

PYROLYSIS, LEACH RESISTANCE, HYGROSCOPICITY, AND DECAY RESISTANCE OF WOOD TREATED WITH ORGANOPHOSPHORUS ESTERS IN COMBINATION WITH ISOPHORONE DIISOCYANATE

W. Dale Ellis

Research Chemist
USDA Forest Service
Forest Products Laboratory
One Gifford Pinchot Drive
Madison, WI 53705-2398

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ABSTRACT

This study evaluated the effectiveness of a difunctional isocyanate to improve the performance of organophosphorus flame retardants. Small southern pine specimens were reacted with isophorone diisocyanate in combination with two organophosphorus ester compounds. The resulting treatments were leach-resistant, not hygroscopic, and moderately decay-resistant, and had thermal degradation patterns like those of effective flame retardants. Pyrolysis of the treated specimens showed lower temperatures at the maximum rate of pyrolysis and greater amounts of residual char compared to untreated specimens. Treated specimens had 2% to 3% less equilibrium moisture content at 27°C and 80% relative humidity than did the untreated specimens. The most leach-resistant specimens lost less than 20% phosphorus during water extraction. This loss of phosphorus did not appreciably change the thermal degradation of the specimens. The treated specimens were more decay-resistant than the untreated ones.

Keywords: Flame retardant, Fyrol 6, Fyrol 51, organophosphorus esters, isophorone diisocyanate, wood, hygroscopicity, decay resistance.

INTRODUCTION

Wood buildings are susceptible to fire. Treating the wood with flame retardants stops or slows the spread of fire and reduces the heat contribution of the wood to the fire. Phosphorus compounds have for many years been among the predominant chemicals used as flame retardants because they change the thermal degradation processes in wood. These compounds reduce the temperature at which pyrolysis occurs and increase the amount of residual char (Browne and Tang 1962; Jain et al. 1985) resulting in a reduction in combustible gases. Phosphorus compounds are acid

precursors that, during combustion or pyrolysis, form acids that cause selective decomposition of the carbohydrate materials. Dehydration and char formation are enhanced, and combustible volatile formation is suppressed (Schuyten et al. 1955; Shafizadeh 1968). Phosphorus compounds, in contrast to many flame retardants, can prevent glowing combustion, which is caused by slow oxidation of the wood (Tang and Neill 1964).

In our past research, we reacted isocyanates and diisocyanates with wood to give the wood dimensional stability and decay resistance (Ellis and Rowell 1984). We reacted a diisocyanate with a diol organophosphorus compound, resulting in an effective, leach-resistant and fire-retardant treatment for wood (Ellis and Rowell 1989).

In this present research, we studied the reactions of two polyol phosphorus compounds

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with a diisocyanate and the properties of wood treated with these chemicals. The isocyanate reacts with hydroxyl groups on the polyols and on the wood to form urethane bonds. Several aspects of the phosphonate-diisocyanate reactions and the resultant flame-retardant wood were evaluated to determine five conditions: (1) the thermal degradation of small specimens, using thermogravimetry as a rapid and inexpensive method for evaluating potential flame retardancy; (2) the equilibrium moisture content (EMC) as a measure of the hygroscopicity of the treatments; (3) the treatability of wood with 16% EMC; (4) the reaction conditions that could affect the leach resistance of these treatments; and (5) the decay resistance of treated wood.

MATERIALS AND METHODS

Chemicals and solution preparation

We used two organophosphorus compounds, OPC1 (Fryol 6 from Akzo Chemical Inc., Chicago, IL) and OPC2 (Fyrol 51 from Akzo Chemical Inc.), as flame retardants.¹ The OPC1 had a molecular weight of 255 and contained 12.4% phosphorus. The OPC2, an oligomer, contained 20.5% phosphorus. Both OPC1 and OPC2 had hydroxyl groups that could react with an isocyanate; the hydroxyl numbers were 450 and 125 mg KOH/g, respectively. Because of its moderate level of reactivity and low vapor pressure, isophorone diisocyanate (IPDI) was used to couple the flame retardant to the wood.

The treating solutions were made by dissolving each organophosphorus compound (OPC) and IPDI in dichloromethane. The OPC1 and IPDI were mixed at a ratio of 1:1.2, by weight. The resulting solution contained 18.25% reactants (8.25 g OPC1 and 10 g IPDI per 100 ml of solution). The OPC2 and IPDI were mixed at a ratio of 1:1.5, by weight. The

resulting solution contained 18.75% reactants (7.5 g OPC2 and 11.25 g IPDI per 100 ml of solution). These amounts were one equivalent of OPC per one equivalent diisocyanate. Dabco, an amine catalyst, was added to a portion of these solutions as 5% of the weight of the isocyanate. Other solutions were prepared containing only 8.25 g OPC1 or 7.5 g OPC2 per 100 ml of solution. Specimens treated with OPC only were prepared for comparison with specimens treated with diisocyanate and OPC.

