Micronized Copper

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ABSTRACT

Micronized copper preservative systems is estimated to be about 80% of the lumber treated with waterborne preservatives in the USA today. Soil block, fungal cellar and field stake test data will be presented for micronized copper systems with primary emphasis on micronized copper quaternary systems. The copper portion of the formulations is present as a fine dispersion of "micro" particulates while the co-biocide is present as either a quat or an azole. Generally, this testing used the amine based counterpart as the control preservative system and the micronized formulations perform as well or better than the amine formulations. For example, in one 5 year field stake test in Gainesville, FL, the micronized copper quaternary formulation significantly outperformed the amine copper quaternary formulations. Strength and fixation testing is also discussed.

Keywords: Efficacy, micronized copper, amine copper, quat, azole, strength, fixation

INTRODUCTION

Water-borne micronized copper formulations

Copper-based preservatives have been widely and successfully used for more than a century (Richardson 1997). The volume of wood products treated with copper-based preservatives grew exponentially during the 1970s and 1980s and remains high today (Archer and Preston, 2006). The focus on predominantly copper-based preservatives has increased following the voluntary withdrawal from the residential market of chromated copper arsenate (CCA) in 2003.

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. These formulations include quats or azoles as cobiocides. Recently micronized copper formulations with the same co-biocides have come into use. This paper presents a comparison of the performance of micronized formulations with their amine solubilized counterparts.

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. A comprehensive review of copper wood preservatives including micronized formulations was recently published (Freeman and McIntyre 2008).

Micronized particles are produced by mechanical grinding of water- or oil-insoluble copper compounds with the 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 dispersing agents are polymeric dispersants, which attach to the surface of particles and repel 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. 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.

Any suitable copper source can be used to obtain micronized particles but basic copper carbonate is most commonly used. 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 systems 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.

Matsunaga et al. (2007) used field emission scanning electron microscopy (SEM) coupled with x-ray microanalysis (EDAX) to examine 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. In further work, Matsunaga et al. (2008) measured the copper concentrations in the middle lamella and secondary cell walls of latewood and found no significant differences between the micronized copper treated products and the amine treated products. They also reported that elemental copper is present within cell walls of the micronized treated wood even though the majority of the copper particles are too large to penetrate the cell wall's nanocapillary network

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).

As well, a recent publication discussed micronized copper containing preservatives and presented results of non-standard procedures (Preston et al. 2008). At first glance, the paper purportedly showed that the micronized formulations are less effective than the soluble ones. However, this runs counter to the voluminous testing on the soluble and the micronized formulations so it appears reasonable to question the conclusion. It seems more likely that the results reported are due to the non-standard 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 non-standardized 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.

This paper presents some of the test data on micronized copper preservatives. More complete data is available in Freeman and McIntyre, 2008 and it is intended to prepare an American Wood Protection Association (AWPA) data package on micronized copper systems for submittal in Fall 2009.

MATERIALS AND METHODS

Testing Organizations

The experimental work reported here was done at test organizations that are third party evaluators and most are ISO 17025 accredited (with the exception of the E19 Test). Standard reports were received from

the test organizations. Review of the reports showed that all critical procedures were followed for the particular test.

The formulation designated as Amine CQ is ACQ-D while Micro CQ is the micronized counterpart. Similarly, Micro CA is the micronized version of CA-B (Wolman E). All retentions are expressed as kg/m^3.

Soil Block Testing

AWPA E10 or E22 Soil Block tests have been conducted at three different organizations: Mississippi State University (MSU), Michigan Technological University (MTU) and FPInnovations—Forintek (FOR). Soil block thresholds for brown-rot fungi are in Table 1 and Table 2 has the thresholds for white-rot fungi. 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.

Ensis conducted similar soil block tests using the Australian Wood Preservation Council (AWPC) protocol (Table 3) using Radiata pine (*Pinus radiata*) for the brown rot fungi and Eucalypt (*Eucalyptus delegatensis)* for the white rot fungi. The first test used one micronized copper quaternary system while the second test used two variants of the micronized azole designated as 1 and 2 in the table.

