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METHOD OF TREATING CELLULOSIC MATERIALS

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This invention relates to a method of preserving cellulosic compositions. More specifically, the invention relates to impregnating wood and other cellulose compositions with a substance resistant to fire, weathering action and fungal attack.

In copending application Serial No. 433,834 filed June 1, 1954, by Songe S. Sakornbut, there is described and claimed an impregnating composition containing chlorinated phenol, highly chlorinated hydrocarbons and esters of phosphoric acid in a volatile hydrocarbon solvent. This application relates to a specific method of utilizing this composition whereby optimum protection against fire is obtained. By the practice of this invention the novel compositions described in the said copending application may be used to preserve wood, paper and other cellulosic products from various destructive agencies including termites, wood borers, fungi and weathering. The method of this invention is especially applicable in rendering usually combustible materials quite resistant to destruction by fire.

Although it is well known that treatment of cellulosic compositions with zinc compounds will result in a substantially fireproof product, such compositions are frequently short-lived due to the fact that the soluble zinc compounds are easily leached out. Furthermore, the use of water-insoluble zinc compounds, or other metal compounds, in coating or impregnating compositions will not result in the deposition of the metal compound within the interstices of the cellulosic product, and the resulting coating is not firmly adherent and may peel or scale off during fires exposing combustible areas to the flames.

The fundamental purpose of this invention is to provide a method of impregnating cellulosic compositions to impart superior resistance to naturally occurring destructive forces. A further purpose of this invention is to provide an optimum method of utilizing the novel compositions of the above-identified copending application. A still further purpose is to provide a method of coating wood, paper or other cellulosic materials with a firmly adhered fireproof surface. Further purposes of this invention will be apparent from the following description.

It has now been found that the useful and novel volatile hydrocarbon solutions of chlorinated phenol, highly chlorinated hydrocarbons and esters of phosphoric acid are especially effective as water-repellent and fire-retardant preservative compositions for porous cellulosic products if the said products have been previously treated with ammoniacal zinc solutions. These zinc solutions are prepared by dissolving zinc oxide, zinc phosphate, zinc borate or other zinc compound in aqueous ammonia, which converts the zinc into a soluble complex, thereby enabling an effective penetration of the zinc compound into the porous wood, paper or fiberboard article. A subsequent drying operation precipitates the zinc in the interstices of the porous article. The product subject to this pre-treatment is then retreated by any of the conventional methods, brushing, spraying, dipping, or vacuum and/or pressure treatment, with the volatile hydrocarbon

solution of chlorinated phenol, highly chlorinated hydrocarbons and esters of phosphoric acid. By this method products usually subject to destruction by fire, and damage by weathering, and by fungal and insect attack are rendered highly resistant to these agencies.

The ammoniacal zinc solutions are preferably prepared with the zinc compound present in substantial concentration, for example from 3 to 12 percent of the compound based on the weight of the ammoniacal zinc solutions. The zinc compound is dissolved in aqueous ammonia, so as to produce a solution containing 10 to 25 percent ammonia. It will be apparent that the amount of zinc compound impregnated and the depth of penetration of the zinc compound into the cellulosic product will depend upon the concentration of the zinc in the solution, the permeability of the cellulosic product and the method of impregnation. Varying degrees of effectiveness can be achieved by increasing the quantity and concentration of the zinc compound retained in the interstices of the cellulosic product.

The cellulosic product containing the desired quantity of zinc compound may then be dried in the open air or with the application of heat, preferably in a dry kiln provided with a suitable vent to dispose of the evolved ammonia gas. When so dried, preferably by application of heat, the zinc complex decomposes with the evolution of ammonia and the insoluble zinc compound precipitates in the interstitial spaces within the cellulosic body. The product so treated is then retreated with the hydrocarbon solution of chlorinated phenol, highly chlorinated hydrocarbons and an ester of phosphoric acid as described hereinafter.

