©Copyright 1984 by The Humana Press Inc.
All rights of any nature whatsoever reserved.
0273–2289/84/1012–0447$02.00

Bonding of Toxic Chemicals to Wood

ROGER M. ROWELL

US Department of Agriculture, Forest Service,
Forest Products Laboratory,
Madison, Wisconsin 53705

Received January 27, 1984; Accepted March 6, 1984

ABSTRACT

A series of chlorinated phenols, derivatives of pentachlorophenol and chlorinated benzene derivatives were prepared and their toxicity to the brown-rot fungi *Gloeophyllum trabeum* was determined in a standard ASTM 12-wk soil-block test. 2,3,5,6-Tetrachlorophenyl isocyanate and pentachlorophenyl isocyanate were synthesized, reacted with southern pine sapwood, and the extracted wood placed in the 12-wk soil-block test.

Pentachlorophenol was found to be the most toxic chemical tested to *Gloeophyllum trabeum* in the soil-block test. Pentachlorophenol is effective in eliminating attack at 0.16 lb/ft^3. Acetylation of pentachlorophenol does not reduce its toxicity. Methylation of the phenol produces a methyl ether derivative that has little observed toxicity even at 1 lb/ft^3. Tetrachlorophenol eliminates attack at 0.33 lb/ft^3. All other partially chlorinated phenols showed little toxicity to *Gloeophyllum trabeum* even at 1 lb/ft^3. Phenol and polychlorinated benzene derivatives showed little toxicity in the soil-block tests. The bonded tetra- and pentachlorophenyl isocyanates reduced attack compared to controls, but the mechanism of effectiveness of the mechanism probably results from substrate modification and enzyme blocking rather than toxicity. The level of treatment (12 wt% gain) corresponds to 4.5 lb/ft^3, or four times higher than the highest treatment for the non-bonded chemicals.

Index Entries: Bonding, of toxic chemicals to wood; phenols, bonding of chlorinated to wood; chlorinated phenols, bonding to wood; wood, bonding of chlorinated phenols to; toxicity, of phenols to wood brown-rot fungi; fungi, wood brown-rot and toxic phenols; brown-rot fungi, effect of phenols on wood; *Gloeophyllum trabeum*, toxicity of wood brown-rot to.

INTRODUCTION

All the commercial wood preservatives currently used in the United States are effective in preventing attack by microorganisms because of their toxic nature. Most of these preservatives are classified as broad-spectrum pesticides—that is, effective against several different types of living organisms. Pentachlorophenol, for example, is effective because it uncouples the biological process of oxidative phosphorylation, an essential function for all living systems—including microbes—that obtain their energy from this respiratory chain.

Because of the concern for toxic chemicals in the environment, the Forest Products Laboratory has initiated a research program to bond or graft toxic chemicals to wood cell-wall polymers to eliminate treatment chemical losses from the weathering of wood products in outdoor use and to limit toxicity to specific organisms. It is questionable, however, whether a chemical such as pentachlorophenol, which is known to be highly toxic to wood-decay fungi in its free form, will retain any toxicity when bonded to a large insoluble polymer.

Pentachlorophenol has been shown to be more toxic to *Lemna minor* and *Trichoderma viride* than less-chlorinated phenols and many times more toxic than phenol (*1*). Acetylation of the hydroxyl group in pentachlorophenol only slightly reduced its toxicity to *Sclerotinia laxa* and *Botrytis fabae,* and was slightly more toxic to *Stereum purpureum* by comparison to pentachlorophenol. Methylation of pentachlorophenol significantly reduced fungitoxic activity against all three of the above fungi (2).

The purpose of this research was to determine the effectiveness of a series of chlorinated phenols and isocyanates bonded to wood in preventing decay by the wood-destroying brown-rot fungus *Gloeophyllum trabeum* in an ASTM standard soil-block test.