Specimens

Southern pine was cut into specimens 10 by 20 by 100 mm (radial by tangential by longitudinal) for use in all the experiments except the decay test, which used specimens 20 by 20 by 20 mm. All specimens were oven-dried overnight at 105 C, and then weighed. One-half the specimens were treated while oven-dry. The others were treated while moist; therefore, they were conditioned at 27 C and 80% relative humidity (RH) to 16% EMC.

For each treatment, 10 specimens, either dry or conditioned to 16% EMC, were placed in a vacuum desiccator. A vacuum was drawn for 30 min to remove air from the wood. While under the vacuum, the specimens were covered with the treating solution, and then the pressure was returned to atmospheric conditions. Specimens were removed from the solution after 2 h of soaking and then cured overnight in an oven at 105 C. Specimens treated with a combination of OPC and diisocyanate were compared to specimens treated with only the OPC and to untreated specimens.

Test methods

Pyrolysis.—Thermogravimetry, using a Perkin-Elmer TGS-2 system, was used to evaluate the thermal degradation of the specimens. The specimens were pyrolyzed in a flow of nitrogen (40 ml/min) as temperatures were programmed from 40 C to 600 C at 20°/min. The specimen weight that remained at 600 C was measured and used to calculate the percentage of residual char. The temperature at the maximum rate of pyrolysis was recorded.

¹ The use of trade or firm names in this publication is for reader information and does not imply endorsement by the U.S. Department of Agriculture of any product or service.

Leach resistance.—Two grams of specimens milled to pass a 20-mesh (841- μ m) screen were extracted with 100 ml of distilled water in a 250-ml Erlenmeyer flask. The water was decanted, and fresh water was added at 2-h intervals for the first 8 h. At the end of 24 h, the specimens were transferred to a funnel containing filter paper, and rinsed with 100 ml of distilled water. Specimens were dried overnight at room temperature and then dried overnight at 105 C. They were then saved for analytical comparisons of extracted and unextracted specimens.

The effects of leaching were evaluated by an analysis of leached and unleached specimens for phosphorus (Galbraith Laboratories, Knoxville, TN), and by thermogravimetry to determine the pyrolysis peak temperatures and amounts of residual char.

Hygroscopicity.—The hygroscopicity of the treated specimens was evaluated by conditioning 10 specimens of each treatment at 27 C and 80% RH, and then at 27 C and 30% RH. The specimens were weighed after 2 weeks at 80% RH and again after 2 weeks at 30% RH. The weight gained after conditioning at 80% RH was measured, and the percent EMC was calculated. Those specimens cured at 27 C and 30% RH were weighed, conditioned at 27 C and 80% RH for 2 weeks, and reweighed, at which point the EMC was calculated. Thermogravimetry was used to measure the moisture not removed by oven-drying at 105 C. The percentage of moisture found by thermogravimetry to be released at 100 C was added to the percentage of moisture calculated from the oven-dry and conditioned weights.

Decay resistance.—Decay resistance was determined using a standard soil block test according to specifications in ASTM D-1413 (ASTM 1991). Six specimens of each treatment were prepared. All specimens were Soxhlet-extracted overnight with dichloromethane, oven-dried at 105 C, and then weighed before treatment with the flame retardant. The controls and the treated specimens were extracted for 4 days with running water. They were then air-dried, oven-dried,

and reweighed. The treatment weight percent gain was then calculated. Specimens were conditioned for 2 weeks at 27 C and 30% RH, and then placed in the soil block test with the brown-rot fungus *Gloeophyllum trabeum* (Pers. ex fr.) Murr. (Madison 617). Specimens were removed from the test after 12 weeks, and the amount of decay was measured as percent weight loss.

Statistical analysis.—The EMC and decay test data were analyzed using *t*-tests to determine if significant differences existed between the means of the different treatments. Because the thermogravimetry and phosphorus data were obtained from composite samples, no statistical analysis was done.

RESULTS AND DISCUSSION

Pyrolysis

Thermogravimetry showed that all treated specimens had lower peak temperatures and greater amounts of residual char than the control specimens (Table 1). All dry specimens treated with an OPC and IPDI or with only OPC had 28% to 30% residual char if they were not extracted with water, whereas those treated after having attained a 16% EMC had 29% to 33% residual char. After pyrolysis, the dry specimens treated with an OPC and IPDI had nearly the same amount of residual char and peak temperatures after leaching as they did before leaching. Specimens treated with only OPC1 or OPC2, and no IPDI, lost 92% and 90%, respectively, of the chemical during water leaching. The effects of this loss can be seen by the reduced amounts of residual char and the higher peak temperatures (Table 1).

