IN SITU THERMAL CONDENSATION OF GLUCOSE–DIAMMONIUM PHOSPHATE INWOOD FOR FIRE AND FUNGAL DECAY PROTECTION[1]

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Abstract. Thermal condensation of glucose–diammonium phosphate in wood at 160 and 190°C will protect wood against fire and decay in one treatment using an aqueous system. For fire protection, treatments at 160 or 190°C led to low flammability as evidenced by fire-tube tests. For nonleached wood, weight losses were 1.9, 2.0, and 2.0% with chemical retentions of 56.7, 44.7, and 64.7%, respectively, for 2-, 4-, and 6-h heating; and for leached wood, weight losses of 5.1, 3.8, and 1.5% with chemical retentions of 24.5, 24.1, and 45.6%, respectively, for 2-, 4-, and 6-h heating compared with 18.8% weight loss for diammonium phosphate-treated wood with chemical retention of 19.4%. The control had 84.4% weight loss. For decay protection, heat treatment at 190°C for 30 min after 2-wk water leaching also prevents degradation by brown and white rot fungi. Weight loss by *Gloeophyllum trabeum* (*Gt*) was 0.4% with 19.5% chemical retention, and weight loss by *Trametes versicolor* (*Tv*) was 1.5% with 17.8% chemical retention. The control had 30.6 and 36.8% weight losses by *Gt* and *Tv*, respectively.

Keywords: Dehydration, diammonium phosphate, fire and fungal decay protection, glucose, thermal condensation, wood.

INTRODUCTION

The degradation of wood by fungi, termites, fire, and UV radiation constitutes four losses of wood in use. Many chemicals have been developed for wood products to control such degradation. In the past, the control of biological degradation was emphasized. Commercial wood preservatives, including chromated copper arsenate (CCA), pentachlorophenol, creosote, and ammoniacal copper quaternary ammonium (ACQ) compounds, were developed for bioprotection. Because of concerns about the effect of arsenic on human health, the US wood preservation industry has recently voluntarily phased out the use of CCA treatment of wood products in residential applications and replaced it with ACQ and copper boron azole compounds. Some other wood preservatives were also developed to lessen the negative health and environmental effects of wood preservatives. These are isothiazolone (Greenley 1986), chlorothalonil (Wood and Bell 1990), propiconazole (Goodwine 1990), and copper dimethyldithiocarbamate (Arsenault et al 1991). Other new copper wood preservatives are isothiazolone and copper–amine complexes (Evan 2003), water-borne copper naphthenates (Freeman et al 2003), and copper HDO (copper xyligen) (Jung 2003).

Proper treatment of wood products with fire retardants for residential uses would decrease the damage to buildings and save lives (Hoebel 1998). This aspect of wood protection, however, has received less attention. Only two commercial fire retardants were adopted by the American Wood Preservers' Association (AWPA 1993). These are FR-1, which is comprised of guanyl urea phosphate (70%) and boric acid (30%), and FR-2, which is comprised of

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phosphoric acid (57.8%), boric acid (18.3%), and ammonia (23.9%). These fire retardants are water-soluble and unsuitable for outdoor use. The amino resin fire retardants are more resistant to water leaching but degrade wood, particularly interior treated wood products because phosphoric acid retained in the products will degrade wood at high humidity.

The amino resin fire retardants were prepared by reacting melamine or dicyandiamide with formaldehyde to form methylolated melamines, which were further polymerized to crosslinked melamine polymers (Juneja 1972; Juneja and Richardson 1974). During formulation, phosphoric acid was introduced into the solution to form complexes with melamine polymers. The phosphate groups in the melamine polymers were unstable and released as phosphoric acid from wood products during service, which decreased wood strength (LeVan and Winandy 1990). There is a need to develop leach-resistant fire retardants with minimum strength loss for wood products.

Historic wood protection has emphasized either decay or fire. If achievable, wood products with dual protection against decay and fire would be more desirable. The dual-protected wood products reported have an amino–resin base formulated by adding biocides, including copper and zinc salts, tertiary and quaternary ammonium compounds, and 3-iodo-2-propynl-butyl carbamate (Ward 1990; Trocino and Amundson 1992). Another formulation involves addition of the quaternary ammonium compounds such as didecyl dimethyl ammonium chloride to the amino–resins—melamine, dicyandiamide, phosphoric acid, and formaldehyde (MDPF), or urea, dicyandiamide, phosphoric acid, and formaldehyde (UDPF) (LeVan and DeGroot 1993).

We have investigated dual protection of wood against decay and fire. In our previous investigations, phosphoramidates prepared in situ from a phosphorus pentoxide–amine system were able to react with wood, and the resulting phosphoramidate-bonded wood resisted water leaching and protected wood from fire and fungal decay (Lee et al 2004a, 2004b) The amino-borates prepared from boric acid and diols resist water leaching and protect wood against fire and decay (Chen 2008a). Phosphortriamidate-impregnated wood prevents thermal degradation but not fungal decay (Chen 2008b). The mentioned treatments use organic solvents that limit practical applications.

In the present study, an aqueous system was used to form thermal condensation products in wood. The chemicals, including glucose and diammonium phosphate, are safe and inexpensive. Glucose–diammonium phosphate mixture was used as an adhesive for wood products (Stofko 1980), but its use for fire and decay protection has not been reported.

The aims of the present study were to investigate the dual protection of wood against fire and fungal degradation in an aqueous system and to learn the mechanisms of fire and fungal decay protection of this modified wood.

