SYNERGISTIC WOOD PRESERVATIVES: TERRESTRIAL MICROCOSMS (TMCs) AND FIELD EXPOSURE EFFICACY STUDIES OF THE SYNERGISTIC COPPER : PYRITHIONE MIXTURE[1]

Tor P. Schultz†
Professor
Forest Products Laboratory
Mississippi State University
Mississippi State, MS 39762

Thomas Nilsson
Professor
Department of Wood Science
Swedish University of Agricultural Sciences
Uppsala, Sweden

and

Darrel D. Nicholas†
Professor
Forest Products Laboratory
Mississippi State University
Mississippi State, MS 39762

(Received June 1999)

ABSTRACT

On the basis of short-term laboratory tests using various wood decay fungi, we previously found that the mixture of copper (II) and sodium pyrithione is highly synergistic. In this study we examined the efficacy of this mixture in protecting wood using terrestrial microcosms (TMCs) with three different Swedish soils, and field stake (ground contact) tests in two different locations in Mississippi. After 12 months of exposure in TMCs, the copper: pyrithione mixture was found to be more effective than either component alone, with only slight degradation due to tunneling bacteria in a compost soil TMC. The field stake test, after 6 years of exposure, showed that a mixture of 0.31 pcf or greater copper (as CuO) and 0.063 pcf or greater pyrithione (as the sodium salt) was approximately as effective as about 0.35 pcf CCA in preventing fungal and termite degradation.

Keywords: Copper, field exposure, fungi, pyrithione, termites, terrestrial microcosms (TMCs), tunneling bacteria, wood preservation.

INTRODUCTION

As a natural organic material, wood is degraded by many organisms, principally fungi and insects. Consequently, in ground contact applications or where the wood is wetted frequently, it should be treated with biocides for protection against wood-destroying organisms. The three major wood preservatives currently used in the United States are the oilborne organic pentachlorophenol and creosote systems and the waterborne, inorganic chromated copper arsenate (CCA) preservative. Most of the treated wood products in the United States, about 80%, are treated with CCA (Mickelwright 1999). CCA is the primary preservative used in lumber for residential construction (Preston 1993).

[1] Approved for publication as Journal Article No. FP144 of the Forest and Wildlife Research Center, Mississippi State University.
† Member of SWST.

Extensive testing and use have shown CCA to be highly effective at protecting wood against a variety of fungi and termites. Chromated copper arsenate is also low-cost, waterborne, and has good leach-resistant properties. However, the perceived environmental hazards of chromium and arsenic will probably limit the use of CCA in the future. Indeed, the use of CCA-treated lumber has already been greatly reduced in the Hawaiian Islands, and the use of CCA in above-ground applications has been banned in Denmark, Germany, Sweden, and other countries. Also, while current U.S. regulations permit disposal of CCA-treated lumber by landfill burial, it is expected that discarding treated lumber will become more expensive and onerous in the future (Preston 1993). Consequently, a need exists for developing alternative, environmentally benign, waterborne, and effective wood preservative(s) for use in residential applications.

As part of our search for new wood preservatives, we have combined various wood preservatives and, using short-term laboratory decay tests, examined these combinations for possible synergism (Schultz and Nicholas 1995). Based on the results obtained from laboratory screening tests, promising mixtures are then selected for long-term field trials. To date, we have examined over 70 combinations in the laboratory and have identified six combinations for further field efficacy testing.

In the intermediate term, most CCA waterborne replacements will likely be based on copper : organic biocide mixtures (Preston 1993; Nicholas and Schultz 1995a). Copper (II) ion is fairly inexpensive, waterborne, and exhibits good biocidal activity; and it is thus a component of most "second generation" wood preservatives. Due to copper-tolerant fungi, however, it is generally recognized that copper alone is not adequate and, consequently, copper-based formulations should contain a co-biocide.

In short-term laboratory decay tests, one of the most highly synergistic mixtures we found was the combination of copper (II) with sodium pyrithione [sodium omadine; 2-mercaptopyridine 1-oxide, sodium salt; 2-pyridenthiol-1-oxide, sodium salt] (Nicholas and Schultz 1995b, 1996). Other advantages of a copper : pyrithione mixture are: (1) both components are waterborne and odorless; (2) the complex should be very leach-resistant as evidenced by a lack of solubility in any solvent we examined and the commercial use of copper pyrithione as an anti-fouling environmentally benign paint additive for ship bottoms (McCoy 1998; Naoki 1998); and (3) metal complexes of pyrithione, sometimes tested with other organic co-biocides, have been examined as wood preservatives (Trotz and Fedynyshyn 1984; Ludwig et al. 1991; Morpeth 1991; Dietrich 1987; Hedley et al. 1979). Disadvantages of copper : pyrithione include the need for a dual treatment process, which will increase the cost, and the lack of any published data with wood under actual or simulated field exposure conditions.

