THERMAL DEGRADATION PROPERTIES OF WOOD REACTED WITH DIETHYLCHLOROPHOSPHATE OR PHENYLPHOSPHONIC DICHLORIDE AS POTENTIAL FLAME RETARDANTS[1]

W. D. Ellis, R. M. Rowell, and *S. L. LeVan*
Research Chemist, Research Chemist, and Chemical Engineer
Forest Products Laboratory,[2] Forest Service
U.S. Department of Agriculture, Madison, WI 53705-2398

and

R. A. Susott
Research Chemist
Intermountain Research Station
Intermountain Fire Sciences Laboratory, Forest Service
U.S. Department of Agriculture, Missoula, MT 59807

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ABSTRACT

Improved thermal degradation properties (an indication of improved flame-retardant properties) were observed when southern pine was reacted with either diethylchlorophosphate (DECP) or phenylphosphonic dichloride (PPDC). These two compounds may prove useful as flame retardants for wood. Thermal degradation was evaluated by thermogravimetric methods; the values were reduced slightly by extraction of the specimens with toluene or ethanol and water. When pyrolyzed in nitrogen, specimens of the reacted wood, extracted or unextracted, showed maximum rates of pyrolysis at lower temperatures and produced more char than control specimens.

Keywords: Flame retardant, diethylchlorophosphate, phenylphosphonic dichloride, southern pine, pyrolysis, thermogravimetry.

INTRODUCTION

The present work is part of a research program at the Forest Products Laboratory designed to enhance wood properties by modifying the cell-wall polymers chemically. By reacting a flame retardant with hydroxyl groups in cell-wall cellulose, hemicellulose, and lignin, it may be possible to reduce the flammability of wood and at the same time eliminate problems of leachability, corrosivity, and hygroscopicity inherent in many existing flame retardants.

As early as 1948 (Toy 1948), flame retardants were used as plasticizers and copolymers in resins and plastics. In a review article, Tesoro (1978) has documented the history of flame retardants used for cellulosic fabrics. Although reactive flame retardants have been used successfully for textiles and plastics, no flame-retardant compounds are commercially available that react with wood and effect

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a leach-resistant, flame-retardant treatment. However, the technology developed in connection with textiles and plastics may be applicable to wood.

Compounds containing phosphorus have been shown to change the thermal degradation properties of wood. They are effective as flame retardants by reducing the temperature at which pyrolysis occurs and greatly increasing the amount of char produced (Browne and Tang 1962). Phosphorus compounds act as acid precursors; during combustion or pyrolysis, they form acids that cause selective decomposition of the cellulosic material to form increased amounts of combustible volatiles (Gottlieb 1956). The effectiveness of such a compound as flame retardant can be measured as a function of the temperature at which maximum pyrolysis occurs and the amount of char formed.

Two phosphorus-containing organic compounds, phenylphosphonic dichloride (PPDC) and diethylchlorophosphate (DECP), when reacted with cellulose textiles, gave them improved flame retardancy (Katsuura and Inagaki 1978; Schwenker and Pacsu 1958). The aim of the present research was to react wood with these two compounds and then use thermogravimetry (TG) to measure the effects on the thermal degradation of the wood, and thus to evaluate the compounds as flame retardants for wood.

Experience shows that reactions that have been reported as working well with cellulose and textiles do not always work with wood. Some of the potential reaction sites in wood are not readily accessible. Often, also, reaction conditions that are useful for textiles are unacceptable for wood. We developed procedures for reacting wood with low-molecular-weight monomers such as propylene oxide, butylene oxide, methyl isocyanate and other isocyanates, and acetic anhydride. When wood was reacted with these compounds, we found the dimensional stability and decay resistance of the wood improved, while its thermal degradation properties as determined by thermogravimetric analysis were unchanged, as were the temperatures of maximum pyrolysis and the residual char of the reacted wood (Rowell et al. 1984).

METHODS

Solutions of PPDC or DECP were made in dimethylformamide (DMF) or pyridine as solvent/catalyst. Solution concentrations varied from 0 to 17% (wt:wt). The PPDC or DECP in solution was reacted with southern pine *(Pinus* sp.) specimens with dimensions 2.5 × 2.5 × 0.6 cm (radial × tangential × longitudinal). All specimens were oven-dried at 105 C before and after treatment. Specimens were submerged in the solution in a stainless steel cylinder (150-ml capacity), then reacted 1 hour at 110 C and 150 lb/in.^{2} of nitrogen. At the end of the reaction time, the cylinder was cooled and the specimens were removed. After air-drying overnight, reacted specimens were then oven-dried at 105 C for 15 hours and weighed; and percent of weight gain was calculated (based on the original oven-dry weight).