Table 1. Soil Block Thresholds for Brown-rot Fungi

			Brown-rot fungi Thresholds, kg/m^3				
Test-Institution	Formula	Cond.[a]	*G. trabeum*	*P. placenta*	*N. lepideus*	*T. lilacino-gilva*	*C. puteana*
E10-MSU	Micro CQ	L	3.5-4.2	8.3-8.6	<2.4	4.5-4.8	--
		NL	3.7-4.2	8.3-8.6	<2.4	6.1-6.4	--
E10-MSU	Amine CQ	L	4.2-4.5	7.0-7.4	<2.4	<2.4	--
		NL	4.2-4.5	<2.4	<2.4	<2.4	--
E10-MTU	Micro CA	L	<0.83	1.5	<0.83	--	--
		NL	<0.83	1.5	<0.83	--	--
E10-MTU	Amine CQ	L	2.1	2.1	<1.2	--	--
		NL	2.1	<1.2	<1.2	--	--
E10-FOR	Micro CA	L	<0.83	0.83	--	--	0.83-1.7
E10-FOR	Micro CQ	L	<1.0	<1.0	--	--	5.5
E22-MSU	Micro CA	NL	<0.80	1.6-2.4	<0.80	--	--
E22-MSU	Amine CQ	NL	1.2-2.4	1.2-2.4	1.2	--	--

[a]L = leached and NL = not leached

Table 2. Soil Block Thresholds for White-rot Fungi

			White-rot fungi Thresholds, kg/m^3		
Test-Institution	Formula	Cond.[a]	*Pl. ostreatus*	*T. versicolor*	*I. lacteus*
E10-MSU	Micro CQ	L	--	4.5-4.8	<2.4
		NL	--	6.1-6.4	<2.4
E10-MSU	Amine CQ	L	--	<2.4	<2.4
		NL	--	<2.4	<2.4
E10-MTU	Micro CA	L	<0.83	<0.83	<0.83
		NL	<0.83	<0.83	<0.83
E10-MTU	Amine CQ	L	<0.83	<0.83	<0.83
		NL	<0.83	<0.83	<0.83
E10-FOR	Micro CA	L	<0.83	--	<0.83
E10-FOR	Micro CQ	L	<1.0	--	<1.0
E22-MSU	Micro CA	NL	--	<0.80	<0.80
E22-MSU	Amine CQ	NL	--	<1.2	<1.2

[a]L = leached and NL = not leached

Table 3. Ensis AWPC soil block test results.

		Threshold, kg/m^3					
	Formula	*C. olivacea*	*F. lilacino-gilva*	*G. abietinum*	*S. lacrymans*	*P. tephropora*	*L. crassa*
	Fungi[a]→	BR	BR	BR	BR	WR	WR
Test 1	Micro CQ	1.9-3.2	1.0-1.9	<1.0	1.9-3.2	<1.0	<1.0
	Amine CQ	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
Test 2	Micro CA-1	<0.60	>1.3	<0.60	1.0-1.3	<0.60	<0.6
	Micro CA-2	<0.60	>1.3	<0.60	>1.3	<0.60	--
	Amine CA	<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

[a]BR = Brown Rot; WR = White Rot

Fixation Testing

AWPA E19 fixation testing was conducted on southern pine (*Pinus sp.*). Figures 1, 2 and 3 present the results for the 4.0, 6.4 and 9.6 kg/m3 retention samples, respectively.

Figure 1. Fixation of 4.0 kg/m^3 retention samples.