The objective of this project was to conduct efficacy trials of copper : pyrithione as a wood preservative. Two different tests were used: terrestrial microcosms (TMCs) with three different Swedish soil types (Nilsson and Edlund 1995; Edlund 1998) [also called soil bed, accelerated field simulation, or fungus cellar tests (Nicholas and Archer 1995)], and field (ground contact) stake tests in two locations in Mississippi. Different copper : pyrithione levels were used in the two different tests.

MATERIALS AND METHODS

Terrestrial microcosms (TMCs)

Scots pine (*Pinus sylvestris* L.) sapwood stakes, 5 × 10 × 100 mm, were treated with two levels of aqueous solutions of sodium pyrithione, copper (II) sulfate, or sodium pyrithione-copper (II) sulfate. Impregnation was carried out by first drawing a vacuum on the submerged stakes for 15 min, then leaving them at atmospheric pressure for 2 h. The pyrithione/copper dual treatments were done in two steps with pyrithione used first, followed by drying and then re-treating with copper. Samples were then dried overnight at 103°C to determine their mass.

The TMCs were created in the laboratory by placing selected soils in plastic boxes. Soils were obtained from three different locations in Sweden based on the known occurrence of different decay microorganisms in each soil [test site soil with brown-rot fungi dominating; forest soil which is acidic (pH ~ 3.5) with mainly white- and soft-rot fungi; and a domestic garden compost soil of neutral pH with soft-rot fungi and tunneling bacteria]. The moisture content of each soil was adjusted to 95% of its water-holding capacity and kept at this level by adding water as necessary. The boxes were loosely covered with plastic sheets, and the TMCs incubated at 25°C and around 85% relative humidity. The stakes were inserted vertically in the soil to a depth of 85 mm, with 5 replicate stakes per treatment per TMC. After exposure for 4, 8 and 12 months, the samples were removed, dried overnight at 103°C, and weighed to determine mass losses, with the mass loss used as the index of decay. Tangential, radial, and cross sections of some of the treated stakes exposed for 12 months were inspected by light microscopy to identify the major types of decay.

Field stake (ground contact) exposure

Defect-free kiln-dried southern yellow pine (SYP) sapwood (*Pinus* spp.) was obtained and machined into samples measuring 19 × 19 × 563 mm. An ammoniacal copper (II) carbonate (ACC) solution was obtained from CSI Corp., and a 40% sodium pyrithione concentrate was obtained from Olin Corp. Wood samples were treated using a full-cell process (30 min of 29 in. Hg vacuum followed by 60 min pressure at 150 psig). The dual-treated samples were first treated with sodium pyrithione, wrapped in plastic for 5 days, and then air-dried for 12 days. Following this, the samples were re-treated with ACC and air-dried for 2 weeks. Target treatment ratios were 3:1 and 5:1 (ACC : sodium pyrithione, weight basis). Retentions for copper were based on CuO and on the sodium salt for pyrithione. The positive controls were CCA-C at two retentions, and the negative controls were untreated stakes. Two sets of samples were treated with 0.17% pyrithione : 0.50% ACC and 0.34 pyrithione : 1.0% ACC to provide samples for later depletion analysis if desired.

The field stakes were installed in the fall of 1993 at the Dorman Lake, MS, and Saucier, MS, test plots, with 10 replicates per treatment per test site. Dorman Lake is located in northeast Mississippi near Mississippi State University, and has a heavy clay soil and an abundance of copper-tolerant fungi. The Saucier test plot is located in the Harrison National Forest near the town of Saucier, MS, and has a sandy loam soil. Since this site is near the Gulf Coast, it has a relatively mild winter and wet summer as compared to the Dorman Lake site. The stakes were visually inspected yearly for fungal and termite damage. Separate decay and termite ratings were recorded, based on a semi-log system of 10 to 0 using AWPA Standard E7-93 (1997) [10 rating, sound to trace of degradation; 9 rating, trace to 3% degradation, etc.].

