

FLAME-RETARDANT TREATMENT OF WOOD WITH A DIISOCYANATE AND AN OLIGOMER PHOSPHONATE

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ABSTRACT

An oligomer phosphonate and isophorone diisocyanate, in a chloroform or dichloromethane solution, were impregnated into wood and cured at 105 C. The leach resistance and thermal degradation of treated wood specimens were evaluated. Leaching milled specimens removed up to 49% of the phosphorus and 12% of the nitrogen. The average weight percent gain of solid specimens leached with three 4-day cycles of running water was reduced from 23% to 17% during the first cycle and from 17% to 16% during the second and third cycles. Toluene : ethanol extraction did not remove the reacted chemicals from the wood. Acetone extraction resulted in a 1% to 2% reduction of the weight percent gain values. Thermal analysis showed that the flame-retardant treatment reduced the temperature at maximum rate of pyrolysis approximately 80 C and increased the amount of residual char to about 30%. Leaching raised the temperature on the average 8 C at the maximum rate of pyrolysis and decreased the amount of residual char an average of 3%. The temperature at maximum rate of pyrolysis and amount of residual char indicate the potential effectiveness of this treatment as a leach-resistant, flame-retardant treatment for wood.

Keywords: Flame retardant, phosphonate, diisocyanate, pyrolysis, thermogravimetry, thermal degradation.

INTRODUCTION

Wood has many inherently good properties, which make it a preferred building material for many applications. However, the flammability of wood can be a problem when wood is used to build permanent structures. The tendency to burn can be greatly reduced by adding fire-retardant chemicals to wood. However, in many instances, these chemicals introduce other problems, including increased hygroscopicity and corrosivity, and reduced adhesive bonding. These problems occur especially when inorganic salts are used as fire retardants (McKnight 1962; Van Kleeck 1942).

A great deal of research has been done to develop treatments that make wood flame retardant but free of the problems associated with leachable inorganic salts. One such treatment is the amino resin system, which uses chemicals such as dicyandiamide, melamine, urea, formaldehyde, and phosphoric acid. The amino resin fire retardants greatly reduce or eliminate hygroscopicity, corrosivity, chemical blooming, and leaching. Leach resistance is attributable to polymerization of the components within the wood (Goldstein and Dreher 1961) and possibly to

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some reaction with the cellulose in wood (Willard et al. 1965). Despite the reported leach resistance of the amino resin treatment, Juneja (1972) reports that water leaching can remove as much as 91% of the phosphorus from shingles treated with dicyandiamide-phosphoric acid-formaldehyde and 71% of the phosphorus from shingles treated with melamine-dicyandiamide-phosphoric acid-formaldehyde.

Urethane foams are commonly made flame retardant by reaction of a phosphorus polyol with an isocyanate. Malz and Kassack (1961) prepared flame-retardant compounds by reacting chemicals having free hydroxyl groups with crosslinking agents such as isocyanates. Von Bonin et al. (1987) propose flame-proofing absorbent substrates used in roofing and packaging with a mixture of a polyisocyanate and a condensate that contains phosphorus and has two or more hydroxyl groups. Isocyanates have been reacted with wood to increase its dimensional stability and decay resistance (Ellis and Rowell 1984).

Chemicals that contain phosphorus change the thermal degradation processes in wood. They are effective as flame retardants because they reduce the temperature at which pyrolysis occurs and increase the amount of residual char (Browne and Tang 1962; Jain et al. 1985). Phosphorus compounds are acid precursors during combustion or pyrolysis, and the acids formed 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).

Objectives of our research were to develop new fire-retardant treatments for wood that are leach-resistant and, at the same time, not hygroscopic or corrosive. To accomplish these objectives, an aliphatic diisocyanate and an oligomer phosphonate were mixed in an appropriate solvent, impregnated into the wood, and cured with heat. Reaction of the diisocyanate with the oligomer phosphonate and the wood should enhance leach resistance.

