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# LABORATORY AND FIELD STUDIES ON THE EFFICACY OF MICRONIZED COPPER AZOLE (MCA) PRESERVATIVE

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## ABSTRACT

Various laboratory and field trials on the efficacy of micronized copper azole (MCA) against decay and termites were conducted. In a laboratory fungal cellar test, MCA treated stakes at retentions of 1.7 kg/m3 and 3.3 kg/m3 showed rating of 9.8 or higher after 27 months exposure while untreated stakes had several failures and an average rating of 5.6. In a laboratory soil block test against four brown rot and two white rot fungi, MCA performed similar to solubilized copper azole (SCA) system and better than CCA. results of an AWPA E-1 termite test showedthat MCA performed comparably to alkaline copper quat (ACQ-D) system. In addition, MCA also demonstrated excellent long-term field efficacy against wood destroying fungi and insects as shown in a 45-month ground contact field stake test in Hawaii and in a 50-month ground contact field stake test in Gainesville, FL.

**Keywords: MCA, Micronized Copper, Azole, Tebuconazole, Soft Rot, Brown Rot, White Rot, Fungi, Wood Decay, 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, water sparsely 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 micronized copper azole (MCA) where tebuconazole is used as a co-biocide.

Numerous studies have been reported on the laboratory and field performance of micronized copper preservatives against wood decay fungi and termites. Larkin *et al.* (2008) reported the biological performance of MCA and MCQ treated stakes when exposed in Hawaii for over 3 years, and they 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 trials on the efficacy of micronized copper system, Cookson *et al.* (2008) reported on the biological efficacies of micronized copper against termites and decay fungi, and they concluded that MCQ and ACQ performed comparably 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 brownrot and two whiterot 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 they concluded that micronized copper formulations perform as well or better than their amine-solubilized counterparts against termites, brown rot, white rot and soft rot fungi. In an attempt to address the mechanism of action of micronized copper preservative, 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 the previous studies, the majority of results have been presented on MCQ system. In this paper, the results of various laboratory and field studies on MCA are reported and the studies include:

1. Soil bed trials on the efficacy against soft rot fungi
2. Laboratory trials on the efficacy against basidiomycete decay fungi and termites
3. Field trials on the efficacy against decay fungi and termites.

## 2. MATERIALS AND METHODS

### 2.1 Soil Bed Fungal Cellar Study

The soil bed study was conducted by Michigan Technological University (MTU) according to the AWPA E14-02 protocol, using southern pine sapwood samples. Three preservatives, ACQ, MCQ and MCA, plus untreated controls were included in the study. Soil temperature was maintained at 25-30°C by heating pipes which are embedded in the concrete blocks forming each fungal cellar and soil moisture was maintained at 100% water holding capacity. The stakes were visually inspected every three months using the rating system specified by E14.

### 2.2 Laboratory Termite Test

The tests were performed in accordance with the AWPA E1-06 protocol by Louisiana State University. The single choice method was used in all tests and the subterranean termite species, *Coptotermes formosanus*, was used in the test. MCA preservative was treated to four retentions at 0.83, 1.66, 2.50 and 3.33 kg/m$^3$. In addition, ACQ-D treated to four retentions, 1.2, 2.4, 4.0 and 6.4 kg/m$^3$, were included as a positive control.

After 28 days of exposure, the samples were removed and cleaned with distilled water to remove termites and sand, rated and oven dried. Each sample was rated based on the following AWPA rating system:

| | |
|---|---|
| 10 | Sound, surface nibbles permitted |
| 9 | Light attack |
| 7 | Moderate attack, penetration |
| 4 | Heavy attack |

0 Failure

**2.3 Laboratory Soil Block Test**

The laboratory decay test of MCA against basidiomycetes was conducted by CSIRO Forest Biosciences following the AWPC protocol. In addition to MCA, two reference preservative systems, CCA and soluble amine-copper tebuconazole (SCA) were also included in the study. Specimens 20 x 10 x 20 mm were cut from seasoned *P. radiata* and *E. delegatensis* sapwood boards. All specimens were air dried to constant moisture content and then treated.