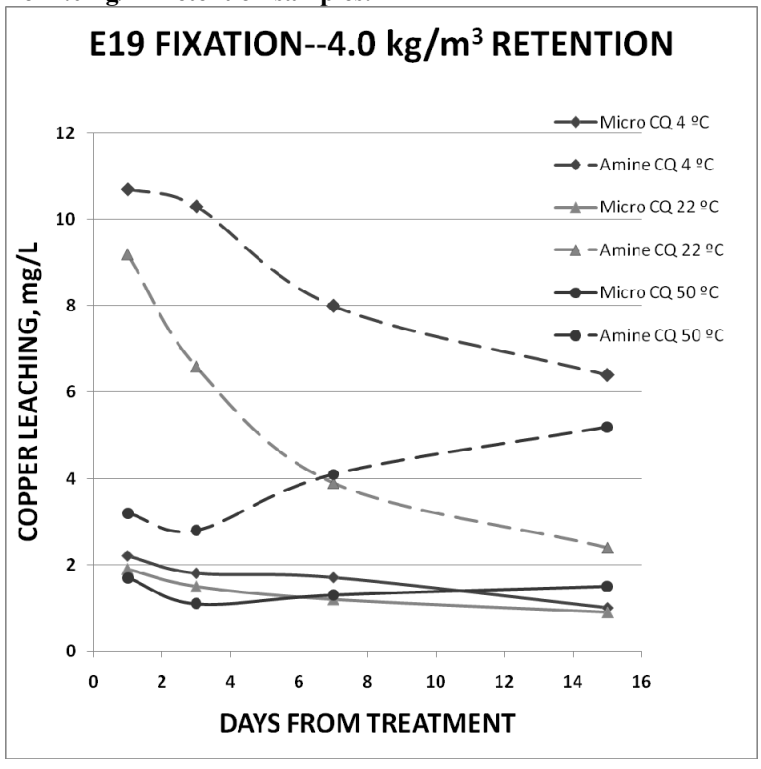


Figure 2. Fixation of 6.4 kg/m^3 retention samples.

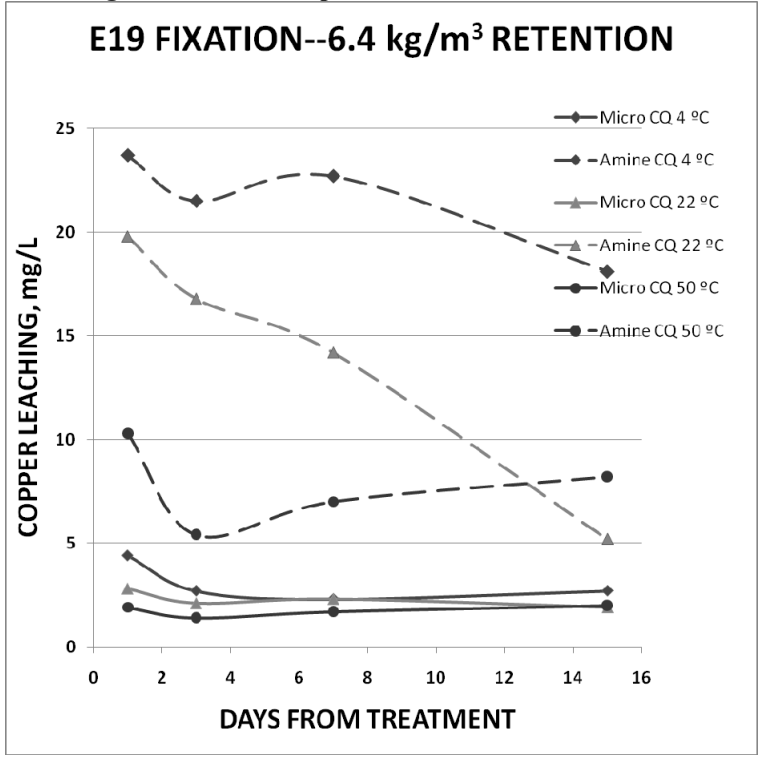
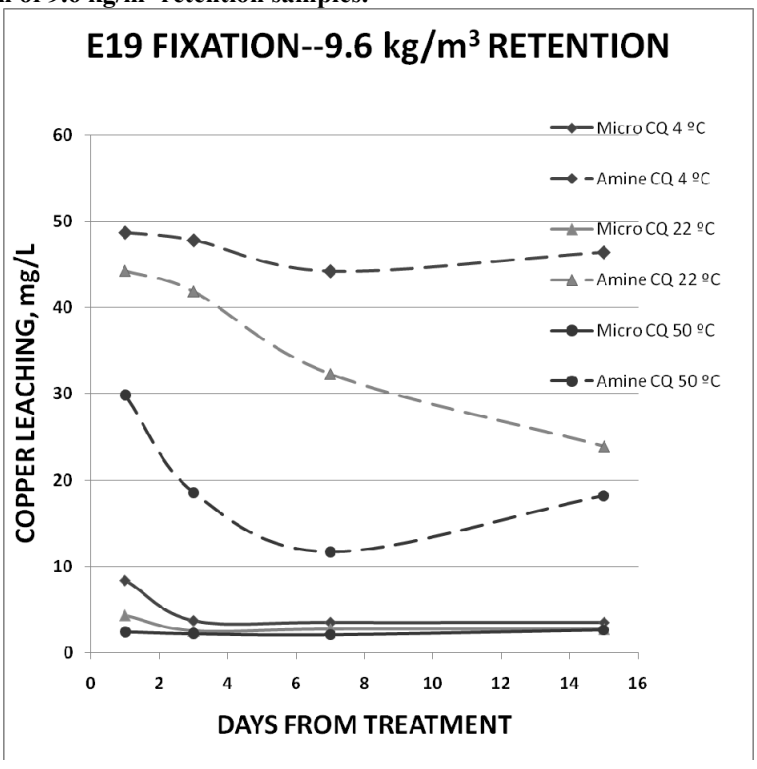