MATERIALS AND METHODS

Characterization

Elemental analysis of the thermal condensation products from glucose–diammonium phosphate and in the presence of loblolly pine (*Pinus taeda* L.) was performed by Galbraith Laboratories, Inc. (Knoxville, TN). IR spectra in KBr of an individual compound, thermal condensation of glucose–diammonium phosphate, and in the presence of loblolly pine were obtained using a Mattson Galaxy series FTIR 5000 spectrophotometer (Unicam, UK).

Wood samples from untreated loblolly pine and loblolly pine heat-treated with 61.2% glucose–diammonium phosphate at 160°C for 2, 4, or 6 h were dried over phosphorus pentoxide in a dessicator for 10 da before IR analysis. Relative intensity of IR peaks of C=C (1644 – 1630 cm^{-1}) and C-H (2925 cm^{-1}) at 160°C for 2, 4, or 6 h and the control was determined by the baseline method (Colthup et al 1964).

Table 1. *Volume of 61.2% aqueous glucose–diammonium phosphate (1:1 molar ratio) used in heat treatments.*

Treatment (°C)	Volume (L)
Fire-tube tests	
160	8.25
190	2.75
Fungal decay tests	
Brown rot fungus (*Gt*)	
160	4.8
190	4.8
White rot fungus (*Tv*)	
160	2.4
190	2.4

Fire Retardant Evaluation

Treatment at 160 °C. Sixty sapwood sticks of loblolly pine (*Pinus taeda* L.), 9.5 × 19 mm in various grain angles in tangential and radial directions and 560 mm in the longitudinal direction, were conditioned at 27°C and 30% RH for 3 wk and weighed. They were then placed under vacuum at 3.74 – 4.0 kPa for 30 min in a treating cylinder and then impregnated with 61.2% aqueous solution of glucose–diammonium phosphate (Table 1) in 1:1 molar ratio at 1.207 kPa for 3 h. The solution was adjusted to pH 9 with 864 mL of 30% ammonium hydroxide solution and soaked for 1 da at room temperature. After soaking, the sticks were removed, excess solution wiped from the surface, and then weighed. The sticks were dried at 60°C for 6 da. The 60 sticks were divided into 3 sets of 20. Each set was heated at 160°C for 2, 4, or 6 h. After heat treatment, one half of the sticks (10) in each set was leached in 8 L of distilled water by changing the water every 24 h for 2 wk. After leaching, nonleached and leached sticks were conditioned at 27°C and 30% RH for 3 wk and weighed before the fire-tube test.

Treatment at 190°C. Procedures of impregnation were similar to the previously mentioned 160°C treatment except 20 loblolly pine sticks and 61.2% aqueous glucose–diammonium phosphate (Table 1) were used. After impregnation, the sticks were heated at 190°C for 15 min. One half of the sticks (10) were leached in 8 L of distilled water by changing the water every 24 h for 2 wk. Then nonleached and leached sticks were conditioned at 27°C and 30% RH for 3 wk and weighed before the fire-tube test.

Treatment with Diammonium Phosphate

Loblolly pine sticks (20 pieces for each concentration) impregnated with 2.75 L of 10, 15, and 20% aqueous diammonium phosphate as described previously were also conditioned at 27°C and 30% RH for 3 wk and weighed before the fire-tube test.

Fire retardancy by the fire-tube test. Loblolly pine sticks without chemical treatment, heat-treated with glucose–diammonium phosphate, and impregnated with diammonium phosphate as described previously, were tested for fire retardancy using the fire-tube test. Tests were run according to ASTM E69-99 (ASTM 2001). The test specimen was 9.5 × 19 mm in cross-section and 1020 mm long and was prepared by connecting two sticks (510 mm long) with similar chemical retentions. The specimen was placed 25 mm above the Bunsen burner and then the flame was adjusted to 280 mm height. The specimen was under flame for 3 min. After the 3-min flame test, flaming and glowing had stopped, and weight loss by flame exposure, duration of flame, and duration of glow was recorded.

Decay Resistance Evaluation

Brown rot fungus treatment at 160°C. Ninety-six loblolly pine sapwood blocks (19 × 19 mm in various grain angles in tangential and radial directions and 19 mm in the longitudinal direction) were conditioned at 27°C and 30% RH for 3 wk and weighed. They were impregnated using procedures similar to those used on the loblolly pine sticks treated for fire-tube tests using a 61.2% aqueous solution of glucose–diammonium phosphate (Table 1). After impregnation and weighing, they were dried at 50°C for 2 da. The blocks were divided into 6 sets and each set (16 blocks) was heated at 160°C for 1, 2, 3, 4, 6, or 8 h. After heat treatment, one half of the blocks (8) were leached in 400 mL distilled water for 6, 24, and 48 h and then every 24 h for 2 wk according to ASTM D-1413-99 (ASTM 2000). The nonleached and leached blocks were then conditioned at 27°C and 30% RH for 3 wk and weighed before the soil block fungal decay tests. Chemical retention in the block was expressed as a weight percentage, which was obtained by multiplying the concentration of solution with the weight of solution absorbed by the block. Retentions of chemicals in wood for fire and fungal decay tests were based on conditioned weights at 27°C and 30% RH for 3 wk before and after heat treatments. Because too few data points existed to establish a threshold relationship, the use of nonlinear regression analysis to determine the threshold retention would not be appropriate (Steel and Torrie 1960; Nance and Amburgey 1976; Gezer et al 1999). Weight losses over 2% were considered to be of fungal origin, and weight losses below 2% could include losses caused by leaching of wood extractives from wood.

