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WOOD PRESERVATION

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The present invention relates to the treatment of wood or similar cellulosic materials and it has particular relation to methods of and compositions for treating wood for purposes of preventing the attacks of various micro-organisms which cause staining or decaying of wood or similar materials.

The main objects of the invention are to provide a composition for destroying organisms of deterioration in wood, and for inhibiting the growth of such organisms; which is relatively inexpensive to prepare; which does not cause staining of the wood; which is relatively free from objectionable odors; which has exceptionally high toxic value against fungous growths and which retains its protective properties over long periods of time, even when exposed to relatively intense weathering.

The action of various fungi in producing stain or decay in wood and cellulosic materials has long been recognized. Among the most common offenders are green mold, the ordinary blue or sap-staining fungus, *Ceratostomella pilifera*, and the decay organism, *Fomes annosus*. These are exceptionally active in relatively warm climates such as exist in the southern part of the United States and are active in green wood still containing much sap. The sap stain organism does not usually produce pronounced decomposition of the wood in which it grows, but instead merely produces its characteristic discoloration which suggests decay and in substantial amounts results in the reduction of the value of the lumber for market purposes. Wood substances, after they have become sufficiently seasoned, are practically immune from sap stain.

It has heretofore been proposed to protect green lumber during the period of seasoning, from sap stain organisms by dipping, spraying, or otherwise applying thereto a suitable toxic substance having the property of inhibiting the growth of the organism. Such substance should possess a relatively large number of characteristics, some of which are more or less the antithesis of others. The following constitutes a partial list of such properties:

- (a) The material must be inexpensive.
- (b) It should possess little or no odor.
- (c) It should be highly toxic to fungi which produce stain and decay in lumber.
- (d) It should be substantially non-toxic to higher animal life.
- (e) It should not produce discoloration of lumber to which it is applied.
- (f) It should be of such nature that it can be

made up into a water solution for application but it should be of only slight solubility and volatility when incorporated into lumber.

(g) It should be non-corrosive to metals or to wood.

(h) It must not operate deleteriously to paints and varnishes which may be applied to the wood.

(i) It must penetrate into or adhere to the wood with relative ease.

But few materials are known to possess a sufficient number of these properties in an adequate degree to permit of commercial application to lumber. Among the materials heretofore proposed are borax and soda ash. These materials are comparatively inexpensive, non-toxic to animals, and non-odorous. However, upon weathering, they leach rapidly away. Among other materials which have been proposed are ethyl mercury chloride, and the sodium salt of tetrachlorophenol. These materials offered some advantage over borax and soda ash; however, under severe conditions they were not entirely satisfactory. Ethyl mercury chloride, for example, is of fairly high volatility and its concentration decreases materially upon exposure. It is also ineffective against green mold. The tetrachlorophenol was not effective in controlling sap stain fungi growing on softwood species such as pine, spruce, etc.

The present invention is based on the discovery that pentachlorophenol constitutes an unusually effective fungicidal material when applied to wood or other cellulosic materials and possesses to an unusual degree the characteristics essential to materials for this purpose.

Pentachlorophenol as well as tetrachlorophenol and trichlorophenol have heretofore been tested by the Petri dish method in malt-agar media against *Ceratostomella pilifera* and *Fomes annosus*. In these tests it was observed that the tetrachlorophenol exhibited a very high degree of toxicity. In contradistinction, it was observed that pentachlorophenol was of comparatively slight toxicity in the ordinary malt-agar medium. For example: it was found that from .002 to .004% of sodium tetrachlorophenolate was effective in the destruction of the ordinary sap stain fungi. About .03% of pentachlorophenol and more than .1% of sodium salt of pentachlorophenol was required to produce complete destruction of the fungus. This degree of toxicity in the pentachlorophenol and its sodium salt was so low as to prohibit its application for destruction of sap stain organism or *Fomes annosus* in or upon wood or similar cellulosic material. In view of this observed extremely

low apparent toxicity for sap stain organisms, pentachlorophenol or its sodium salt have not heretofore been suggested for protection of wood. However, tetrachlorophenol, because of its known high toxicity in cultures, has enjoyed wide commercial use.

