Copper Based Wood Preservative Systems- are used Treating Solutions as Efficacious as Virgin Solutions?

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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 copper systems with co-biocides performed very well while copper 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.

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 several 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 and micronized copper systems

For this paper, virgin treating solutions are defined as solutions that are created in a small batch for initial laboratory efficacy screening as a wood treatment. Usually, these early results are used for subsequent listing efforts but it is uncommon for more small scale efficacy testing such as soil block testing to be done later in the product cycle. It is uncommon that used solutions from industrial work tanks are taken for efficacy screenings. For this work, it was decided to conduct efficacy testing with both virgin and used treating solutions. It was thought that any deleterious depletion of actives or agglomeration of actives due to "treating conditions" would be apparent in performance differences between the virgin and used solutions. Used treating solution (TS) as defined in this study represents solution that has been in contact with wood inside the treatment cycle.

EXPERIMENTAL METHODS

Formulations and Treatments

Copper formulations used for wafer treatments in this test are: Micronized Copper Quat Type A (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 of the formulations 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". However, the MCQ from the treating plant was Type A as compared to the ACQs which were Type D. 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. Used treated solutions were not collected for Micronized Copper Azole Type B (MCA) and Copper Azole Type B (CA) because of time constraints and availability of solutions.

Wafers were treated with the solutions using laboratory cylinders and the various treatments were adjusted to provide groups with nominal copper as metal retentions of 0.80, 1.6, 2.4 and 3.2 kg/m^3 (0.05, 0.10, 0.15 and 0.20 pcf). The intent of maintaining the same copper retentions was to evaluate the effects of the co-biocides if present.

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. The 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. Ten wafers were treated with each given solution concentration and the 8 replicate wafers were chosen that were closest to the target retention. Eight of the wafers were exposed (4 per container) to the fungus and the remaining two wafers were used for preservative analysis. A matched set of untreated southern pine sapwood controls were treated with water only and tested along with each set of solution treatments. Table 1 presents the treating information.

Chemical Analysis

The virgin formulations were prepared from common copper sources such as copper carbonate and blended with co-biocides in the proper ratios according to AWPA P5. The used treating solutions were commercial formulations. Chemical analysis was done according to AWPA Standards A9 for copper, A28 for azoles and A36 for quats, as appropriate.

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).

Samples were sterilized by gamma irradiation prior to soil block 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) (Figure 1). (Thus the eight replicates for a particular formulation would be in two separate containers.) 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 according to the procedures of AWPA E22. The strength loss results are in Table 2. After drying to constant weight, the weight losses of the samples were determined with the results in Table 3.

Analysis of variance (ANOVA, SAS 9.1 2009) was used to determine significant differences between means of the strength and weight losses. 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.

RESULTS AND DISCUSSION

As shown in Tables 1, 2, and 3, and Figure 2, 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.

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 close, it is reasonable to surmise that no deleterious effects are exerted on the treating solutions during repetitive, multiple treatment usage. Recall though that the MCQ-TS had a higher proportion of quaternary than the virgin solution, so the slightly better performance of the treating plant solution may be due to its higher proportion of quat. 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, there is no meaningful difference in the thresholds 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 against this particularly highly aggressive strain of copper tolerant fungus. This was expected and the necessity of an effective co-biocide is clearly demonstrated.

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 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. As noted earlier, decay affects strength faster and to a larger degree than weight.

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.

CONCLUSIONS

This soil block test with the highly copper tolerant fungus, *Postia placenta*, showed that there is no meaningful difference in the strength losses determined for micronized systems compared to their amine soluble counterparts. One micronized product, MCA, was slightly more effective than amine copper azole but the remaining systems showed the micronized and amine formulations to have similar strength losses.

Similar strength losses for similar copper retentions were also found in comparing virgin with used treating solutions. This indicates that there is no significant change in concentration of the co-biocide or other measured effects were experienced in the work tank solution after the use of a solution of repetitive treatments when compared to new solutions.

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.