Throughout this paper, any discussion of percent weight gain is on the basis of unextracted specimens. Weight gains could not be calculated for extracted specimens because of the loss of wood substance during extraction.

A representative portion of each specimen was milled to pass 40-mesh screen. One-half of the milled specimen was extracted for 8 hours with toluene : ethanol (2:1, v:v) in a Soxhlet extractor. Extracted specimens were dried at 105 C, then

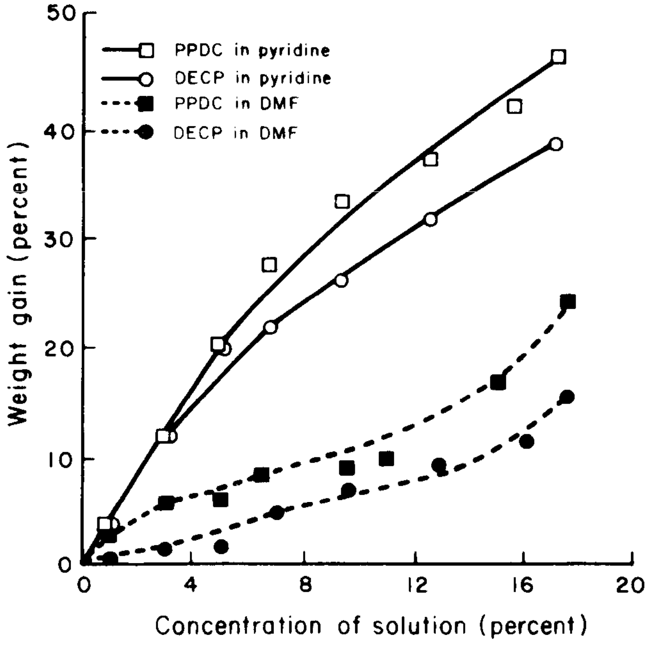

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Fig. 1. Weight gain of wood specimens reacted with phenylphosphonic dichloride (PPDC) diethylchlorophosphate (DECP) in pyridine or dimethylformamide (DMF). (ML86 5404)

leached with water for 7 days, the water being changed daily. Specimens were redried at 105 C. Milled specimens, both extracted and unextracted, were subjected to thermogravimetric analysis.

Derivative thermogravimetry (DTG) and TG were done using a Perkin-Elmer TGS-2 system. Specimens were pyrolyzed in a flow of nitrogen (200 ml/min) by heating at 20 C per minute. The weight remaining was monitored at 1 C intervals. A microcomputer processed this information and calculated the fractional weight of the specimen remaining as a function of temperature, and plotted this as the TG curve. The rate of weight loss as a function of temperature was calculated and plotted as a DTG curve. The percentage of char remaining at 500 C was used as a relative measure of retardant effectiveness since char formation reduces the amounts of burning volatile products and the heat they produce. The temperature at the maximum rate of pyrolysis was measured from the DTG curve. Because, during pyrolysis, phosphorus compounds form acids that cause decomposition of the cellulose to occur at lower temperatures, the pyrolysis temperature indicates the compound's ability to cause selective decomposition of the wood and, indirectly, its effectiveness as a flame retardant.

RESULTS AND DISCUSSION

Reaction chemistry

The extent of reaction of PPDC or DECP with the wood depended on the compound, its concentration, the solvent, and the reaction time. In this study the amount of chemical reacted with wood was controlled by changing solution concentrations while holding reaction time and temperature constant.

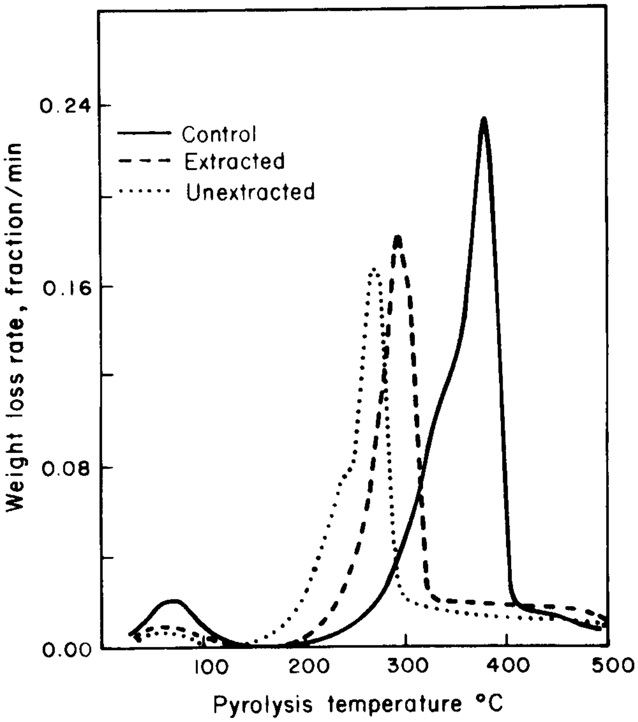

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FIG. 2. Derivative thermogravimetry curves for control, extracted reacted, and unextracted reacted wood specimens. Wood was reacted to 15% weight gain with diethylchlorophosphate in dimethylformamide. (ML86 5405)