RESULTS AND DISCUSSION

Terrestrial microcosms

Weight losses are given in Table 1, and principal microorganism type(s) that caused wood degradation are shown in Table 2. The untreated (control) samples had high weight losses in all three Swedish soils. The pyrithione-treated wood also performed poorly, probably due to the water solubility of the sodium salt of pyrithione resulting in rapid leaching from the wood. The data in Tables 1 and 2 indicate that pyrithione does exhibit good activity against brown-rot fungi but is susceptible to soft-rot, with soft-rot the dominating decay type in stakes treated with pyrithione alone. This suggests that pyrithione, like triazoles (Edlund and Nilsson 1999), is active against several basidiomycete fungi but less active against soft-rot fungi. White-rot attack was observed in the Forest Soil (Table 2) and was due to an

TABLE 1. *Average weight loss for TMC samples exposed to three Swedish soils for 4, 8 and 12 months. The soils were selected from previous studies for the occurrence of different decay organisms.*

Chemical treatment[2]		Average weight loss (%)[1]								
		Test site soil[3]			Forest soil[3]			Compost soil[3]		
		4 mo	8 mo	12 mo	4 mo	8 mo	12 mo	4 mo	8 mo	12 mo
Pyrithione,	0.1 M	3.4	4.6	4.3	6.2	25.4	24.4	17.4	42.4	62.0
Pyrithione,	0.15 M	4.6	6.4	38.9	6.5	19.4	25.5	12.3	46.7	64.5
Cu,	0.05 M	3.0	3.4	3.7	3.1	27.9	40.1	5.8	22.4	49.2
Cu,	0.075 M	4.6	4.0	5.2	4.6	20.0	31.4	1.7	4.4	3.5
Pyrithione, + Cu[2],	0.1 M 0.05 M	2.5	2.7	3.4	1.7	2.7	3.8	0.9	1.9	2.5
Pyrithione, + Cu,	0.15 M 0.075 M	3.5	2.3	4.4	3.2	3.8	4.3	1.9	1.9	3.9
Control	—	57.1	56.4	59.9	6.6	42.9	37.8	35.8	48.1	66.4

[1] Average of five replicates.
[2] Pyrithione is sodium pyrithione, and Cu is copper (II) sulfate, with the biocide molarity (M) of the treating solution given.
[3] Test Site Soil has predominately brown-rot fungi; Forest Soil mainly has white- and soft-rot fungi; and Compost Soil has mainly soft-rot fungi and tunneling bacteria.

unknown species with an unusual capacity to degrade treated wood. Edland and Nilsson (1999) observed attack by such white-rot fungi in a variety of treated pine stakes. Wood treated at both copper levels gave poor results in the Forest Soil TMC (Table 1) due to an unusual appearance of brown-rot, and possibly some leaching of the copper in the acidic soil (Edlund and Nilsson 1999). In the Compost Soil, high weight losses were observed with the lowest copper level, with degradation due to the combined activities of soft rot and tunneling bacteria (Table 2). In contrast, wood treated with the copper : pyrithione mixture had little weight loss for all three soil types, even at the lower biocide levels (Table 1). Also, no visual degradation was observed for wood treated with the copper : pyrithione mixture for the Test Site Soil and Forest Soil TMCs, but some tunneling bacteria degradation was observed for samples in the Compost Soil TMC.

TABLE 2. *Microscopic identification of the principal microorganism type that caused wood degradation in the TMC test.*

Chemical treatment		Type of microbial attack[1]		
		Test site soil	Forest soil	Compost soil
Pyrithione	0.1 M	SR	SR	SR/TB
Pyrithione	0.15 M	SR	SR/WR	SR/TB
Cu	0.05 M	SR	BR	SR/TB
Cu	0.075 M	SR	BR	SR/TB
Pyrithione + Cu	0.1 M 0.05 M	na	na	TB
Pyrithione + Cu	0.15 M 0.075 M	na	na	TB

[1] SR = soft-rot; TR = tunneling bacteria; WR = white-rot; BR = brown-rot; and na = no attack.
Samples were analyzed after 12 months of exposure in the Test Site, Forest Soil, and Compost Soil TMCs.

Based on the TMC data, we conclude that the copper : pyrithione mixture was more effective than either biocide alone. In addition, mass losses below 5% for all three TMCs indicate good efficacy for this mixture at the two retention levels examined.

