#### MICRONIZED COPPER AZOLE (MCA) EFFICACY UPDATE

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#### ABSTRACT

This paper provides a field biological efficacy update on the micronized copper azole (MCA) wood preservative. MCA treated stakes, along with reference system of ACQ and CA-B, were installed at Hawaii, Gainesville, FL, Dorman Lake, MS, Saucier, MS, Maple Ridge, BC and Kincardine, ON. The inspection results showed that MCA preservative provided excellent long-term efficacy against decay fungi and termite attack. Overall, the field test results indicated that MCA has performed similar to its soluble counterpart CA-B and at least as well as ACQ.

# Keywords: MCA, Micronized Copper Azole, Triazole, Tebuconazole, Brown Rot, White Rot, Fungi, Efficacy, Wood Decay, and Termites.

#### **1. INTRODUCTION**

Micronized copper wood preservatives are based on a novel copper technology and are widely used in today's North American wood preservation market. Unlike the traditional alkaline copper preservatives where copper is solubilized in aqueous ethanolamine solution, micronized copper formulations do not use the organic solvent mono-ethanolamine. Instead, sparsely water soluble copper compounds, such as basic copper carbonate, are "micronized" into sub-micron particles and dispersed in water instead of using water soluble forms of copper compounds or complexes. There are currently two commercially available micronized copper systems, namely micronized copper quat (MCQ) where dimethyldidecylammonium carbonate/bicarbonate is used as a co-biocide, and MCA where either tebuconazole or a tebuconazole/propiconazole combination is used as a co-biocide.

Numerous studies have been reported on laboratory and field performance of micronized copper preservatives against wood decay fungi and termites. Larkin *et al.* (2008) reported on the biological performance of MCA and MCQ treated stakes exposed in ground contact in Hawaii for over 3 years, and concluded that MCA and MCQ performed similar to an alkaline copper quat system (ACQ-D). They further concluded that all field stakes with retentions at or above the commercial loadings for ground contact applications were performing very well with little or no decay damage. In Australian field trials on the efficacy of micronized copper against termites and decay fungi, and concluded that MCQ and ACQ performed similar in an in-ground stake trial. They also reported on a laboratory soil block test which showed that MCQ and ACQ gave similar performance against four brown rot and two white rot fungi. They further reported that MCQ

performed similar to ACQ against two aggressive subterranean termites, *Coptotermes* acinaciformis and Mastotermes darwiniensis, in an H3 (outside, above-ground) field test. In a comprehensive review of all the copper based wood preservatives, Freeman and McIntyre (2008) reviewed over a dozen laboratory and field exposure studies focusing on the biological performance of micronized copper preservative systems, and concluded that micronized copper formulations perform as well or better than their aminesolubilized counterparts against termites, brown rot, white rot and soft rot fungi. In an attempt to address the mechanism of action of micronized copper preservatives, Zhang and Ziobro (2009) conducted a 20-week water leaching study, and the result showed the micronized copper in treated wood continuously released cupric ion when exposed to water and the level of cupric ion released is similar to that of amine soluble copper counterpart, and slightly higher than CCA preservative. In addition, electron microscopic studies by Matsunaga et al. (2007) and Stirling et al. (2008) confirmed cell wall penetration of copper in the wood treated with micronized copper system. Additional results of laboratory and field tests were reported by Zhang and Ziobro (2010) and McIntyre et.al (2012) which again demonstrated the effectiveness of MCA against wood destroying organisms.

In this paper, the results of various field studies on the bio-efficacy of MCA are updated.

## 2. MATERIALS AND METHODS

### 2.1 Formulations

MCA – contains micronized copper particles dispersed in water plus tebuconazole with the ratio of elemental copper to tebuconazole as 25 to 1.

CA-B – contains amine soluble copper plus tebuconazole with an elemental copper to tebuconazole with the ratio of elemental copper to tebuconazole as 25 to 1.

ACQ-C – contains amine soluble copper plus alkylbenzylammonium carbonate/bicarbonate quat with a copper oxide (CuO) to quat ratio of 2:1.