Figure 3. Fixation of 9.6 kg/m^3 retention samples.



Generally, the fixation testing at room temperature (22 ºC) shows that the micronized formulation loses from 1-4 mg/L depending on the initial retention while the amine formulation loses from 5 to 10 times as much. At the same starting retention, the micronized formulation would maintain more actives in the wood with time. This and other data should allow a slight reduction in the starting retention for the micronized formulations since they will have an "aged" retention as that of the equivalent amine solubilized formulation.

Cooper et al (2008) showed that the leaching from MCQ treated wood approximated the copper losses from CCA and was always much smaller than the losses from ACQ. Cooper conducted laboratory tests and found that the MCQ leaching was about 10% that of ACQ while in 2 year field tests, the losses from MCQ were also about 10% those of ACQ. Soil tests done by Cooper showed that MCQ lost about half of the copper that ACQ did.

Termite Testing

Termite Testing was conducted by CSIRO with both *Coptotermes acinaciformis* and *Mastotermes darwiniensis*. These results were discussed by Cookson *et al.* (2008).

The "Lunch Box" protocol of the AWPC was used in which termites are attracted into a steel container that contains the test specimens. After 12 months of exposure, the mass loss of the various formulations was determined. The tests with Radiata Pine (*P. radiata*) are in Table 4 and the tests with Spotted Gum (*Corymbia maculata*) are in Table 5. Note that the water treated controls were completely destroyed by the *M. darwiniensis* and severely attacked by the *C. acinaciformes*.

Table 4. CSIRO AWPC Lunch Box Termite test results with Radiata Pine.

Radiata Pine		Mass Loss, %	
Formula	Retention, kg/m^3	*C. acinaciformes*	*M. darwiniensis*
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	94.0

Table 5. CSIRO AWPC Lunch Box Termite test results with Spotted Gum.

Spotted Gum		Mass Loss, %	
Formula	Retention, kg/m^3	*C. acinaciformes*	*M. darwiniensis*
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

Field Stake Tests

Various field stake tests have been conducted. The tests reported here follow the AWPA protocol which allows various sizes of stakes. Note that some tests were conducted with the small, Fahlstrom size stake (4 x 38 x 254 mm). Southern pine was used in all cases.