Specimens were treated to three retentions for each system by drawing a vacuum of -95 kPa for 30 minutes, introducing the preservative while under vacuum, and then immediately releasing the vacuum. *P. radiata* specimens were left to absorb preservative for 30 minutes at atmospheric pressure, while *E. delegatensis* specimens received 30 minutes pressure at 900 kPa. After treatment, specimens (except the water-treated controls) were wrapped in plastic bags, to allow for the completion of any chemical fixation or preservative immobilization that might occur. The blocks were placed on trays and left to air dry for two weeks.

Four brown-rot fungi and two white-rot fungi were used to evaluate the treatments in *P. radiata* and *E. delegatensis* respectively.

| **Brown-rotting fungi** | **DFP number** | **White-rotting fungi** | **DFP number** |
|---|---|---|---|
| *Coniophora olivacea* | 1779 | *Perenniporia tephropora* | 7904 |
| *Fomitopsis lilacino-gilva* | 1109 | *Lopharia crassa* | 10644 |
| *Gloeophyllum abietinum* | 13851 | | |
| *Postia placenta* | 7290 | | |

**2.4 In-Ground Field Stake Test**

<u>*Test in Hawaii*</u>*:* This study was conducted by MTU following the AWPA E7-03 protocol. Southern pine stakes measuring 19 x19 x 450mm were treated with MCA, MCQ as well as 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, MCQ and ACQ-D. 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. Stakes were inspected annually according to the rating system described in AWPA E7.

**3. RESULTS AND DISCUSSION**

### 3.1 Soil Bed Fungal Cellar Study

The fungal cellar study was conducted to evaluate the preservative performance against soft-rot. Table 1 summarizes the results of a fungal cellar test in the wet soil condition. After 27-month exposure, untreated controls had an average rating of 5.6. Stakes treated with ACQ-D, MCA and MCQ preservatives all performed well at the two retentions, and no evidence of decay was observed in the treated stakes.

### 3.2 Laboratory Termite Test

Table 2 provides a summary of the means for the primary data of interest, i.e., percent mortality, percent weight loss, and treatment ratings. The control samples showed a mortality of 5.8%, which is an indicative of acceptable termite vigor. Mean percent mortality for MCA treated samples ranged from 27.8% to 53.1%, and mean percent mortality for ACQ-D treated samples ranged from 17.7% to 22.1%. The control samples showed a mean weight loss of 27.4%, and the mean weight loss for samples treated with MCA and ACQ-D ranged from 0.8% to 5.1%. The results showed that MCA and ACQ-D provided similar performance against the Formosan termite.

### 3.3 Soil Block Decay Test

The soil block decay test compared the performance of MCA to CCA and soluble amine copper azole systems. The average weight loss against the six decay fungi is given in Table 3, and the major results of the study are summarized below:

- Water-treated controls were severely decayed by most of the decay fungi, with mean mass losses of 28.3% to 61.7%.
- All concentrations of MCA were able to control the two white rotting fungi, *Perenniporia tephropora* and *Lopharia crassa* in *Eucalyptus delegatensis* substrate, and the brown rotting fungi *Gloeophyllum abietinum* and *Coniophora olivacea* in *Pinus radiata* substrate. The lowest and highest retentions of MCA (0.15% and 0.32% m/m) were able to control the brown rotting fungus *Postia placenta* in *P. radiata* substrate.
- The CCA reference preservative was able to control the brown rotting fungi *G. abietinum* and *C. olivacea* at all retentions. In comparison, all CCA retentions had some level of significant decay from *Fomitopsis lilacino-gilva* and *P. placenta*. Both white rotting fungi were also able to cause decay to *E. delegatensis* treated to the lowest CCA retention.
- The SCA reference preservative at all retentions was able to control the brown rotting fungi *G. abietinum* and *C. olivacea*, and the white rotting fungus *P. tephropora*. In comparison, all SCA retentions had some level of significant decay from *F. lilacino-gilva* and *Postia placenta*. The white rotting fungus *L. crassa* caused some decay to *E. delegatensis* treated to the lowest SCA retention.