MATERIALS AND METHODS

An aliphatic diisocyanate was selected for this study because it is less reactive than aromatic diisocyanates, which allows the reaction to be controlled. Reaction does not occur at room temperature in most cases but can be initiated by increasing the temperature. Aliphatic diisocyanates are less likely to yellow than aromatic diisocyanates when exposed to sunlight. Isophorone diisocyanate (IPDI) was used in this study. It has a relatively high molecular weight (222) and a low vapor pressure, which make its use and handling relatively safe.

Fyrol 51 (Stauffer Chemical Co.)² used in this study is an oligomer phosphonate containing 20.5% phosphorus and having hydroxyl groups that will react with an isocyanate. Fyrol 51 is soluble in water, methanol, ethanol, 2-propanol, chloroform, and dichloromethane. Water and alcohols are not appropriate as reaction solvents for isocyanates, and none of the solvents known to swell wood dissolve both Fyrol 51 and IPDI. Chloroform and dichloromethane were selected as the

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most appropriate solvents for making solutions of Fyrol 51 and IPDI. The ratio of the fyrol : diisocyanate : solvent solutions was 1:2:20 (by volume). The amount of solvent was increased or decreased to control chemical weight gains in the reacted wood.

Preparation of specimens

Specimens of ponderosa pine and southern pine were cut into 25 by 25 by 6 mm (radial by tangential by longitudinal) pieces for dimensional stability tests. Specimens 140 by 7 by 3 mm were cut for leaching, thermogravimetric analysis, and elemental analysis. All specimens were oven-dried at 105 C before weighings and reactions.

Treatment of specimens

Specimens were placed in a container inside a desiccator, and a vacuum was drawn for 1 h using a water aspirator. Specimens were then covered with solution and the pressure returned to atmospheric. After a 1-h soak, the solution was drained and a vacuum drawn for 10 min to remove excess chemicals and solvent. The specimens were then cured overnight at 105 C, reweighed, and the weight percent gain (WPG) calculated based on the original oven-dry weight. Ten specimens of each size were treated at each level of treatment.

Leaching

Three different methods of leaching were used. The method used depended on what was to be done later with the specimens. Method 1 was used with specimens milled to pass a 40-mesh screen. One-half of the milled specimens were soaked 24 h in distilled water followed by several rinses with distilled water. Next, these specimens were rinsed with several 50-ml portions of acetone, then oven-dried at 105 C. Each half of the milled specimens was subjected to thermogravimetric, phosphorus, and nitrogen analyses, and unleached and leached portions were compared.

Method 2, a combination of water and solvent leachings, was done using solid specimens (140 by 7 by 3 mm). Leaching data represent the average of four specimens in each group. The specimens were (1) leached 4 days in running water, (2) extracted 18 h with toluene : ethanol (2:1,v:v) in a Soxhlet extractor, (3) extracted 18 h with acetone in a Soxhlet extractor, and (4) leached 4 days with running water. Before and after each cycle of leaching or extraction, the specimens were oven-dried and weighed, and the WPG was calculated based on the original untreated weight.

Method 3 consisted of 4-day cycles of leaching in running water. Solid specimens (140 by 7 by 3 mm) were subjected to three cycles of leaching, with oven-drying and weighing before and after each cycle. The WPG based on the original untreated weight was calculated after each cycle. Data reported are the average of four specimens per group.

Dimensional stability tests

Dimensional stability was determined using a flat bed micrometer by measuring the increase in volume (swelling) of treated and untreated specimens. Specimen volume was determined oven-dry and after specimens were soaked in water. The

TABLE 1. Phosphorus (P) and nitrogen (N) in unleached and leached ponderosa pine specimens reacted with Fyrol 51-IPDI.¹

Weight percent gain	Percentage of specimen weight			
	Unleached		Leached	
	P	N	P	N
0	0	0.04	—	—
14.5	1.11	0.89	0.64	0.80
22.8	1.88	1.21	0.96	1.06
34.3	2.40	1.48	1.46	1.48
39.6	2.71	1.77	1.63	1.67
42.6	2.72	1.81	1.84	1.80

¹ Specimens milled to pass a 40-mesh screen were leached first with water and then with acetone.

volume was measured after each hour for the first 5 h, then after 24 h. The percentage of swelling was calculated from the wet volume of the specimen compared to its treated oven-dry volume.