ACQ-D – contains amine soluble copper plus dimethyldidecylammonium carbonate/bicarbonate quat with a copper oxide (CuO) to quat ratio of 2:1.

MCQ – contains micronized copper particles dispersed in water plus dimethyldidecylammonium carbonate/bicarbonate quat with a copper oxide (CuO) to quat ratio of 2:1.

## 2.2 Ground Contact Field Stake Test

<u>*Test in Hawaii*</u>: This study was conducted by MTU following AWPA Standard E7-03. Southern pine stakes measuring  $19 \times 19 \times 450$ mm were treated with MCA and ACQ-D.

The treated stakes, along with untreated controls, were installed at two Michigan Technological University (MTU) field sites in November 2004. The stakes were initially exposed in the first site in Keaau, Hawaii (near Hilo), and then removed in November 2005 and re-installed in the second test site Maunawili, Hawaii (near Honolulu) in February 2006. The characteristics of these sites were described previously (Stirling *et al.* 2008).

<u>*Test in Florida:*</u> Southern pine stakes measuring 19 x19 x 450mm were treated with MCA and ACQ-D following AWPA Standard E7-03. The treated stakes, along with untreated controls, were installed at Austin Cary Forest near Gainesville, FL in February 2005. This site has a mean temperature of 20°C an annual precipitation of 128cm, and has a Scheffer Index of approximately 110. The soil is sandy.

<u>Test in Saucier and Dorman Lake, Mississippi</u>: Both tests were conducted by Mississippi State University following AWPA Standard E7-03. Southern pine stakes measuring 19 x19 x 450mm were treated with MCA and CA-B. The treated stakes, along with untreated controls, were installed at Dorman Lake and Saucier, MS in 2005.

<u>Test in Maple Ridge, BC and Kincardine, ON</u>: Both tests were conducted by FPInnovation, CA. Canadian wood species, Pacific silver fir and white spruce, were treated with MCA and ACQ-C. The treated stakes, along with untreated controls, were installed at Maple Ridge, BC near Vancouver in December 2009 and Kincardine, ON near Toronto in May 2010.

The test stakes installed in all the testing plots were rated annually according to the grading system described in AWPA E7, where a rating of 10 stands for sound or no sign of decay, wood softening or discoloration caused by microorganism attack and a rating of 0 for complete failure due to attack by microorganisms.

## 3. RESULTS AND DISCUSSION

### 3.1 10-years field stake test in Hawaii

The result for the 19mm stakes treated with MCA and ACQ-D and exposed in Hawaii for 10 years are summarized in Figure 1. Untreated controls had almost complete failures after about 21-months exposure, indicating the aggressiveness of the testing sites. After 10-years exposure, MCA treated stakes at retention of 1.6kg/m<sup>3</sup> and ACQ-D treated stakes at 2.4 and 4.0 kg/m<sup>3</sup> had severe deterioration with average decay ratings below 5. MCA stakes at the two higher retentions at 2.6kg/m<sup>3</sup> and 3.4kg/m<sup>3</sup> showed average ratings of 8.0 and 7.0, respectively. ACQ-D treated stakes at retentions of 6.4 kg/m<sup>3</sup> had average decay ratings of 7.0.

### 3.2 10-years field stake test in Gainesville, FL

Figure 2 presents the results of 19mm stakes treated with MCA and ACQ-D and exposed in Gainesville, FL for 10 years. All the untreated stakes failed after 38-months exposure, indicating the severity of the decay/termite hazards at the Gainesville test site. After 10-years exposure, MCA stakes at retention of 1.8 kg/m<sup>3</sup> and ACQ-D treated stakes at both lower and higher retentions had shown a significant decline in decay ratings, while MCA treated stakes at the retention of 3.4 at kg/m<sup>3</sup> only showed an average decay rating of 9.7, indicating negligible decay and/or termite attack.