The cellulosic composition impregnated with the zinc compound is then impregnated with a preservative solution of which the principal component is a volatile solvent which may be any one in which the critical components of the preservative solutions are soluble. These solvents may include the aliphatic hydrocarbons, such as petroleum ether, gasoline or kerosenes of low volatility; the aromatic hydrocarbons, such as toluene, xylenes, naphthalenes or mixtures thereof; or chlorinated hydrocarbons such as ethylene dichloride, tetrachlorethane or chlorinated propanes, or a mixture of solvents of any one or more of these classes. The solvents should have a boiling point or a boiling point range between 110° C. and 220° C. and should preferably have an initial boiling point above 125° C.

The active toxicant in the novel preservative compositions is the chlorinated phenol, which has the characteristic toxicity of a phenol and the well known stability to the composition due to the high chlorine content. The chlorinated phenols may be phenol, cresol or similar toxic phenol having a plurality of chlorine substituents as in tetrachlorocresol and pentachlorophenol. If desired, a mixture of chlorinated hydrocarbons containing varying numbers of chlorine substituents, but preferably having an average of at least four per molecule, may be used. This chlorinated phenol may be present in the amount of 3 to 8 percent and preferably 4 to 6 percent.

A critical component in both the prior art preservatives and in the novel highly effective preservative is the chlorinated hydrocarbon. This component may be an aromatic or an aliphatic hydrocarbon containing a very high proportion of chlorine, for example in excess of 40 percent by weight of the compound and preferably in excess of 50 percent. This component is added to provide body to the solution and to impart fire retardancy. Specific compounds and mixtures of compounds such as obtained by the direct chlorination of petroleum fractions are useful. Compounds which may be used include chlorinated biphenyl, chlorinated terphenyl, or mixtures thereof, chlorinated naphthalene and chlorinated

paraffin of varying chain length and various mixtures of chlorinated hydrocarbons sold commercially as Aroclors, Chloraffins and Chlorowaxes. The chlorinated hydrocarbons may be present from 8 to 20 percent of the weight of the solution and preferred compositions may contain from 12 to 16 percent of the highly chlorinated hydrocarbons based upon the weight of the solution.

The esters which are of exceptional utility in the improvement of the prior art solutions are the esters of phosphoric acid in which each of the three organic radicals has from four (4) to eight (8) carbon atoms. Suitable examples of the phosphates which are useful in the practice of this invention are the trialkyl phosphates, including tributyl phosphate, trioctyl phosphate, trihexyl phosphate, tricyclohexyl phosphate, tri(2-ethylhexyl) phosphate and triamyl phosphate; the triaryl phosphates, including triphenyl phosphate, tricresyl phosphate and tribenzyl phosphate and the mixed phosphates such as octyl diphenyl phosphate, cresyl diphenyl phosphate, phenyl dicresyl phosphate, butyl dioctyl phosphate and other mixed esters prepared by the esterification of phosphoric acid with mixtures of alcohols, mixtures of phenols or mixtures of alcohols and phenols having the specific number of carbon atoms and specified configurations. From 3 to 10 percent of the weight of the solution of the above described aliphatic and aromatic esters of phosphoric acid may be used. Other compositions containing from 4 to 6 percent of the esters of phosphoric acid are preferred with respect to their utility in impregnating cellulosic compositions.

The valuable compositions made in accordance with this invention are preferred to be of superior water repellency and contain for this purpose from 0.1 to 2 percent of the solution and preferably from 0.2 to 0.8 percent of a petroleum wax may be added. Either microcrystalline wax or paraffin wax may be used.

Wood, wood products and fabricated cellulosic compositions, such as paper, pressed board and other compositions containing varying proportions of cellulosic derivatives, can be rendered resistant to the action of insects, weathering and fungus decomposition by applying the above described solutions by brushing, spraying or treating them under pressure and/or vacuum as is conventional in the impregnating art.

The preparation of the treated composition involves the heating of the solvent, the phosphate esters and the chlorinated phenol to effect a solution and thereafter combining the chlorinated hydrocarbons and the petroleum wax with agitation until a homogeneous solution is obtained.