It has now been observed that when pentachlorophenol or, preferably, its sodium salt, are applied to wood they are substantially more effective as sap stain inhibitors than tetrachlorophenol compounds. The reason for this reversal of the order of merit is obscure and at the present time is not understood. In view of the poor showing of the compound in culture media the results with pentachlorophenol compounds were highly surprising.

The pentachlorophenol or its sodium salt are applicable to hard woods or soft woods of various types, including gum, pine, and the like. Treating solutions are prepared by dissolving the sodium salt of pentachlorophenol in water in any suitable ratio. Good results have been obtained by the addition of three or four pounds of the sodium salt of the phenol compound to 50 gallons of water. Higher concentrations may be employed but in general are not required. Substantial reduction of the concentration results in considerable impairment of the results. The solution of the sodium salt of pentachlorophenol may be applied to the wood in any convenient manner. As a general rule it is preferable to apply it to the wood promptly after it has been sawed. It is also desirable that the logs themselves be sawed into lumber within a short period after they have been felled in order to prevent premature discoloration by sap stains. The application of the water solution may be made by spraying, brushing or dipping. However, for most commercial purposes dipping seems to constitute the most satisfactory method. The sawed timber is simply submerged in a suitable bath of the above indicated concentration of the sodium salt solution until it is adequately wetted. The timber is then withdrawn from the bath, drained and permitted to dry. Exposure of the sodium salt of pentachlorophenol to the carbon dioxide of the air results in the liberation of the pentachlorophenol in or upon the wood fibers. The free phenol is of very low solubility in water and forms a much more permanent fungicide than the salt. Accordingly, after dipping, it is desirable that the wood be dried and exposed to the air as thoroughly as possible prior to exposure to rain or other weathering agencies. The phenol may be precipitated more quickly by dipping the freshly treated wood into an acid bath or by exposure to an atmosphere containing carbon dioxide in high concentration. Precipitation of insoluble salts of the phenolate may be effected by treatment of the wood after it has been treated with sodium pentachlorophenolate, with a solution of a heavy metal salt such as sulfates of zinc, copper or cadmium, or with chloride of barium, mercuric chloride, etc.

The relative merit of pentachlorophenol and certain common and well-recognized sap stain control chemicals was determined by application to freshly cut sticks of pine lumber of 2 inch width, 1 inch thickness, and 18 inch length. These sticks were dipped into solutions of the various protective materials in concentrations of 160 grams per 6 gallons of water and were then stacked in piles along with similar control sticks which had not been treated. The sticks were exposed to spores of the sap stain and green mold organisms carried by wind and various insects, for a period of sixty days. The piles were then

taken down and the specimens were examined for the presence of sap stain. The percentage of the lumber which was stained was then estimated. The results of the test are tabulated as follows:

	Percent stained	Percent mold
Untreated controls.....	65.4	-----
160 gms. sodium trichlorophenolate per 6 gals. water.....	13.1	0.2
160 gms. sodium tetrachlorophenolate per 6 gals. of water.....	12.8	0.4
160 gms. mixture of equal parts of sodium tri- and tetrachlorophenolate per 6 gals. of water.....	11.8	1.1
160 gms. sodium pentachlorophenolate per 6 gals. of water.....	3.1	0.2
64.4 gms. ethyl mercury chloride per 6 gals. of water.....	5.5	11.2

The materials were tested under actual mill conditions upon sawed pine at Crossett, Arkansas; Clarks, Louisiana; and Natalbany, Louisiana and the results of the test indicating the percentage stained are supplied in the following table:

Chemical concentration	Crossett, Ark.	Clarks, La.	Natalbany, La.
Untreated controls.....	45.6	78.7	87.8
Ethyl mercury chloride 1 lb./50 gal.....	6.9	16.5	31.1
Na-pentachlorophenolate 4 lb./50 gal.....	1.55	8.5	9.5
Na-pentachlorophenolate 3 lb./50 gal.....	-----	16.9	15.3
Na-tetrachlorophenolate 4 lb./50 gal.....	2.35	29.1	26.8
Na-tetrachlorophenolate 3 lb./50 gal.....	3.65	32.2	31.6

Ethyl mercury chloride was employed in the amount of 1 pound per 50 gallons of water, which is the concentration recommended by its manufacturer. At materially higher concentrations it is not economically feasible. It is also understood that higher concentrations do not proportionally increase its effectiveness. Lumber which has been treated with pentachlorophenol after drying in the stack is found to have a rich yellow tint very similar to that of well-cured kiln dried lumber.

