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WOOD PRESERVATION

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This invention relates to the preservation of wood and similar organic materials which are subject to decay and attack by termites, and more particularly to compositions and processes for impregnating such materials with a zinc chloride-sodium dichromate solution containing acidic substances.

Zinc chloride-sodium dichromate solutions have been found to be particularly efficient preservatives for preventing decay and deterioration of wood and similar organic materials due to the growth of bacteria or fungi, and to prevent destruction by termites. Wood impregnated with this solution is markedly resistant to decay and attack by termites; is markedly resistant to weathering or leaching when in contact with the ground or under similarly severe conditions; and is well adapted for the reception of surface coatings such as paint.

The use of zinc chloride-sodium dichromate solutions, however, has been accompanied by the disadvantage that an insoluble residue of a bright yellow color, that forms in the solution, results in objectionable deposits upon the surface of the treated material. With solutions of usual concentrations the amount of the insoluble residue is small but, nevertheless, sufficient to give the wood a dirty appearance and to interfere with subsequent finishing operations. With solutions of greater concentration, such as are used for empty cell treatment of wood, the difficulty is more pronounced as much more residue is formed.

Notwithstanding the advantages of the zinc chloride-sodium dichromate treatment, it has not been more generally adopted in the building industry primarily due to the presence of the objectionable yellow deposit just mentioned. Finished and semi-finished lumber is practically unmarketable in the condition of discoloration which results from the deposition of this insoluble residue. Consequently, finishing operations or other means for removing the insoluble deposit must be relied on for producing a marketable product. Moreover, such finishing operations are complicated by the deposit. Altogether the advantages of the zinc chloride-sodium dichromate treatment, insofar as the building industry is concerned, are materially offset by this single disadvantage—the formation of an insoluble residue.

I have found that by incorporating a small amount of an acidic substance into the zinc chloride-sodium dichromate solution the formation of an insoluble residue is prevented. In this manner I am able to impregnate wood and like fibrous cellulosic material with zinc chloride-sodium dichromate solutions without the deposition of any objectionable residue on the surface of the wood, and without impairing the efficacy of zinc chloride sodium-dichromate treatment. Thus my invention not only makes it possible to produce zinc chloride-sodium dichromate treated wood which is as clean and free of objectionable deposits as untreated wood, but also opens up the way to a more extended application of the treatment in the building industries.

The prevention of the formation of an insoluble residue is particularly desirable because once the insoluble residue has formed it can be redissolved only with difficulty and then only by the use of undesirably large amounts of acidic material. It is accordingly particularly advantageous to add the acidic material prior to the formation of the insoluble residue as otherwise the increased quantity of acidic material required would result in severe corrosion of the treating equipment and would tend to impair the strength and permanence of the material treated.

Without intending to limit myself to any particular theory, I believe that the insoluble material results from the formation of a zinc chromate, probably of complex form, due to the presence of zinc oxide in the zinc chloride and that the difficulty involved in redissolving it is due in part to the complex form in which it precipitates. Whatever the mechanism of the reaction, however, the fact remains that more than five times as much acidic material must be added to redissolve the precipitate, once formed, than to prevent the formation of the precipitate. This is materially in excess of the amount which would be expected for a simple metathetical reaction of precipitation and redissolution.

In a more particular and preferred aspect of my invention, I use chromic acid as the acidic substance preferably compounded with the zinc chloride and sodium dichromate as a dry mixture suitably proportioned for the preparation of solutions required for any particular treatment. By the use of chromic acid the formation of an insoluble residue is prevented without the introduction of any foreign ions or radicals, so that the high efficiency of the zinc chloride-sodium dichromate treatment is preserved. By the use of a dry mixture, as described, the chromic acid is dissolved simultaneously with the zinc chloride and the sodium dichromate so that it is active to prevent the formation of an insoluble residue.

Chromic acid, as previously pointed out, is particularly advantageous in that no foreign ions or radicals are introduced which might interfere with the efficacy of the zinc chloride-sodium dichromate treatment. Without imposing any limitations of theory, I believe that the mechanism of the reaction may be explained by the following.