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Table 1. Treatment of wafers

		RETENTION [kg/m^3]			
Treatment	**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	0.80	0.96	0.11
	0.24% MCQ (TS)	736.5	1.76	1.76	0.22
	0.35% MCQ (TS)	738.4	2.56	2.72	0.33
	0.37% MCQ (TS)	729.1	2.72	2.72	0.34
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	0.80	0.64	0.09
	0.24% ACQ-D (TS)	699.4	1.60	1.28	0.18
	0.35% ACQ-D (TS)	706.1	2.40	1.92	0.27
	0.47% ACQ-D (TS)	705.6	3.36	2.56	0.37
CA	0.12% CA	746.4	0.88	0.64	0.92
	0.24% CA	753.9	1.78	1.12	1.85
	0.37% CA	755.0	2.67	1.76	2.77
	0.49% CA	760.6	3.58	2.24	3.73
MCA	0.12% MCA	723.5	0.85	0.48	0.88
	0.24% MCA	716.0	1.68	1.12	1.75
	0.37% MCA	743.5	2.62	1.76	2.74
	0.49% MCA	739.7	3.49	2.24	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.

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

System	Copper Retention [kg/m^3]	Strength Loss [%]	Standard Deviation	Significance	Equal to Unexposed
MCQ	0.83	**70.8**	5.6	CBD	No
	1.58	**30.6**	14.3	GF	No
	2.4	**-15.1**	4.9	KNML	Yes
	3.31	**-26.6**	4.6	O	Yes
MCQ (TS)[a]	0.86	**54.5**	6.9	E	No
	1.73	**-7.6**	5.7	KJ	Yes
	2.61	**10.1**	10.6	IH	Yes
	2.7	**-13.2**	10.1	KML	Yes
ACQ-D	0.88	**61.5**	7.0	ED	No
	1.78	**3.7**	12.6	IH	Yes
	2.61	**-10.1**	8.7	KJL	Yes
	3.54	**-16**	4.6	CED	Yes
ACQ-D (TS)[a]	0.82	**62.4**	13.0	ED	No
	1.65	**-10.6**	9.2	IH	Yes
	2.5	**-19.9**	8.5	KJL	Yes
	3.33	**-21.1**	5.1	KNML	Yes
CA	0.88	**77.5**	8.0	B	No
	1.78	**23.3**	9.6	G	No
	2.67	**11.2**	11.5	H	No
	3.58	**7.9**	8.8	IH	Yes
MCA	0.85	**68**	6.6	BCD	No
	1.68	**-7.1**	10.9	KJ	Yes
	2.62	**-25**	11.1	ON	Yes
	3.49	**-28**	5.7	O	Yes
MCu	0.8	**96**	0.4	A	No
	1.63	**96.4**	0.1	A	No
	2.45	**91.7**	1.6	A	No
	3.28	**90**	2.5	A	No
CuMEA	0.82	**94.9**	0.7	A	No
	1.63	**95**	1.0	A	No
	2.43	**72.4**	31.0	CBA	No
	3.25	**39.9**	22.0	F	No
Water Exposed	--	**95.1**	--	A	--
Water Unexposed	--	--	--	IJ	--

[a]TS indicates treating plant liquid, see text.
Mean values expressed for copper retention and strength loss.