Brown rot treatment at 190°C. The impregnation procedures were the same as for the 160°C treatment, except 48 loblolly pine blocks and 61.2% aqueous glucose–diammonium phosphate (Table 1) were used. After impregnation, the blocks were divided into 3 sets, and each set of 16 blocks was heated at 190°C for 10, 20, or 30 min. After heat treatment, one half of the blocks (8) from different heat treatments were leached in 400 mL of distilled water as described previously. The nonleached and leached blocks were then conditioned at 27°C and 30% RH for 3 wk and weighed before soil block fungal decay tests.

White rot fungus treatment at 160 and 190°C. Sweet gum (*Liquilambar stysflua* L.) sapwood blocks (19 mm in all anatomical directions) were used. Number of blocks, treating method, and concentrations of chemical were the same as for loblolly pine blocks (Table 1), except heat treatments at 190°C were 20 and 30 min. Treated blocks were leached with the procedures used for the loblolly pine blocks. Fungal decay evaluations were tested by ASTM D 1413-99 (ASTM 2000).

RESULTS AND DISCUSSION

Elemental Analysis

Elemental analysis of thermal condensation products from heat treatment of loblolly pine with glucose–diammonium phosphate at 160 and 190°C showed that nitrogen and phosphorus were retained in the wood (Table 2). Heat treatment of loblolly pine with 61.2% glucose–diammonium phosphate in 1:1 molar ratio at 160°C for 2 h (Table 2) indicated that a total of 14% phosphorus and 58% nitrogen was retained in the products for leached compared with nonleached products. Results for heating at 160°C for 4 h indicated that a total of 29% phosphorus and 67% nitrogen was retained in the products. High-temperature treatments (180 – 190°C) led to wood degradation.

Therefore, heat treatment at 190°C was only for 15 min. Results indicated a total of 17% phosphorus and 56% nitrogen was retained in the products. These results indicated that heat treatment at 160°C for 4 h retained more phosphorus and nitrogen than other heat treatments. Heat treatments of glucose–diammonium phosphate may form water-insoluble, heat-stable polyphosphoramidates as a result of thermal condensation of glucose–diammonium phosphate (Kaur et al 1986). Polyphosphoramidates are good dehydration agents that promote char formation in wood through dehydration of wood polysaccharides to chars and produce fewer and less volatile compounds (Lyons 1970).

Fourier transform infrared analysis. Infrared bands of glucose, diammonium phosphate, loblolly pine, and thermal condensation products from glucose–diammonium phosphate and thermal condensation products from glucose–diammonium phosphate in loblolly pine are described in Table 3. Only IR bands of thermal condensation products from glucose–diammonium phosphate and glucose–diammonium phosphate in loblolly pine are described subsequently.

Fourier transform infrared analysis of thermal condensation products from reaction of glucose with diammonium phosphate. Thermal condensation of glucose–diammonium

Table 2. *Elemental analysis of thermal condensation products from heat treatments of loblolly pine with glucose–diammonium phosphate.*

	Nonleached		Leached	
Treatment	P[a] (%)	N[b] (%)	P (%)	N (%)
160°C (2 h)	4.2	3.64	0.59 (14)[c]	2.12 (58)[c]
160°C (4 h)	5.9	5.14	1.72 (29)	3.46 (67)
190°C (15 min)	4.88	4.25	0.83 (17)	2.36 (56)
Control	15×10^{-6}	<0.5		

[a] Phosphorus.
[b] Nitrogen.
[c] Retention (%) after water leaching.

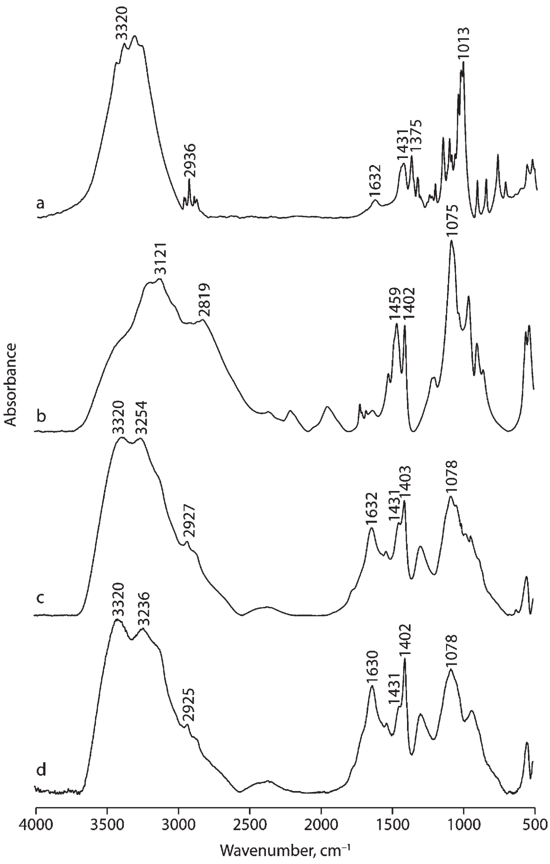

Figure 1. Fourier transform infrared (FTIR) bands of glucose (a), diammonium phosphate (b), and their condensation products at 160°C for 2 h (c) and 4 h (d).

phosphate in 1:1 molar ratio at 160°C for 2 and 4 h showed the following characteristic IR absorptions (Fig 1; Table 3). The strong absorption at 3320 cm^{-1} is attributed to H-bonded OH absorption of glucose and at 3254 – 3236 cm^{-1} is attributed to $NH4^{+}$ stretching of diammonium phosphate. The strong absorption at 1630 – 1632 cm^{-1} is attributed to OH stretching of adsorbed water and also attributed to C=C stretching vibration. The intensity of this absorption increased from 2 to 4 h heating, which indicated that more double bonds are formed in the glucose molecular. The strong absorption at 1402 cm^{-1} is attributed to $HPO4^{-3}$ stretchings and at 1431 cm^{-1} is attributed to CH2 stretching vibration. The strong absorption at 1078 cm^{-1} is attributed to $HPO4^{-3}$ stretching and C-O stretching of glucose (Bellamy 1964; Colthup et al 1964).