As pointed out above, I believe that the zinc oxide, which is present in all commercial grades of zinc chloride, is responsible for the formation of the insoluble residue. By the addition of chromic acid prior to the formation of the insoluble residue, zinc oxide may be converted to zinc

dichromate according to the following equation:

$$ZnO+2CrO_3 \rightarrow ZnCr_2O_7$$

or by the addition of an equimolecular mixture of chromic acid and sodium chloride to zinc chloride and sodium dichromate according to the following equation:

$$ZnO+2CrO_3+2NaCl \rightarrow Na_2Cr_2O_7+ZnCl_2$$

Thus by the use of chromic acid with or without sodium chloride the basicity of the zinc chloride is overcome without the introduction of any foreign ions or radicals.

In order that my invention may be more fully understood the following examples are given:

Example I

A dry mixture of the following composition was prepared:

	Per cent
Zinc chloride ($ZnCl_2$)	81.2
Sodium dichromate dihydrate ($Na_2Cr_2O_7.2H_2O$)	13.3
Chromic acid (CrO_3)	3.5
Sodium chloride (NaCl)	2.0

The materials used in the above mixture were commercial products of the following grades: Technical granulated zinc chloride having a basicity of 1.75 per cent zinc oxide (ZnO), technical sodium dichromate crystals, technical flake chromic acid, and rock salt.

The above mixture represents a commercial form of my invention which is particularly suitable for transportation and sale. Suitable zinc chloride-sodium dichromate solutions free of any insoluble residue may be made simply by dissolving this mixture in the proper quantity of water.

Five parts by weight of the mixture described in Example I were dissolved in 95 parts of water. White pine sash lumber was impregnated with this solution by the full cell process. After kiln drying, the lumber so treated was as clean and free of insoluble residue as the untreated wood; it worked readily into the finished condition and was in all respects comparable, insofar as finishing operations were concerned, with the untreated lumber.

In comparison, the same type of wood treated with a zinc chloride-sodium dichromate solution containing 81.5 per cent of technical granulated zinc chloride and 18.5 per cent sodium dichromate was covered with a yellow scum which not only gave it a dirty appearance but also interfered with the finishing operations. The solution contained an appreciable amount of a bright yellow insoluble residue.

The above example illustrates the use of equimolecular proportions of chromic acid and sodium chloride. The following example shows that the same results may be achieved with chromic acid alone.

Example II

A dry mixture of the following composition was prepared from materials of the same grade as in Example I:

	Per cent
Zinc chloride ($ZnCl_2$)	83.0
Sodium dichromate dihydrate ($Na_2Cr_2O_7.2H_2O$)	13.3
Chromic acid (CrO_3)	3.7

A five per cent solution prepared from this mixture was used in the treatment of white pine sash lumber in the same manner as in Example I. The treated wood was quite clean and worked up equally as well as that of Example I.

Solutions were prepared from both mixtures described in Examples I and II ranging up to fifty per cent concentration without formation of an insoluble residue. Thus the concentration may be varied over wide limits to adapt the solution to various commercial practices of full cell and empty cell treatment of lumber, and to the transportation and storage of the concentrated solutions in available tanks.

Although I have specifically described my invention with reference to chromic acid, it is to be understood that other acidic substances may be employed. For the purpose of my invention any substance which is capable of neutralizing the basicity of the zinc chloride may be considered an "acidic substance", and any such substance may be considered as coming within the broader aspects of my invention. It is obvious, of course, but worthy of mention that the use of an acidic substance which is acted upon by the dichromate, which is itself insoluble in the system or which would precipitate any of the constituents of the solution, should be avoided. In other words, the acidic substance should be compatible with the zinc chloride-sodium dichromate system.

In its preferred aspects my invention relates to dry mixtures of zinc chloride-sodium dichromate and an acidic substance. For this purpose I prefer chromic acid, not merely because it is a convenient and economical dry acidic substance but because it may be used without the introduction of any foreign ions or radicals. Although chromic acid is more desirable in these respects, it is to be understood that other suitable solid acids such as furoic, sulfamic, citric or tartaric acid, and that suitable acid salts such as sodium bisulfate may be used. In the selection of dry acidic substances other than chromic acid, however, care should be exercised, as foreign ions or radicals are introduced which may be incompatible with the zinc chloride-sodium dichromate system, either in the respect that they may form insoluble compounds or in the respect that they may impair the efficacy of the zinc chloride-sodium dichromate treatment. Oxalic acid, for example, cannot be used as it is not compatible with the zinc chloride-sodium dichromate system, the zinc ion being precipitated as zinc oxalate.

