ACQ-D	4.0	14.0	2.7	—	
		6.4	20.4	3.7	—	
3-TPI	Micro CA	1.6	2.14	—	BDL	
		3.2	2.18	—	BDL	
		4.8	1.86	—	BDL	
3-TPI	CA-B	1.6	5.42	—	27.59	
		3.2	6.29	—	20.33	
		4.8	9.74	—	18.32	

Table 19. — MSU E20 soil leaching test results.

	Component loss (%)	
	Copper	Quat
<b>4 kg/m<sup>3</sup> Retention</b>		
Micro CQ-SOIL 1	3.7	29.6
Micro CQ-SOIL 2	6.2	16.8
Micro CQ Average	5.0	23.2
ACQ-SOIL 1	15.8	29.8
ACQ-SOIL 2	23.4	15.1
ACQ Average	19.6	22.4
<b>6.4 kg/m<sup>3</sup> Retention</b>		
Micro CQ-SOIL 1	-4.1	22.3
Micro CQ-SOIL 2	9.3	19.2
Micro CQ Average	2.6	20.7
ACQ-SOIL 1	11.5	22.1
ACQ-SOIL 2	24.8	12.9
ACQ Average	18.2	17.5

Table 20. — TPI E20 soil leaching test results.

Formula	Retention, kg/m <sup>3</sup>	Component loss (%)		
		Copper	Quat	Tebuconazole
Micro CA	3.2	14.1	—	10.8
ACQ-D	6.4	26.6	7.3	—

this case, the Micro CQ did not perform as well as the Micro CA.

Ensis (formerly CSIRO) used the Australasian Wood Preservation Committee (AWPC) protocol for soil block testing that is functionally the same as the AWPA E10 test. After 12 weeks of exposure, the mass losses for leached blocks of radiata pine with brown rot fungi or eucalypt with white rot fungi were as shown in **Table 6**. In this case, the brown rot fungi used were: *Coniophora olivacea*, *Fomitopsis lilacino-gilva*, *Gleophyllum abietinum* and *Serpula lacrymans*. The white rot fungi used were *Perenniporia tephropora* and *Lopharia crassa*. The results show fungal control for micronized formulations at retentions comparable to or lower than the soluble ACQ-D and CA-B used in the test.

A second soil block test using AWPC procedures was conducted by Ensis using lower retentions. The copper tolerant *Postia placenta* was used in lieu of *S. lacrymans* in this second test. In both Ensis tests, the micronized products generally performed similar to or better than the soluble copper azole or CCA-C controls.

To summarize the above 8 soil block tests, the performance of the micronized systems is essentially the same as the soluble control formulations for a wide variety of brown rot and white rot fungi. In one test, the micronized formulations had a meaningful difference in the thresholds, but other tests contradict that result.

### Soil bed test summaries

The AWPA E23 Soil Bed test can be controlled to favor brown rot (*Basidiomycete* sp.) attack by keeping the soil moisture content in the range of 40 to 80 percent. Two soil bed tests were conducted favoring brown rot conditions by Mississippi State University researchers and the results are summarized in **Table 7**. It should be noted that the average percent strength loss is used to evaluate decay attack in this test. The two brown rot tests show similar performance for the two micronized formulations in **Table 7** with their matched soluble counterparts.

Similarly, the AWPA E23 test can be conducted where soft rot attack is favored by controlling the soil moisture near saturation (>90%). **Table 8** presents the results of the MSU E23 test under soft rot favoring conditions and there does not appear to be any differences in performance between the micronized and the soluble products in this soft rot test. It should be noted that the testing in **Table 7** and **8** was done at the same overall copper retention for both the azole and quaternary products.

Scion (formerly New Zealand Forest Research Institute) is currently conducting a

soft rot test. The AWPC protocol is being used with stock soil taken from the Scion forest nursery. The soil was wetted to more than 100 percent water holding capacity before stake installation and high soil moisture was maintained during exposure. Soil temperature was maintained at 79 °F (26 °C). There is no significant difference in the micronized and soluble products at comparable retentions in this soft rot test after 22 months (Fig. 1).

The results of the MSU and the Scion accelerated laboratory tests show that the soluble and micronized formulations have similar performance against soft rot fungi.

### Termite test summaries

AWPA E1 No Choice testing with Formosan Subterranean Termites (FST, *Coptotermes formosanus*) was done at Louisiana State University (LSU) and Mississippi State University with micronized formulations with the results shown in Table 9. As explained above, the co-biocide portions of the micronized formulations are slightly different and therefore designated by a numerical suffix. Also, note that consid-

Table 21. — TPI E12 coupon corrosion test results.

Coupon Type	Formula	Retention, kg/m <sup>3</sup>	Corrosion (mpy)
C1010 Steel	Micro CA	1.1	5.5
		2.3	8.0
		3.2	14.0
	CA-B	1.2	4.2
		2.6	8.3
		3.7	10.5
		Water only	0.2
Hot Dipped Galvanized	Micro CA	1.1	0.9
		2.3	1.3
		3.2	3.5
	CA-B	1.2	2.0
		2.6	3.3
		3.7	2.2
		Water only	-0.1
CDA 110 Copper	Micro CA	1.1	0.1
		2.3	0.1
		3.2	0.1
	CA-B	1.2	0.2
		2.6	0.3
		3.7	0.3
		Water only	0.1
2024 Aluminum	Micro CA	1.1	0.7
		2.3	2.2
		3.2	6.6
	CA-B	1.2	-0.1
		2.6	0.1
		3.7	0.1
		Water only	-0.1

Table 22. — E12 coupon corrosion test results.

