United States Patent Office 3,501,339
Patented Mar. 17, 1970

3,501,339

PROCESS FOR IMPROVING THE FLAME RETARDANCY OF WOOD

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No Drawing. Filed Nov. 9, 1966, Ser. No. 592,965
Int. Cl. C09d 5/18
U.S. Cl. 117—118 3 Claims

ABSTRACT OF THE DISCLOSURE

Process for treating natural wood materials to impart flame resistance thereto which comprises impregnating the wood material with an alkyl or aryl halogenated phosphite, or phosphonate and thereafter heating.

This invention relates to the treatment of normally flammable natural wood materials to render the same fire retardant. More particularly, it relates to the treatment of wood with a water, fire, and weather resistant composition containing a phosphorus compound.

Because of its ready availability, ease of fabrication, and other reasons, wood is still widely used in construction of bridges, trestles, wharves, mine shafts, and other structures. In many such applications, costly measures are required to prevent and to extinguish fires. The use of oil-soluble wood preservatives is necessary in many instances to prevent decay of the wood. Such preservatives frequently increase the susceptibility of the wood to combustion. It would be desirable if a means could be found that would render the wood fire retardant. Many solutions to the problem of raising the ignition temperature of wood have been presented. Some of those methods involve coating the wood surface with a fire retardant composition. However, in such a method, when the wood is cut or trimmed, the freshly exposed surfaces are no longer protected and require a new treatment. Other methods use water-soluble inorganic salts impregnated into the wood. Such salts are incompatible with the common oil-soluble preservatives and, in addition, are easily leached out of the wood by standing water or by rain. Still other methods precipitate a water-insoluble resin within the fibrous structure of the wood. Such methods, however, affect the important structural properties of the wood.

The provision of a means for rendering normally flammable natural wood materials fire retardant is the principal object of this invention.

It has now been found that natural wood materials can be rendered very resistant to burning by treatment with alkyl or aryl halogenated phosphites or phosphonates, of which the haloalkylphosphonates are exceptionally effective for this purpose, followed by heating to fix the phosphorus compound in the wood.

Phosphites and phosphonates that are advantageously used in the process of this invention are those wherein the alkyl groups contain from 1 to 8 carbon atoms, preferably 1 to 4 carbon atoms, and those aryl substituted compounds wherein the aryl group may contain from 6 to 10 carbon atoms. Compounds which are particularly useful include, for example, tris-(2-bromoethyl) phosphite, tris-(bromopropyl) phosphite, bis-(2-bromoethyl) 2 - bromoethylphosphonate, bis - (bromopropyl) bromopropyl phosphonate, di(chloroethyl) vinylphosphonate, di(2-chloropropyl) 2-chloropropyl phosphonate, di(2-chloroethyl) 2-chloroethylphosphonate and the nuclearly chlorinated and brominated mono-, di-, and triphenyl phosphites.

Any method of impregnation of the wood materials with the phosphorus compound is effective and solvent can be used if desired. The impregnation may be done by merely soaking the wood in the phosphorus compound (when it is a liquid) or in a solution of the compound. (The phosphites and phosphonates are soluble in numerous solvents, and may be applied as an emulsion in solvents such as water.) The wood may be impregnated using increased pressure to force the phosphorus compound to penetrate the wood deeper, or the wood may be put under reduced pressure to remove air and gases from the pores of the wood and then admit the phosphorus compound or its solution so that it will fill the wood pores in place of air.

After impregnation, the wood is heated at a temperature of 100° C. to 200° C. and preferably 140° C. to 180° C. in order for chemical reaction to occur between the wood fibers and the halogenated phosphorus compound. (It is believed that transesterification occurs between hydroxy groups of the wood and the phosphorus ester.)

The time that the treated wood must be heated varies inversely with the temperature employed. For example, at 100° C., heating is advantageously carried out for about 15 minutes. At 200° C., a heating time of about 5 minutes is sufficient.

The following examples further illustrate the present invention.

Example 1

A tongue depressor of white pine wood was cut into one inch sections and put in a flask, along with 20 ml. of bis(2-chloroethyl) chloroethylphosphonate (BCP) and heated to 200° C. The wood and solution became dark in color. The flask and contents were cooled and the wood removed. The wood pieces were washed with acetone to remove excess phosphonate, then washed with water and dried.

A wood section thus treated would not burn when held in an igniting flame and removed. Only on holding in the igniting flame until phosphonate was driven out by the heat would the wood burn, and then the flame immediately went out on removal of the burning wood strip from the igniting flame. On burning, the wood tended to char only.

Example 2

To demonstrate the effectiveness of various phosphonates as SE (self-extinguishing) additives for wood, clean dry white ash applicator sticks were tagged with a piece of adhesive tape on one end and numbered for identification. The sticks were then baked at 150° C. for 5 minutes to remove extraneous moisture in the interior of the wood. The sticks after cooling were weighed to the tenth of a mg. on an analytical balance. These sticks were 5¾ inches long and 1/16 inch in diameter.