Leach resistance

The IPDI was included in the flame-retardant treatments to increase the leach resistance. Peak temperatures, amounts of residual char, and amounts of phosphorus were used to measure the effects of water extraction on the treatments. Experiments confirmed that the IPDI prevented leaching of the flame-retardant compounds.

TABLE 1. Temperature at maximum rate of pyrolysis and amount of residual char for extracted and unextracted specimens.^a

Treatment	Treated oven-dry				Treated at 16% EMC			
	Residual char (%)		Peak temp (°C)		Residual char (%)		Peak temp (°C)	
	NEX	EX	NEX	EX	NEX	EX	NEX	EX
Control	17.6	15.7	405	410	17.6	15.7	405	410
OPC1	30.8	17.4	329	392	31.9	16.7	327	392
OPC1-IPDI	29.8	28.9	345	345	29.1	23.5	341	356
OPC1-IPDI-Dabco	29.8	27.6	348	348	30.3	23.1	337	359
OPC2	33.0	24.3	306	343	32.6	24.3	304	337
OPC2-IPDI	30.9	28.0	335	344	32.4	24.2	315	353
OPC2-IPDI-Dabco	28.8	26.9	337	344	32.3	25.7	327	351

^a NEX is not extracted, EX extracted. Specimens were milled to pass a 20-mesh (841- μ m) screen, then extracted with water.

Dry specimens.—The dry specimens that were reacted with OPC1 and IPDI were leach-resistant, as shown by both the peak temperatures being unchanged by extraction and the fact that water extraction reduced the amount of residual char by less than 2%. Water extraction removed from 18% to 22% of the phosphorus from these specimens, leaving a phosphorus content of 0.72%. Dry specimens that were reacted with OPC2 and IPDI were slightly less leach-resistant than those treated with OPC1 and IPDI. The peak temperatures of specimens treated with OPC2 and IPDI were increased by about 10°. The amount of residual char was reduced by 3 percentage points (Table 1), and water extraction removed from 32% to 34% of the phosphorus (Table 2). The OPC2 without IPDI appeared to have some leach resistance when only peak temperatures and residual char were considered (Table 1); however, over 90% of the phosphorus was extract-

ed, leaving 0.12% phosphorus content in the specimens (Table 2). Water extraction caused specimens treated with OPC1 without IPDI to lose enough flame retardant that the amounts of residual char were only slightly more than those of untreated specimens. The peak temperatures also were increased by more than 60°, indicating a considerable loss of flame retardant (Table 1). More than 90% of the phosphorus was extracted from specimens treated with OPC1 only, leaving 0.06% phosphorus (Table 2).

Moist specimens.—Specimens having 16% EMC prior to reaction with treatments with OPC and IPDI were less leach-resistant than the comparable dry specimens. The extracted residual char values for the 16% EMC specimens were from 1.2 to 4.7 percentage points less than the values for extracted dry specimens. The moist specimens had peak temperatures that were from 7° to 11° higher than

TABLE 2. Percentage of phosphorus in extracted and unextracted specimens.^a

Treatment	Treated oven-dry			Treated at 16% EMC		
	NEX	EX	Amount extracted	NEX	EX	Amount extracted
Control	0	0	—	0	0	—
OPC1	0.80	0.06	92.5	0.98	0.06	93.9
OPC1-IPDI	0.88	0.72	18.2	0.80	0.40	50.0
OPC1-IPDI-Dabco	0.92	0.72	21.7	0.88	0.31	64.8
OPC2	1.21	0.12	90.1	1.49	0.18	87.9
OPC2-IPDI	1.32	0.90	31.8	1.37	0.32	80.2
OPC2-IPDI-Dabco	1.37	0.90	34.3	1.14	0.38	66.7

^a NEX is not extracted, EX extracted. Specimens were milled to pass a 20-mesh (841- μ m) screen, then extracted with water.

those of the dry specimens, and from 50% to 80% of their phosphorus was extracted by water, compared to 18% to 34% lost from the dry specimens (Table 1). Isocyanate reacts with water to form final products of carbon dioxide and an amine. The amine probably is more soluble and more easily leached from the specimens than are the polyurethanes formed by the reactions of the polyols and isocyanate.