Test-Institution	Formula	Retention, kg/m <sup>3</sup>	Corrosion (mpy)					
			Steel	HDG	Alum.	Brass	Copper	SS
1-TPI	Micro CA	1.9	2.56	1.10	0.19	0.07		
		3.7	2.06	2.14	-0.27	0.06		
	ACQ-D	4.5	8.67	-0.17	0.33	0.15		
		7.0	13.74	0.80	0.23	0.24		
	Untreated	—	-0.07	-0.66	0.38	0.03		
2-SUNY	Micro CA-1	3.4	1.7	1.9	0.1	0	0	0
		3.4	2.6	2.7	0.1	0	0	0.1
	CA-B	3.4	7.1	3.0	0	0	-0.2	0
	Micro CQ	6.4	1.6	1.6	0	-0.1	-0.1	0
	ACQ-D	6.4	7.7	3.2	0.1	0	-0.2	0
	CCA-C	6.4	1.6	2.1	0.1	0	-0.1	0
	Untreated	—	0.3	0.5	0	-0.1	-0.1	0
3-SUNY	Micro CQ-1	4.0	2.8	0.9	0.3	0.1		
		6.4	2.7	0.8	0.5	0.1		
	Micro CQ-2	4.0	3.5	1.0	0.4	0.1		
		6.4	4.4	1.1	0.4	0.1		
	ACQ-D	4.0	12.1	1.1	0.4	0.1		
		6.4	15.7	1.4	0.3	0.3		
	CCA-C	4.0	3.0	0.8	0.2	0.1		
		6.4	3.7	1.0	0.3	0.1		
	UNT		1.7	0.4	0.1	0.1		

Table 23. — Michigan State ISANTA fastener corrosion test results.

	Retention, kg/m <sup>3</sup>	Coated Screw	Dry Wall Screw	Sheet Metal Screw	Average weight loss (%)			
					HDG Nail	Common Nail	Aluminum Nail	Copper Nail
Micro CA-1	3.4	0.51	0.33	0.01	1.59	2.85	0	0.01
Micro CA-2	3.3	0.56	0.33	0.01	1.79	3.4	0.02	0
CA-B	3.3	1.29	0.38	0	2.82	5.2	0	0.01
Micro CQ	6.2	0.58	0.34	0	1.71	2.52	0.02	0
ACQ-D	6.2	1.38	0.4	0	3.35	6.28	0	0
CCA-C	6.4	0.69	0.37	0.01	1.64	2.23	0.01	0.01
UNT		0.65	0.37	0	1.51	1.41	0.01	0

Table 24. — ASTM D—143 bending strength test results.

Test	Institution	Formula	MOR <sup>a</sup>	MOE <sup>b</sup>	WML <sup>c</sup>
Test 1	MSU	Micro CQ (3.4 kg/m <sup>3</sup> )	0.99	0.97	1.09
		Micro CA-1 (3.4 kg/m <sup>3</sup> )	0.99	0.97	1.04
		Micro CA-2 (3.4 kg/m <sup>3</sup> )	1.03	0.98	0.95
		UNT	1	1	1
Test 2	SUNY-ESF	Micro CQ (6.1 kg/m <sup>3</sup> )	0.97	1.00	0.85
		ACQ (5.9 kg/m <sup>3</sup> )	1.03	1.06	0.69
		UNT	1	1	1
Test 3	TPI	Micro CA (5.4 kg/m <sup>3</sup> )	1.00	1.04	0.90
		CA-B (5.3 kg/m <sup>3</sup> )	0.98	1.01	1.04
		Water	1	1	1

<sup>a</sup> Modulus of Rupture <sup>b</sup> Modulus of Elasticity <sup>c</sup> Work to Maximum Load

erably lower retentions of some of the micronized formulations are tested in comparison to their respective soluble controls.

In the first LSU test, the results were consistent for the 3 micronized copper azole formulations since tebuconazole does not have insecticidal properties and the copper content was the same in each formulation. There was slight weight loss in both the experimental and ACQ-D (control) treatments but this is due to “nibbling” by these voracious termites.

Another No Choice E1 Formosan test at LSU compared two micronized formulations, Micro CA and Micro CQ, with ACQ-D, CA-B, CCA-C and untreated wood. In this test, at similar copper retentions, the performance of the micronized formulations was similar to that of the soluble systems.

Mississippi State University (MSU) also performed AWP E1 Formosan testing using the No Choice procedure. Essentially 100 percent termite mortality was obtained with all treatments and the two controls had <33 percent termite mortality. The micronized and the soluble treatment had similar weight losses and ratings in this test.

In a second E1 test conducted at MSU, the Choice procedures were followed and both Formosan and the common subterranean termite (*Reticulitermes flavipes*) were used. The samples were also tested in the leached and non-leached condition. The results comparing Micro CQ and ACQ-D are in **Table 10**. Again the various treatments had 100 percent termite mortality while the controls were

<33 percent, and again the performances of both the micronized and the soluble formulations were similar.

As shown by the above four tests, there is no meaningful difference in the performance of micronized formulations compared to their soluble counterparts or to other waterborne formulations for either common subterranean or Formosan termites. This is as expected since copper is the dominant termiticide in the formulations and it is present in equal amounts whether or not the formulation is micronized.

### Field efficacy tests

For most wood preservation researchers, the most important criteria for judging performance of a system is the comparative performance of that system against well-known standardized preservative systems in field efficacy tests. For many decades, the key indicator of long-term performance has been the relative ranking of the various retentions of the formulation compared to similar retentions of CCA-C. More recently, CA-B or ACQ-D have been the primary comparators but it should be kept in mind that these formulations were standardized based on their relative performance to CCA-C.

For this paper, the primary focus is on the relative performance of the micronized formulations compared to the soluble versions of the same formulation. There is no reason to believe that this relative performance between the micronized and the soluble systems will not continue

for longer periods of time. This provides a mechanism to gauge properties for micronized formulations for durations longer than the tests themselves.