Figure 4. Stake Test 1 in Gainesville, FL with Fahlstrom Stakes

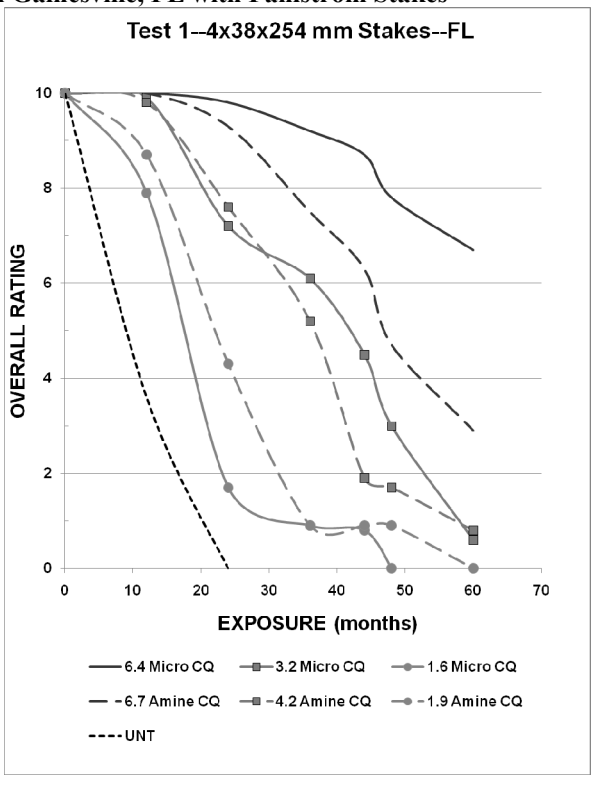


Figure 5. Stake Test 2 in Gainesville, FL with Fahlstrom Stakes

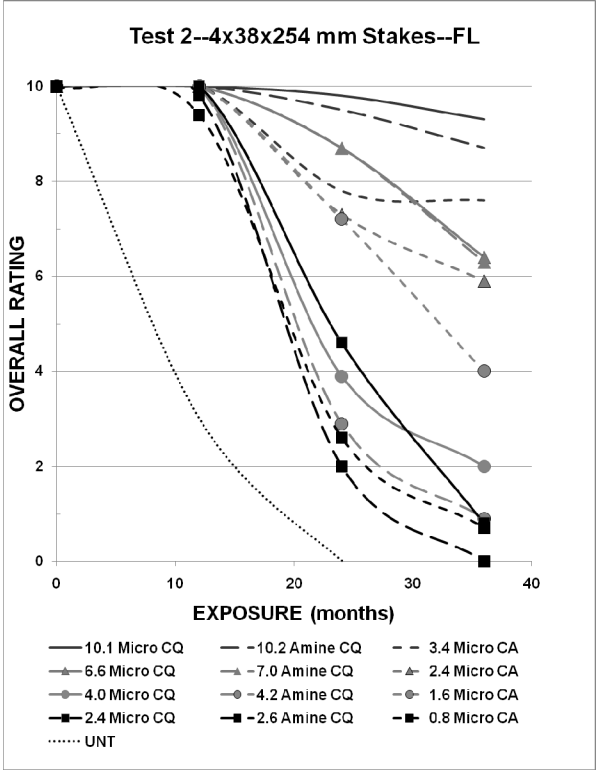
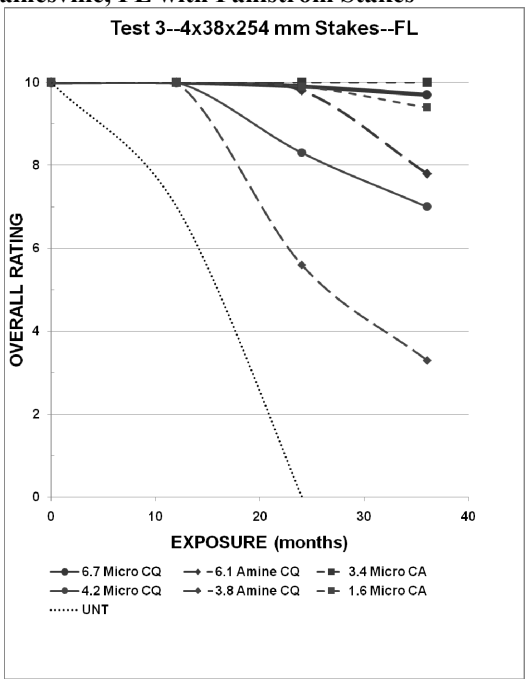
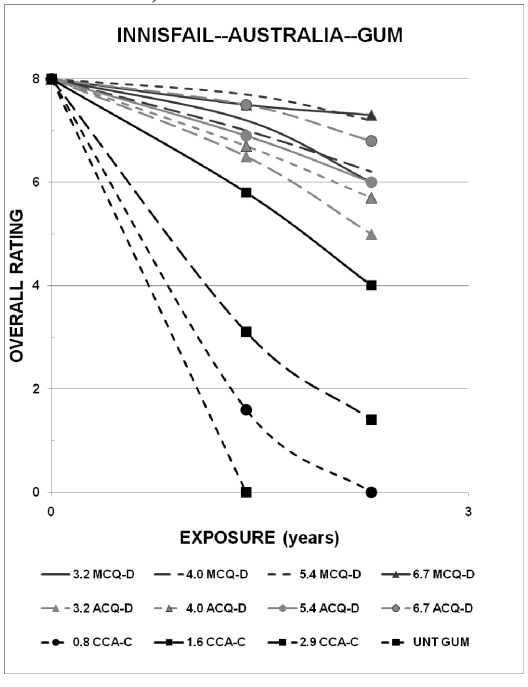