Thermogravimetric analysis

Thermogravimetric analyses (TGAs) were done using a Perkin Elmer TGS-2 system. Specimens were pyrolyzed in a flow of nitrogen (40 ml/min). Pyrolysis temperatures were programmed from 30 to 600 C at 20 C per minute. The specimen weight remaining at 600 C was used to calculate the percentage of residual char. The temperature at maximum rate of pyrolysis was recorded.

RESULTS AND DISCUSSION

Treatment of specimens

The chemicals were in the void spaces of the wood, not in the cell walls, because the solvents and chemicals used did not swell the wood and the reaction of IPDI with Fyrol 51 and the wood caused no increase in wood volume or dimensional stability. Weight gains greater than 50% were achieved. The color and appearance of untreated and treated specimens were the same except that specimens with the highest level of treatment sometimes had a crusty deposit on their surfaces.

Ponderosa pine and southern pine gave similar results in all tests; therefore, only the data for ponderosa pine are reported.

TABLE 2. Weight ratio of phosphorus and nitrogen (P/N) in treating solutions and in unleached and leached specimens.¹

Weight percent gain	P/N ratio		
	Treating solution	Unleached specimens	Leached specimens
14.5	1.05	1.25	0.80
22.8	1.41	1.55	0.90
34.3	1.41	1.69	0.95
39.6	1.41	1.50	0.98
42.6	1.41	1.50	1.00

¹ Specimens milled to pass a 40-mesh screen were leached first with water and then with acetone.

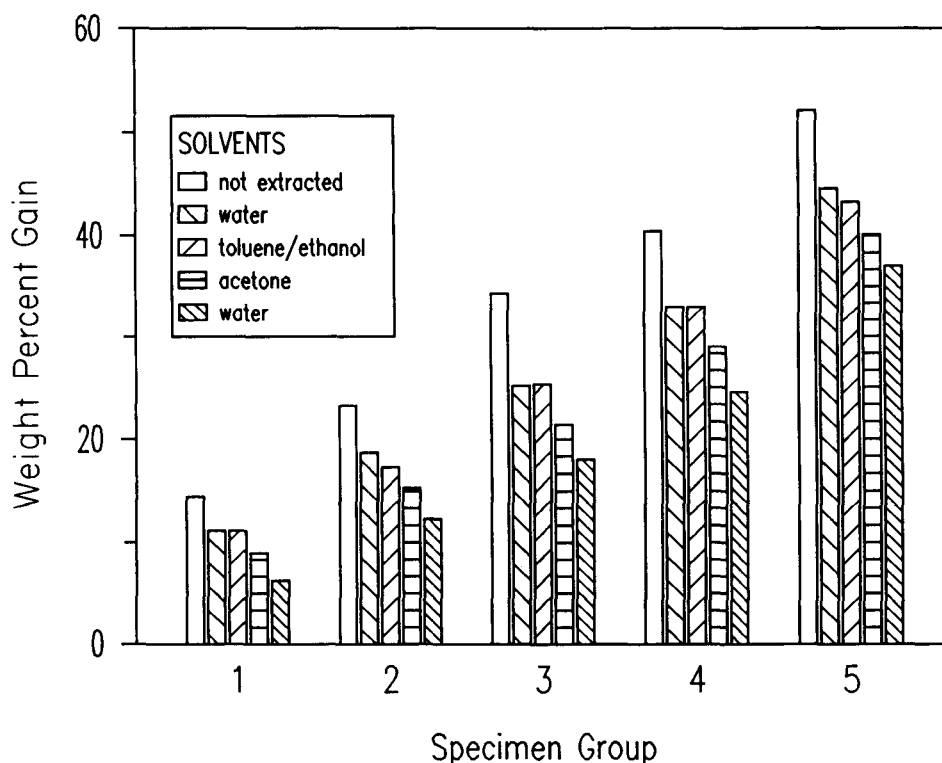


FIG. 1. Effect of successive water and solvent leachings (method 2) on weight of solid ponderosa pine specimens treated with Fyrol 51-IPDI.

