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## ABSTRACT

The efficacy of various micronized and amine copper preservative systems was evaluated using soil block testing with the copper tolerant brown rot fungi, *Postia placenta.* The American Wood Protection Association E22 protocol was used to compare the relative efficacy of preservatives by monitoring compressive strength losses of the systems in southern pine wood. As information, the weight losses were also measured and the relative ranking of the systems was the same by either methodology. Generally, the micronized and amine systems with co-biocides performed very well while systems without a cobiocide did not. Used treating liquids obtained from operating plants did not show any significant differences in performance compared to virgin liquids of the same system.

**Keywords:** micronized copper, amine copper, soil block, E22, used treating solutions

## 1. INTRODUCTION

Historically wood preservatives have been screened by laboratory methods prior to testing by field trials. In the late 1940's and early 1950's, the seminal work in the development of screening tests was performed by Duncan and Richards (1950, 1953, 1954, 1958a,b). Numerous publications then used the "new" soil block method to determine the toxic threshold of many chemicals to specific monocultures of fungi (Duncan and Lombard 1965). This methodology used weight loss as the evaluation criteria and the method was slightly altered over the next fifty years with minor, but significant improvements, including sterilization techniques, addition of feeder strips, new supporting mesh materials and others.

In 2005, Darrel Nicholas, Mississippi State University presented a Preliminary Evaluation Method (PEM) to the American Wood Protection Association (AWPA) where compressive strength loss instead of weight loss was used as the gauging mechanism to evaluate attack by decay fungi. Since compressive strength loss in wood wafers was deemed to be roughly nine times more sensitive to attack by decay fungi than weight loss and the wood wafer was reduced in thickness and volume, general trends of attack could be determined in periods as short as four weeks, instead of the classic weight loss soil block incubation period of 12 to 26 weeks (Nicholas and Jin, 1996; Jansen and

Nicholas, 2002; Crawford and Nicholas, 2003). Additionally, an instrumental method added to the method allowed for quantitative, precise and accurate measurements of compressive strength loss (AWPA 2006). The methodology was standardized by the AWPA as Standard Method E22 in 2006. The E22 method is used worldwide by multiple labs today.

This report provides a snapshot of threshold data of three sets of parameters against one, highly copper resistant strain of brown rot fungi, *Postia placenta*, with three main sets of variables:

(1) Influence of used treating solutions vs. virgin treating solutions,
(2) Influence of co-biocide on the effectiveness of a primary copper system, and
(3) Effects of different co-biocides on amine vs. micronized copper systems

## 2. EXPERIMENTAL METHODS

### 2.1 Formulations and Treatments

Copper formulations used for wafer treatments in this test are: Micronized Copper Quat (MCQ), Micronized Copper Azole Type B (MCA), Copper Azole Type B (CA), Alkaline Copper Quat Type D (ACQ-D), micronized copper only (MCu), and an amine base copper only (CuMEA). Each formulation was decay tested in its virgin form, i.e. as it was freshly prepared and unused. In addition, MCQ and ACQ formulations were collected from active treating plants to test the efficacy between the treating process liquids and compare it to the efficacy of the "virgin solutions". The material from the treating plants is designated for convenience as TS for treating solution even though some materials were actually dispersions. No additional preparation (other than dilution for retention purposes) was done to the formulations designated as TS.

### 2.2 Fungal Exposure

Fungal testing was performed in accordance with the AWPA E22-09 Standard Accelerated Laboratory Method for Testing the Efficacy of Preservatives against Wood Decay Fungi Using Compression Strength (AWPA 2007). The 256 samples of southern pine sapwood were treated using full cell treatment cycles using solutions or dispersions diluted with tap water to achieve the desired copper level. Sample wafers were 18 mm x 18 mm x 5 mm (tangential x radial x longitudinal) specimens containing 2 to 8 rings per 18 mm. Matched untreated (water only) southern pine sapwood controls were used. Table 1 presents the treating information.

Samples were sterilized by gamma irradiation prior to testing. Testing containers were assembled containing 200 grams of soil, 60 ml of distilled water, and two southern pine feeder strips. The feeder strips were inoculated with the copper tolerant brown rot fungi *Postia placenta* and incubated until the feeder strips were completely covered with mycelia. After incubation, four samples from the same treatment group were placed in each container on top of the southern pine feeder strips (two samples per feeder strip). The *P. placenta* (Fr.) M.J. Larsen & Lombard strain (ATCC 11538) was obtained through the courtesy of R.M. Rentmeester at the Center for Forest Mycology Research, USDA Forest Products Laboratory, Madison, WI.