The results demonstrate that MCA has performed as well as the two reference preservatives, SCA and CCA, at all retentions examined.

### 3.4 In-Ground Stake Test

Table 4 shows the average decay ratings of the 19mm stakes treated with MCA, MCQ and ACQ-D and exposed in Hawaii. Untreated controls had almost complete failures after about 21 exposure, indicating the aggressiveness of the testing sites. After 45 months exposure, MCA treated stakes at the lowest retention still have a decay rating of 8.4, and the two higher retentions showed high rating of 9.8 and 9.7, respectively. The MCA at the two highest retentions demonstrated similar performance as MCQ and ACQ-D at the retention of 6.4 kg/m$^3$.

Table 5 shows a performance comparison between MCA, MCQ and ACQ-D treated stakes after 50 months exposure in Gainesville, FL. All untreated stakes failed completely due to the decay and termite attack after 25 months exposure. At the lower retention, MCA outperformed both ACQ-D and MCA, and at the higher retention, MCA and MCQ performed similarly and both showed better performance than ACQ-D in this test.

## 4. CONCLUSIONS

The results of both laboratory and field trials clearly show that micronized copper preservatives are effective against wood decay fungi and insects and that micronized copper preservatives perform at least as well as reference systems of CCA and ACQ-D.

## 6. REFERENCES

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**Table 1. Summary of Soil Bed Fungal Cellar Test Results by MTU**

| Preservative System | Retention (kg/m3) | Exposure Time (Months) | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | **9** | **13** | **15** | **18** | **21** | **24** | **27** |
| **ACQ-D** | **4.0** | 10 | 10 | 9.95 | 10 | 9.9 | 9.6 | 9.9 |
| | **6.4** | 10 | 10 | 10 | 10 | 10 | 9.9 | 10 |
| **MCA** | **1.7** | 10 | 10 | 9.9 | 10 | 9.95 | 9.6 | 9.8 |
| | **3.3** | 10 | 10 | 9.9 | 9.9 | 9.8 | 9.5 | 9.9 |
| **MCQ** | **4.0** | 10 | 10 | 10 | 10 | 9.95 | 9.8 | 10 |
| | **6.4** | 10 | 9.9 | 9.9 | 9.9 | 9.9 | 9.7 | 9.8 |
| **SYP Control** | **---** | 8.5 | 8.0 | 8.0 | 7.75 | 7.3 | 6.4 | 5.6 |

**Table 2. Summary Data for Mortality, Weight Loss and Rating**

| Preservative | Retention kg/m3 | Weight Loss % | Rating | Mortality |
|---|---|---|---|---|
| **MCA** | 0.8 | 5.0 | 8.3 | 27.8 |
| | 1.7 | 5.1 | 8.3 | 45.1 |
| | 2.5 | 3.3 | 8.5 | 53.1 |
| | 3.3 | 3.1 | 8.7 | 52.8 |
| **ACQ-D** | 1.2 | 4.1 | 8.0 | 19.6 |
| | 2.4 | 1.9 | 8.9 | 22.1 |
| | 4.0 | 0.8 | 9.4 | 21.5 |
| | 6.4 | 1.7 | 10.0 | 17.7 |
| **SYP Control** | ---- | 27.4 | 2.0 | 5.8 |