Further details of the preparation and use of the new compositions and of their desirable physical properties are set for with respect to the following examples.

Example 1

A 20 percent aqueous ammonium hydroxide solution was used to dissolve 10 percent by weight of zinc phosphate. This solution was then applied to a Ponderosa pine wafer by immersion. After drying, the sample contained about 4 percent by weight of the zinc compound. The sample was then retreated in the same manner with a solution comprising 75 percent by weight of mineral spirits, 5 percent of pentachlorophenol, 14.5 percent of a commercially available chlorinated paraffin hydrocarbon (Chlorowax 70), 5 percent cresyl diphenyl phosphate and 0.5 percent of a microcrystalline wax.

The sample was subjected to the Standard Swellograph Method of the National Wood Products Manufacturers Association (N. W. M. A.–M–2–51) and was found to have a water repellency of 73 percent. When tested by the horizontal flame spread method, the average flame-out period was 0 seconds, indicating substantial fireproofness.

Example 2

To demonstrate the effect of the pre-impregnation with the water solution of soluble zinc compounds, samples were treated without the zinc solution application. When tested as described in the preceding example, it was found to have a water-repellency of 68.3 percent and a flame-out time of 15 seconds.

What is claimed is:

1. The method of treating porous cellulosic materials which comprises applying to the porous materials an aqueous ammoniacal solution of a zinc compound, drying the said material and then treating the material with a composition comprising a hydrocarbon oil boiling between 110° C. and 220° C., from 3 to 8 percent by weight of a chlorinated phenol, from 8 to 20 percent of a chlorinated hydrocarbon containing at least 40 percent chlorine, from 3 to 10 percent of an ester of phosphoric acid and from 0.1 to 2 percent of petroleum wax, all percentages of the components of said composition being based on the weight of the resulting solution.

2. The method of treating porous cellulosic materials which comprises applying to the porous materials an aqueous ammoniacal solution of a zinc compound, drying the said material and then treating the material with a composition comprising a hydrocarbon oil boiling between 110° C. and 220° C., from 3 to 8 percent by weight of a chlorinated phenol, from 8 to 20 percent of a chlorinated hydrocarbon containing at least 40 percent chlorine and from 3 to 10 percent of an ester of phosphoric acid, all percentages of the components of said composition being based on the weight of the resulting solution.

3. The method of treating porous cellulosic materials which comprises applying to the porous materials an aqueous ammoniacal solution of a zinc compound, drying the said material and then treating the material with a composition comprising a hydrocarbon oil boiling between 110° C. and 220° C., from 3 to 8 percent by weight of a chlorinated phenol, from 8 to 20 percent of a chlorinated hydrocarbon containing at least 40 percent chlorine, from 4 to 6 percent of an ester of phosphoric acid and from 0.1 to 2 percent of petroleum wax, all percentages of the components of said composition being based on the weight of the resulting solution.

4. The method of treating porous cellulosic materials which comprises applying to the porous materials an aqueous ammoniacal solution of a zinc compound, drying the said material and then treating the material with a composition comprising a hydrocarbon oil boiling between 110° C. and 220° C., from 4 to 6 percent by weight of a chlorinated phenol, from 12 to 16 percent of a chlorinated hydrocarbon containing at least 40 percent chlorine, from 4 to 6 percent of an ester of phosphoric acid and from 0.2 to 0.8 percent of petroleum wax, all percentages of the components of said composition being based on the weight of the resulting solution.

5. The method of treating porous cellulosic materials which comprises applying to the porous materials an aqueous ammoniacal solution of a zinc compound, drying the said material and then treating the material with a composition comprising a hydrocarbon oil boiling between 110° C. and 220° C., from 4 to 6 percent by weight of a chlorinated phenol, from 12 to 16 percent of a chlorinated hydrocarbon containing at least 40 percent chlorine and from 4 to 6 percent of an ester of phosphoric acid, all percentages of the components of said composition being based on the weight of the resulting solution.