After six weeks exposure, the samples were strength tested per AWPA E22 with the results in Table 2. After drying to constant weight, the weight losses of the samples were determined with the results in Table 3.

Means and standard deviations of the strength and weight losses were determined. This data was also analyzed via analysis of variance using Fisher's least significant difference test. Groupings were determined using the least significant difference (LSD) procedure at alpha = 0.05.

Table 1. Treatment of wafers

| | | RETENTION [kg/m$^3$] | | | |
|---|---|---|---|---|---|
| **Sample** | **Concentration** | **Solution** | **Cu** | **Co-Bio** | **Total a.i.** |
| MCQ | 0.19% MCQ | 709.9 | 0.83 | 0.53 | 1.36 |
| | 0.38% MCQ | 675.2 | 1.58 | 0.99 | 2.58 |
| | 0.57% MCQ | 679.5 | 2.40 | 1.50 | 3.90 |
| | 0.76% MCQ | 703.0 | 3.31 | 2.06 | 5.38 |
| MCQ (TS)[a] | 0.12% MCQ (TS) | 739.0 | 0.86 | 0.89 | 1.76 |
| | 0.24% MCQ (TS) | 736.5 | 1.73 | 1.77 | 3.50 |
| | 0.35% MCQ (TS) | 738.4 | 2.61 | 2.66 | 5.26 |
| | 0.37% MCQ (TS) | 729.1 | 2.70 | 2.76 | 5.47 |
| ACQ-D | 0.19% ACQ-D | 752.0 | 0.88 | 0.58 | 1.43 |
| | 0.38% ACQ-D | 757.6 | 1.78 | 1.12 | 2.90 |
| | 0.57% ACQ-D | 740.8 | 2.61 | 1.63 | 4.26 |
| | 0.76% ACQ-D | 751.4 | 3.54 | 2.21 | 5.74 |
| ACQ-D (TS) | 0.12% ACQ-D (TS) | 699.4 | 0.82 | 0.65 | 1.47 |
| | 0.24% ACQ-D (TS) | 699.4 | 1.65 | 1.30 | 2.94 |
| | 0.35% ACQ-D (TS) | 706.1 | 2.50 | 1.97 | 4.46 |
| | 0.47% ACQ-D (TS) | 705.6 | 3.33 | 2.63 | 5.95 |
| CA | 0.12% CA | 746.4 | 0.88 | 0.04 | 0.92 |
| | 0.24% CA | 753.9 | 1.78 | 0.07 | 1.85 |
| | 0.37% CA | 755.0 | 2.67 | 0.11 | 2.77 |
| | 0.49% CA | 760.6 | 3.58 | 0.14 | 3.73 |
| MCA | 0.12% MCA | 723.5 | 0.85 | 0.03 | 0.88 |
| | 0.24% MCA | 716.0 | 1.68 | 0.07 | 1.75 |
| | 0.37% MCA | 743.5 | 2.62 | 0.11 | 2.74 |
| | 0.49% MCA | 739.7 | 3.49 | 0.14 | 3.62 |
| MCu | 0.12% MCu | 684.5 | 0.80 | N/A | 0.80 |
| | 0.24% MCu | 695.7 | 1.63 | N/A | 1.63 |
| | 0.35% MCu | 693.8 | 2.45 | N/A | 2.45 |
| | 0.47% MCu | 698.1 | 3.28 | N/A | 3.28 |
| CuMEA | 0.12% CuMEA | 689.6 | 0.82 | N/A | 0.82 |
| | 0.24% CuMEA | 694.4 | 1.63 | N/A | 1.63 |
| | 0.35% CuMEA | 688.8 | 2.43 | N/A | 2.43 |
| | 0.47% CuMEA | 688.8 | 3.25 | N/A | 3.25 |
| Water - Exposed | -- | -- | -- | -- | -- |
| Water Unexposed | -- | -- | -- | -- | -- |

[a]TS indicates treating plant liquid, see text.

## 3. RESULTS AND DISCUSSION

As shown in Tables 2 and 3, the results are arranged by the copper (as metal) retention values. This allows comparison of the formulations that do not have co-biocides with those that do.