Leach resistance

Water leaching followed by acetone leaching of milled specimens (method 1) removed from 32% to 49% of the phosphorus, while the amount of nitrogen was unchanged or slightly reduced in some specimens (Table 1). The theoretical phosphorus to nitrogen (P/N) ratio of the treating solution used to treat most specimens was 1.41 (Table 2). The P/N ratio of unleached specimens ranged from 1.50 to 1.69. Fyrol 51 seemed to penetrate the wood somewhat better than diisocyanate. The P/N ratio of leached specimens ranged from 0.9 to 1.0, indicating the phosphorus component was also more easily removed from the wood than the nitrogen component. The ratio in the treating solution of six isocyanate groups to each hydroxyl group provided an excess of isocyanate for reaction with hydroxyl groups. All the Fyrol 51 should have reacted with isocyanate. Further experiments are needed to determine why some phosphorus could be leached from the wood.

In successive leachings of solid specimens (method 2) with (1) water, (2) toluene : ethanol, (3) acetone, and (4) water, most weight loss was caused by water leaching, small weight losses were caused by acetone, and little or no weight loss was caused by toluene : ethanol (Fig. 1).

Solid specimens leached in three 4-day cycles of running water (method 3) showed that most of the weight loss occurred during the first cycle, with little or no weight loss during the second and third cycles. The first cycle removed the

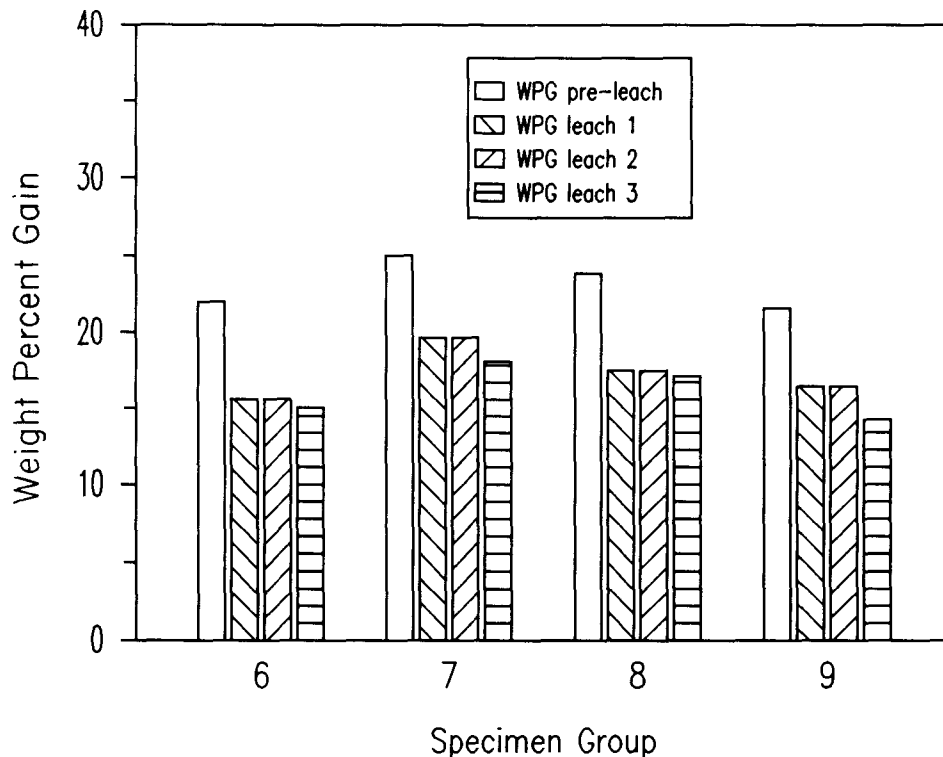


FIG. 2. Effect of successive water leachings (method 3) on weight of solid ponderosa pine specimens treated with Fyrol 51-IPDI.

soluble chemicals, and the reacted chemicals were then resistant to leaching by water (Fig. 2).