These tests all show that pentachlorophenol and its sodium salt, contrary to what is shown by tests in malt-agar culture media, when applied to wood, is substantially higher in value than the phenols of lower chlorine content. However, it is found that mixtures of pentachlorophenol and trichlorophenols are of relatively higher merit as agencies of sap stain control than mixtures of pentachlorophenol with any of the other phenols of lower chlorine content. The results of tests of mixtures of equal parts of tri and tetra, tetra and penta, and penta and trichlorophenols as applied to sawed pine lumber are given in the following table. In these tests 160 grams of the mixture of phenols was incorporated into 6 gallons of water and applied to the lumber by dipping.

	Percent of sap stain	Percent of green mold
Tri+tetra.....	11.8	1.1
Tetra+penta.....	7.9	0.7
Tri+penta.....	4.9	0.7

It will be noted that as applied to sap stain, trichlorophenol by itself is slightly inferior to tetrachlorophenol. However, the mixture of tri and pentachlorophenol is substantially superior

to the corresponding mixture of tetra and pentachlorophenols.

It also has been observed that certain compounds of relatively slight toxicity for sap stain organisms, when incorporated with some sap stain control chemical such as pentachlorophenol or its sodium salt exhibit an adjuvant action. The sodium salt of sulphonated and butylated phenylphenol designated herein as S. B. P. is an outstanding example of a compound of this class. The results of comparative tests on pine lumber of this compound in combination with pentachlorophenol are tabulated as follows:

Chemical concentration	Grams of S. B. P. added to 8 gals. of toxic solution	Percent stain
Sodium tetrachlorophenolate 4 lbs./50 gal. water.....	112	27.2
Do.....		11.9
Sodium pentachlorophenolate 4 lbs./50 gal. water.....		11.2
Do.....	37.5	9.4
Do.....	75	6.9
Do.....	300	2.2

Other aryl phenols containing alkyl and sulpho groups may also be substituted for the butylated and sulphonated phenylphenol; examples of such material are mono and di propylated or butylated derivatives of sulphonated naphthols or phenol.

Pentachlorophenol forms various metallic salts with zinc, magnesium, copper, cadmium, mercury, barium, and the like which may also be employed for the destruction or prevention of the growth of decay organisms. These heavy metal salts are preferably made into solutions with organic solvents such as a lubricating oil, light oils, naphtha, dimethyl ether, wood alcohol and the like. The solutions may be applied to the dry or seasoned wood by spraying, dipping, or brushing. However, most effective results are obtained by application of the solution under pressure, thereby causing relatively deep penetration of the compounds in the wood. Methods such as the full cell method of impregnating wood are well understood and need not be described. In the case of oil solutions the oil prevents leaching out of the toxic material from the wood and relatively permanent protection is thus obtained. In the case of dimethyl ether the solvent upon evaporation leaves relatively insoluble pentachlorophenol or its insoluble salts deposited in the fibers of the wood itself. Pentachlorophenol and its sodium salt may also be dissolved in organic solvents such as dimethyl ether and used to impregnate lumber against organisms of decay.

Dry or seasoned wood which has been impregnated with pentachlorophenol dissolved in a volatile organic solvent or by the sodium salt of pentachlorophenol dissolved in water or an organic solvent may be further impregnated with soluble salts of copper, zinc, cadmium, mercury, barium or the like, to precipitate a heavy metal pentachlorophenolate in situ. These pentachlorophenolates are, in most instances, insoluble in water and provide relatively permanent protective agents for the wood.

Barium pentachlorophenolates is insoluble in cold water but is relatively soluble in hot water. Accordingly, wood may be impregnated with a hot water solution of barium pentachlorophenolate. Upon cooling, the barium salt is permanently precipitated in the wood. Wood which has been treated with pentachlorophenol or any of its salts

dissolved in any volatile solvent may be further treated with oil by conventional methods.