Table 2. Mean strength loss of wafers after exposure to *P. placenta*.

| System | Copper Retention [kg/m$^3$] | Strength Loss [%] | Significance | Equal to Unexposed |
|---|---|---|---|---|
| **MCQ** | 0.83 | **70.8** | CBD | No |
| | 1.58 | **30.6** | GF | No |
| | 2.40 | **-15.1** | KNML | Yes |
| | 3.31 | **-26.6** | O | Yes |
| **MCQ (TS)[a]** | 0.86 | **54.5** | E | No |
| | 1.73 | **-7.6** | KJ | Yes |
| | 2.61 | **10.1** | IH | Yes |
| | 2.70 | **-13.2** | KML | Yes |
| **ACQ-D** | 0.88 | **61.5** | ED | No |
| | 1.78 | **3.7** | IH | Yes |
| | 2.61 | **-10.1** | KJL | Yes |
| | 3.54 | **-16.0** | CED | Yes |
| **ACQ-D (TS)** | 0.82 | **62.4** | ED | No |
| | 1.65 | **-10.6** | IH | Yes |
| | 2.50 | **-19.9** | KJL | Yes |
| | 3.33 | **-21.1** | KNML | Yes |
| **CA** | 0.88 | **77.5** | B | No |
| | 1.78 | **23.3** | G | No |
| | 2.67 | **11.2** | H | No |
| | 3.58 | **7.9** | IH | Yes |
| **MCA** | 0.85 | **68.0** | BCD | No |
| | 1.68 | **-7.1** | KJ | Yes |
| | 2.62 | **-25.0** | ON | Yes |
| | 3.49 | **-28.0** | O | Yes |
| **MCu** | 0.80 | **96.0** | A | No |
| | 1.63 | **96.4** | A | No |
| | 2.45 | **91.7** | A | No |
| | 3.28 | **90.0** | A | No |
| **CuMEA** | 0.82 | **94.9** | A | No |
| | 1.63 | **95.0** | A | No |
| | 2.43 | **72.4** | CBA | No |
| | 3.25 | **39.9** | F | No |
| **Water Exposed** | -- | **95.1** | A | |
| **Water Unexposed** | -- | -- | IJ | |

[a]TS indicates treating plant liquid, see text.

### 3.1 Compressive Strength Loss

The strength loss data in Table 2 shows MCQ to have a threshold between 1.6 and 2.4 kg/m$^3$ of copper while the used MCQ solutions obtained from treating plants (MCQ-TS) had a threshold between 0.9 and 1.7 kg/m$^3$. Since the thresholds are essentially the same, it is reasonable to surmise that no deleterious effects are exerted on the treating solutions during repetitive, multiple treatment usage. For comparison, the ACQ threshold is between 0.9 and 1.8 kg/m$^3$ of copper while the used treating solution ACQ-TS has a similar threshold between 0.8 and 1.7 kg/m$^3$. For the various copper quat systems, the thresholds are essentially the same no matter if the copper is present as a micronized particulate or dissolved in amine or if the solution had been repetitively used or was freshly prepared.

The MCA threshold was also between 0.9 and 1.7 kg/m$^3$ of copper while its amine counterpart, CA, had a threshold between 2.75 and 3.6 kg/m$^3$ of copper. In this case, there is a significant difference in the efficacies with the micronized product performing better than the amine version.

Neither the micronized copper only nor the amine copper only performed well at all against this particularly highly aggressive strain of copper tolerant fungus. This was expected and the necessity of an effective co-biocide is clearly demonstrated.

### 3.2 Weight Loss

First, it should be noted that weight loss is currently not a part of the E22 Standard but that this data was collected to provide additional information for comparative purposes. Also, it was thought that it would be disruptive to excessively dry the samples before the test so the samples were air-dried to constant weight. The mean moisture content of spare samples was then used to calculate a starting dry weight for the samples after exposure to the fungus.

The weight loss data in Table 3 shows two distinct groups: a continuum of weight losses from 0 to 11% and then weight losses from 24% to 50%. For this reason, the judgement of acceptability was simply whether or not the system was in the low or the high weight loss class.

Not too surprisingly, the weight loss data was similar to the strength loss data. For MCQ, the weight loss threshold was between 1.6 and 2.4 kg/m$^3$ and the MCQ-TS was 0.9 to 1.7 kg/m$^3$ of copper. The ACQ weight loss threshold was between 0.9 and 1.8 and the ACQ-TS was 0.8 to 1.7 kg/m$^3$ of copper.

In weight loss, the MCA and the CA exhibited similar weight loss thresholds of 0.9 to 1.7 kg/m$^3$ and 0.9 to 1.8 kg/m$^3$ of copper, respectively. This suggests that the significant difference seen in the strength loss is a further demonstration of the sensitivity of the strength loss versus the weight loss in this type of testing.

Only the highest loading, 3.3 kg/m$^3$ of copper, of the CuMEA gave acceptable performance while the remaining copper alone samples gave high weight losses.