Dimensional stability

The Fyrol 51-IPDI fire-retardant treatment did not result in significant dimensional stability. The treated specimens swelled slightly slower than untreated specimens, but after 3 h in water, the swelling of treated specimens was only 0.8% less than that of control specimens (Fig. 3). The chemicals were not in the cell walls because the solvents did not swell the wood structure; swelling permits the reaction within the cell walls that is necessary for increased dimensional stability.

Thermal degradation

Pyrolysis temperatures.—The treatment of wood with an oligomer phosphonate and a diisocyanate lowered the temperature at the maximum rate of pyrolysis (Fig. 4). The addition of as little as 5% Fyrol 51-IPDI flame retardant lowered the pyrolysis temperature by 58 C. The addition of 20% of this flame retardant lowered the pyrolysis temperature approximately 80 C. Increasing the amount of flame-retardant treatment to 50% of the specimen weight decreased the pyrolysis temperature by an additional 10 C only.

The pyrolysis temperature of specimens leached with water and acetone was

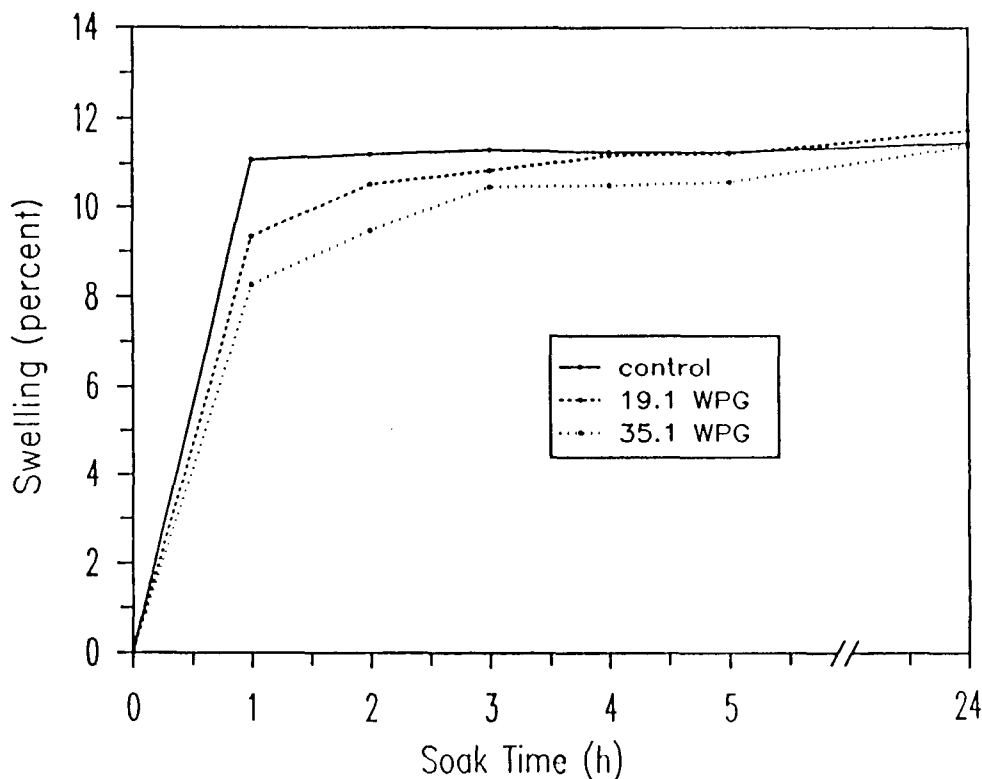


FIG. 3. Effect of water soaking on swelling of solid ponderosa pine specimens treated with Fyrol 51-IPDI.