Field stake exposure

Tables 3 and 4 show the average decay and termite ratings for the Saucier and Dorman Lake test sites, respectively, after 6 years of exposure. The untreated (control) and pyrithione-treated samples all showed rapid degradation, with none of these samples lasting more than 3 years. Samples treated with 1% ACC had essentially no attack at Saucier, but one sample was totally degraded by fungi (likely a copper-tolerant fungus) at Dorman. Of the copper: pyrithione samples, those treated at the lowest biocide levels (0.125% ACC with 0.042 or 0.025% pyrithione) gave

TABLE 3. *Average decay and termite rating for field stakes at the Saucier, MS plot, and 10 replicate stakes per treatment.*

		Exposure time, years											
	Average retention[2]	1		2		3		4		5		6	
Treatment	kgm^{-3} (pcf)	Decay[3]	Termite[3]	Decay	Termite	Decay	Termite	Decay	Termite	Decay	Termite	Decay	Termite
0.042% Pyrithione + 0.125% Cu	0.27 (0.017) 0.77 (0.048)	9.8	9.8	9.8	9.6	8.4	8.9	6.9	7.0	5.7	5.3	4.3	3.7
0.025% Pyrithione + 0.125% Cu	0.16 (0.010) 0.72 (0.045)	9.6	8.9	8.0	8.9	7.2	7.1	6.6	6.2	4.5	5.6	4.1	4.0
0.084% Pyrithione + 0.25% Cu	0.56 (0.035) 1.46 (0.091)	10	9.9	10	10	9.7	10	9.7	9.7	8.2	9.2	7.7	7.6
0.050% Pyrithione + 0.25% Cu	0.30 (0.019) 1.62 (0.101)	10	9.8	10	10	9.8	10	8.9	9.5	8.2	8.8	7.7	8.1
0.170% Pyrithione + 0.50% Cu	1.15 (0.072) 3.42 (0.214)	10	10	10	10	10	10	10	10	10	9.9	10	9.9
0.170% Pyrithione + 0.50% Cu	1.14 (0.071) 3.33 (0.208)	10	10	10	10	10	10	10	10	9.9	10	9.9	10
0.10% Pyrithione + 0.50% Cu	0.67 (0.042) 3.33 (0.208)	10	10	10	10	10	10	10	10	10	10	10	9.9
0.25% Pyrithione + 0.75% Cu	1.68 (0.105) 5.45 (0.340)	10	10	10	10	10	10	10	10	10	10	9.7	10
0.15% Pyrithione + 0.75% Cu	1.10 (0.063) 4.98 (0.311)	10	10	10	10	10	10	10	10	10	10	9.9	10
0.34% Pyrithione + 1.0% Cu	2.56 (0.160) 5.21 (0.325)	9.9	10	9.9	10	9.9	10	8.9	8.8	8.7	8.8	8.0	8.8
0.34% Pyrithione + 1.0% Cu	2.35 (0.147) 6.95 (0.434)	10	10	10	10	10	10	10	10	10	10	9.8	10
0.20% Pyrithione + 1.0% Cu	1.36 (0.085) 6.86 (0.428)	10	10	10	10	10	10	10	10	10	10	9.9	10
0.34% Pyrithione	2.34 (0.146)	6.6	4.7	0	1.7	0	0	0	0	0	0	0	0
1.0% Cu	6.47 (0.404)	10	10	10	10	10	10	10	10	10	10	9.9	10
Water Control	—	4.8	2.0	0.8	1.1	0.7	0.4	0	0	0	0	0	0
CCA-C (0.18 pcf)[4]	2.88 (0.18)	10	10	10	9.8	9.8	9.6	9.8	9.3	9.5	9.0	9.4	8.9
CCA-C (0.33 pcf)[4]	5.29 (0.33)	10	10	10	10	10	10	10	10	9.9	9.6	9.8	9.4

[1] Pyrithione is sodium pyrithione, and Cu is ammoniacal copper (II) carbonate with the retention based on CuO.
[2] Rententions are given in both kilograms per cubic meter (kg m^{-3}) and pounds per cubic feet (pcf); with the number an average of 10 stakes.
[3] A rating of 10 indicates no attack and a 0 rating indicates complete failure.
[4] CCA-C data were obtained from another study at the Saucier test site, with stakes read by Amburgey/Barnes/Landers at the FPL/MSU.

