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PERFORMANCE OF NEW SILVER BASED WOOD PRESERVATIVES

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Summary

Research programs sponsored by the Silver Research Consortium have established that commercial aqueous dispersions of biocidal silver are effective as wood preservatives. Research carried out independently by US Forest Products Laboratory (Madison, WI) has established that these same biocidal silver formulations also repel termites. These products work in almost all naturally occurring soil pH levels and have very low leaching propensities in soil and water environments.

1. Introduction

Several drivers have converged that allow the development of silver based wood preservatives to be attractive. The first was the voluntary withdrawal announced on February, 12, 2002 of Chromated Copper Arsenate (CCA) from the residential applications market, as a result of an agreement with the US Environmental Protection Agency by leading manufacturers of preserved wood. Between 1933 and 2004, CCA was the dominant chemical for pressure treating of such applications, however its withdrawal has opened this application to at least 30 organic and inorganic biocides and preservatives.(1) Also, wood/plastic composite materials have entered the market and have seen steady growth.(2)

Silver has been registered for use as a pesticide in the USA since December 1954 when the Federal government issued the first registration for silver as an antimicrobial agent.(3) At present, products emitting silver for antimicrobial purposes as pesticides are regulated under the US Federal Insecticide, Fungicide and Rodenticide Act (FIFRA). Silver has a long history of use as a biocide in medical, water purification and other applications. At the same time, silver colloids have been developed and used in many of the above applications. The ability to stabilize fine dispersions of silver and maintain their chemical activity, particularly in the presence of light, has been developed for many years and one example of control release technology involving silver ions is shown in reference 4. The confluence of discoveries on the ability of finely divided silver to be incorporated in a form compatible with wood pressure treatment technology led to interest in examining its usefulness in preventing degradation of Southern yellow pine lumber. Several research projects have been sponsored by the Silver Research Consortium at Florida International and Mississippi State Universities to develop such information. In this paper the following characteristics of three selected silver-based wood preservative treatments are described: maintenance of compressive strength after soil bed exposure, retention of preservative, leaching of preservative into water and soil environments and toxic threshold levels with selected fungi. Independent research with these same products carried out at the US Forest Products laboratory has also shown that these products also provide termite repellency.(5) Recent studies have also shown that nano particles of silver and nano silver in combination with nano zinc oxide can also be effective wood preservatives. (6) (7)

2. Methodology

a. Application of Preservative Formulations:
Three liquid silver containing wood preservative chemicals were chosen for study. These have been screened to be the best of 11 available chemicals in an earlier study, where it was found that solid biocides, dispersed in silicone, gave inferior results. The three treatments used in this work are coded as:

β: Silver iodide dispersion, diluted with deionized water
κ: Titanium dioxide and silver chloride dispersion used as-is
ω: Zeolite slurry containing silver and zinc

Southern pine was purchased from lumber stores in the southeast USA without any chemical treatment. Samples were free of knots and did not show any visible evidence of mold, stain, decay or insect attack. Blocks of 3.24 cm^3 (0.198 in^3) volume were cut and weighed to the nearest 10 mg before chemical treatment. The weighed samples were used for untreated controls and for treatment with the silver formulations. Wood samples taken from purchased stock were randomized across the applied treatments. The test blocks including controls were conditioned using an oven at 40°C. They were brought to a constant moisture equilibrium and weighed to the nearest 0.1 grams just before treatment. Blocks were conditioned before and after treatment with the preservative chemical by placing in a forced draft oven at 40°C until two consecutive weighing were equal, which required 8 – 12 hours. Impregnations were carried out in a vacuum desiccator being exposure for 30 minutes under a vacuum of approximately 300 mm of mercury in a Pyrex vessel. The treated blocks were then exposed to atmospheric pressure for 30 minutes to allow for equilibration to occur, followed by the 40°C conditioning described above.

b. Soil Bed Exposures:
Soil bed exposures were carried out in the laboratory using a relative humidity at a level that would prevent excessive soil drying. Free draining containers were used with a layer of gravel on the bottom of each bed with a ratio of soil to gravel of 3:1. Fresh soil was used with a water holding capacity between 40 and 60%. pH levels were adjusted to 5.0, 7.0 and 9.0, representing almost all levels of pH found in soil. The soil samples were

passed through a 4 mm sieve to remove large matter. A soil moisture content corresponding to 100% of water holding capacity was maintained: soil beds were watered using soft water. Wood samples were installed with 75 mm (3 in.) spacing and samples immersed to half their length. Soil was then compacted around each sample after placement. Samples were randomly distributed throughout the soil bed. Samples were then visually inspected.

c. Leaching Experiments:
Experiments similar to those described in Section 2b were conducted with treated cubes, 2.54 cm (1 in.) per side using soil, fresh (pond) water and sea water. Samples were half exposed to air and half to the test environment. Soil, fresh water and sea water pH was measured bi-weekly. Soil samples (10 grams), pond water and sea water samples (10 ml each) were collected after one day, one week and two months and analyzed for silver content. The amount of silver was measured by adding 20.0 mm of DTPA (diethylene triamine penta acetic acid) extraction reagent, shaking the solution at 180 rpm for 15 minutes and filtering immediately thereafter using No. 42 Whatman's filter paper. Extracts were saved in labeled scintillation vials in a refrigerator for further analysis of silver in the flame atomic absorption spectrometer at 328.07 nm wavelength.

d. Compressive Strength and Fungi Resistance:
AWPA Standard E10-01, "Standard Method of Testing Wood Preservatives by Laboratory Soil Block Culture" and AWPA Standard E22, "Standard Accelerated Laboratory Methods to Determine the Efficacy of Preservatives Against Wood Decay Fungi Using Compressive Strength" were used to evaluate the three selected silver-based formulations using the three fungi *Gloeophylum trabeum, Postia placenta*, and *Trametes versicolor*. According to the standard, samples were sterilized before exposure to the fungi. Cube samples were placed in test jars and incubated for eight weeks in accordance with the E-10 test standard, while wafers were placed in cups, with four wafers per cup an incubator for four weeks, per the E-22 standard.