on the average 8 C higher than that of unleached specimens (Fig. 4). The temperature at maximum rate of pyrolysis was changed very little by water and acetone leaching. A WPG of 10 represents approximately 0.7% phosphorus. At this weight gain, the temperature at maximum rate of pyrolysis was 350 C, 50 C lower than that of untreated specimens. Pyrolysis temperatures indicate that wood treated to 10 WPG had a minimum level of flame-retardant properties, but optimal treatment levels were 20 to 30 WPG.

Residual char.—The amount of residual char formed during pyrolysis of flame-retardant-treated wood is important because it indicates the influence the chemical has on degradation reactions. An effective flame retardant facilitates degradation reactions and increases the amount of residual char formed. The more char formed early during a fire, the greater the protective layer against further burning.

Fyrol 51-IPDI treated specimens formed more residual char than untreated specimens (Fig. 5). The amounts of char ranged from 16% for untreated specimens to a maximum of 33% for specimens with 50 WPG. Specimens with ≥ 15 WPG all had close to 30% residual char. The amount of residual char was decreased an average of 3% by leaching of milled specimens with water and acetone. The efficiency of the flame-retardant treatment was therefore reduced very little by leaching with water and acetone.

Pyrolysis temperatures and amounts of residual char remained essentially un-

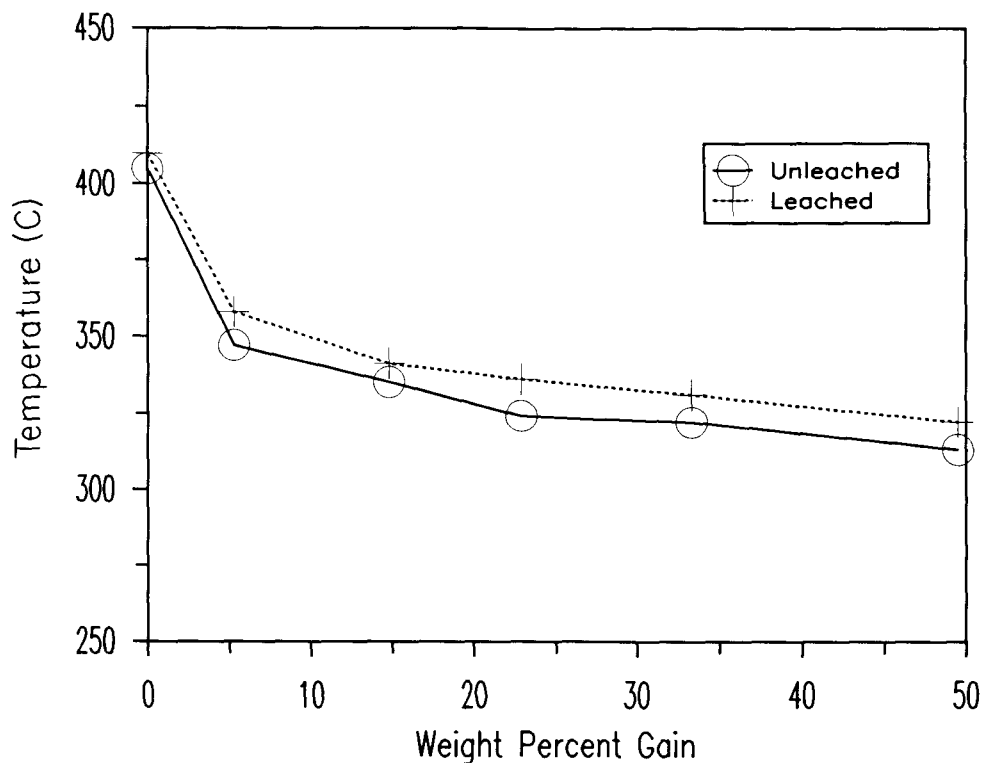


FIG. 4. Effect of Fyrol 51-IPDI treatments on temperature at maximum rate of pyrolysis of leached (method 1) and unleached ponderosa pine specimens.

changed as treatment levels increased from 25 to 50 WPG. Thermal degradation properties changed very little at ≥ 25 WPG, indicating only small increases in the flame-retardant effect of treatments can be expected with weight gains greater than 25%.