More PPDC than DECP reacted with the wood when the same reaction time, temperature, and solvent were used (Fig. 1). Specimens generally had 5 to 10% more weight gain when reacted with PPDC than with DECP. The molecular weights of the portions of PPDC and DECP reacted with the specimens were very close, thus excluding the possibility that the larger weight gains for PPDC-reacted specimens might have been caused by a heavier molecule being reacted with the wood.

When pyridine rather than DMF was used as solvent, weight gains for the PPDC and DECP reactions were approximately three times larger (Fig. 1). Schwenker and Pacsu (1958) have suggested that pyridine is an effective catalyst because it forms a pyridinium complex which aids the substitution of phosphorus compounds for a labile hydrogen in the cellulose.

Despite the higher weight gains when pyridine was the solvent, reacted specimens had better thermal degradation properties when DMF was the solvent/catalyst. At this time we cannot explain the differences in thermal degradation properties associated with these solvents.

Thermogravimetry

Similar DTG curves were observed for all specimens. The reaction of PPDC or DECP with wood shifted the pyrolysis peaks to lower temperatures (Fig. 2). The peaks shifted more or less according to the level of reaction. The peak tem-

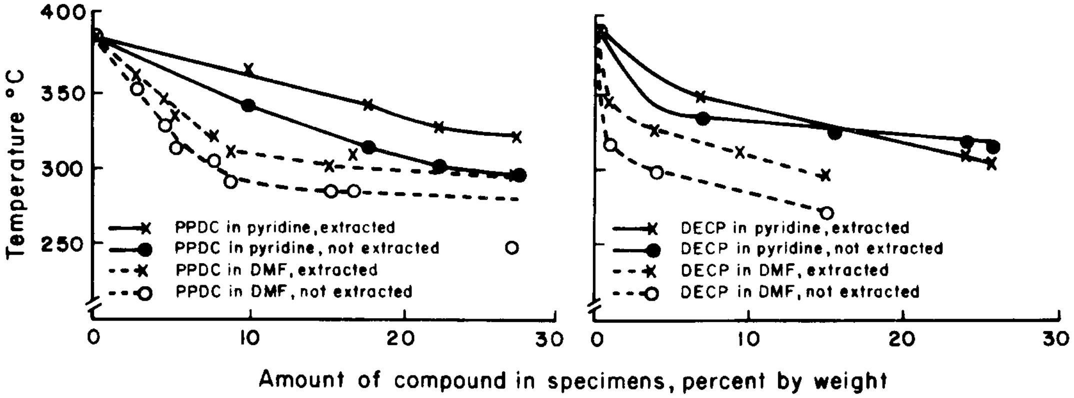

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FIG. 3. Temperature at maximum rate of pyrolysis of wood specimens reacted with increasing amounts of phenylphosphonic dichloride (PPDC) or diethylchlorophosphate (DECP). (ML86 5406)

perature for maximum rate of pyrolysis of control specimens of wood was 386 C. The specimens began to lose weight at about 200 C, weight-loss increase slowed forming a shoulder on the peak at about 350 C, and most of the weight loss occurred below 400 C.

When DMF was used as the solvent, reaction of wood with either PPDC or DECP lowered the temperature for maximum rate of pyrolysis by 100 to 120 C. As the amount of chemical reacted with the wood increased, the temperature of pyrolysis decreased (Fig. 3). The temperature range for pyrolysis, from the beginning to the completion of weight loss, was about 50 C narrower for reacted specimens than for control specimens.

The effects of the phosphorus compounds and the solvents on the temperature of pyrolysis can be seen from Table 1. DECP in DMF as solvent was most effective, while PPDC in pyridine as solvent was the least effective in lowering the pyrolysis temperature of reacted specimens.

Extraction of reacted specimens slightly increased the pyrolysis temperatures (Fig. 3). This was seen as a shift of the pyrolysis peak (Fig. 2). Extraction presumably removed some of the compound that was not reacted with the wood. The shoulder seen on the DTG peak of control and reacted specimens was absent from that of reacted specimens that had been extracted. The shoulder probably arose

TABLE 1. *Temperature at maximum rate of pyrolysis of reacted wood specimens.*[1]

Amount of chemical[3] in specimens	Temperature[2]			
	DECP/pyr	DECP/DMF	PPDC/pyr	PPDC/DMF
pct		*C*		
0	386	386	386	386
10	335	305	360	305
15	325	290	345	300
20	315	—	330	295
25	300	—	320	290

[1] All specimens unextracted.