MATERIALS AND METHODS

Chemicals Tested

The chemicals used to treat wood (Table 1) were all purchased and recrystallized except pentachlorophenol acetate and pentachlorophenol anisole. The acetate was prepared by acetylating pentachlorophenol with acetic anhydride in pyridine and crystallizing from hot ethyl alcohol (*2,3*). The methyl ether was prepared by methylating pentachlorophenol with methyl iodide and silver oxide and crystallizing from hot methyl alcohol (*2,4*).

Wood Treatments

Southern pine (*Pinus* sp.) Sapwood blocks (¾ × ¾ × ¾ in.) were treated with each separate chemical listed in Table 1. A 3% solution was

TABLE 1
Chemicals Used to Treat Southern Pine for Fungal Toxicity in the Soil-Block Test

Chemical	Recrystallized melting point, °C
Pentachlorophenol	189
2,3,5,6-Tetrachlorophenol	114
2,4,6-Trichlorophenol	64
2,4-Dichlorophenol	42
4-Chlorophenol	43
Phenol	39
Pentachlorophenol acetate	148
Pentachlorophenol anisole	107
Pentachlorobenzene	83
1,2,4,5-Tetrachlorobenzene	138
Pentachloroaniline	232
2,3,5,6-Tetrachloroaniline	106

prepared for each chemical dissolved in toluene. Treating wood with this solution gave retentions of 1 pound per cubic foot (lb/ft^3). Dilutions of each were made with toluene to prepare treatment levels of 0.5, 0.3, 0.16, 0.08, and 0.04 lb/ft^3. Several of the chemicals were tested at up to 12% solutions (4 lb/ft^3). Some were diluted with toluene to prepare a treating level of 2 lb/ft^3.

Five blocks were treated with each solution. The blocks were placed in a vacuum chamber and evacuated for 30 min. The treating solution was added to the chamber through a separatory funnel until all blocks were completely submerged. The vacuum was then released and the blocks soaked for 60 min. The treated blocks were blotted dry and weighed. Weight gains were determined based on the amount of chemical added.

The treated blocks along with untreated controls were conditioned at 27°C, 30% relative humidity (RH) prior to soil-block testing.

Soil-Block Tests

Standard soil-block tests were conducted according to specifications as outlined in ASTM D 1413 (5). The blocks were put in test with the brown-rot fungus *Gloeophyllum trabeum* (Pers. ex Fr.) Murr. (Madison 617). Specimens were removed after 12 wk and the extent of decay was determined by ovendry weight loss (Table 2).

Synthesis of Isocyanates

2,3,5,6-Tetrachlorophenyl Isocyanate

To a solution of phosgene (70.2 g, 709.6 mmol) dissolved in toluene (300 mL) was added 1,1,3,3-tetramethylurea (3.8 mL, 32.2 mmol). The so-

TABLE 2
Oven-Dry Weight Loss in 12-wk Test of Treated Southern Pine in Soil-Block Test with *Gloeophyllum trabeum*

	Average weight loss (%) for treatment levels of (lb/ft^3)								
Chemical	0.00	0.04	0.08	0.16	0.33	0.5	1.0	2.0	4.0
Pentachlorophenol	—	54.1	5.9	0.2	0	0	0	—	—
Pentachlorophenol acetate	—	60.2	21.4	2.4	0	0	0	—	—
Pentachlorophenol anisole	—	62.2	60.9	62.6	61.8	62.6	55.2	—	—
2,3,5,6-Tetrachlorophenol	—	60.7	53.1	20.7	0.4	0	0	—	—
2,4,6-Trichlorophenol	—	66.7	66.0	67.1	55.5	38.3	22.7	1.5	2.6
2,4-Dichlorophenol	—	67.3	69.0	65.7	66.5	63.9	53.6	59.1	52.5
4-Chlorophenol	—	63.4	60.7	61.3	58.0	51.9	28.3	0.8	2.1
Phenol	—	61.7	59.7	61.7	60.8	59.1	53.1	48.7	10.4
Pentachlorobenzene	—	65.6	65.4	66.7	63.5	42.9	36.4	31.6	33.0
1,2,4,5-Tetrachlorobenzene	—	64.3	—	66.6	64.6	60.5	65.5	—	—
Pentachloroaniline	—	—	—	—	65.8	66.6	57.0	55.6	—
2,3,5,6-Tetrachloroaniline	—	—	—	—	29.4	1.3	0.3	0.7	1.3
Control	64.3	—	—	—	—	—	—	—	—