### Field stake test summaries

The AWPA E7 Field Stake test method allows a variety of stake sizes which range from the relatively small Fahlstrom size (4 by 38 by 254 mm) up to the IUFRO size of 25 by 50 by 500 mm. The cross-section of the IUFRO stake is more than 8 times that of the Fahlstrom stake so the fastest approach to determine decay and termite attack is to use the small Fahlstrom stakes. The large surface to volume ratio provides an acceleration factor so performance can be determined in shorter exposure periods.

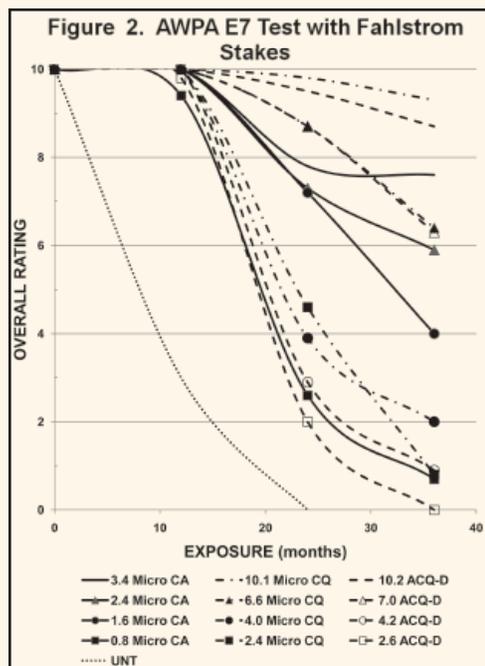
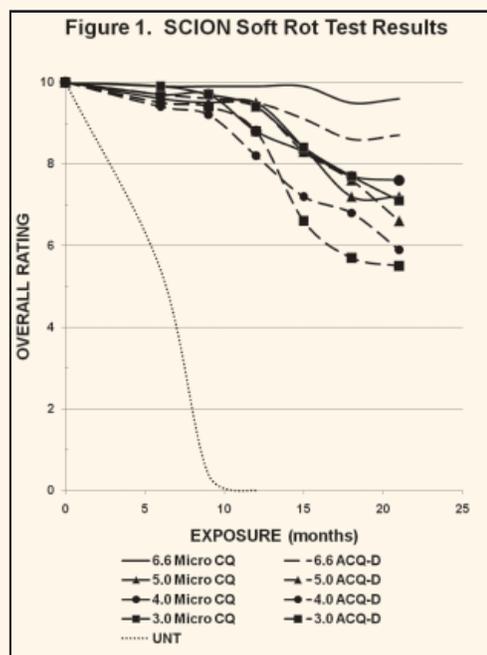
**Figure 2** shows a comparison of Micro CA, Micro CQ and ACQ-D at four different retention groups using Fahlstrom stakes in an AWPA E7 test in Gainesville, Florida. After 3 years of exposure, the highest retentions of the three formulations are rated at 8 or 9 while the next highest retentions are all grouped near a 6 rating. The third retention group is rated from 1 to 4 while the lowest retention group is at 1 or less. Importantly, the performance of the two micronized formulations matches that of the soluble formulation throughout the various retention groups. It should be noted that the last rating of all of the stakes was independently done by MSU personnel to avoid any bias.

A longer term AWPA E7 test with Fahlstrom stakes is shown in **Figure 3**. After 5 years of exposure in Gainesville, the Micro CQ at 6.4 kg/m<sup>3</sup> retention is clearly outperforming the ACQ-D at 6.7 kg/m<sup>3</sup> retention. The performance of the two systems in the two lower retention groups is the same though. Again the last inspection of these stakes was performed by MSU personnel.

An AWPA E7 test with 19 by 19 by 450 mm stakes is underway at Gainesville. The last inspection of these stakes was also performed by MSU personnel and the results are summarized in **Table 11**. The higher retention approximates the ground contact retention for each formulation while the lower retention is approximately the above ground retention. It is apparent that Micro CA and Micro CQ in this test are outperforming ACQ-D at both retention levels.

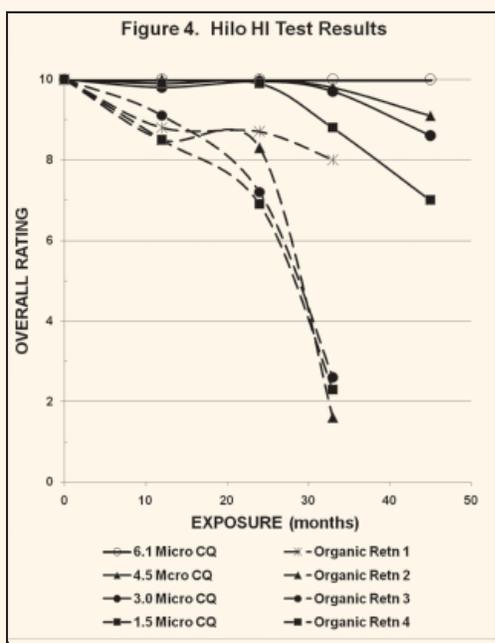
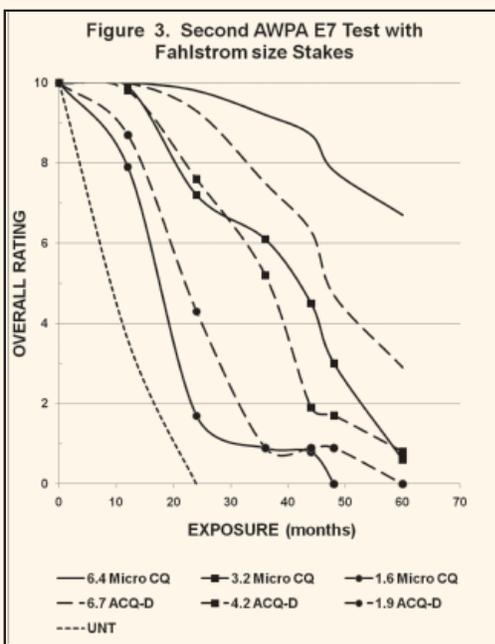
A second 19 mm stake test is currently being conducted by MSU at two sites in Mississippi and 2 year data are presented in **Table 12**. There is little differentiation between the formulas in this test and more exposure time will be needed for the treated specimens. The untreated controls are completely destroyed so there is good activity at these sites.