Hygroscopicity.—All treated specimens were significantly less hygroscopic at 27 C and 80% RH than the untreated specimens (Table 3). Specimens treated with only OPC1 or OPC2 were slightly but significantly less hygroscopic than the control specimens, having about 1% less moisture. Specimens treated with OPC1 and IPDI or OPC2 and IPDI had 5% and 3.5% less moisture, respectively, than the untreated specimens. This indicates that the isocyanate reacted with the hydroxyl groups of the wood. The presence of pretreatment moisture did affect the EMC of treated specimens. Specimens with 16% EMC prior to treatment were less hygroscopic than the dry specimens; their EMC values were about 1.5% lower at 27 C and 80% RH. Specimens equilibrated at 27 C and 30% RH followed the same order of EMC as specimens equilibrated at the higher humidity, except that the EMC values were lower by 6 to 8 percentage points.

Decay resistance

Untreated specimens lost 45.7% of their weight during the 12-week decay test (Table 4). The amount of decay seen in the untreated specimens did not differ significantly from that seen in specimens treated with only Dabco or only IPDI. Specimens treated with only OPC1 or OPC2 had 36% and 40% less decay, respectively, than the untreated specimens. The inclusion of IPDI with the OPC reduced the amount of decay below that found for the OPC-treated specimens alone. The weight losses for dry specimens, and for moist specimens treated with OPC1 and IPDI, were 31% and 19%, respectively. The weight losses for dry and moist specimens treated with OPC2 and IPDI were 16% and 6%, respectively. Compared to

TABLE 3. *Percentage of equilibrium moisture content in specimens.^a*

Treatment	Treated oven-dry		Treated at 16% EMC	
	80% RH	30% RH	80% RH	30% RH
Control	16.28 e	8.22	16.28 e	8.22
OPC1	15.25 c	7.78	15.34 d	7.55
OPC1-IPDI	11.91 a	5.78	11.07 a	4.90
OPC1-IPDI-Dabco	11.80 a	5.19	10.96 a	4.33
OPC2	15.48 d	7.41	14.47 c	6.57
OPC2-IPDI	13.07 b	6.56	11.84 b	4.99
OPC2-IPDI-Dabco	13.01 b	6.08	11.68 b	4.66

^a Values are means of 10 specimens. Values within a column followed by the same letter are not significantly different at 99% confidence level.

the dry specimens, the greater decay resistance of the specimens treated while moist could have been a result of their lower hygroscopicity; the specimens treated while moist had less moisture than the dry specimens during the decay test. Moist specimens treated to a 17.4% weight gain with OPC2 and IPDI had a 5.7% weight loss during the decay test. This indicates that treating to higher weight gains might give improved decay resistance (Table 4).

CONCLUSIONS

Adding IPDI to OPC1 and OPC2 resulted in leach-resistant and flame-retardant wood

TABLE 4. *Soil block decay test of southern pine treated with flame retardant and inoculated with Gloeophyllum trabeum.^a*

Treatment	Percentage of weight	
	Gain from treatment	Loss through decay
OPC2-IPDI ^b	17.4	5.7 a
OPC2-IPDI-Dabco ^c	13.6	10.9 b
OPC2-IPDI ^c	14.0	16.3 c
OPC2-IPDI-Dabco ^b	12.0	17.0 c
OPC1-IPDI-Dabco ^b	10.1	17.7 c
OPC1-IPDI ^b	10.8	19.3 c
OPC1-IPDI-Dabco ^c	13.6	25.4 d
OPC2	2.9	27.6 d
OPC1	0.8	29.4 d
OPC1-IPDI ^c	14.1	31.0 d
IPDI	5.7	40.5 e
Control	0.0	45.7 e
Dabco	0.4	49.7 e

^a Specimens leached for 4 days with running water before subjected to decay test. Values are means of six specimens.

^b Specimens had 16% moisture content when treated.

^c Specimens were oven-dry when treated.

treatments. After water extraction, both treatments were present at levels sufficient to significantly increase amounts of residual char and reduce pyrolysis temperatures of the wood, but the presence of IPDI was essential to make the treatments leach-resistant. The pyrolysis of the specimens reacted with OPC2 and IPDI, and of those reacted with OPC1 and IPDI, showed that these treatments lowered the pyrolysis temperature and increased the amount of residual char, with the OPC2 and IPDI treatment succeeding slightly better than the OPC1 and IPDI treatment. Observations of the amount of residual char and pyrolysis temperatures were made because effective flame retardants will generally increase the amount of residual char and reduce the temperature at the maximum rate of pyrolysis (peak temperature). All specimens treated with either OPC1 and IPDI or OPC2 and IPDI were less hygroscopic and more decay-resistant than the untreated specimens.

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