Fourier transform infrared analysis of thermal condensation products from glucose–diammonium phosphate in loblolly pine. The IR band of wood in the region of 1630 – 1644 cm^{-1} is associated with sorbed water and also with stretching vibration of aromatic orthohydroxy ketone of polyphenolic flavonols (Hergert and Kurth 1953). This band is intense in wood species, including larch, western red cedar, redwood, and ponderosa pine. It also appeared in thermal degradation of cellulose xanthate attributable to the creation of double bonds in the cellulose molecular (Zahbankov 1966). In our study, thermally treated wood with glucose–diammonium phosphate was dried thoroughly over phosphorus pentaoxide for 10 da. The samples should not have sorbed water. The increase in intensity of IR absorption at 1630 – 1644 cm^{-1} (Fig 2; Table 4) is attributed to the increase in double bonds of cellulose and hemicelluloses in wood as a result of dehydration by thermal condensation products from glucose–diammonium phosphate. Indeed, the relative intensity of C=C peak compared with peak at C-H (C=C/CH) (Table 4) increases from control of 1.14 – 1.57 (38%; 2 h heating), 2.11 (85%; 4 h), and to 2.43 (113%; 6 h).

Similar conclusions were reported for thermal degradation of cellulose xanthate (Zahbankov 1966) and wood (Sekiguch et al 1983). In addition to the previously reported IR absorptions, a very strong and broad absorption at 3419 –

Table 3. *Assignment of fourier transform infrared (FTIR) bands and thermal condensation products of glucose–diammonium phosphate in loblolly pine.*

Compound or wood	Frequency	Intensity[a]	Assignment
Glucose[b]	3320	vs	Bonded OH stretching
	1431	m	CH_2 stretching
	1375	m	CH_2 stretching
	1013	s	C-O stretching
Diammonium phosphate[c]	3121	vs	NH_4^+ stretching
	1402	m	NH_4^+ deformation
	1075	vs	$HP0_4^{-2}$ stretching
Loblolly pine[d]	3600 – 3000	vs	H-bonded OH stretching
	2929	m	C-H stretching
	1632	m	Adsorbed water; orthohydroxy ketone of flavonols
	1600, 1515	m	Aromatic C=C (lignin)
	1425	s	CH_2 symmetrical bending
	1380	s	C-H bending
	1059	s	C-O stretching
Condensation products of glucose–diammonium phosphate: 160°C (2 or 4 h)[e]	3320	s	H-bonded OH stretching
	3254 – 3236	s	NH_4^+ stretching
	2925	s	C-H stretching
	1630 – 1632	s	Adsorbed water; C=C stretching from dehydration of glucose
	1403 – 1402	s	NH_4^+ deformation
	1078		C-O stretching, $HP0_4^{-2}$ stretching
Condensation products of glucose–diammonium phosphate in loblolly pine: 160°C (2, 4, 6 h)[f]	3440 – 3419	vs	H-bonded OH stretching
	2924 – 2922	m	C-H stretching
	1644 – 1630	s	C=C stretching from dehydration of cellulose and hemicelluloses
	1512 – 1509	m	Aromatic C=C stretching
	1061 – 1056	s	C-O stretching

[a] m, medium intensity; vs, very strong intensity; s, strong intensity.
[b] Colthup et al (1964).
[c] Bellamy (1964).
[d] Hergert and Kurth (1953); Marchessault (1962); Sarkanan et al (1967).
[e] Bellamy (1964); Colthup et al (1964).
[f] Marchessault (1962); Bellamy (1964); Zahbankov (1966).

3440 cm^{-1} is attributable to H-bonded O-H stretching vibration, and a strong absorption at 1056 – 1061 cm^{-1} is attributable to C-O stretching vibration, which decreased after 4 and 6 h heating compared with the control. The IR intensity of aromatic peak at 1509 – 1512 cm^{-1} remained unchanged. This suggested that dehydration in wood took place mainly in hemicelluloses and cellulose. These IR absorptions are characteristic of wood that has been chemically modified (Marchessault 1962).

Evaluation for Fire Retardancy

Treatment at 160°C. Loblolly pine was treated with a 61.2% aqueous solution of glucose–diammonium phosphate in a 1:1 molar ratio at 160°C for 2, 4, and 6 h. The retentions of chemicals in wood (Table 5) were 56.7, 44.7, and 64.7% for nonleached wood and 24.5, 24.1, and 45.6% for leached wood. This indicated that 43, 54, and 70% of water-insoluble thermal condensation products were formed in wood after 2, 4, and 6 h heating. The results indicated that longer heating produced more water-insoluble thermal condensation products in wood. Weight losses by fire-tube tests of loblolly pine treated with glucose–diammonium phosphate at 160°C (Table 5) were small for both nonleached and leached wood. For nonleached wood, weight losses by fire-tube tests at chemical retentions of 56.7, 44.7, and 64.7% were 1.9, 2.0,