TABLE 4. *Average decay and termite ratings for field stakes at the Dorman Lake, MS plot, with 10 replicate stakes per treatment.*

Treatment	Average retention[2] kgm^{-3}/pcf	Exposure time, years 1		2		3		4		5		6	
		Decay[3]	Termite[3]	Decay	Termite	Decay	Termite	Decay	Termite	Decay	Termite	Decay	Termite
0.042% Pyrithione + 0.125% Cu	0.30 (0.019) 0.66 (0.041)	10	10	9.7	9.6	8.4	9.3	6.2	5.0	4.2	4.7	3.0	4.5
0.025% Pyrithione + 0.125% Cu	0.16 (0.010) 0.82 (0.051)	10	10	9.9	9.9	9.1	9.8	7.3	8.6	7.1	7.5	6.6	6.7
0.084% Pyrithione + 0.25% Cu	0.56 (0.035) 1.54 (0.096)	10	10	10	10	9.4	9.9	9.4	9.4	7.7	9.6	7.0	9.3
0.05% Pyrithione + 0.25% Cu	0.34 (0.021) 1.67 (0.104)	9.8	10	9.8	9.9	8.2	9.8	7.9	8.1	6.1	8.4	5.7	6.2
0.170% Pyrithione + 0.50% Cu	1.30 (0.081) 3.38 (0.211)	10	10	10	10	9.9	10	9.9	9.8	9.6	9.7	9.0	9.7
0.170% Pyrithione + 0.50% Cu	1.07 (0.067) 3.32 (0.207)	10	10	9.8	10	8.5	10	8.4	8.8	8.3	8.4	7.0	8.2
0.10% Pyrithione + 0.5% Cu	0.64 (0.040) 3.41 (0.213)	10	10	10	10	9.8	10	9.5	10	9.0	9.8	8.8	9.6
0.25% Pyrithione + 0.75% Cu	1.70 (0.106) 0.31 (0.303)	10	10	10	10	9.9	10	9.8	9.9	9.9	9.9	9.9	9.8
0.15% Pyrithione + 0.75% Cu	0.99 (0.062) 5.00 (0.312)	10	10	10	10	10	9.9	10	9.9	9.9	10	9.9	9.9
0.34% Pyrithione + 1.0% Cu	2.24 (0.140) 5.00 (0.312)	10	10	10	10	10	10	9.8	9.9	9.7	9.8	9.7	9.7
0.34% Pyrithione + 1.0% Cu	2.31 (0.144) 6.84 (0.422)	10	10	10	10	10	10	10	10	10	9.9	9.9	9.9
0.20% Pyrithione + 1.0% Cu	1.38 (0.086) 6.89 (0.430)	10	10	10	10	10	10	10	10	10	10	9.7	10
0.34% Pyrithione	2.26 (0.141)	6.4	9.1	2.2	5	1.1	1.6	0	0	0	0	0	0
1.0% Cu	6.92 (0.432)	10	10	10	10	9.4	9.6	9.0	9.3	9.0	9.0	8.9	8.9
Water Control	—	0	9.3	0	0	0	0	0	0	0	0	0	0
CCA-C (0.16 pcf)[4]	2.56 (0.16)	10	9.9	9.8	9.8	9.8	9.6	9.6	9.2	9.3	9.0	9.2	8.8
CCA-C (0.36 pcf)[4]	5.77 (0.36)	10	10	10	10	10	9.9	10	9.8	10	9.4	9.9	9.4

[1] Pyrithione is sodium pyrithione, and Cu is ammoniacal copper (II) carbonate with the retention based on CuO.
[2] Retentions are given in both kilograms per cubic meter (kgm^{-3}) and pounds per cubic feet (pcf), with the number an average of 10 samples.
[3] A rating of 10 indicates no attack and a 0 rating indicates complete failure.
[4] CCA-C data was obtained from another study at the Dorman Lake test site, with stakes read by Amburgey/Barnes/Landers at the FPL/MSU.

relatively poor results. For samples treated with 0.25% ACC and 0.084 or 0.050% pyrithione, decay and termite ratings were similar to those of the 0.16 pcf CCA samples at Dorman Lake, but poorer decay ratings were obtained for these samples at Saucier as compared to the 0.18 pcf CCA samples.