Figure 6. Stake Test 3 in Gainesville, FL with Fahlstrom Stakes



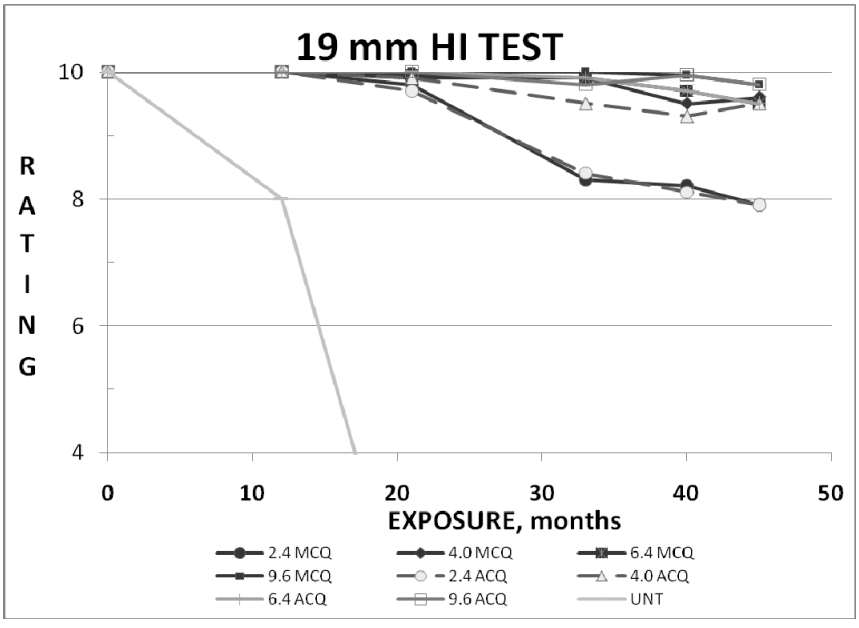
Additional field testing using AWPC procedures was reported by Cookson *et al* (2008) using both radiata pine and gum. There is little differentiation for the pine but the gum is shown in Figure 7.

Figure 7. CSIRO Stake Test in Innisfail, Australia with Gum Stakes



Larkin *et al* (2008) reported on 19 mm stake tests being conducted in Hawaii using AWPA E7 procedures.

Figure 8. AWPA 19 mm Stake Test in Hawaii

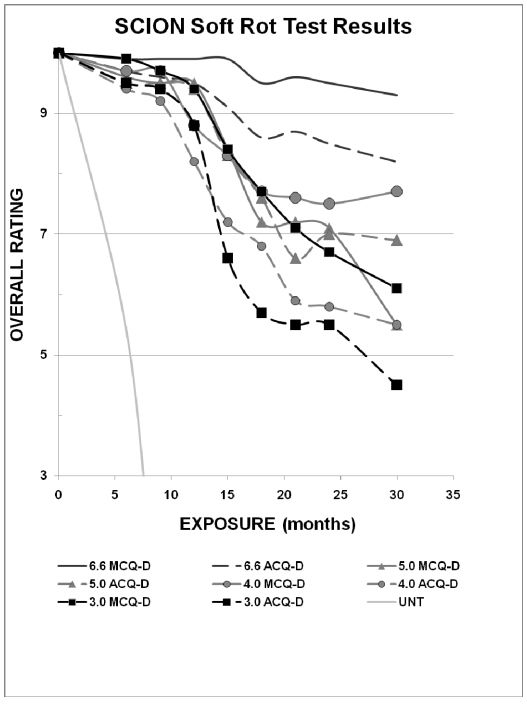


As shown, the micronized formulations perform the same as or better than the amine formulations in the various stake tests. Since there is less leaching for the micronized versions, lower initial retentions can be used to give equivalent performance.