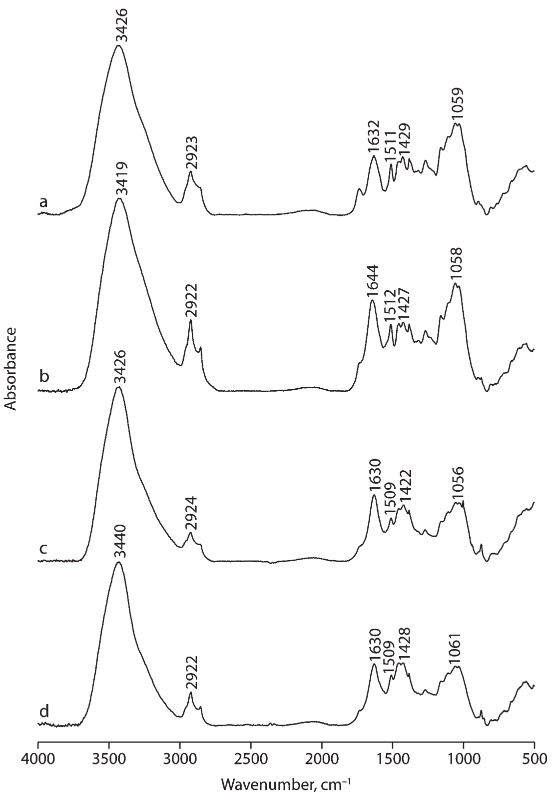

Figure 2. Fourier transform infrared (FTIR) bands of loblolly pine (a) and thermal condensation products from glucose–diammonium phosphate in loblolly pine at 160°C for 2 h (b), 4 h (c), and 6 h (d).

Table 4. *Infrared (IR) peaks of C=C (1644 – 1630 cm^{-1}) and C-H (2925 cm^{-1}) of loblolly pine treated with glucose–diammonium phosphate at 160°C.*

Treatment	Relative intensity of IR peak[a]
Control	1.14
2 h	1.57 (38%)[a]
4 h	2.11 (85%)
6 h	2.43 (113%)

[a] C=C/C-H stretching vibrations. Percent (%) IR intensity increases relative to the control.

and 2.0% for 2, 4, and 6 h heating, respectively. For leached wood, weight losses were 5.1, 3.8, and 1.5% with chemical retentions of 24.5, 24.1, and 45.6%. The control had a large weight loss of 84.4%, and wood treated with diammonium phosphate with retentions of 10.6, 14.5, and 19.4% had weight losses of 51.9, 35.4, and 18.8%, respectively, in fire-tube tests. These fire-tube tests showed that heat treatments with glucose–diammonium phosphate at 160°C in wood resulted in smaller weight losses than wood impregnated with diammonium phosphate. Weight losses and chemical retentions for wood heat-cured with glucose–diammonium phosphate were 3.8 – 5.1% with 24.1 – 24.5% chemical retentions, and wood impregnated with diammonium phosphate with chemical retention of 19.5% had 18.55% weight loss. This implied that wood that had been heat-cured with glucose–diammonium phosphate had lower flammability than wood impregnated with diammonium phosphate.

Treatment at 190°C. Loblolly pine was treated with 61.2% glucose–diammonium phosphate in a 1:1 molar ratio at 190°C for 15 min. Retentions of thermal condensation products in wood (Table 5) were 60 and 27.3% for nonleached and leached wood with 1.5 and 3.9% weight losses by fire-tube tests, respectively. This indicated that heating at 190°C for only 15 min can also produce 46% water-insoluble products that had low flammability as shown by a small weight loss by the flame test.

The duration of flame after a 3-min flame exposure test (Table 5) showed that no flame persisted for nonleached and leached wood treated with glucose–diammonium phosphate at all concentration levels (24.1 – 64.7%) for heating at 160°C for 2, 4, and 6 h. Wood impregnated with diammonium phosphate with various weight gains of 10.6, 14.5, and 19.4% had much longer duration of flame for 291, 216, and 55 s, respectively. The treated wood had no residual burning after the flame was removed, indicating that wood heat-cured with glucose–diammonium phosphate had good fire retardancy compared with wood impregnated with diammonium phosphate. The duration of glow for wood heat-cured with glucose–diammonium phosphate (Table 5) was 0 s at all concentration levels (24.1 – 64.7%) and 0 s for wood impregnated with diammonium phosphate at all concentration levels (10.6 – 19.4%) after removing flame from treated wood.

Table 5. *Fire-tube test of loblolly pine sticks treated with glucose–diammonium phosphate at various temperatures and times.*

Treatment	Concentration of solution (%)	Retention[a] (%)	Final weight loss (%)	Duration of flame (s)	Duration of glow (s)
160°C					
2 h					
Nonleached	61.2	56.7	1.9	0	0
Leached	61.2	24.5	5.1	0	0
4 h					
Nonleached	61.2	44.7	2.0	0	0
Leached	61.2	24.1	3.8	0	0
6 h					
Nonleached	61.2	64.7	2.0	0	0
Leached	61.2	45.6	1.5	0	0
190°C					
15 min					
Nonleached	61.2	60.0	1.5	0	0
Leached	61.2	27.3	3.9	0	0
Diammonium phosphate					
Nonleached	10	10.6	51.9	291	0
	15	14.5	35.4	216	0
	20	19.4	18.8	55	0
Control			84.4		

[a] Retentions of chemicals in wood based on conditioned weights at 27°C and 30% RH for 3 wk before and after heat treatments.

Evidence of increased IR intensity in the region of 1630 – 1634 cm^{-1} attributable to C=C stretching vibration of wood reacted with glucose–diammonium phosphate at 160°C from 2 – 6 h (Table 4; Fig 2b – d) indicated that dehydration of cellulose and hemicelluloses in wood took place. The insoluble products from heat treatments of glucose–diammonium phosphate act as dehydration agents to wood during thermal degradation by way of the dehydration pathway (Shafizadeh 1984) to produce more chars and less volatile compounds. This thereby protects wood from thermal degradation. The fire-tube tests showed that high char yields ranging from 94.9 – 98.5% for nonleached and leached wood treated with diammonium phosphate at 160 and 190°C compared with 15.6% for the control further supported that dehydration of wood by thermal condensation products from glucose–diammonium phosphate took place.