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

System	Copper Retention [kg/m^3]	Weight Loss %	Standard Deviation	Significance	Acceptable
MCQ	0.83	**37**	**0.02**	C	No
	1.58	**24**	**0.01**	G	No
	2.4	**7**	**0.01**	IHJ	Yes
	3.31	**2**	**0.02**	LKM	Yes
MCQ (TS)[a]	0.86	**25**	**0.04**	GF	No
	1.73	**8**	**0.04**	IHJ	Yes
	2.61	**2**	**0.04**	LKM	Yes
	2.7	**2**	**0.01**	LKM	Yes
ACQ-D	0.88	**35**	**0.02**	DC	No
	1.78	**11**	**0.01**	H	Yes
	2.61	**5**	**0.01**	LIKMJ	Yes
	3.54	**1**	**0.01**	LM	Yes
ACQ-D (TS)	0.82	**30**	**0.01**	FE	No
	1.65	**7**	**0.02**	IHJ	Yes
	2.5	**4**	**0.01**	LKMJ	Yes
	3.33	**2**	**0.02**	LKM	Yes
CA	0.88	**34**	**0.04**	DCE	No
	1.78	**6**	**0.04**	LIKHJ	Yes
	2.67	**1**	**0.05**	LKM	Yes
	3.58	**0**	**0.02**	M	Yes
MCA	0.85	**31**	**0.01**	DE	No
	1.68	**10**	**0.01**	IH	Yes
	2.62	**7**	**0.03**	IKHJ	Yes
	3.49	**6**	**0.03**	LIKHJ	Yes
MCu	0.8	**50**	**0.01**	A	No
	1.63	**42**	**0.03**	B	No
	2.45	**47**	**0.02**	A	No
	3.28	**45**	**0.01**	AB	No
CuMEA	0.82	**49**	**0.02**	A	No
	1.63	**46**	**0.01**	A	No
	2.43	**25**	**0.01**	GF	No
	3.25	**9**	**0.01**	IHJ	Yes
Water Exposed	--	**48**	**0.04**	A	--

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

Figure 1. Photo is a depiction of one container holding 4 exposed wafers of a particular retention covered by mycelium of *P. placenta*.

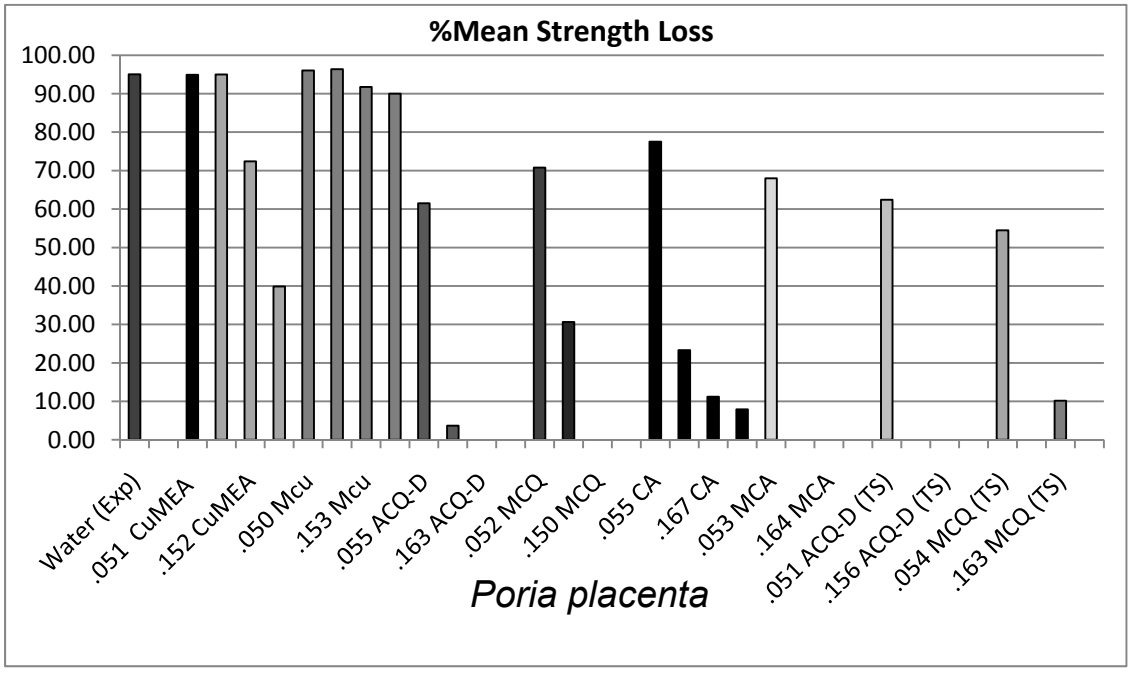

Figure 2. Mean percent strength loss (as compared to untreated, unexposed) for treated and untreated samples exposed to (*P. placenta*).