**Figure 4** shows test results with 19 mm stakes being conducted in Hilo, Hawaii, by Michigan Technological University. In this case, the comparator is a proprietary organic biocide system that was tested at comparable retention levels as the Micro CQ. Obviously, the Micro CQ is performing much better than the organic system. Soft rot cavities and narrow bore holes were found in the organic biocide stakes as well as the untreated stakes in this test (Stirling et al. 2007). This further demonstrates the soft rot resistance of the micronized formulations in test at this site.



A second MTU test in Hilo with 19 mm stakes has the results shown in **Table 13**. In this test, the lowest retention of Micro CA has about half the copper of the lowest retentions of the quaternary formulations so it is not surprising that these stakes are beginning to show some attack. There is considerable activity at the site since the untreated controls have failed completely.

A field stake test using Australasian Wood Preservation Committee (AWPC) procedures is being conducted by Ensis in Innisfail, Australia using 20 mm stakes. The 17-month ratings are available and these have been adjusted to the 10 scale familiar to North America researchers (**Table 14**). The micronized formulation has ratings that are somewhat better than the soluble formulation for the hardwood (Eucalypt) samples while there is



basically no attack on the softwood samples. The site is very aggressive as shown by the attack on the CCA treated Eucalypt and both the micronized and the amine formulations are performing better than the CCA treated hardwood. This suggests that soft rot control with the alternate formulations is better than the control with CCA. Soft rot control in hardwoods has been a long known problem with CCA (Hulme and Butcher 1977).

Overall, the 7 field stake tests show good efficacy of the micronized formulations. In every case, the performance of the micronized system was similar to or better than its soluble counterpart at equivalent retentions. The tests are being conducted in well-known, high hazard sites in Australia, Florida, Hawaii and Mississippi. There is no reason to believe

that the long-term performance of micronized systems will not match that of other waterborne systems.

### Ground proximity test summaries

Two AWP E18 ground proximity tests are underway in Hilo, Hawaii, and Saucier, Mississippi, under the auspices of MSU personnel. The first has only 12 months of exposure (Table 15) and has limited decay. The second has 27 months duration, and the Hawaii untreated controls are severely decayed. However, the two ground proximity tests need more exposure time to provide more discriminatory results.

### Field termite test summary

A field termite test was conducted by CSIRO personnel according to AWPC procedures. Blocks of either radiata pine (*Pinus radiata*) or spotted gum (*Corymbia maculata*) were treated with formulations, leached and then exposed to either *Coptotermes acinaciformis* or *Mastotermes darwiniensis* termites. The latter termite is a voracious feeder while the former is similar in aggressiveness to the Formosan subterranean termite found in the United States. For this test, the treated blocks were placed in metal "lunch box" containers that were attached by plastic pipe to termite infested trees. The test exposure continued until the untreated controls were destroyed, which was 12 months for the *C. acinaciformes* and 5 months for the *M. darwiniensis* (Table 16). The micronized formulation performed similarly to ACQ-D in this field test with these two termite species.

## Laboratory property tests

### Water leaching test summaries

AWPA E11 Leaching tests were conducted by Michigan State University (Table 17), Mississippi State University (Table 18) and twice by Timber Products (Table 18). The results of these tests show that the micronized systems lose considerably less copper than the amine-solubilized systems when evaluated in this aggressive leaching regime. In the first two tests, the micronized systems had about half of the copper losses as the soluble systems while in the third test, the losses of copper from the micronized system were only a tenth of the soluble system. Generally, the co-biocide losses are approximately the same — which is to be expected — except in the second TPI test where the tebuconazole losses were below the detection limit.

### Laboratory soil leaching test summaries

Mississippi State University researchers conducted AWP E20 Soil Leaching using two different soils (Table 19). One was obtained from the Saucier field test site while the other was purchased from a local agricultural cooperative. Surprisingly, the two soils had similar chemical and physical properties considering the considerably different sources. However the copper losses were generally higher in the agricultural soil. Overall though, the average copper losses from the micronized system were about one-fourth of the copper losses from the soluble system.

The second AWWA E20 test was done by Timber Products (**Table 20**), and the copper losses from the micronized formulation were about half those of the soluble system.

Results of the two soil leaching tests show that the micronized systems lose considerably less copper than the amine-solubilized systems. This is in agreement with the water leaching tests discussed above.

## Effects on treated wood properties

### Treated wood-metal coupon corrosion test results

All of the following AWWA E12 coupon corrosion testing was conducted with 10 replicates of each condition. This is a significant improvement over the 3 replicates used in the test standard since the test variability is considerably less with more replicates.

E12 coupon corrosion testing has been conducted by Timber Products Inspection on a number of micronized formulations. The results from one study are in **Table 21** where the micronized and amine treating solutions were chosen to cover the range of above ground and ground contact retentions for the formulation. Generally the rates for the Micro CA were similar to the rates for the soluble treatment except for aluminum. There the micronized version appeared to be more corrosive which is somewhat surprising in light of other tests.