Evaluation of Fungal Decay Resistance

Brown rot fungus. Heat treatment of loblolly pine with 61.2% glucose–diamonium phosphate in a 1:1 molar ratio at 160°C for 2 h without leaching prevented decay by *G. trabeum*. Weight loss was 2.1% with 56.8% chemical retention. Leached wood required 6 h heating to prevent decay. Weight loss was 1.4% with 21.3% chemical retention. The control had 30.6% weight loss by *G. trabeum*. Wood heated for 8 h had 31.6% weight loss by *G. trabeum*. However, test results indicated that wood heated for 8 h without chemical treatment did not affect the decay tests (Table 6).

For 190°C treatments, nonleached wood required 10 min to prevent decay by *G. trabeum*. Weight loss was 2.2% with 56.5% chemical retention. Leached wood required 30 min heating to prevent decay by *G. trabeum* and weight loss was 0.4% with 19.5% chemical retention. The control had 30.6% weight loss by *G. trabeum*. Wood heated for 30 min had 33.7% weight loss by *G. trabeum*. This indicated that heating wood without chemical treatment for 30 min did not affect the decay tests (Table 6).

White rot fungus. Heat treatment of sweet gum with 61.2% glucose–diammonium phosphate in a 1:1 molar ratio at 160°C for 4 – 8 h showed that only nonleached wood prevented

Table 6. *Weight losses of glucose–diammonium phosphate-treated loblolly pine blocks decayed by Gloeophyllum trabeum in a 12-wk soil block fungal decay test.*

		Nonleached		Leached	
Treatment	Concentration of solution (%)	Retention (%)[b]	Weight loss (%)[a] by *G. trabeum*	Retention (%)[b]	Weight loss (%)[a] by *G. trabeum*
160°C					
1 h	61.2	59.3	5.0 (5.8)	10.0	11.5 (1.8)
2 h	61.2	56.8	2.1 (2.4)	17.7	7.6 (3.4)
3 h	61.2	54.0	1.2 (0.8)	20.7	3.9 (2.2)
4 h	61.2	54.2	2.2 (2.6)	20.7	2.9 (2.1)
6 h	61.2	50.3	1.3 (1.6)	21.3	1.4 (1.7)
8 h	61.2	47.0	2.6 (3.2)	19.5	0.4 (0.9)
No chemicals					
2 h			41.0 (6.1)		
4 h			34.3 (2.7)		
8 h			31.6 (3.3)		
190°C					
10 min	61.2	56.5	2.2 (2.5)	7.8	15.7 (3.2)
20 min	61.2	48.9	2.8 (2.8)	22.3	6.7 (2.7)
30 min	61.2	47.0	2.6 (3.6)	19.5	0.4 (0.2)
No chemicals					
10 min			36.4 (2.5)		
30 min			33.7 (2.8)		
Control			30.6 (5.0)		

[a] Average of five replicates, numbers in parentheses are standard deviations. Weight losses over 2% were considered to be of fungal origin and below 2% may include losses of wood extractives.

decay by *T. versicolor*. Results from nonleached wood showed 1.5% weight loss with 43.7% chemical retention. Leached wood, even after 8 h heating, was unable to prevent decay by *T. versicolor,* but had a small weight loss of 4.1% with 19.0% chemical retention. The control had 36.8% weight loss by *T. versicolor*. Untreated wood heat treatment at 160°C for 8 h had 38.2% weight loss by *T. versicolor*. This indicated that heating wood without chemical treatment for 8 h at 160°C does not affect the decay tests (Table 7).

For 190°C treatment of sweet gum with glucose–diammonium phosphate, nonleached wood prevented decay by *T. versicolor* after 20 min heating. Weight loss was 0% with 43.2% chemical retention. Leached wood prevented decay by *T. versicolor* after 30 min heating. Weight loss was 1.5% with 17.8% chemical retention. The control had 36.8% weight loss by *T. versicolor*. Results from wood heated without chemicals for 30 min had 37.6% weight loss by *T. versicolor*. This indicated that heating untreated wood for 30 min at 190°C does not affect the decay tests (Table 7).

The decay tests described showed that heat treatment of wood with glucose–diammonium phosphate at 190°C for 30 min protected loblolly pine and sweet gum from both *G. trabeum* and *T. versicolor* even after 2 wk water leaching (Tables 6 and 7). Weight loss by *G. trabeum* was 0.4% and by *T. versicolor* was 1.5% with chemical retentions of 19.5% and 17.8%, respectively. Heat treatment of wood with glucose–diammonium phosphate at 190°C was more effective to both brown and white rot fungi than at 160°C. The decay protection of wood treated with thermal condensation products from glucose–diammonium phosphate may have been attributed to the inability of fungal decay enzymes to metabolize the modified wood substrate, which was one of the mechanisms to explain the fungal decay resistance of hydrothermally modified wood (Stamm 1960; Subramanian 1984; Tjeerdsma et al 2002; Hakkou et al 2006). However, hydrothermally

Table 7. *Weight losses of glucose–diammonium phosphate-treated sweet gum blocks decayed by Trametes versicolor in a 12-wk soil block fungal decay test.*

