# Long-term ground-contact efficacy studies of two synergistic biocide mixtures that laboratory decay studies suggested may be promising wood preservative systems

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**Abstract**

The development of new preservative systems requires considerable time, and initially promising systems are often discarded after considerable time and expenses have been borne. With the trend to employ multiple biocides many combinations could conceivably be tested for many years, which clearly is neither practical nor economical. It is necessary to employ initial laboratory decay screening tests to rapidly select only those systems that will likely perform well in outdoor exposure and discard the majority that appear inadequate. This choice is extremely difficult and fraught with the likelihood of both erroneously rejecting good systems and selecting others for further testing that later prove inadequate. We had previously identified two mixtures that, based on rapid initial laboratory screening with the agar plate test and subsequent verification employing the soil block test, were found to be highly synergistic; Cu(II) and sodium pyrithione (Cu:P), and Cu(II) and copper-8-quinolinolate/oxine copper/Cu-8 (Cu:Cu-8). These two promising systems, selected from more than 60 mixtures, were used to treat stakes that were then installed in two outdoor test plots in areas with high or severe decay and termite deterioration hazards. After nine and 14 years of exposure for the Cu:Cu-8 and Cu:P systems, respectively, these systems generally performed equally or only slightly worse than the highly effective preservative CCA-C at mid to high retentions. We conclude that it is possible to use rapid laboratory screening tests to dramatically reduce the number of possible combinations studied in lengthy and expensive outdoor exposure tests. However, investigators need to fully understand the limitations and advantages of the particular laboratory screening test(s) employed to optimize the data obtained from the laboratory screening procedure while minimizing the test's drawbacks.

Wood products are used extensively in applications where the wood can be degraded by many different organisms. To prevent degradation, nondurable wood products used in applications where they are susceptible to biodeterioration are treated with biocides. Wood preservation has recently undergone dramatic changes worldwide, driven by both real and perceived environmental concerns and governmental regulations (Preston 1993, 2000; Schultz et al. 2007). As the older preservatives are removed, new systems that are environmentally-benign need to be developed (Freeman et al. 2006, Schultz et al. 2007).

The development of new wood preservative systems is a difficult and long-term process. Among the reasons for this lengthy process is the need for multiple year outdoor efficacy testing at two or more sites (Preston 2003). Also, new systems are usually composed of a combination of two or more biocides with other nonbiocidal additives sometimes added (Freeman et al. 2006, Schultz et al. 2007). This results in numerous potential combinations, and it simply is not practical to test all possible combinations in outdoor efficacy tests. Thus, laboratory screening tests are employed to greatly reduce the large number of possible candidates to an economically acceptable few for long-term and costly outdoor testing. How laboratory screening data are used to reduce the large

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number of possible candidates to a small number is, however, a thorny assessment. Undoubtedly, in the past sometimes "the baby was thrown out with the bathwater." For example, CCA, the dominant preservative systems in the latter half of the 20th century in North America, showed poor efficacy against some decay fungi in laboratory soil block screening tests. Thus, scientists need to be cognizant of the advantages and limitations of the particular screening test(s) employed.

The initial laboratory screening test first employed to determine efficacy in North America is usually the soil block test (Behr 1973, Archer et al. 1995). The soil block test typically requires about 4 months, is an established procedure, and initial leaching experiments can be run on the wood prior to inoculation. For single-component biocide systems, such as the first-generation organic systems penta and creosote, this screening test is usually very good. However, with the trend to employ multiple biocides and additives in the third-generation organic systems (Preston 2003, Schultz et al. 2007), the number of possible combinations can be quite large and require much time and expense to test all possible combinations.

The agar plate method offers several advantages in rapid screening of many potential wood preservatives (Archer et al. 1995, Behr 1973). It is extremely rapid compared to other screening methods, with results usually obtained within a week. Also, it is easy to quickly run many biocides with a wide variety of decay fungi, and the results are often reproducible unlike many other decay tests. However, the results obtained give only a relative "fungicidal" activity value, and the test does not indicate how well the biocide(s) performs in wood or if biodeterioration and/or leaching may be a problem during the long service life expected from treated wood.

The overall objective of this paper was to determine how well wood treated with systems that were identified as promising using rapid laboratory screen tests performed in long-term ground-contact exposure at two sites in high or severe deterioration zones.