In some instances it may be found desirable to market zinc chloride-sodium dichromate in the form of a solution or to prepare such a solution at the treating plant. When zinc chloride-sodium dichromate compositions are so marketed, or are prepared, a wider selection of acidic substances is afforded, as such compositions are not confined to the use of solid acids. The more common acids, such as hydrochloric and sulfuric acid, are suitable for this purpose. It is to be understood, however, that a strong mineral acid is not essential but that weaker mineral acids, as well as the organic acids and acid salts previously mentioned, may be used.

In the preparation of a zinc chloride-sodium dichromate solution it may be found expedient to adopt any of several procedures. Thus the solution may be prepared by dissolving the dry mixture which has been described in detail above, or it may be prepared by dissolving a zinc chloride-sodium dichromate mixture in acidulated water, sodium dichromate in an acidulated solution of zinc chloride, or zinc chloride in an acidulated solution of sodium dichromate. By any of these

procedures the acidic substance will be actively present to prevent the formation of an insoluble residue.

The quantity of acidic substances required in any particular case is determined by the basicity of the zinc chloride used. This basicity may be determined by titrating a sample of commercial zinc chloride to the methyl orange endpoint with standard hydrochloric acid and calculating the titration in terms of zinc oxide (ZnO).

The minimum amount required is that which will prevent the formation of any appreciable quantity of insoluble residue. I have found that the minimum quantity required for this purpose is approximately three-fourths times the number of equivalents of acidic substance required to produce a soluble zinc salt per equivalent basicity of the zinc chloride, the basicity being calculated as zinc oxide as indicated above. For example, one equivalent of sulfuric acid per equivalent of zinc oxide is required to produce zinc sulfate, whereas two equivalents of chromic acid are required to produce zinc dichromate. Thus the minimum amount of sulfuric acid would be about three-fourths equivalents, whereas that for chromic acid would be about one and one-half equivalents. A somewhat lower concentration of acidic substance may be used, but ordinarily a smaller amount is too close to the absolute minimum for safe operation, particularly under the variable conditions of temperature and pressure used in impregnation treatments.

The maximum amount of acidic substance permissible may be varied considerably. As already pointed out, however, it is desirable that it be kept as low as possible, in order to prevent corrosion of the treating equipment and possible impairment of the material treated. I have found that for most purposes the most satisfactory results are obtained if the amount of acidic substance is maintained about three-fourths to about one and one-fourth times the number of equivalents of acid required to produce a soluble zinc salt, per equivalent basicity of the zinc chloride.

The limits given above have been figured on the basis of chemical equivalents in view of the wide diversity of acid substances which may be employed. These limits, however, may be easily converted to proportions by weight for any given substance. For chromic acid the proportion by weight will range from approximately 1.85 to 3.1 times the basicity of the zinc chloride calculated as zinc oxide on a weight basis. Thus in Example I the amount of chromic acid is about two and one-half times the basicity of the zinc chloride calculated as zinc oxide on a weight basis.

The relative amounts of zinc chloride and sodium dichromate may be varied over a wide range according to the various commercial practices. As a general rule, however, the zinc chloride is the predominating ingredient and usually constitutes more than two-thirds of the mixture.

Solutions prepared according to this invention may be employed with advantage in the preservation of wood and similar organic materials subject to decay and attack by termites, either by the empty cell or full cell processes, in all applications where zinc chloride and zinc chloride-sodium dichromate solutions are customarily employed. In addition, they may be used in applications requiring subsequent finishing steps where the use of the zinc chloride-sodium dichromate treatment would be impractical because of the deposition of insoluble material.

I claim:

1. A zinc chloride-sodium dichromate composition useful for the preservation of wood and similar organic materials subject to decay and prepared from zinc chloride containing basic zinc constituents, having incorporated therein a compatible acidic substance in an amount sufficient at least to prevent formation of any appreciable quantity of insoluble residue.