Treatment	Concentration of solution (%)	Nonleached Retention (%)[b]	Nonleached Weight loss (%)[a] by *G. trabeum*	Leached Retention (%)[b]	Leached Weight loss (%)[a] by *G. trabeum*
160°C					
1 h	61.2	45.6	7.9 (2.2)	0.6	32.8 (4.2)
2 h	61.2	44.3	3.0 (2.2)	14.2	14.7 (5.6)
3 h	61.2	43.3	2.0 (1.6)	16.0	13.2 (3.8)
4 h	61.2	43.7	1.5 (0.6	19.2	6.2 (3.7)
6 h	61.2	41.0	1.5 (0.7)	19.2	6.2 (3.7)
8 h	61.2	41.5	2.0 (0.5)	19.0	4.1 (4.2)
No chemicals					
2 h			31.4 (2.7)		
4 h			32.6 (6.3)		
8 h			38.2 (3.8)		
190°C					
20 min	61.2	43.2	0.0 (0)	11.5	13.1 (5.1)
30 min	61.2	39.4	2.1 (0.6)	17.8	1.5 (1.3)
No chemicals					
10 min			37.3 (5.5)		
30 min			37.6 (4.2)		
Control			36.8 (2.5)		

[a] Average of five replicates, numbers in parentheses are standard deviations. Weight losses over 2% were considered to be of fungal origin and below 2% may include losses resulting from wood extractives.

[b] Retentions of chemicals in wood based on conditioned weights at 27°C and 30% RH before and after heat treatments.

modified wood requires high temperatures between 165 and 190°C for 16 h to be effective against decay.

The high temperatures and long heating times led to wood degradation as evidenced by the decrease in modulus of rupture (MOR) of 5 – 18% (Tjeerdsma et al 1998). In the early investigations, Seborg et al (1953) reported that toughness of basswood decreased 32 – 63% at 250 and 300°C for 20 and 60 min, respectively. Troughton and Rozen (1974) reported that tensile strength of Douglas-fir by either oven-drying or hot pressing decreased 45% at 200°C for 10 min, whereas white spruce decreased only 3%. Davis and Thompson (1964) reported that for southern red oak and Douglas-fir heated to 200°C for 20 min, toughness decreased 20 – 30% compared with the control. MacLean (1955) reported that work to maximum load and MOR of Douglas-fir decreased 30% at 150°C for 8 h. Whether heat treatments of wood with glucose–diammonium phosphate affect the strength properties of wood requires investigation. There is a need to search for safe dehydration agents that can dehydrate wood at lower temperatures without causing it to degrade. Research in this area should lead to environmentally acceptable wood protection.

The advantages of *in situ* heat treatment of wood with glucose–diammonium phosphate are the use of an aqueous system and safe and inexpensive chemicals. Dual protection of wood with good fire and decay protection can be achieved with this treatment. The disadvantages are that high temperatures and high concentrations of chemicals are required, and over half of the reaction products were lost by water leaching. Further work on decreasing the concentrations of chemicals at 190°C treatment with varied heating times may help to lower the chemical concentrations.

CONCLUSIONS

Thermal condensation of glucose–diammonium phosphate in wood at 160 and 190°C protects wood from both fire and fungal degradation. For fire protection, either 160°C for 2 h or 190°C for 15 min protects wood from fire degradation even after 2 wk water leaching. For fungal decay protection, heat treatment at 190°C for 30 min after water leaching prevents decay by *Gt* and *Tv*, and, at 160°C for 6 to 8 h, also prevents decay by *Gt* and *Tv*. IR evidence suggested that dehydration of cellulose and hemicelluloses in wood may play an important role in fire and decay resistance. The advantages of these treatments are the use of an aqueous system and safe and inexpensive chemicals. The disadvantages of these treatments are the requirements for high concentrations of chemicals and high temperatures. Research is needed to find chemicals able to dehydrate cell wall polymers in wood at lower temperatures without degradation.

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REFERENCES

Arsenault R, Kressbach J, Fox R (1991) Laboratory and field evaluation of copper dimethyldithiocarbamate as a wood preservative. American Wood-Preservers' Association, Birmingham, AL. Pages 1 – 23.

ASTM (2000) Standard method of testing wood preservatives by laboratory soil-block cultures. D143-99. American Society for Testing and Materials, West Conshohocken, PA.

——— (2001) Standard test method for combustible properties of treated wood by the fire-tube apparatus. E69-99. American Society for Testing and Materials, West Conshohocken, PA.

AWPA (1993) Report of subcommittee P-7: Fire retardant systems. Pages 415 – 417 *in* Proc American Wood-Preservers' Association, Birmingham, AL.

Bellamy LJ (1964) The infrared spectra of complex molecules. John Wiley & Sons, Inc., New York. Pages 343 – 349.

Chen GC (2008a) Synthesis and evaluation of aminoborates derived from boric acid and diols for protecting wood against fungal and thermal degradation. Wood Fiber Sci 40(2):248 – 257.

——— (2008b) Synthesis and evaluation of phosphortriamidates in wood for thermal and fungal decay protection. Holzforschung 62:318 – 321.

Colthup NB, Daley IH, Wiberley SE (1964) Chapter 2. Experimental considerations. Pages 37 – 97, Chapter 10. Ethers, alcohols, and phenols. Pages 269 – 277, Chapter 12. Compounds containing boron, silicone, phosphorus, sulfur, or halogen. Pages 291 – 318 *in* Introduction to infrared and raman spectroscopy. Academic Press, New York, NY.

Davis WH, Thompson WS (1964) Influence of thermal treatments of short duration on the toughness and chemical composition of wood. Forest Prod J 8:350 – 356.

Evan P (2003) Emerging technologies in wood protection. Forest Prod J 47:14 – 22.

Freeman MH, Kamdem P, Brient JA (2003) Water-born copper naphthanates: A chromium and arsenic free preservative for wood and composites *in* Proc American Wood-Preservers' Association. 99:194 – 211.