lution was stirred for 30 min and 2,3,5,6-tetrachloroaniline (20.0 g, 86.6 mmol) was added. The solution was heated to 45–50°C for 2 h and 80–85°C for 2 h, and then refluxed for 1.5 h while more phosgene was bubbled in. Excess phosgene was removed from the reaction mixture under vacuum. The bottom solution containing an oil layer was discarded. The upper-layer solution was collected by decantation and dried under vacuum to give a white solid (22.1 g, 99.2%). The nuclear magnetic resonance (NMR) spectrum of the product showed no amine protons, which indicated a complete conversion of the amine to the isocyanate. The infrared (IR) spectrum of the product showed a strong isocyanate (2276 cm^{-1}) absorption and a trace of urea carbonyl (1655 cm^{-1}) absorption. The product (1 g) was dissolved in dry hexane, and an insoluble solid was removed by filtration. Crystallization from dry hexane gave the isocyanate as white shiny needles (0.4 g, 43.5%), melting point (mp) 62.5–63.5°C.

Analytical calculation for C_7HNOCl_4: C, 32.72; H, 0.39; N, 5.45. Found: C, 32.85; H, 0.31; N, 5.37.

Pentachlorophenyl Isocyanate

To a solution of phosgene (87.0 g, 879.4 mmol) dissolved in toluene (300 mL) was added 1,1,3,3-tetramethylurea (1.8 mL, 15.0 mmol). The solution was stirred for 30 min, and pentachloroaniline (15.0 g, 56.5 mmol) was added. The solution was heated to 80–83°C for 6 h while more phosgene was passed in. Phosgene was removed from the solution containing an oil layer and a white precipitate. The upper layer solution was collected by decantation, and the bottom layer containing the oil and precipitates was discarded. The solution was evaporated to give a white solid (16.4 g, 99.8%). The NMR spectrum of the product showed no amine protons, which indicated a complete conversion to the isocyanate. The IR spectrum of the product showed a strong isocyanate (2280 cm^{-1}) absorption and a trace of urea carbonyl (1655 cm^{-1}) absorption. The product (1 g) was dissolved in dry hexane, and an insoluble solid was removed by filtration. The filtrate was evaporated to give a white solid that was crystallized from dry hexane to give the isocyanate as white shiny flakes (0.6 g, 59.2%), mp 100.5–102°C (lit. mp 99–101°C) (*6*).

Analytical calculation for C_7NOCl_5: C, 28.86; N, 4.81. Found: C, 28.75; N, 4.74.

Bonding of Isocyanates to Wood

Southern pine blocks (¾ × ¾ × ¾ in.) were reacted for 2 h with either 2,3,5,6-tetrachlorophenyl isocyanate or pentachlorophenyl isocyanate, dissolved in *p*-dioxane at 110°C, under 150 psi, as previously described (*7,8*). After reaction, the blocks were ovendried for 3 h, extracted in a Soxhlet extractor for 2 h with benzene/ethanol (2/1 vol/vol), and again oven dried. The weight gain from bonding was calculated on the original and final oven dry weight (Table 3). The level of treatment for the bonded isocyanates (12% weight gain) corresponded to 4.5 lb/ft^3. The blocks were then conditioned at 27°C, 30% RH prior to soil-block testing.