Corrosion rates for additional E12 coupon corrosion tests conducted by TPI and the State University of New York—Environmental Science and Forestry (SUNY) are shown in **Table 22**. In the TPI test, the rates for the micronized formulation were similar to the soluble formulation for aluminum, brass and hot dipped galvanized and considerably lower for the mild steel.

SUNY-ESF researchers determined that the micronized formulations appeared to have lower or similar corrosion depending on the metal in one test. In a second corrosion test, SUNY-ESF determined the micronized formulations again show good corrosive properties relative to the other water-bornes. In this test, the corrosion rates for the micronized formulations were about one-third those of the soluble counterparts for mild steel.

These four tests show that, within the experimental variation, the corrosion rates determined for the micronized formulations were the same or better than those for the soluble formulations. In one case, it appeared that the micronized rate was high with aluminum but the other three tests showed that the micronized formulas perform well with this metal.

The protocol developed by the AWWA in cooperation with the International Staple, Nail and Tool Association (ISANTA) was used by Michigan State University researchers to evaluate fastener corrosion in contact with micronized formulations. The results in **Table 23** demonstrate that the micronized formulations had less corrosion with the seven screws and nails tested. In most cases, the micronized formulations had weight losses similar to or less than those for CCA-C.

### ASTM D-143 bending strength tests results

A number of bending strength tests have been performed

following ASTM D-143 procedures. Within a test series, the results can be compared to either the untreated or water-treated control. The results for 3 such tests are presented in **Table 24** and show that the micronized formulations do not impact strength properties to any significant degree. In fact, the micronized strength properties are usually within a few percent of those of the water treated or the untreated controls.

## Other test results

Two recent publications discussed copper-containing preservatives and presented results of nonstandard procedures (Goodell et al. 2007, Preston et al. 2008). At first glance, one would reach the conclusion that the first publication demonstrated that none of the commercially available (and soluble) copper preservatives are very effective while the second showed that the micronized formulations are even less effective than the soluble ones. Since these two conclusions run counter to the voluminous testing on the soluble and the micronized formulations, it appears reasonable to question the conclusions. It seems more likely that the results reported in these two papers are due to the nonstandard test procedures used where test samples were cut from larger pieces and little to no data were given on co-biocide analysis of the test specimens. The results of these nonstandardized tests are consistent with attack by copper tolerant fungi on internal parts of treated products rendered vulnerable by stripping of co-biocides and exposed to attack by cutting out test samples.

## Summary and conclusions

The results of the laboratory and field tests summarized above show that micronized formulations perform as well or better than their amine-solubilized counterparts. The laboratory biological efficacy tests for fungal decay, soft rot attack and termite resistance demonstrate similar thresholds or performance levels across the board. The field efficacy tests show good performance of the micronized systems at appropriate retentions for both above ground and ground contact applications. Property testing demonstrated that micronized systems leach less than the soluble counterparts and have improved corrosion properties. No deleterious effects were noted on strength properties.

The variety of copper-based wood preservatives has increased in recent years since copper exhibits good biocidal activity. However, any formulation of copper-based wood preservatives must be efficacious against copper-tolerant fungi. Several co-biocides are used to enhance efficacy against copper tolerant fungi. Copper remains the primary biocide component used to protect wood used in ground contact or fully exposed to the weather.

Copper can be fixed in wood through complexing, ligand exchange, chelating, and precipitation with wood components. Copper toxicity is associated with free cupric ion in a biological system and copper interferes with the metabolism of wood decay fungi.

Most copper-based products have found good growth markets in Europe and Japan, but only Copper Quarternaries and copper azole have seen large commercial success in the United States. Considerable research continues with copper-based preservatives, and the recent introduction of numerous micronized versions is an offshoot of that research. Extending the growth of copper-based preservatives into the future will depend on continued research improvements.

### Authors' Notes

This paper contains proprietary data that is the property of the owners of the original studies. The technology that is the subject of this paper is or may be subject to claims for protection under various U.S. and foreign patents and patent applications. By providing information to the authors for use in the preparation of this paper none of the parties providing such information in any way waive their rights pursuant to such patents and patent applications or intend in any manner to grant any license or permission, express or implied, to any other party (including without limitation the other parties providing information to the authors for use in the preparation of this paper) to use the technology.

The authors believe that in good faith no data or findings have been withheld from them in preparing this review and base their conclusions on data furnished to them under secrecy agreements and under waiver of non-disclosure terms.

### About the authors

Mike H. Freeman is an independent wood scientist in Memphis, Tennessee; (wooddoc@aol.com). Craig R. McIntyre is principal of McIntyre Associates, Inc. in Walls, Mississippi (craig@mcintyre-inc.com).

**The authors dedicate this article in loving memory of Mrs. Craig (Marie) McIntyre.**

### Precautions

This publication reports research and data involving pesticides. It does not contain recommendations for their specific or individual use, outside of the registered pesticide U.S. EPA label, nor does it imply that the uses discussed here have been registered. Appropriate State and/or Federal agencies must register all uses of pesticides before they can be recommended. Some pesticides discussed in this article are restricted use pesticides (RUP's) and can only be purchased and used by a certified pesticide applicator.

Pesticides can be injurious to humans, domestic animals, desirable plants, and fish or other wildlife if they are not handled or applied properly. Use all pesticides selectively and carefully. Follow recommended practices for the disposal of surplus pesticides and pesticide containers. Always read and follow U.S. EPA approved labeling and use the product only for its intended use and at the approved use rate. Remember, the label is the law; Material Safety Data Sheets are for guidance only.