[2] Approximations made from graph to enable comparisons of chemical treatments at the same level of treatment.

[3] DECP = diethylchlorophosphate; PPDC = phenylphosphonic dichloride; DMF = dimethylformamide; pyr = pyridine.

TABLE 2. *Residual char formed during pyrolysis of reacted wood specimens.*[1]

Amount of chemical[3] in specimens	Residual char[2]			
	DECP/pyr	DECP/DMF	PPDC/pyr	PPDC/DMF
pct	pct			
0	20	20	20	20
10	30	48	25	44
15	34	49	29	46
20	36	—	33	46
25	38	—	34	46

[1] All specimens unextracted.

[2] Approximations made from graph to enable comparisons of chemical treatments at the same level of treatment.

[3] DECP = diethylchlorophosphate; PPDC = phenylphosphonic dichloride; DMF = dimethylformamide; pyr = pyridine.

from the pyrolysis of wood substances that were later removed from the reacted specimens by extraction.

It was not possible to quantify, by weight, losses of flame-retardant chemicals caused by solvent and water extraction because of the simultaneous loss of wood substances during extraction.

Char

The amount of residual char formed during the 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.

Both DECP and PPDC had the desired effect of increasing the amount of residual char of reacted specimens above the 20% formed from the pyrolysis of control specimens (Table 2). PPDC in pyridine was least effective, the maximum amount of char from this treatment being 34%. DECP in DMF was the most effective; 48 to 49% char was formed from specimens with as little as 10% reacted chemical. Specimens reacted using DMF as solvent formed considerably more residual char than specimens reacted using pyridine as solvent (Fig. 4).

SUMMARY

PPDC and DECP can be reacted with wood using either DMF or pyridine as solvent/catalyst. The reaction proceeded easily at 110 C, and adequate weight gains were obtained after 1 hour of reaction time. Higher weight gains occurred with pyridine than with DMF at identical reaction conditions, but better flame-retardant properties were found in specimens reacted with DMF as solvent.

The temperature at maximum rate of pyrolysis was lowered by reaction of either PPDC or DECP with wood. This pyrolysis temperature was lowered most effectively by DECP in DMF at weight gains of 10% and above (the temperature was lowered 100 to 120 C). Extracted specimens had a temperature at maximum rate of pyrolysis about 20 C higher than unextracted specimens.

The amount of char formed during pyrolysis was increased considerably by reacting wood with PPDC or DECP. Wood reacted with DECP in DMF as solvent produced 49% char compared to 20% char for control specimens. Extraction of reacted specimens reduced the amount of char formed. The lower pyrolysis temperatures and increased amounts of char formed by wood reacted with PPDC or

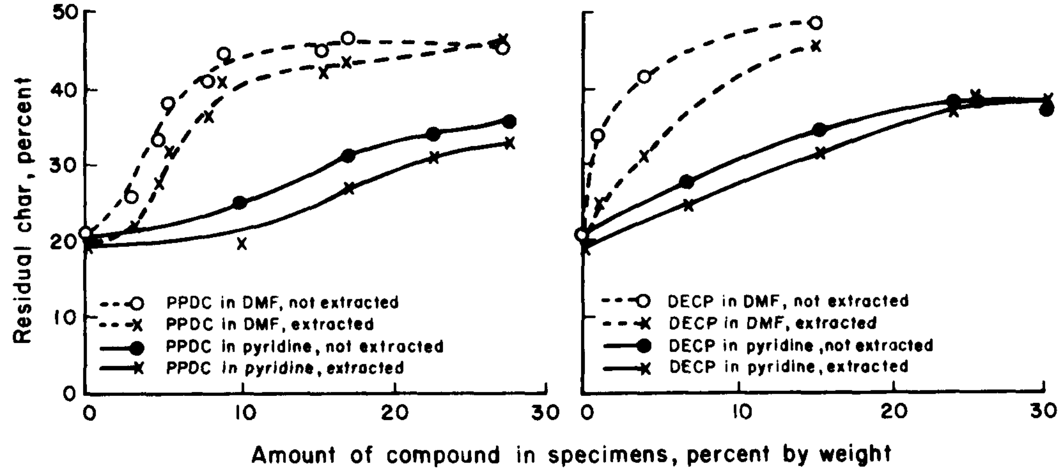

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FIG. 4. Residual char formed during pyrolysis of wood specimens reacted with increasing amounts of phenylphosphonic dichloride (PPDC) or diethylchlorophosphate (DECP). (ML86 5407)

DECP show that both these chemicals could prove effective flame retardants. Extraction of specimens did not cause major changes in the results of pyrolysis of the specimens, from which it appeared that both PPDC and DECP were acceptably reacted with the wood.

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