6. The method of treating porous cellulosic materials which comprises applying to the porous materials an aqueous ammoniacal solution of a zinc compound, drying the said material and then treating the material with a composition comprising a hydrocarbon oil boiling between 110° C. and 220° C., from 3 to 8 percent by weight of pentachlorophenol, from 8 to 20 percent of a chlorinated hydrocarbon containing at least 40 percent chlorine, from 3 to 10 percent of an ester of phosphoric acid and from 0.1 to 2 percent of petroleum wax, all percentages of the

components of said composition being based on the weight of the resulting solution.

7. The method of treating porous cellulosic materials which comprises applying to the porous materials an aqueous ammoniacal solution of a zinc compound, drying the said material and then treating the material with a composition comprising a hydrocarbon oil boiling between 110° C. and 220° C., from 3 to 8 percent by weight of pentachlorophenol, from 8 to 20 percent of chlorinated paraffin containing at least 40 percent chlorine, from 3 to 10 percent of an ester of phosphoric acid and from 0.1 to 2 percent of petroleum wax, all percentages of the components of said composition being based on the weight of the resulting solution.

8. The method of treating porous cellulosic materials which comprises applying to the porous materials an aqueous ammoniacal solution of a zinc compound, drying the said material and then treating the material with a composition comprising a hydrocarbon oil boiling between 110° C. and 220° C., from 3 to 8 percent by weight of pentachlorophenol, from 8 to 20 percent of chlorinated paraffin containing at least 40 percent chlorine, from 3 to 10 percent of cresyl diphenyl phosphate and from 0.1 to 2 percent of petroleum wax, all percentages of the components of said composition being based on the weight of the resulting solution.

9. The method of treating porous cellulosic materials which comprises applying to the porous materials an aqueous ammoniacal solution of a zinc compound, drying the said material and then treating the material with a composition comprising a hydrocarbon oil boiling between 110° C. and 220° C., from 3 to 8 percent by weight of pentachlorophenol, from 8 to 20 percent of chlorinated paraffin containing at least 40 percent chlorine and from 3 to 10 percent of cresyl diphenyl phosphate, all percentages of the components of said composition being based on the weight of the resulting solution.

10. The method of treating porous cellulosic materials which comprises applying to the porous materials an aqueous ammoniacal solution of a zinc compound, drying the said material and then treating the material with a composition comprising a hydrocarbon oil boiling between 110° C. and 220° C., from 4 to 6 percent by weight of pentachlorophenol, from 12 to 16 percent of a chlorinated hydrocarbon containing at least 40 percent chlorine, from 4 to 6 percent of an ester of phosphoric acid and from 0.2 to 0.8 percent of petroleum wax, all percentages of the components of said composition being based on the weight of the resulting solution.

11. The method of treating porous cellulosic materials which comprises applying to the porous materials an aqueous ammoniacal solution containing from 3 to 12 percent of a zinc compound and from 10 to 25 percent ammonia, drying said material and then treating the material with a composition comprising a solvent oil boiling between 110° C. and 220° C., from 4 to 6 percent by weight of pentachlorophenol, from 12 to 16 percent of chlorinated paraffin containing at least 40 percent chlorine, from 4 to 6 percent of an ester of phosphoric acid and from 0.2 to 0.8 percent of petroleum wax, all percentages of the components of said composition being based on the weight of the resulting solution.

12. The method of treating porous cellulosic materials which comprises applying to the porous materials an aqueous ammoniacal solution containing from 3 to 12 percent of a zinc compound and from 10 to 25 percent ammonia, drying said material and then treating the material with a composition comprising a solvent oil boiling between 110° C. and 220° C., from 4 to 6 percent by weight of pentachlorophenol, from 12 to 16 percent of chlorinated paraffin containing at least 40 percent chlorine, from 4 to 6 percent of cresyl diphenyl phosphate and from 0.2 to 0.8 percent of petroleum wax, all percentages of the components of said composition being based on the weight of the resulting solution.