Soft Rot Tests

Soft rot tests were conducted according to the AWPC protocol by SCION using Radiata pine (Figure 9). These show slightly better performance for the micronized formulation compared to the amine system.

Figure 9. Soft Rot Test



Property Testing

Strength testing using the procedures of ASTM D143 was conducted at the State University of New York in Syracuse, NY (Table 6) using southern pine.

Table 6. Strength Testing Normalized to Untreated Controls

Formula	Modulus of Rupture	Modulus of Elasticity	Work to Max. Load
6.1 Micro CQ	0.97	1	0.85
5.9 Amine CQ	1.03	1.06	0.69
UNT	1	1	1

Corrosion testing of micronized formulations has been discussed by Freeman and McIntyre (2008). Generally the corrosion for micronized products with a particular metal was much less than that for the amine formulation.

RESULTS AND DISCUSSION

Soil Block Tests

Generally, the micronized formulations show similar or better performance than the amine formulation in soil block test. For Brown-rot fungi (Table 1), the copper tolerant *Postia placenta* gave somewhat anomalous results in that little control was shown in one test but other tests contradict this result. Similarly, *Trametes lilacino-gilva*, showed poor control in one test (Table 2) but tests with the synonymous *Fometes lilacino-gilva* gave good control (Table 3).

Termite Tests

Tests with the extremely aggressive *Mastotermes darwiniensis* showed that ground contact retentions of micronized copper quaternary would adequately protect wood from attack by this termite.

Stake Tests

Stake Test 1 shows that the Amine CQ (ACQ-D) performance does not match that of the micronized counterpart at equal retentions. Generally, the performance of the micronized systems is as good as or better than the amine formulations in the other stake tests also. Since the amine formulations have been in use for many years, it seems reasonable to conclude that the micronized systems will also give good performance lives.

Soft Rot Tests

Again the micronized formulations show performance as good as or better than the amine counterparts in this test. In other work, micronized copper field stakes were examined and there was no evidence of soft rot attack (Stirling *et al* 2008). Other stakes from that field site with organic preservatives did have soft rot attack so this test also showed that micronized formulations do not seem to be susceptible to soft rot.

Fixation Tests

The fixation data shows that the micronized formulations lose much less copper than amine systems. Thus, the micronized formulations provide a higher residual copper content in wood treated to the same original retentions.

Strength Test

Neither the amine or the micronized systems had any significant impact on wood strength properties.

RECENT ISSUES

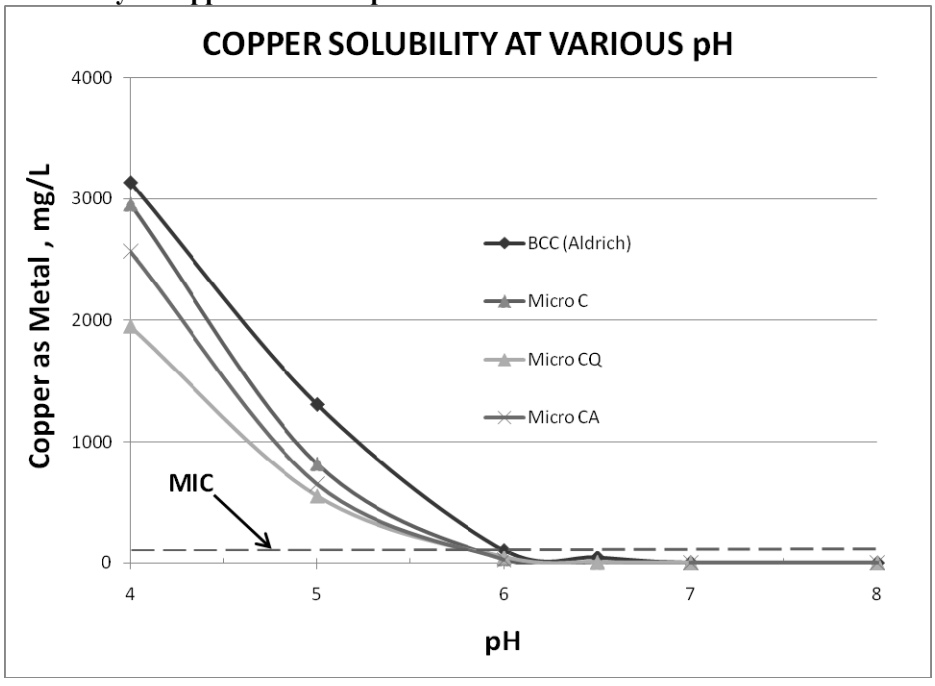
Recently there have been allegations that the performance of all micronized copper formulations is suspect. These claims are based on the results of limited tests but nonetheless there have been various hypotheses advanced for the “poor performance”.