TABLE 3
Oven-Dry Weight Loss in 12-wk Test of Southern Pine Reacted with Chlorinated Phenyl Isocyanates in Soil-Block Test with *Gloeophyllum trabeum*

Chemical	Weight percent gain on treatment	Average weight loss, %
Control (none)	0	60.6
2,3,5,6-Tetrachlorophenyl isocyanate	12.1	27.1
Pentachlorophenyl isocyanate	12.2	39.1
Methyl isocyanate (*7*)	7.3	15.8
	10.8	9.2
Ethyl isocyanate (*8*)	7.0	23.0
	15.0	6.0
n-Propyl isocyanate (*8*)	10.0	4.0

RESULTS

Of the chemicals tested in Table 1, pentachlorophenol was found to be the most toxic to *Gloeophyllum trabeum* in soil-block tests; it eliminated attack at 0.16 lb/ft^3 (Table 2). Acetylation of pentachlorophenol did not greatly reduce its toxicity. The ester bond may have hydrolyzed, giving back the free phenol. Methylation of the phenol, however, apparently produced a stable ether bond that was not hydrolyzed, and the methyl ether derivative had little observed toxicity even at 1 lb/ft^3. Tetrachlorophenol was not quite as toxic as pentachlorophenol, but eliminated attack at 0.33 lb/ft^3. All other partially chlorinated phenols showed little toxicity to *Gloeophyllum trabeum,* even at 1 lb/ft^3. Pentachloroaniline showed little toxicity, whereas the 2,3,5,6-tetrachloroaniline eliminated attack at about 0.5 lb/ft^3. Phenol and polychlorinated benzene derivatives showed little toxicity in the soil-block test.

Bonding tetrachlorophenyl and pentachlorophenyl isocyanates to wood through a urethane bond reduced attack compared to the control (Table 3).

DISCUSSION

The toxicity of chlorinated phenols to *Gloeophyllum trabeum* is primarily caused by the presence of the free phenol and at least four chlorine groups. Loss of the phenolic group results in reduced fungitoxicity, so it cannot be eliminated. Because the two chemicals bonded to wood do not contain this free phenolic group, no apparent toxicity is observed in the cell wall-bonded derivatives. The mechanism of effectiveness is probably the result of substrate modification and enzyme blocking rather than toxicity, as was shown in bonding methyl, ethyl, and *n*-propyl isocyanates to wood in earlier research (*7,8*). From these observations, tetrachlorophenol isocyanate reacted with wood might provide an interesting chemical for testing. Even this chemical derivative might not be toxic to microorganisms when bonded to wood since the toxicity of the chlorinated phenol is caused by an intercellular mechanism, and the chlorophenol could not get through the cell wall while attached to a large insoluble polymer.

Future research in this area will concentrate on bonding chemicals to wood that act through extracellular toxic mechanisms.

ACKNOWLEDGMENTS

The author acknowledges the assistance of Rebecca Schumann for soil-block testing and George Chen for synthesis of isocyanate derivatives. This article was written and prepared by US Government employees on official time and is therefore in the public domain.

REFERENCES

1. Blackman, G. E., Parke, M. H., and Garton, G., *Arch. Biochem. Biophys.* **54,** 45 (1955).
2. Byrde, R. J. W., and Woodcock, D., *Ann. Appl. Biol.* **44**(1), 138 (1956).
3. Barral, E., *Bull. Soc. Chim.* **13**(3), 341 (1895).
4. Weber, A., and Wolff, N., *Ber. Dtsch. Chem. Ges.* **18,** 335 (1885).
5. American Society for Testing and Materials. ASTM Stand. Desig. D 1413, Philadelphia, Pa., 1976.
6. Holtschmidt, H. O., Bayer, O., and Degener, E., US Patent 3,277,138, Oct. 4, 1966.
7. Rowell, R. M., and Ellis, W. D., *Wood Sci.* **12**(1), 52 (1979).
8. Rowell, R. M., and Ellis, W. D., *ACS Symp. Ser.* **172,** 263 (1981).