At the Saucier plot (Table 3), all copper: pyrithione-treated stakes with 0.5% or greater copper gave results equal to or better than the 0.33 pcf CCA set, except for one sample of the 1.0%/0.34% copper/pyrithione treatments. In reviewing the individual data for this particular set, it was observed that one sample, which had received one of the lower retention levels in that set, failed in the fourth year and this was the reason for this set's lower rating. Amburgey (personal communication, FPL/ MSU, 1999) mentioned that he has observed some scattered locations at Saucier that have copper-tolerant fungi, and suggested that may have been the cause for the failure. At the Dorman Lake site where copper-tolerant fungi are abundant (Table 4), all copper : pyrithione treatments with 0.75% or greater copper gave results approximately equal to that obtained with 0.36 pcf CCA.

CONCLUSIONS

Good results were obtained with all three soils in the simulated field exposure (TMCs) test for the synergistic copper : pyrithione mixture, while the individual components gave poorer results. Copper : pyrithione-treated samples were only attacked by tunneling bacteria in the Compost Soil TMC. After 6 years of ground exposure at two different sites, field stakes treated with the copper : pyrithione mixture at the higher biocide levels (0.75 and 1.0% copper) generally performed equal to, or better than, samples treated to about 0.35 pcf CCA for all except one sample. In addition to good efficacy in these soil-contact tests, a copper : pyrithione mixture has other advantages, but the need for a dual treatment is a major detriment. The generally good efficacy data suggest that the use of short-term laboratory decay tests to identify promising mixtures for further long-term field-exposure testing is reasonable, and we are currently conducting field tests on other promising mixtures found to be synergistic in laboratory tests.

REFERENCES

AWPA STANDARDS. 1997. American Wood-Preservers' Association Standards 1997. Gransbury, TX.

DIETRICH, W., E. GIEBELER, G. GEROMIN, AND W. WEISS. 1987. Synergistic wood preservatives comprising quaternary ammonium compounds and pyridine N-oxide derivatives. German Patent Application: DE 87-3718012.

EDLUND, M.-L. 1998. Durability of wood in ground contact tested in field and laboratory. Doctoral thesis, Swedish University of Agricultural Sciences, Uppsala, Sweden. 24 pp.

———, AND T. NILSSON. 1999. Performance of copper and non-copper based wood preservatives in terrestrial microcosms. Holzforschung 53:369–375.

HEDLEY, M. E., A. F. PRESTON, D. J. CROSS, AND J. A. BUTCHER. 1979. Screening of selected agricultural and industrial chemicals as wood preservatives. Int. Biodeterior. Bull. 15(1):9–18.

LUDWIG, G. W., O. EXNER, AND H. G. SCHMITT. 1991. Synergistic wood preservative compositions comprising phenol and pyrithione derivatives. German Patent Application: DE 91-4122654.

MCCOY, M. 1998. Biocides succeed despite regulations. Chem. Eng. News, Nov. 9, 1998:21–39.

MICKELWRIGHT, J. T. 1999. Wood preservation statistics, 1997. AWPA, Gransbury, TX.

MORPETH, F. F. 1991. Synergistic industrial antimicrobial compositions comprising an isothiazolone derivative. European Patent Application: EP 91-311043.

NAOKI, Y. 1998. Application example of tin replacement agent in ship bottom paint. Toso Gijutsu 37(7):93–96.

NICHOLAS, D. D., AND K. J. ARCHER. 1995. Soil beds for testing wood preservatives. Pages 110–115 *in* Wood preservation in the '90s and beyond. FPS Proceedings No. 7308, Forest Products Society, Madison, WI.

———, AND T. SCHULTZ. 1995a. Biocides that have potential as wood preservatives—An overview. Pages 169–173 *in* Wood preservation in the '90s and beyond. FPS Proceedings No. 7308, Forest Products Society, Madison, WI.

———, AND ———. 1995b. Synergistic wood preservative compositions. U.S. Patent 5,462,589.

———, AND ———. 1996. Synergistic wood preservative compositions. U.S. Patent 5,540,954.

NILSSON, T., AND M.-L. EDLUND. 1995. Laboratory versus field tests for evaluating wood preservatives: A scientific view. Int. Research Group Paper IRG/WP 95-20076.

PRESTON, A. F. 1993. Wood preservation: Extending the forest resource. J. Forestry 91(11):16–18.

SCHULTZ, T. P., AND D. D. NICHOLAS. 1995. Utilizing synergism to develop new wood preservatives. Pages 187–191 *in* Wood preservation in the '90s and beyond. FPS Proceedings No. 7308, Forest Products Society, Madison, WI.

TROTZ, S. I., AND T. H. FEDYNSHYN. 1984. Pyrithione-containing bioactive polymers and their use in paint and wood preservative products. U.S. Patent Application: 84-660208.