## Methods

We decided to use the agar plate test as an initial screening tool to examine a large number of biocide combinations for synergism. We focused on four low-cost biocides as one component, three of which are already employed in wood preservation (Nicholas and Schultz 1995) [boric acid/borates; the quat didecyldimethylammonium chloride (DDAC); and Cu(II)], and one low-cost organic that had been previously examined as a possible preservative and once apparently sold in South America, tribromophenol (TBP). For the second component we employed a number of biocides that either are commercial wood preservatives or have been extensively examined as possible biocides (Nicholas and Schultz 1995): 3-iodo-2-propynylbutyl carbamate; copper naphthenate, copper-8-quinolinolate (Cu-8); 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one; propiconazole; tebuconazole, diiodomethyl-p-tolysulfone, and chlorothalonil. These biocides are relatively expensive compared to the four biocides employed as the first component. We also examined one biocide not previously examined as a wood preservative, sodium pyrithione. These mixtures were examined in a three:one ratio, employing more of the low-cost component and less of the usually more expensive second biocide. Each mixture, and the individual components, were tested against four wood-destroying fungi, two brown-rots (*Gloeophyllum trabeum* (ATCC 11539) and *Postia placenta* (ATCC 11538), and two white-rot fungi (*Trametes versicolor* (ATCC 12679) and *Irpex lacteus* ATCC 11245). The data were analyzed to determine which mixtures were synergistic (Schultz and Nicholas 1995). Promising systems were then rerun with the agar plate test using a wider range of biocide ratios, and then the synergism verified using the soil-block test.

Defect-free kiln-dried southern pine sapwood (*Pinus* spp. L.) was machined into ground-contact field stakes measuring 19 by 19 by 457 mm (0.75 by 0.75 by 18 inches). The stakes were treated by a full-cell process using a dual treatment for each preservative. For the Cu(II):pyrithione (Cu:P) mixture, stakes were first treated with sodium pyrithione (sodium omadine™), wrapped in plastic for 5 days, then air-dried (Schultz et al. 2000). Following this, the samples were retreated with an ammoniacal copper(II) carbonate (ACC) solution and air-dried again. Retentions were based on weight gain and the solution concentrations and are reported on the basis of CuO for Cu(II) and sodium pyrithione for pyrithione. For the Cu(II) and Cu-8 system (Cu:Cu-8), the stakes were first treated with ACC in water, air-dried, then treated with an oil-soluble Cu-8 (Nytek 10) in mineral spirits, then air-dried again (Schultz et al. 2005). As above, retentions were based on weight gain with the copper retentions based on CuO.

The field stakes were installed at the Dorman Lake, Mississippi, and Saucier, Mississippi, test plots, with 10 replicate stakes per treatment installed at both sites. Dorman Lake is located in northeast Mississippi, has a heavy clay soil that is poorly drained, and is classified as a high American Wood-Preservers' Association (AWPA Zone 4) deterioration zone. Copper-tolerant brown-rot fungi are abundant at the Dorman Lake test plot (Schultz et al. 2000) and, consequently, this is a good site to evaluate copper-based systems. The Saucier plot is located in the Harrison National Forest near the Gulf Coast, has a sandy loam soil that is well drained, and is classified as a severe (AWPA Zone 5) deterioration zone with aggressive termites. The climate and soils at these two sites are fully described elsewhere (Schultz et al. 2002). The stakes were visually inspected periodically, with separate decay and termite ratings based on a rating system using AWPA Standard E7–01 [a 10 rating, sound to trace of degradation; a 9 rating, trace to 3 percent degradation; etc., down to a 0, or failed], with the average ratings reported for the 10 stakes in each treatment set at each location.

The last inspection occurred in the summer of 2007. Hurricane Katrina had caused considerable damage to the Saucier test site in 2005, with the relatively small Cu:P test plot particularly hard hit with six trees felled. This and the clean-up resulted in about 15 percent of the remaining stakes being destroying, with the averages calculated based on the remaining stakes.

## Results and discussion

By the initial and relatively rapid agar plate screening process over 60 mixtures were run. Four mixtures were found to be synergistic, and two had relatively high synergistic factors. By employing mostly biocides that either were used commercially as wood preservatives or had been extensively studied we felt that some of the disadvantages of the agar plate were overcome, specifically:

- Although the agar plate gives only a relative fungicidal value, by just looking for enhanced efficacy we could detect those mixtures which would perform at least as well as the individual components, most of which are biocides already employed or being considered as wood preservatives;
- While the agar plate does not give any idea of the extent of biocide leaching and/or biodegradation in long-term exposure applications, by employing mostly biocides that were already extensively examined or commercially employed as wood preservatives, these two factors should not be a problem; and
- By employing mixtures containing relatively large amount of a low-cost biocide, Cu(II), DDAC, TBP, or boric acid, the cost of a mixture should be relatively low.