The first hypothesis advanced was that the micronized formulations would be susceptible to attack by soft rot decay fungi. The reason for this susceptibility was that there would not be sufficient copper in the cell wall to prevent soft rot. As noted earlier, a number of scanning electron microscopy papers have

shown that there is copper present in the cell wall. Matsunaga et al (2008) measured the relative amounts in the latewood of micronized and amine formulations and found no significant difference between the two systems. A number of laboratory and field tests have also shown that the micronized systems are not susceptible to soft rot attack.

The second hypothesis was that there is insufficient "available copper" in the micronized formulations due to the insolubility of copper carbonate (Jin et al 2008). The proponents of this hypotheses point out that basic copper carbonate (BCC) is essentially insoluble in water. This is true at pH 7 but wood typically has a pH of 4 to 5. For example, southern pine is pH 4.75 (Stamm, 1964). At that pH, various copper systems have solubilities of about 1000 mg/L or more (Figure 10). The degree of solubility at pH 4.75 vastly exceeds the Minimum Inhibitory Concentration (MIC) of 100 mg/L for ACQ determined by Archer et al (1995) for a number of brown-rot fungi. Thus it would appear that copper ions are "available" in the wood and the copper ions are in the right form to prevent fungal attack. Further discussion of this issue is available (McIntyre et al, 2009).

Figure 10. Solubility of copper at various pH.



The third hypothesis was that there is a sharp distinction between the retentions for the earlywood bands as opposed to the retentions for the latewood bands within southern pine. This is supposedly due to the density differences and the smaller cells in the latewood not allowing the penetration of the micronized particles.

To investigate this possibility, two samples of micronized wood were compared with two samples of amine wood. The wood was commercially treated so the retentions would be representative of the "real world" and reflect modern treating practices. The earlywood and latewood bands of the wood were carefully cut and the retentions of the various segments determined (Table 7). As shown, the micronized product had a relative even distribution of retentions with good balance of the preservative actives in each band. In contrast, the amine product had a greater variation in the retentions and the balance of actives was also more variable. Thus, one would expect that the performance of the amine formulation to be more variable relative to the distribution between the earlywood and latewood bands since the micronized formulation is more uniform. This comparison data counters the original hypothesis which suggests that the original hypothesis may be incorrect.

Table 7. Earlywood-Latewood Distribution of Components

FORMULATION	BAND	RETN, kg/m^3	% CuO	% Quat
MCQ-D 1	EARLY	5.3	66	34
MCQ-D 1	LATE	5.0	64	36
MCQ-D 2	EARLY	5.2	64	36
MCQ-D 2	LATE	7.5	62	38
ACQ-D 1	EARLY	3.9	58	42
ACQ-D 1	LATE	7.9	59	41
ACQ-D 2	EARLY	3.9	68	32
ACQ-D 2	LATE	5.9	74	26

SUMMARY AND CONCLUSIONS

A voluminous series of standardized laboratory and field tests performed at third party laboratories show that the biological efficacy of micronized copper formulations is as good as or better than the amine counterparts. Other properties such as strength and corrosion also show the micronized products to perform well. Generally, there is no reason to suspect that micronized copper formulations will not give service lives equivalent to their amine counterparts.

Recent hypotheses regarding micronized formulations were investigated but the available evidence suggests that the hypotheses may not be correct.

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