2. A zinc chloride-sodium dichromate composition useful for the preservation of wood and similar organic materials subject to decay and prepared from zinc chloride containing basic zinc constituents, having incorporated therein a compatible acidic substance in an amount equivalent at least to about three-fourths times the equivalents of acidic substance required to form a soluble zinc salt per equivalent basicity of the zinc chloride.

3. A zinc chloride-sodium dichromate composition useful for the preservation of wood and similar organic materials subject to decay and prepared from zinc chloride containing basic zinc constituents, having incorporated therein a compatible acidic substance in an amount equivalent to from about three-fourths to about one and one-quarter times the equivalents of acidic substance required to form a soluble zinc salt per equivalent basicity of the zinc chloride.

4. A zinc chloride-sodium dichromate composition useful for the preservation of wood and similar organic materials subject to decay and prepared from zinc chloride containing basic zinc constituents, having incorporated therein chromic acid in an amount sufficient at least to prevent formation of any appreciable quantity of insoluble residue.

5. A zinc chloride-sodium dichromate composition useful for the preservation of wood and similar organic materials subject to decay and prepared from zinc chloride containing basic zinc constituents, having incorporated therein chromic acid in an amount equivalent to at least about one and one-half equivalents of the basicity of the zinc chloride.

6. A zinc chloride-sodium dichromate composition useful for the preservation of wood and similar organic materials subject to decay and prepared from zinc chloride containing basic zinc constituents, having incorporated therein chromic acid in an amount equivalent to from about one and one-half to about two and one-half equivalents of the basicity of the zinc chloride.

7. As a dry mixture a zinc chloride-sodium dichromate composition useful for the preservation of wood and similar organic materials subject to decay and prepared from zinc chloride containing basic zinc constituents, having incorporated therein a compatible acidic substance in an amount sufficient at least to prevent formation of any appreciable quantity of insoluble residue.

8. As a dry mixture a zinc chloride-sodium dichromate composition useful for the preservation of wood and similar organic materials subject to decay and prepared from zinc chloride containing basic zinc constituents, having incorporated therein a compatible acidic substance in an amount equivalent at least to about three-fourths times the equivalents of acidic substance required to form a soluble zinc salt per equivalent basicity of the zinc chloride.

9. As a dry mixture a zinc chloride-sodium dichromate composition useful for the preservation of wood and similar organic materials subject to decay and prepared from zinc chloride containing

basic zinc constituents, having incorporated therein a compatible acidic substance in an amount equivalent to from about three-fourths to about one and one-quarter times the equivalents of acidic substance required to form a soluble zinc salt per equivalent basicity of the zinc chloride.

10. As a dry mixture a zinc chloride-sodium dichromate composition useful for the preservation of wood and similar organic materials subject to decay and prepared from zinc chloride containing basic zinc constituents, having incorporated therein chromic acid in an amount sufficient at least to prevent formation of any appreciable quantity of insoluble residue.

11. As a dry mixture a zinc chloride-sodium dichromate composition useful for the preservation of wood and similar organic materials subject to decay and prepared from zinc chloride containing basic zinc constituents, having incorporated therein chromic acid in an amount equivalent to at least about one and one-half equivalents of the basicity of the zinc chloride.

12. As a dry mixture a zinc chloride-sodium dichromate composition useful for the preservation of wood and similar organic materials subject to decay and prepared from zinc chloride containing basic zinc constituents, having incorporated therein chromic acid in an amount equivalent to from about one and one-half to about two and one-half equivalents of the basicity of the zinc chloride.

13. As a dry mixture a zinc chloride-sodium dichromate composition containing about 3.5 per cent chromic acid, about 13 per cent sodium dichromate dihydrate, about 2 per cent sodium chloride, and the balance substantially zinc chloride having a basicity calculated as zinc oxide in the order of 1.75 per cent.

14. As a dry mixture a zinc chloride-sodium dichromate composition comprising about 3.7 per cent chromic acid, about 13 per cent sodium dichromate dihydrate, and the balance substantially zinc chloride having a basicity calculated as zinc oxide in the order of 1.75 per cent.

15. In a process for the preservation of wood and similar organic materials subject to decay and attack by termites by impregnation with a zinc chloride-sodium dichromate solution, the steps comprising preparing a zinc chloride-sodium dichromate solution containing basic zinc constituents, incorporating therein a compatible acidic substance in amount sufficient at least to prevent formation of any appreciable quantity of insoluble residue and then impregnating the material to be preserved with said solution.