**Table 3. The average weight loss after exposure to six decay fungi for 12 weeks.**

| Preservatives | % m/m actives in OD wood | Mean Mass Loss (%) | | | | | |
|---|---|---|---|---|---|---|---|
| | | *C. olivacea* 1779 BR | *F.lilacino-gilva* 1109 BR | *G. abietinum* 13851 BR | *P. placenta* 7290 BR | *P. tephropora* 7904 WR | *L. crassa* 10644 WR |
| MCA | 0.15% | 0.5 (0.1) | 29.8 (2.0) | 0.5 (0.1) | 2.7 (0.7) | 1.4 (0.4) | 1.8 (0.2) |
| | 0.23% | 0.8 (0.0) | 16.6 (1.1) | 0.8 (0.1) | 9.6 (2.8) | 0.8 (0.0) | 1.1 (0.3) |
| | 0.32% | 0.5 (0.1) | 7.5 (1.3) | 0.6 (0.0) | 2.1 (0.4) | 0.5 (0.1) | 0.4 (0.0) |
| SCA | 0.15% | 0.6 (0.1) | 32.2 (1.9) | 0.8 (0.3) | 15.2 (3.6) | 2.2 (1.2) | 7.3 (2.1) |
| | 0.23% | 0.3 (0.1) | 18.6 (2.1) | 0.4 (0.1) | 16.4 (6.0) | 1.5 (0.8) | 2.5 (1.0) |
| | 0.32% | 0.4 (0.1) | 12.6 (1.1) | 0.5 (0.1) | 23.4 (10.3) | 1.0 (0.3) | 1.9 (0.5) |
| CCA | 0.14% | 0.4 (0.1) | 32.6 (3.7) | 1.1 (0.4) | 48.2 (6.0) | 11.3 (2.0) | 12.3 (2.1) |
| | 0.28% | 0.6 (0.0) | 8.8 (2.8) | 0.5 (0.1) | 28.4 (2.0) | 1.3 (0.4) | 5.6 (1.3) |
| | 0.47% | 0.3 (0.0) | 3.2 (0.6) | 0.3 (0.0) | 25.9 (1.3) | 0.9 (0.1) | 0.9 (0.1) |
| Water-treated | -- | 61.7 (0.5) | 47.1 (1.5) | 28.3 (1.7) | 52.3 (1.5) | 40.7 (1.9) | 55 0 (1.7) |

BR = brown rot   WR = white rot
The boxes with average weight loss below 3% are highlighted.

**Table 4. Summary of Stake Decay Ratings in Hawaii**

| Preservative System | Retention (kg/m3) | Exposure Time, Months | | | | |
|---|---|---|---|---|---|---|
| | | 12 | 21 | 33 | 40 | 45 |
| ACQ-D | 4.0 | 10.0 | 9.9 | 9.5 | 9.3 | 9.5 |
| | 6.4 | 10.0 | 10.0 | 9.9 | 9.7 | 9.5 |
| MCQ | 4.0 | 10.0 | 9.9 | 9.9 | 9.5 | 9.6 |
| | 6.4 | 10.0 | 9.95 | 9.9 | 9.7 | 9.5 |
| MCA | 1.7 | 10.0 | 10.0 | 9.8 | 9.1 | 8.4 |
| | 2.5 | 10.0 | 10.0 | 10.0 | 9.9 | 9.8 |
| | 3.3 | 10.0 | 10.0 | 10.0 | 10.0 | 9.7 |
| SYP Control | --- | 8.0 | 0.9 | 0.0 | 0.0 | 0.0 |

**Table 5. Summary of Stake Decay Ratings in Gainesville, FL**

| Preservative System | Retention (kg/m3) | Exposure Time, Months | | | |
|---|---|---|---|---|---|
| | | 12 | 25 | 38 | 50 |
| ACQ-D | 3.8 | 10.0 | 5.4 | 2.7 | 2.8 |
| | 6.2 | 10.0 | 9.8 | 8.6 | 8.8 |
| MCQ | 4.2 | 10.0 | 8.3 | 6.6 | 6.5 |
| | 6.7 | 10.0 | 9.9 | 9.6 | 9.7 |
| MCA | 1.7 | 10.0 | 9.9 | 9.4 | 9.9 |
| | 3.4 | 10.0 | 10.0 | 10.0 | 10.0 |
| SYP Control | --- | 7.0 | 0.0 | 0.0 | 0.0 |