13. The method of treating porous cellulosic materials which comprises applying to the porous materials an aqueous ammoniacal solution containing from 3 to 12 percent of a zinc compound and from 10 to 25 percent ammonia, drying said material and then treating the material with a composition comprising a solvent oil boiling between 110° C. and 220° C., from 4 to 6 percent by weight of pentachlorophenol, from 12 to 16 percent of chlorinated paraffin containing at least 40 percent chlorine and from 4 to 6 percent of cresyl diphenyl phosphate, all percentages of the components of said composition being based on the weight of the resulting solution.

14. The method of treating porous cellulosic materials which comprises applying to the porous materials an aqueous ammoniacal solution containing from 3 to 12 percent of a zinc compound and from 10 to 25 percent ammonia, drying said material and then treating the material with a composition comprising mineral spirits boiling between 110° C. and 220° C., from 4 to 6 percent by weight of a chlorinated phenol, from 12 to 16 percent of a chlorinated hydrocarbon containing at least 40 percent chlorine, from 4 to 6 percent of an ester of phosphoric acid and from 0.2 to 0.8 percent of petroleum wax, all percentages of the components of said composition being based on the weight of the resulting solution.

15. The method of treating porous cellulosic materials which comprises applying to the porous materials an aqueous ammoniacal solution containing from 3 to 12 percent of a zinc compound and from 10 to 25 percent ammonia, drying said material and then treating the material with a composition comprising mineral spirits boiling between 110° C. and 220° C., from 4 to 6 percent by weght of a chlorinated phenol, from 12 to 16 percent of a chlorinated hydrocarbon containing at least 40 percent chlorine and from 4 to 6 percent of an ester of phosphoric acid, all percentages of the components of said composition being based on the weight of the resulting solution.

16. The method of treating porous cellulosic materials which comprises applying to the porous materials an aqueous ammoniacal solution containing from 3 to 12 percent of a zinc compound and from 10 to 25 percent ammonia, drying said material and then treating the material with a composition comprising mineral spirits boiling between 110° C. and 220° C., from 3 to 8 percent by weight of pentachlorophenol, from 8 to 20 percent of a chlorinated hydrocarbon containing at least 40 percent chlorine, from 3 to 10 percent of an ester of phosphoric acid and from 0.1 to 2 percent of petroleum wax, all percentages of the components of said composition being based on the weight of the resulting solution.

17. The method of treating porous cellulosic materials which comprises applying to the porous materials an aqueous ammoniacal solution containing from 3 to 12 percent of a zinc compound and from 10 to 25 percent ammonia, drying said material and then treating the material with a composition comprising mineral spirits boiling between 110° C. and 220° C., from 3 to 10 percent of an ester of phosphoric acid, from 3 to 8 percent of pentachlorophenol, from 8 to 20 percent of a chlorinated terphenyl containing at least 40 percent chlorine and from 0.1 to 2 percent of paraffin wax, all percentages of the components of said composition being based on the weight of the resulting solution.

18. The method of treating porous cellulosic materials which comprises applying to the porous materials an aqueous ammoniacal solution containing from 3 to 12 percent of a zinc compound and from 10 to 25 percent ammonia, drying said material and then treating the material with a composition comprising mineral spirits boiling between 110° C. and 220° C., from 3 to 8 percent by weight of pentachlorophenol, from 8 to 20 percent of chlorinated paraffin containing at least 40 percent chlorine, from 3 to 10 percent of cresyl diphenyl phosphate

and from 0.1 to 2 percent of microcrystalline wax, all percentages of the components of said composition being based on the weight of the resulting solution.

19. The method of treating porous cellulosic materials which comprises applying to the porous material an aqueous ammoniacal solution containing from 3 to 12 percent of a zinc compound and from 10 to 25 percent ammonia, drying said material and then treating the material with a composition comprising mineral spirits boiling between 110° C. and 220° C., from 3 to 8 percent by weight of pentachlorophenol, from 8 to 20 percent of chlorinated paraffin containing at least 40 percent chlorine and from 3 to 10 percent of cresyl diphenyl phosphate, all percentages of the components of said composition being based on the weight of the resulting solution.

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