The four synergistic mixtures were examined further using additional agar plate tests with a wider range of biocide ratios followed by soil-block tests. The two mixtures which initially showed high synergism, Cu(II) and sodium pyrithione (Cu:P), and Cu(II) and Cu-8 (Cu:Cu-8), continued to show high efficacy against a variety of decay fungi and, consequently, were chosen for outdoor exposure testing.

*Table 1. — Average decay and termite ratings for SYP field stakes treated with sodium pyrithione and Cu(II) after 14 years of exposure at the Dorman Lake and Saucier test sites. Generally based on an average of 10 replicate stakes per site per treatment, but some stakes in the Saucier site were missing after hurricane Katrina. Stakes were dual-treated, with sodium pyrithione (pyrithione) in water treated first with the stakes then dried, followed by Cu(II) as water-borne ammoniacal copper carbonate (ACC) with the retention based on CuO. Decay and termite ratings were based on AWPA standard E7 –01, with a 10 rating sound to trace of degradation, etc., down to a 0 [failed] rating.*

| | | Average rating after 14 years of exposure | | | |
|---|---|---|---|---|---|
| | Retention | Dorman Lake | | Saucier | |
| Treatment | ($kg/m^3$) | Decay | Termite | Decay | Termite |
| 1% ACC | 6.47 | 5.7 | 6.9 | 4.9 | 7.1 |
| 0.34% Pyrithione | 2.34 | 0 | 0 | 0 | 0 |
| 0.042% Pyrithione/0.125% ACC | 0.27/0.77 | 0 | 0 | 0 | 0 |
| 0.025% Pyrithione/0.125% ACC | 0.16/0.72 | 0.4 | 0.8 | 0 | 0 |
| 0.084% Pyrithione/0.25% ACC | 0.56/1.46 | 2.3 | 2.2 | 0 | 0 |
| 0.05% Pyrithione/0.25% ACC | 0.30/1.62 | 2.0 | 1.6 | 0 | 1.1 |
| 0.17% Pyrithione/0.50% ACC | 1.15/3.42 | 5.1 | 5.4 | 8.0 | 9.6 |
| 0.17% Pyrithione/0.50% ACC | 1.14/3.33 | 4.6 | 5.3 | 6.9 | 7.9 |
| 0.10% Pyrithione/0.50% ACC | 0.67/3.33 | 3.4 | 5.2 | 6.3 | 7.3 |
| 0.25% Pyrithione/0.75% ACC | 1.68/5.45 | 5.7 | 7.9 | 9.0 | 9.4 |
| 0.15% Pyrithione/0.75% ACC | 1.10/4.98 | 7.6 | 8.9 | 8.4 | 8.7 |
| 0.34% Pyrithione/1.0% ACC | 2.56/5.21 | 4.0 | 6.5 | 3.4 | 3.6 |
| 0.34% Pyrithione/1.0% ACC | 2.35/6.95 | 8.3 | 8.2 | 6.0 | 6.3 |
| 0.20% Pyrithione/1.0% ACC | 1.36/6.86 | 7.7 | 8.2 | 5.9 | 7.4 |
| 0.2% CCA* | 1.6 | 0 | 0.5 | 0 | 0 |
| 0.4% CCA* | 3.2 | 3.7 | 3.8 | 2.4 | 1.1 |
| 0.7% CCA* | 4.8 | 4.6 | 5.1 | 7.7 | 3.8 |
| 0.9% CCA* | 6.4 | 7.7 | 8.0 | 8.6 | 6.9 |
| 1.3% CCA* | 9.6 | 8.4 | 9.3 | 9.3 | 8.3 |

*The CCA-treated stakes were rated by Terry Amburgey, H. Mike Barnes, Brian Lindsey, and Mike Sanders from another study at the Dorman Lake and Saucier plots and they kindly provided the data.

## Long-term ground-contact exposure testing

The results from earlier ratings of the two systems in ground-contact exposure has been previously reported (Cu:P, Schultz et al. 2000; and Cu:Cu-8, Schultz et al. 2005). This paper only reports results from the latest inspections, 14 years for the Cu:P (**Table 1**) and 9 years for the Cu:Cu-8-treated stakes (**Table 2**). The control/untreated stakes, which were destroyed by decay and/or termites within 3 years, are not reported.