3. Results and Discussion

Soil Bed Exposures: After 180 days of exposure, test cubes impregnated with treatment β were firm, corners were intact and no change in color had taken place. A weight loss of 1.5% was measured for blocks exposed to all three pH levels of soils after 180 days. Treatment κ also resulted in test cubes that were firm with intact corners and no change in color. Weight losses of <5% were observed for samples in each of the three pH soils after 180 days. Test cubes impregnated with treatment omega showed a minimum change in appearance: sides exposed to soil lost their original yellow/green color, whereas sides exposed to air were intact. However the blocks were firm and no sign of decay or fungal growth in all three pH level soils were seen. The weight loss was found to be <0.15% for blocks exposed to soil at all three pH levels for 180 days. The conditioned and unconditioned control samples showed the presence of a green fungus, growing on the surface of the blocks above the soil. By comparison, the untreated blocks lost about 63% of their weight in these tests.

Leaching Behavior: Results from the leaching behavior are shown in Figure 1. About 0.5g of formulations β and κ were initially taken up in the separately treated 3- 3.5g blocks, of which 0.01g of the formulations was silver. Formulation ω is a slurry in a form that prevented measurement of initial uptake in the test blocks. Formulation β had very low leach rates in sea water and soil, but relatively high levels in fresh water. Formulation κ had low leaching behavior in soil and fresh water, and moderate leach levels in sea water. Formulation ω had the highest leach rates of the three formulations in both soil and sea water, but a significantly lower leach rate than formulation β in fresh water. In ocean water and soil, leach concentrations after 60 days were always <1 ppm. In fresh water, formulations κ and ω had leach concentrations below 0.25 ppm, while formulation β showed a leach concentration of 2.4 ppm after 60 days, the highest of the entire set of results.

Toxic thresholds for each of the three formulations are shown in Table 1. These levels were established by diluting concentrated formulations with deionized water to determine the toxic threshold value, however it should be noticed that this value is based on the silver content of the formulation. All of these formulations contain other ingredients that may contribute to the overall efficacy. This factor must be taken into account in future studies. Compression strength values of wafers exposed to Postia placenta according to AWPA Standard E-22 are shown in Table 2. The Southern pine sapwood wafers, 5 X 18 X 18 mm (0.197 X 0.71 X 0.71 in.) specified in this procedure were treated with only two of the formulations, κ and ω. These formulations were diluted with deionized water to achieve the desired treating solution concentrations.

All three treatments tested were effective in controlling fungal growth. Except for treatment ω in the fresh water environment, the leachability of these formulations pressure treated with samples can be characterized as low, with local silver leachate concentrations <1 ppm. The silver content of the leachate from these conditions can be expected to be in a combined form with other compounds in the solution, or adsorbed onto the soil. Therefore the quantity of ionic silver in the leachate using water quality criteria measurements, is likely to be much lower then the indicated leachate concentration. Of the two formulations tested for compressive strength, formulation κ proved very effective in preserving compression strength using AWPA Standard E-22. At the same levels of silver content, formulation ω proved less effective. Toxic threshold values of silver in these formulations, within pressure treated Southern yellow pine, were typically 0.16-0.48 kg/m^3 (0.01-0.03 lb/ft^3).

4. Conclusions

Commercial aqueous dispersions of silver that are formulated for controlled release of silver ion are effective against wood destroying bacteria, and, at a level of 200 parts per million per weight of wood, are effective against certain wood decay fungi. The wood retains its natural color. Additional research has found these formulations also to be effective in repelling termites. Leaching studies into soil and water indicate the only parts per million of silver are eluted from treated wood. Bioassay evaluations of the effects of leachates in soil and water are now being undertaken at Florida International University. Further research is continuing at Mississippi State University to determine if more economical formulations can be developed using antimicrobial silver with organic fungicides.

5. References

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3. U.S. Environmental Protection Agency, Re-Registration Eligibility Document for Silver, Case 4082, Published 1993 (www.epa.gov/oppsrrd1/reds/old_reds/silver.pdf)
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5. F. Green III and R. Arango, "Wood Protection by Commercial Silver Formulations Against Eastern Subterranean Termites" – IRG-WP 07-30422. Proceedings of IRP-WP 38th Annual Conference, May 2007.
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Tables

Table 1. Toxic threshold levels of silver in the three formulations tested

PRODUCT	**FUNGUS**	**TOXIC THRESHOLD (pcf Ag)**
β	G. trabeum	0.025--0.027
β	T. versicolor	0.0014--0.0069
κ	G. trabeum	0.006—0.007
κ	P. placenta	0.012
ω	G. trabeum	<0.009
ω	P. placenta	>0.036

Table 2. Average compressive stresses (of three samples) of wafer samples after exposure to Postia Placenta, tested in accordance with AWPA Standard E-22

Formula and retention level (pcf)	Average compression stresses (g/m2)
κ 0.0045	22.02
κ 0.0112	156.40
κ 0.0172	175.37
κ 0.0224	175.90
κ 0.0345	168.41
exposed control	0
unexposed control	180.88
ω 0.0045	0
ω 0.0115	0
ω 0.0142	0
ω 0.0233	34.79
ω 0.0358	79.73
exposed control	0
unexposed control	164.70

Figures

Figure 1 Leaching behavior of the three wood preservative formulations from impregnated test blocks into soil, pond water and seawater after 1,7 and 60 days