Table 3. Mean weight loss of wafers after exposure to *P. placenta*.

| System | Copper Retention [kg/m$^3$] | Weight Loss % | Significance | Acceptable |
|---|---|---|---|---|
| **MCQ** | 0.83 | **37** | C | No |
| | 1.58 | **24** | G | No |
| | 2.40 | **7** | IHJ | Yes |
| | 3.31 | **2** | LKM | Yes |
| **MCQ (TS)[a]** | 0.86 | **25** | GF | No |
| | 1.73 | **8** | IHJ | Yes |
| | 2.61 | **2** | LKM | Yes |
| | 2.70 | **2** | LKM | Yes |
| **ACQ-D** | 0.88 | **35** | DC | No |
| | 1.78 | **11** | H | Yes |
| | 2.61 | **5** | LIKMJ | Yes |
| | 3.54 | **1** | LM | Yes |
| **ACQ-D** | 0.82 | **30** | FE | No |
| | 1.65 | **7** | IHJ | Yes |
| | 2.50 | **4** | LKMJ | Yes |
| | 3.33 | **2** | LKM | Yes |
| **CA** | 0.88 | **34** | DCE | No |
| | 1.78 | **6** | LIKHJ | Yes |
| | 2.67 | **1** | LKM | Yes |
| | 3.58 | **0** | M | Yes |
| **MCA** | 0.85 | **31** | DE | No |
| | 1.68 | **10** | IH | Yes |
| | 2.62 | **7** | IKHJ | Yes |
| | 3.49 | **6** | LIKHJ | Yes |
| **MCu** | 0.80 | **50** | A | No |
| | 1.63 | **42** | B | No |
| | 2.45 | **47** | A | No |
| | 3.28 | **45** | AB | No |
| **CuMEA** | 0.82 | **49** | A | No |
| | 1.63 | **46** | A | No |
| | 2.43 | **25** | GF | No |
| | 3.25 | **9** | IHJ | Yes |
| **Water** | -- | **48** | A | -- |

[a]TS indicates treating plant liquid, see text.

## 4. CONCLUSIONS

This soil block test with the highly copper tolerant fungus, *Postia placenta*, showed that there is usually no difference in the strength losses determined for micronized systems compared to their amine soluble counterparts. The only difference was for amine copper azole which was slightly less effective than the micronized product, MCA.

Similar strength losses for similar copper retentions were also found in comparing virgin with used solutions. This indicates that there is no significant stripping of the co-biocide or other deleterious effect experienced during the use of a solution for repetitive treatments.

Not too surprisingly, this test with the highly copper tolerant fungus, *Postia placenta*, showed that a co-biocide was definitely necessary to protect the wood. Basically, any copper only system did not perform well whether it was evaluated by strength loss or weight loss.

## 5. REFERENCES


Duncan, C G, 1953. Soil-block and agar-block techniques for evaluations of oil-type wood preservatives: creosote, copper naphthenate and pentachlorophenol. Special Release No. 37, USDA Div. of Forest Pathology, Beltsville, MD, 35 pp.

Duncan, C G, 1957. Evaluating wood preservatives by soil-block tests: 9. Influence of different boiling fractions of the petroleum carrier on the effectiveness of pentachlorophenol and copper naphthenate. Proceedings American Wood-Preservers' Association, 53:13-21.

Duncan, C G, 1958a, Evaluating wood preservatives by soil-block tests: 10. Effect of species of wood on preservatives threshold values, Proceedings American Wood-Preservers' Association, 54:172-177.

Duncan, C G, 1958b, Studies of methodology of soil-block testing. U.S. Forest Service, Forest Products Laboratory. Rpt. 2114.

Duncan, C G and F F Lombard. 1965. Fungi Associated With Principal Decays in Wood Products in the United States. USDA Forest Service, Research Paper W0-4. 31 pp.

Duncan, C G and C A Richards, 1950, Evaluating wood preservatives by soil-block tests: 1. Effect of the carrier on pentachlorophenol solution, 2. Comparison of a coal tar creosote, a petroleum containing pentachlorophenol or copper naphthenate and mixtures of them, Proceedings American Wood-Preservers' Association, 46:131-145.

Jansen, S and D D Nicholas, 2002, Use of transverse compression properties as a measurement of wood biodegradation, Part 1 of 2 - Effect of white-rot on yellow poplar. International Research Group on Wood Preservation. IRG/WP 02-40239.

Nicholas, D D and D Crawford, 2003, Concepts in the development of new accelerated test methods for wood decay. In: Wood Deterioration and Preservation: Advances in Our Changing World, eds. B Goodell, D Nicholas and T Schultz, American Chemical Society Symposium Series, Washington, D.C.

Nicholas, D D and Z Jin, 1996, Use of compression strength loss for measuring decay in the soil block test. International Research Group on Wood Preservation, IRG/WP 96-20083.