### 3.3 Field stake test in Dorman Lake and Saucier, MS

A comparison of field stake performance between MCA and its soluble counterpart CA-B is illustrated in Figures 3 & 4, where the treated stakes were exposed in Dorman Lake for nearly 10 years and in Saucier for over 9 years. At the Dorman Lake test plot after 117-months exposure, MCA at  $1.3 \text{kg}^3$  had a rating of 5.5, while the corresponding CA-B at the same retention had a rating of 3.6. Both MCA and CA-B at the medium retention had average ratings of 9.1 and 8.6, respectively. At the higher retention, the average decay ratings for MCA and CA-B are 9.7 and 9.1, respectively. At the Saucier test plot, all the untreated stakes failed completely after 51-months exposure. Both MCA and CA-B treated stakes at the low retention of  $1.3 \text{kg}^3$  had average decay ratings of 7.8 and 7.6, respectively, while MCA and CA-B stakes at the two higher retentions still had average decay rating of 9.1 or higher.

### 3.4 Field stake test in Maple Ridge, BC and Kincardine, On

Figures 5 & 6 demonstrate the decay rating of Pacific silver fir and white spruce stakes treated with MCA after 5-years exposure in Maple Ridge, BC and Kincardine, ON. ACQ-D treated stakes at a retention of 5.1 kg/m<sup>3</sup> for Pacific silver fir, and 3.7 kg/m<sup>3</sup> for white spruce were used as references. For Pacific silver fir stakes, untreated controls were subject to severe deterioration at both sites with decay ratings below 2. The ACQ treated stakes had a slight degree of decay attack, while MCA treated stakes at all retentions still performed well with rating 9.7 or higher.

For the white spruce stakes, untreated stakes were also subject to moderate to severe deterioration at both sites, with average rating of 4.5 and 4.6. ACQ-treated stakes had an average rating of 8.9 at the BC site and 7.5 at the Ontario site. All the MCA stakes were still sound after 5 years of exposure at both sites.

### 4. CONCLUSIONS

The results of long-term field stake tests at various test plots clearly show MCA preservative is effective against wood decay fungi and insects and that MCA performs at least as well as reference systems of ACQ and CA-B.

### 6. REFERENCES

Cookson, L.J., Creffield, J.W., McCarthy, K.J., and Scown, D.K. (2008): Australian trials on the efficacy of micronized copper. International Research Group on Wood Protection. Document No. IRG/WP/08-30480

Freeman, M.H. and McIntyre, C.R. (2008): A comprehensive review of copper-based wood preservatives with a focus on new micronized or dispersed copper systems. Forest Product Journal 58(11): 6-27

Larkin, G.M., Zhang, J., Richter, D.L., Ziobro, R.J., and Laks, P.E. (2008): Biological performance of micronized copper wood preservative formulations in field and laboratory tests. International Research Group on Wood Protection. Document No. IRG/WP/08-30488

Matsunaga, H. et al., 2007; IRG/WP 07-40360

McIntyre, C.R., Freeman M.H., Fox, R.F., and Zhang, J. (2012): Addressing the need for service life estimates for newer preservatives. 2012 American Wood Protection Association Proceedings

Stirling, R. et al., 2008; IRG/WP 08-30479

Zhang, J. and Ziobro, R. (2009): Micronized copper preservative systems: observations on the release of cupric ion (Cu<sup>2+</sup>) from treated wood and performance against wood decay fungi. International Research Group on Wood Protection. Document No. IRG/WP/09-30519

Zhang, J. and Ziobro, R. (2010): Laboratory and field studies on the efficacy of micronized copper azole (MCA) preservative. 2010 American Wood Protection Association Proceedings



Figure 1. Ground Contact Stake Test Results from Hawaii

Figure 2. Ground Contact Stake Tests from Gainesville, FL



Figure 3. Ground Contact Stake Tests from Dorman Lake, MS



Figure 4. Ground Contact Stake Test Results from Saucier, MS



Figure 5. Decay Ratings of MCA Treated Pacific Silver Fir





#### Figure 6. Decay Ratings of MCA Treated White Spruce