Gezer ED, Yalinkilic MK, Kizilkaya K, Michael JH (1999) Estimation of preservative toxic threshold retention from laboratory decay tests: A new method. Wood Sci Technol 33:63 – 71.

Goodwine W (1990) Suitability of propiconazole as a new generation wood preserving fungicide. Pages 206 – 214 *in* Proc American Wood-Preservers' Association.

Greenley DE (1986) Laboratory and field evaluation of a substituted isothiazolone as a potential wood preservative. Pages 206 – 214 *in* Proc American Wood-Preservers' Association.

Hakkou M, Petrissans M, Gerardin P, Zoulalian A (2006) Investigations of the reasons for fungal durability of heat-treated beech wood. Polym Degrad Stabil 91:393 – 397.

Hergert HL, Kurth EF (1953) The infrared spectra of lignin and related compounds. I. Characteristic carbonyl and hydroxyl frequencies of some flavanones, flavones, charcones and acetophenones. J Am Chem Soc 75:1622 – 1625.

Hoebel JF (1998) US consumer product safety commission activities related to polymer flammability. Pages 303 – 307 *in* Proc on Recent Advances in Flame Retardancy of Polymeric Materials.

Juneja SC (1972) Stable and leach-resistant fire retardants for wood. Forest Prod J 22(6):17 – 23.

———, Richardson LR (1974) Versatile fire retardants from amino–resins. Forest Prod J 24(5):19 – 23.

Jung M (2003) Copper HDO (Copper xyligen) *in* Proc American Wood-Preservers' Association 99:190 – 193.

Kaur B, Gur IS, Bhatnagar (1986) Studies on thermal degradation of cellulose and cellulose phosphoramides. J Appl Polym Sci 31:667 – 683.

Lee HL, Chen GC, Rowell RM (2004a) Thermal properties of wood reacted with a phosphorus pentaoxide–amine system. J Appl Polym Sci 91:2465 – 2481.

——— (2004b) Fungal decay resistance of wood reacted with a phosphorus pentoxide–amine system. Holzforschung 58:311 – 315.

LeVan SL, DeGroot RC (1993) One step process for imparting resistance and fire retardancy to wood products. US Patent 5185214.

———, Winandy JE (1990) Effect of fire retardant treatments on wood strength: A review. Wood Fiber Sci 22 (1):113 – 131.

Lyons WJ (1970) Mechanisms of fire retardation with phosphorus compounds: Some speculation. J Fire Flammability. 1:302 – 311.

MacLean JD (1955) Effect of oven heating and hot pressing on strength properties of wood *in* Proc American Wood-Preservers' Association 5:227 – 250.

Marchessault RH (1962) Application of infra-red spectroscopy to cellulose and wood polysaccharides. Pure Appl Chem 5:107 – 129.

Nance WL, Amburgey TL (1976) Statistical analysis of data from laboratory decay tests. Pages 161 – 171 *in* Proc American Wood-Preservers' Association Annual Meeting, April 25 – 28, 1976, Atlanta, GA.

Sarkanan KV, Chang HM, Ericksson B (1967) Species variation in lignins I. Infrared spectra of guaiacyl and syringyl models. TAPPI 50(11):572 – 575.

Seborg RM, Tarkow H, Stamm AJ (1953) Effect of heat upon the dimensional stabilization of wood. Forest Prod J 3(9):59 – 67.

Sekiguch Y, Frye JS, Shafidadeh F (1983) Structure and formation of celluosic chars. J Appl Polym Sci 28:3513 – 3525.

Shafizadeh F (1984) Pyrolysis and combustion. Pages 489 – 529 *in* Rowell RM, ed. The chemistry of solid wood. Advanced in chemistry series 207. American Chemical Society, Washington, DC.

Stamm AJ, Baechler RH (1960) Durability and dimensional stability of five modified woods. Forest Prod J 1:22 – 26.

Steel RGD, Torrie JH (1960) Principles and procedures of statistics. Pages 332 – 345 *in* Non-linear regression analysis. (Steel and Torrie, eds). McGraw-Hill Book Company, Inc., New York, NY.

Stofko J (1980) Bonding of solid lignocellulosic materials. US Patent 4183997.

Subramanian RV (1984) Bioactive wood–polymer composites. Pages 292 – 305 *in* Rowell RM, ed. The chemistry of solid wood. Advances in chemistry series 207. American Chemical Society, Washington, DC.

Tjeerdsma BF, Boonstra M, Militz H (1998) Thermal modification of non-durable wood species. 2. Improved wood properties of thermally treated wood. International Research Group on Wood Preservation. IRG/MP 98-40124.

———, Stevens M, ———, Van Acker J (2002) Effect of process conditions on moisture content and decay resistance of hydro-thermally treated wood. Holzforsch Holzverw 53(5):94 – 99.

Trocino FS, Amundson FJ (1992) Fire-retardant chemical compositions. US Patent 5162394.

Troughton GE, Rozen LR (1974) Heat effects on tensile properties of Douglas-fir and white spruce thin section. Wood Sci 7(2):116 – 122.

Ward HA (1990) Wood preservatives. US Patent 4950685.

Wood T, Bell J (1990) *In* Proc Development of chlorothalonil as a wood preservative. American Wood-Preservers' Association. Pages 190 – 196.

Zahbankov RG (1966) Infrared spectra of cellulose and it derivatives. Pages 97 – 102 *in* New types of cellulose derivatives: investigation of the new products of thermal decomposition of cellulose methylxanthate. Chapter VI. Stepanov BI (Ed.) Translated from Zhurnal Prikladnoi Spektroskopii 19(1):145 – 147. Consultants Bureau, New York, NY.