### References

- Archer, K. 2007. Cell wall penetration of particulate copper wood Preservative systems in southern pine. Unpublished oral presentation at 38<sup>th</sup> Annual Meeting. Int. Res. Group on Wood Pres., IRG Secretariat, Stockholm.
- Archer, K and Preston, A. 2006. An overview of copper based wood preservatives. Wood protection 2006. <http://www.forestprod.org/woodprotection06archer.pdf>.
- American Wood Protection Association (AWPA). Book of Standards. 2008. pp. 5–07.
- Arsenault, R.D. (1973). Factors influencing the effectiveness of preservative systems. In: Wood Deterioration and Its Prevention by Preservative Treatments, D.D. Nicholas (ed.). Vol 2, pp. 121–278. Syracuse University Press, New York.
- Barnes, H. M.; Amburgey, T. L.; Freeman, M. H.; Brient, J. A. 2001. Copper naphthenate-treated hardwoods. Proc., American Wood-Preservers' Association 97:15–23.
- Bull D. C. 2001. The chemistry of chromated copper arsenate II. Preservative-wood interactions. Wood Science and Tech. 34(6): 459–466.
- Buschhaus, H-U and A.R. Valcke, 1995. Triazoles: Synergism between Propiconazole and Tebuconazole. IRG/WP/95-30092. Int. Res. Group on Wood Pres., IRG Secretariat, Stockholm.
- Byrne, Tony. 1994. Technical Note of Anti-Sapstain Chemicals Effectiveness to the Forintek Stakeholders. 4 pp.
- Cao, J. and D.P. Kamdem, 2005. Microdistribution of Copper in Copper-Ethanolamine (Cu-EA) treated southern yellow pine (*Pinus spp.*) related to Density Distribution. *Holzforschung*, 59:82–89.
- Cao, J. and Yu, L. 2007. Copper fixation in ACQ-D treated Chinese fir at various temperature and relative humidity conditions. IRG/WP/07–30436. Int. Res. Group on Wood Pres., IRG Secretariat, Stockholm.
- Cervantes, C. and Gutierrez-Corona, F. 1994. Copper resistance mechanisms in bacteria and fungi. *Microbiology Reviews*. 14(2):121–137.
- Choi, S.M., J.N.R. Ruddick and P.I. Morris. 2002. The copper tolerance of mycelium vs spores for two brown rot fungi. IRG/WP 02–10422. Int. Res. Group on Wood Pres., IRG Secretariat, Stockholm.
- Clausen, C.A and F. Green. 2003. Oxalic acid overproduction by copper-tolerant brown-rot basidiomycetes on southern yellow pine treated with copper-based preservatives. *International Biodeterioration & Biodegradation*. 51(2):139–144.
- Clausen, C.A., Green III, F., Woodward, B. M., Evans, J.W and DeGroot R.C. 2000. Correlation between oxalic acid production and copper tolerance in *Wolfiporia cocos*. *International Biodeterioration & Biodegradation* 46:69–76.
- Cooper, P.A. 1991. Cation exchange adsorption of copper on wood, *Wood Preservation* 1(1): 9–14.
- Cooper, P.A., D. Jeremic, L.L. Taylor, Y.T. Ung and F. Kazi. 2001. Effect of Humic Acid on leaching of CCA from treated Wood., *For. Prod. J.*, 51(9):73–77.
- Dawson-Andoh, B.E. and D.P. Kamdem, 1998. Application of environmental scanning electron microscopy to the study of macrodistribution of copper in copper naphthenate treated hardwoods, *Holzforschung* 52: 603–606
- De Groot R.C. and Woodward, B. 1999. Using copper-tolerant fungi to biodegrade wood treated with copper-based preservatives. *International biodeterioration & biodegradation* 44:17–27. 26.
- Freeman, M.H. 2002. Waterborne Copper Naphthenate– A Chromium and Arsenic Free Wood Preservative Chemical. Proceedings of the 2002 FPS Wood Preservation Workshop, Orlando, Florida. FPS, Madison, Wisconsin.
- Freeman, M., Kamdem, P. and Brient, J. A. 2004. Water-borne copper naphthenate: a chromium and arsenic free preservative for wood and composites. Poster presented at Environmental Impacts of Preservative-Treated Wood Conference. Orlando, Florida.
- Goodell, B., J. Jellison, J. Loferski and S.L. Quarles, 2007. Brown Rot Decay of ACQ and CA-B Treated Lumber, *For. Prod. J.*, 57: 31–33.
- Grace, K., R.T. Yamamoto and P.E. Laks, 1993. Laboratory evaluation of copper naphthenate pressure treatments against the Formosan subterranean termite. IRG/WP/93–10005. Int. Res. Group on Wood Pres., IRG Secretariat, Stockholm.
- Groenier, J.S. and S. Lebow. 2006. Preservative-Treated Wood and Alternative Products in the Forest Service. USDA Forest Service. TE42G01—Technical Services ECAP.
- Gunther, M.R., Hanna, P.M., Mason, R.P. and Cohen, M.S. 1995. Hydroxyl radical formation from cuprous ion and hydrogen peroxide: A spin-trapping study. *Archives of Biochemistry and Biophysics*. 316(1):515–522.
- Hale, M.D. and Eaton R.A. 1986. Soft-rot cavity formation in five preservative-treated hardwood species. *Trans. Br. Mycol. Soc.*, 86:585–590.
- Hughes, A.S. 2004. The tools at our disposal. Final Workshop COST Action E22 'Environmental optimisation of Wood Protection' Lisboa – Portugal, 22nd – 23rd March 2004.
- Hulme, M.A. and J.A. Butcher. 1977. Soft-rot control in hardwoods treated