Three sticks each were immersed in various phosphonates as shown in the accompanying table. The phosphonates were in test tubes and the sticks were immersed to a depth of 2.5 inches. The sticks were soaked for two hours at 25° C. The sticks were then removed and excess

phosphonate wiped off. The sticks were then again wiped just before weighing to determine the weight pick-up of phosphonate. One stick of each series was then burned according to the technique described below, and its self extinguishing characteristic observed and recorded. The remaining two sticks of each series were then placed in a hot air oven at 140° C. for exactly thirty minutes, removed, cooled and reweighed. This gave the amount of residual phosphonate in the stick. One stick of each series was now burned to determine its self extinguishing characteristic at this stage. The remaining sticks were immersed in acetone for 30 minutes to a depth of 2.5 inches to leach out any "non-fixed" phosphonate in the wood fibers. These sticks were then rinsed with fresh acetone and dried 5 minutes at 100° C. The sticks were cooled and reweighed to determine the amount of residual phosphonate still left in the wood. These sticks were then burned according to the following test to determine its self extinguishing characteristics.

The sticks as treated above were held in the flame of a "Meeker" burner at an angle of 30° from the horizontal until they caught fire. They were then removed and observed for continuance of burning. If the flame went out it was reignited and removed from the flame—still at a 30° angle and observed for continuance of burning. If it again went out, it was classed as self-extinguishing (SE). If the flame struggled to burn and succeeded for a while on both ignitions or if it burned readily after removal from the flame, it was classified as flammable (B). Untreated wood, in this test, continued to burn after the first ignition and was consumed completely.

The data are compiled in the following table.

TABLE I

Stick No.	Solution* No.	Weight percent Phosphonate absorbed	Weight percent Phosphonate remaining after heating	Weight percent Phosphonate remaining after extracting with Acetone	Results
1	A	22.1			SE
2	A	23.0	5.6		B
3	A	23.7	4.9	2.1	B
4	B	18.9			SE
5	B	9.6	.29		B
6	B	14.6	2.1	1.8	B
7	C	22.7			SE
8	C	12.5	4.5		SE
9	C	9.7	5.4	2.6	SE
10	D	17.8			SE
11	D	12.3	2.4		SE
12	D	10.6	3.1	2.5	SE
13	E	15.6			SE
14	E	15.2	6.6		SE
15	E	12.6	5.1	3.9	SE

*A—Diethyl ethylphosphonate.
B—Dibutyl butylphosphonate.
C—Di(chloroethyl) vinylphosphonate.
D—Di(2-chloropropyl) 2-chloropropylphosphonate.
E—Di(2-chloroethyl) 2-chloroethylphosphonate.

NOTE.—All percentages based on dry weight of stick.

RESULTS OF BURNING TESTS

(I) Treated wood, wiped dry:					
Stick No	1	4	7	10	13
Results	SE	SE	SE	SE	SE
(II) Baked wood, 140° C., 30 min.:					
Stick No	2	5	8	11	14
Results	B	B	SE	SE	SE
(III) Acetone extracted wood:					
Stick No	3	6	9	12	15
Results	B	B	SE	SE	SE

SE=Self Extinguishing. B=Burns.

Example 3

Five grams of wood fiber were charged to a 500 cc. flask and 150 grams of bis-(bromopropyl)-bromopropylphosphate were added. The mixture was heated for 2 hours at 147° to 155° C., cooled and filtered on a vacuum filter. The fiber was washed with 100 ml. of isopropyl alcohol in two portions and dried under vacuum at 25° C. 112 grams of the bromopropylphosphonate was recovered. The fiber sample was found to contain 7.0 percent bromine and 3.9 percent phosphorus by neutron activation. It did not burn even when held in a flame, although it did char and disintegrate.

I claim:

1. Process for treating natural wood materials to impart flame resistance thereto which comprises impregnating the wood material with an alkyl or aryl halogenated phosphite or phosphonate and thereafter heating the impregnated wood at a temperature of 100° to 200° C. for a time sufficient to fix the phosphite or phosphonate in the wood.

2. Process of claim 1 wherein the wood is treated with bis(2-chloroethyl) chloroethylphosphonate or bis-(bromopropyl) bromopropylphosphonate.

3. Flame retardant wood materials whenever made by the process of claim 1.

References Cited

UNITED STATES PATENTS

1,936,985	11/1933	Lommel et al.	
2,143,639	1/1939	Caprio	117—147
2,662,834	12/1953	Paist et al.	117—136 X
2,666,078	1/1954	Ferguson	252—8.1 X
2,803,562	8/1957	Erbel et al.	117—136
2,811,469	10/1957	Costello	117—136
3,046,236	7/1962	Jahn.	
3,265,681	8/1966	Friedman	106—15 X
3,285,774	11/1966	Goldstein et al.	117—136
3,321,330	5/1967	Mohney	106—15 X

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U.S. Cl. X.R.

117—136, 147

PO-1050
(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,501,339 Dated March 17, 1970

Inventor(s) Arthur E. Gurgiolo

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In Col. 4, line 14, delete "phosphate" and insert in its place --phosphonate--.

SIGNED AND
SEALED
SEP 15 1970

(SEAL)
Attest:

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