CONCLUSIONS

The Fyrol 51-IPDI treatment changes the thermal degradation properties of wood. The temperature at maximum rate of pyrolysis was lowered and the amount of residual char was increased. These changes indicate improved flame-retardant properties.

The solvents used did not swell the wood, which means the chemicals were not in the cell walls but reacted in the lumen structure. It was possible to leach some but not all phosphorus from the specimens. More work is needed to develop a solvent system that will swell the wood to facilitate entry of the reacting chemicals into the cell wall. Such a system would increase both leach resistance and dimensional stability.

Physical properties of the treated wood were not evaluated. The physical appearance was not changed, and there was no apparent loss of integrity or strength. Strength properties will be evaluated in future studies. Fire performance of larger specimens needs evaluating by fire tests such as the fire tube, tunnel, and fire brand tests.

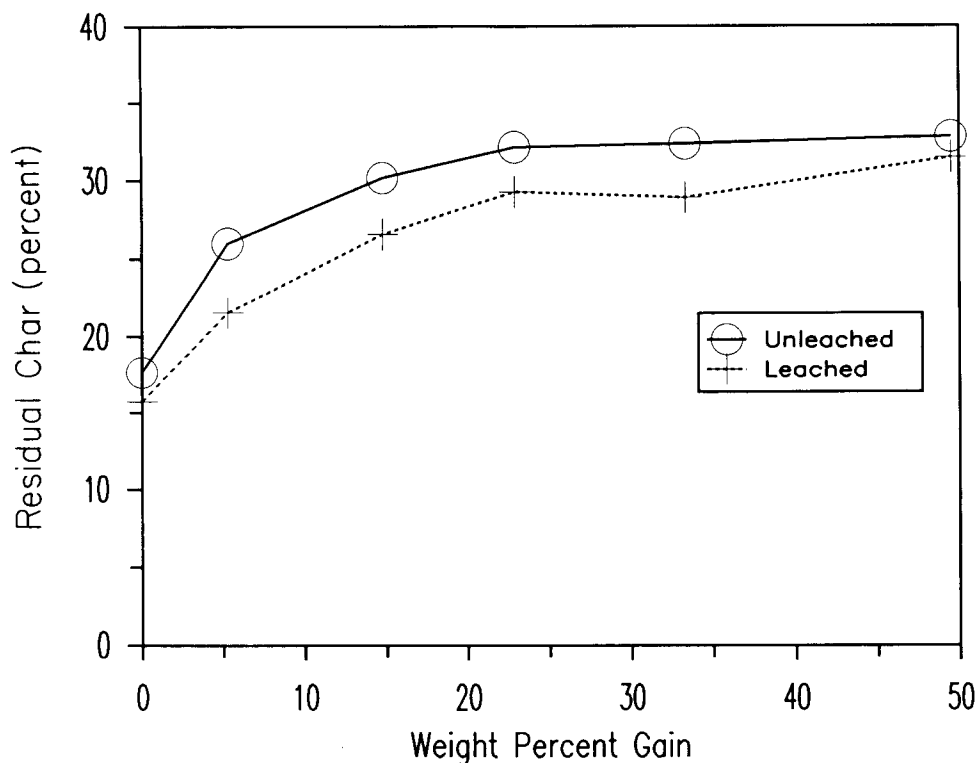


FIG. 5. Residual char resulting from pyrolysis of leached (method 1) and unleached ponderosa pine specimens treated with Fyrol 51-IPDI.

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