- with chromated copper arsenate preservatives. I. Treatment problems. *Material und Organismen* 12 (2): 81–95
- Humar, M., Sentjurc, M., Amartey, S.A and Pohleven, F. 2005. Influence of acidification of CCB (Cu/Cr/B) impregnated wood on fungal copper tolerance. *Chemosphere*. 58(6): 743–749.
- Humar, M., Bucar, B., Zupancic, M., Zlindra, D and Pohleven, F. 2007. Influence of ethanolamine on lignin depolymerization and copper leaching from treated Norway spruce and beech wood. IRG/WP/07–30423. Int. Res. Group on Wood Pres., IRG Secretariat, Stockholm.
- Kamdem, D.P., Fair R., and Freeman, M. 1996. Efficacy of waterborne emulsion of copper naphthenate for northern red oak (*Quercus rubra*) and soft maple (*Acer rubrum*). *Holz als Roh- und Werkstoff* 54 :183–187.
- Leach, R. M. and Zhang, J. 2006. Micronized wood preservative compositions. United States Patent Application 20060288904.
- Lebow, S. 1996. Leaching of wood preservative components and their mobility in the environment: summary of pertinent literature. Forest Products Laboratory General Technical Report. FPL-GTR-93. 36 pp.
- Lebow, S. 2007. Preservative treatments for building components. In: *Wood Protection 2006*. Forest Prod. Society. Pub. No. 7229. [www.fpl.fs.fed.us/documnts/pdf2007/fpl\\_2007\\_lebow001.pdf](http://www.fpl.fs.fed.us/documnts/pdf2007/fpl_2007_lebow001.pdf)
- Lebow, S., Winandy, J. and Bender, D. 2004. Treated Wood in Transition: A Look at CCA and the Candidates to Replace It. *Wood Design Focus*. Summer 2004. 4–8.
- Matsunaga, H., Kiguchi, M and Evans, P. 2007. Micro-distribution of metals in wood treated with a nano-copper wood preservative. IRG/WP/07–40360. Int. Res. Group on Wood Pres., IRG Secretariat, Stockholm.
- Matsunaga, H., Kiguchi, M, B. Roth and Evans, P. 2008. Visualisation of metals in pine treated with preservative containing copper and iron nanoparticles, IAWA J (In Press).
- Mitsuhashi, J., Morrell, J.J., Jin, L., Preston, A.F. 2007. The effect of additives on copper losses from alkaline copper treated wood. IRG/WP/07–50246. Int. Res. Group on Wood Pres., IRG Secretariat, Stockholm.
- Morrell, J.J. 1991. Copper tolerant fungi: a brief review on their effects and distribution. *Proceedings, American Wood-Preservers' Association* 87:265–70.
- Morrell, J.J. 2005. Protection of wood based materials. In *Handbook of environmental degradation of materials*. ed. Kutz, M. pp. 313. William Andrew Publishing.
- Murphy, R.J. and Levy J.F. 1983. Production of copper oxalate by some copper tolerant fungi. *Transactions of the British Mycological Society* 81:165–168.
- Myers, D.F., Fyler, J.M., Palmer, C.H and Rosebery, G. D. 1989. Oxine copper (NYTEK R GD) for the control of mold and sapstain on lumber in North America. International Research Group on Wood Preservation. IRG/WP/3517. Int. Res. Group on Wood Pres. IRG Secretariat, Stockholm.
- Nicholas, D.D. and Schultz, T.P. 1997. Comparative performance of several ammoniacal copper preservative systems., IRG/WP 97–30151. Int. Res. Group on Wood Pres., IRG Secretariat, Stockholm.
- Nilsson, K. and J. Bjurman, 1998. Chitin as an indicator of the biomass of two wood-decay fungi in relation to temperature, incubation time, and media composition. *Can. J. Microbiol.* 44(6): 575–581.
- Petri, M., Murphy, R.J and Morris, I. 2000. Microdistribution of Some Copper and Zinc Containing Waterborne and Organic Solvent Wood Preservatives in Spruce Wood Cell Walls. *Holzforschung* 54:(1) 23–26.
- Pizzi, A. 1982a. The chemistry and kinetic behavior of Cu-Cr-As /B wood preservatives. III. Fixation of the Cu/Cr system on wood. *J. Polym. Sci.: Polym. Chem. Ed.* 20: 725–738.
- Pizzi, A. 1982b. The chemistry and kinetic behavior of Cu-Cr-As /B wood preservatives. Part 4. Fixation of CCA to wood. *J. Polym. Sci.: Polym. Chem. Ed.* 20: 739–764.
- Pohleven, F and Humar, M. 2006. Addition of boron compounds and octanoic acid for improvement of biocidal properties and copper fixation at copper-ethanolamine based wood preservatives. IRG/WP/06–30408. Int. Res. Group on Wood Pres., IRG Secretariat, Stockholm.
- Preston, A. F., Walcheski, P. J. and McKaig, P. A. 1985. Recent studies with ammoniacal copper carboxylate preservatives. *Proceedings, American Wood-Preservers' Association* 81:30–39.
- Preston, A.F., L. Jin, D. D. Nicholas, A. Zahora, P. Walcheski, K. Archer and T. Schultz. 2008. Field stake tests with copper-based preservatives. IRG/WP 08–30459. Int. Res. Group on Wood Pres., IRG Secretariat, Stockholm.
- Rhatigan, R.G., J.J. Morrell, and A.R. Zahora. 2000. Marine performance of preservative treated Southern pine panels. Part-I. Exposure in Newport, Oregon. IRG/WP/00–10368. Int. Res. Group on Wood Pres., IRG Secretariat, Stockholm.
- Richardson, H.W. 1997. A handbook of copper compounds and applications. Richardson, H.W. and R.L. Hodge 2004. Particulate Wood Preservative and Method for Producing Same. United States Patent Application 20040258768.