The results from the Cu:P stakes after 14 years of exposure are shown in **Table 1**. The stakes treated with relatively low levels of pyrithione and Cu are doing equivalent to or better then stakes treated to about the same general retention with 0.2 or 0.4 percent CCA at both locations. Stakes treated with mid to high levels of pyrithione and Cu are doing about as well as or only slightly worse than stakes treated to about the same actives retention with 0.7, 0.9 or 1.3 percent CCA. However, one of the two Cu:P sets treated with 0.34 percent pyrithione and 1.0 percent Cu is doing poorly at both locations; specifically, the set with less copper has poor decay and termite efficacy. The pryithione:copper ratio in this poorly performing set is about 2:1, the lowest ratio among all the Cu:P sets. It is possible that the copper level was too low to complex with all the pyrithione and, consequently, more pyrithione leached, resulting in lower levels of both copper and pyrithione. In summary, it appears that at an approximately equal actives retention Cu:P performs about the same as CCA, with one exception.

The results of the Cu:Cu-8 treated stakes after 9 years of exposure are given in **Table 2**. Stakes treated with relatively low retentions are generally performing as well as stakes treated with 0.5 percent CCA to a 3.0 $kg/m^3$ retention. Stakes treated with higher levels of Cu are performing about equivalent to CCA provided that the Cu-8 treatment level was greater than 0.1 percent.

## Conclusions

More than 60 biocides mixtures were examined by a rapid screening agar plate test that was designed to optimize the strengths and minimize the disadvantages of the initial test. Promising mixtures were then examined by additional agar plate tests followed by the soil block test, with two mixtures selected as the most promising. In long-term ground-contact exposure at two locations with high or severe decay and termite hazards, these two systems performed roughly equal to stakes treated with the highly effective CCA preservative

*Table 2. — Average decay and termite ratings for SYP field stakes treated with Cu(II) and Cu-8 after approximately 9 years of exposure at the Dorman Lake and Saucier test sites. Based on an average of 10 replicate stakes per site per treatment. Copper was water-borne ammoniacal copper carbonate (ACC) with the retention based on CuO. Cu-8 was Nytek 10 using mineral spirits as the solvent. Decay and termite ratings were based on AWPA standard E7 –01, with a 10 rating sound to trace of degradation, etc., down to a 0 [failed] rating.*

| | | Average rating after 9 years of exposure | | | |
|---|---|---|---|---|---|
| | Retention | Dorman Lake | | Saucier | |
| Treatment | ($kg/m^3$) | Decay | Termite | Decay | Termite |
| ACC, 0.50% | 2.4 | 5.2 | 7.1 | 6.7 | 8.9 |
| ACC, 1.0% | 5.1 | 5.0 | 6.1 | 6.6 | 7.6 |
| Cu-8, 0.13% | 0.3 | 0 | 0 | 1.0 | 1.0 |
| Cu-8, 0.30% | 0.96 | 1.6 | 1.3 | 1.9 | 1.1 |
| Cu-8, 0.69% | 1.92 | 3.4 | 3.1 | 5.4 | 6.5 |
| 0.125% ACC/0.08% Cu-8 | 0.6/0.3 | 2.4 | 3.1 | 4.0 | 4.5 |
| 0.25% ACC/0.04% Cu-8 | 1.6/0.2 | 2.8 | 4.4 | 7.1 | 8.5 |
| 0.25% ACC/0.08% Cu-8 | 1.3/0.3 | 5.0 | 6.1 | 5.1 | 5.3 |
| 0.50% ACC/0.08% Cu-8 | 2.4/0.3 | 8.0 | 7.9 | 9.3 | 9.6 |
| 0.50% ACC/0.17% Cu-8 | 3.2/0.5 | 7.6 | 8.0 | 8.5 | 8.7 |
| 0.75% ACC/0.08% Cu-8 | 5.0/0.2 | 7.0 | 9.4 | 8.0 | 6.8 |
| 0.75% ACC/0.13% Cu-8 | 5.0/0.3 | 8.9 | 9.8 | 9.0 | 10.0 |
| 0.75% ACC/0.25% Cu-8 | 3.7/0.6 | 9.9 | 9.9 | 8.9 | 9.4 |
| 1.00% ACC/0.10% Cu-8 | 6.1/0.3 | 9.0 | 8.4 | 6.6 | 6.6 |
| 1.00% ACC/0.17% Cu-8 | 5.0/0.5 | 8.3 | 9.6 | 9.8 | 9.8 |
| 1.00% ACC/0.30% Cu-8 | 5.0/1.1 | 7.6 | 8.8 | 9.7 | 9.9 |
| CCA, 0.50% | 3.0 | 7.4 | 6.4 | 9.8 | 9.4 |
| CCA, 1.0% | 6.1 | 9.6 | 8.8 | 9.8 | 10.0 |

system at similar actives retentions. We conclude that our approach of employing a "designed" screening approach successfully selected two mixtures that performed very well in long-term outdoor exposure.

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