Green or wet wood containing substantial amounts of moisture may be submerged in a hot solution of pentachlorophenol or any of the salts thereof until the wood is thoroughly heated. The moisture is thus partly or completely vaporized, and upon cooling of the wood while it is submerged, the vapor is condensed and the solution of pentachlorophenol or the salt thereof is drawn deep into the fibers of the partially evacuated wood to provide permanent protection.

Although only the preferred forms of the invention have been described, it will be apparent to those skilled in the art that numerous modifications may be made therein without departure from the spirit of the invention or the scope of the appended claims.

What I claim is:

1. A method of treating green wood to prevent the growth of the decay organism, *Fomes annosus*, green mold and the sap-staining fungus, *Ceratostomella pilifera*, without increasing substantially the resistance of the wood to fire and water or operating deleteriously to paints and varnishes which may be applied to the wood, which comprises applying to the wood a solution of a preserving agent selected from the class consisting of pentachlorophenol and the metallic salts thereof, said solution being so dilute as not to impart any substantial fire or water resisting qualities to said wood or to affect deleteriously any paints or varnishes which may thereafter be applied to the wood and being of sufficient concentration to provide substantially adequate protection against the growth of said organisms.

2. A method of treating green wood to prevent the growth therein of the decay organism, *Fomes annosus*, green mold and the sap-staining fungus, *Ceratostomella pilifera*, without increasing substantially the resistance of the wood to fire and water or operating deleteriously to paints and varnishes which may be applied to the wood, which comprises submerging the wood at atmospheric pressure in a solution of a preserving agent selected from the class consisting of pentachlorophenol and the metallic salts thereof, said solution being so dilute as not to impart any substantial fire or water resisting qualities to said wood or to affect deleteriously any paints or varnishes which may be thereafter applied to the wood and being of sufficient concentration to provide substantially adequate protection against the growth of said organisms, and subsequently subjecting the resulting wood to drying and seasoning in air.

3. A method of treating green wood to prevent the growth therein of the decay organism, *Fomes annosus*, green mold and the sap-staining fungus, *Ceratostomella pilifera*, without increasing substantially the resistance of the wood to fire and water or affecting deleteriously paints and varnishes which may be applied to the wood, which comprises applying to the wood a solution of pentachlorophenol, said solution being so dilute as not to impart any substantial fire or water resisting qualities to said wood or to affect deleteriously any paints or varnishes which may be thereafter applied to the wood and being of sufficient concentration to provide substantially adequate protection against the growth of said organisms.

4. A method of treating green wood to prevent the growth therein of the decay organisms, *Fomes annosus*, green mold and the sap-staining fungus,

- Ceratostomella piliifera*, without increasing substantially the resistance of the wood to fire and water or affecting deleteriously paints and varnishes which may be applied to the wood, which comprises applying to the wood an aqueous solution of sodium pentachlorophenolate, said solution being so dilute as not to impart any substantial fire or water resisting qualities to said wood or to affect deleteriously any paints or varnishes which may be thereafter applied to the wood and being of sufficient concentration to provide substantially adequate protection against the growth of said organisms.
5. A method of treating green wood to prevent growth of sap stain organisms therein, comprising applying thereto an aqueous solution of a mixture of the metallic salts of tri and pentachlorophenols.
6. A wood preservative which comprises a mixture of a pentochlorphenol salt and an alkylated and sulphonated aryl phenol.
7. A wood preservative which comprises a mixture of a pentachlorphenol salt and a di-propyl sulphonated naphthol.
8. A wood preservative which comprises a mixture of a pentachlorphenol salt and a di-butyl sulphonated naphthol.
9. A wood preservative which comprises a mixture of a pentachlorphenol salt and a sodium salt of sulphonated and butylated phenyl phenol.
10. A wood preservative which comprises a mixture of a pentachlorphenol salt and an alkylated and sulphonated phenol.
11. A method of protecting wood from fungous growths which comprises applying to the wood a solution of a salt of pentachlorophenol, in which solution water is employed as a solvent and an alkylated and sulphonated phenol is employed as an adjuvant.
12. A method of treating green wood to prevent the growth of sap stain organisms thereupon which comprises treating the lumber with a water solution of sodium pentachlorophenolate and an alkylated and sulfonated phenol.
13. A method as defined in claim 12 in which the alkylated and sulphonated phenol is a sulphonated and butylated phenylphenol.

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