- Richardson, H.W. and R.L. Hodge 2006. Milled submicron organic biocides with narrow particle size distribution, and uses thereof. United States Patent Application 20060086841.
- Roussel, C. J.P. Haluk, A. Pizzi and M-F. Thevenon, 2000. Copper based wood preservative – a new approach using fixation with resin acids of rosin. IRG/WP/00–30249. Int. Res. Group on Wood Pres., IRG Secretariat, Stockholm.
- Ruddick, J.N.R. and Xie, C. 1994. Influence of the enhanced nitrogen in ammoniacal copper treated wood on decay by brown and white rot fungi. *Material und Organismen*. 29(2): 93–104.
- Ruddick, J.N.R., Xie, C. and Herring F.G. 2001. Fixation of amine copper preservatives. Part 1. Reaction of vanillin, a lignin model compound with monoethanolamine copper sulphate solution. *Holzforschung* 55(6): 585–589.
- Rui, C. and Morrell J.J. 1994. Assessing biocide effects on protoplasts of wood decay fungi. *Wood Fiber Sci.* 26:205–211.
- Ryan, K.G. and J.A. Drysdale, 1988. X-ray analysis of copper, chromium and arsenic within the cell walls of treated hardwoods – new evidence against the microdistribution theory. *J. Institute Wood Sci.*, 11: 108–113.
- Scalbert A., Cahill, D., Dirol, D., Navarrete M.A., De Troya, M.T., Van Leemput, M. 1998. A Tannin/Copper preservation treatment for wood. *Holzforschung* 52(2):133–138.
- Schultz, T.P., Nicholas, D.D and Henry W.P. 2003. Efficacy of a copper(II)/oxine copper wood preservative mixture after 69 months of outdoor ground-contact exposure and a proposed mechanism to explain the observed synergism. *Holzforschung*. 59(3):370–373.
- Simpson, J.A., K.H. Cheeseman, S.E. Smith, and R. T. Dean. 1988. Free-radical generation by copper ions and hydrogen peroxide. *The Biochemical journal*. 254: 519–523.
- Smart, R and Wall, W. 2006. Copper borate for the protection of engineered wood composites. IRG/WP/06–40334. Int. Res. Group on Wood Pres., IRG Secretariat, Stockholm.
- Somers, E. 1963. The uptake of copper by fungal cells. The uptake of copper by fungal cells. *Annals of Applied Biology* 51(3):425–437.
- Steenkjaer Hastrup, S.C., Green III, F., Clausen, C.A., Jensen, B. 2005. Tolerance of *Serpula lacrymans* to copper-based wood preservatives. *International Biodeterioration & Biodegradation* 56 :173–177.
- Stirling, R., J. Drummond, J. Zhang and R. Ziobro. 2008. Micro-distribution of micronized copper in southern pine. IRG/WP/ 08–30479. Int. Res. Group on Wood Pres., IRG Secretariat, Stockholm.
- Sutter, H.P., Jones, E.B.G. and Walchli, O. 1983. The mechanism of copper tolerance in *Poria placenta* (Fr.) Cke. and *Poria vaillantii* (Pers.). *Fr. Material und Organismen* 18(4):241–262.
- Thomason, S.M. and E.A. Pasek. 1997. Amine copper reaction with wood components: acidity versus copper adsorption. IRG/WP/ 97–30161. Int. Res. Group on Wood Pres., IRG Secretariat, Stockholm.
- Ung, T.Y and Cooper, P.A. 2005. Copper stabilization in ACQ-D treated wood: retention, temperature and species effects. *Holz als Roh- und Werkstoff*. 63(3):186.
- Vesentini D., Dickinson D. J. and Murphy R. J. 2006a. Analysis of the hyphal load during early stages of wood decay by basidiomycetes in the presence of the wood preservative fungicides CuSO<sub>4</sub> and cyproconazole. *Holzforschung*. 60:637–642.
- Vesentini D., Dickinson D. J. and Murphy R. J. 2006b. Fungicides affect the production of extracellular mucilaginous material (ECMM) and the peripheral growth unit (PGU) in two wood-rotting basidiomycetes. *Mycological Research* 110: 1207–1213.
- Wakeling, R. 2006. Above and below-ground depletion of copper, chromium and arsenic from *Pinus radiata* and *Fagus sylvatica* at thirteen test sites in New Zealand and Australia. IRG/WP/06–30402. Int. Res. Group on Wood Pres., IRG Secretariat, Stockholm.
- Woodward, B. and De Groot R. 1999. Tolerance of *Wolfiporia cocos* isolates to copper in agar media. *Forest products journal*. 49(4):87–94.
- Xie, C, J.N.R. Ruddick, S.J. Tettig and F.G. Herring. 1995. Fixation of ammoniacal copper preservatives: Reaction of vanillin, a lignin model compound with ammoniacal copper sulphate solution, *Holzforschung* 49: 483–490.
- Zahora, A.R., A.F. Preston, K.J. Archer, and S. Kleinschmidt. 2000. Marine performance of preservative treated southern pine panels. Part-II. Exposures at Mourilyan Harbour, Queensland, Australia. IRG/WP/00–10337. Int. Res. Group on Wood Pres., IRG Secretariat, Stockholm.
- Zhang, J. and Kamdem, D.P. 2000. FTIR characterization of copper ethanolamine—wood interaction for wood preservation. *Holzforschung* 54: 119–122.
- Zhang, J. and Leach, R.M. 2005. Non-alkaline micronized wood preservative formulations. United States Patent Application 20060086284.
- Zhang, Y. and Jiang, M. 2006. Corrosiveness of metal by copper-based preservatives. IRG/WP 06–40329. Int. Res. Group on Wood Pres., IRG Secretariat, Stockholm.