16. In a process for the preservation of wood and similar organic materials subject to decay and attack by termites by impregnation with a zinc chloride-sodium dichromate solution, the steps comprising preparing a zinc chloride-sodium dichromate solution containing basic zinc constituents, simultaneously incorporating therein a compatible acidic substance in amount sufficient at least to prevent the formation of any appreciable insoluble residue and then impregnating the material to be preserved with said solution.

17. In a process for the preservation of wood and similar organic materials subject to decay and attack by termites by impregnation with a zinc chloride-sodium dichromate solution, the steps comprising preparing a dry mixture comprising zinc chloride containing basic zinc constituents, sodium dichromate, and a compatible acidic substance in an amount equivalent at least to about three-fourths times the equivalents of acidic substance required to form a soluble zinc salt per equivalent basicity of the zinc chloride, dissolving said mixture to form a clear aqueous solution and impregnating the material to be preserved with the resulting solution.

18. In a process for the impregnation of wood and similar organic material subject to decay and attack by termites with a zinc chloride-sodium dichromate solution prepared from zinc chloride containing basic zinc constituents, the step of preventing the deposition of an insoluble residue on the materal during the impregnation by incorporating in the zinc chloride-sodium dichromate solution simultaneously with the preparation of the solution a compatible acidic substance in an amount equivalent at least to about three-fourths times the equivalents of acidic substance required to form a soluble zinc salt per equivalent basicity of the zinc chloride.

19. In a process for the impregnation of wood and similar organic material subject to decay and attack by termites with a zinc chloride-sodium dichromate solution prepared from zinc chloride containing basic zinc constituents, the step of preventing the deposition of an insoluble residue on the material during the impregnation by incorporating in the zinc chloride-sodium dichromate solution simultaneously with the preparation of the solution chromic acid in an amount equivalent at least to about three-fourths times the equivalents of acidic substance required to form a soluble zinc salt per equivalent basicity of the zinc chloride.

20. A zinc chloride-sodium dichromate composition useful for the preservation of wood and similar organic materials subject to decay and prepared from zinc chloride containing basic zinc constituents, having incorporated therein sulfamic acid in an amount sufficient at least to prevent formation of any appreciable quantity of insoluble residue.

21. A zinc chloride-sodium dichromate composition useful for the preservation of wood and similar organic materials subject to decay and prepared from zinc chloride containing basic zinc constituents, having incorporated therein sulfamic acid in an amount equivalent to at least about one and one-half equivalents of the basicity of the zinc chloride.

22. A zinc chloride-sodium dichromate composition useful for the preservation of wood and similar organic materials subject to decay and prepared from zinc chloride containing basic zinc constituents, having incorporated therein sulfamic acid in an amount equivalent to from about one and one-half to about two and one-half equivalents of the basicity of the zinc chloride.

23. As a dry mixture a zinc chloride-sodium dichromate composition useful for the preservation of wood and similiar organic materials subject to decay and prepared from zinc chloride containing basic zinc constituents, having incorporated therein sulfamic acid in an amount sufficient at least to prevent formation of any appreciable quantity of insoluble residue.

24. As a dry mixture a zinc chloride-sodium dichromate composition useful for the preservation of wood and similar organic materials subject to decay and prepared from zinc chloride containing basic zinc constituents, having incorporated therein sulfamic acid in an amount equivalent to at least about one and one-half equivalents of the basicity of the zinc chloride.

25. As a dry mixture a zinc chloride-sodium di-

chromate composition useful for the preservation of wood and similar organic materials subject to decay and prepared from zinc chloride containing basic zinc constituents, having incorporated therein sulfamic acid in an amount equivalent to from about one and one-half to about two and one-half equivalents of the basicity of the zinc chloride.

26. In a process for the impregnation of wood and similar organic mat erialsubject to decay and attack by termites with a zinc chloride-sodium dichromate solution prepared from zinc chloride containing basic zinc constituents, the step of preventing the deposition of an insoluble residue on the material during the impregnation by incorporating in the zinc chloride-sodium dichromate solution simultaneously with the preparation of the solution sulfamic acid in an amount equivalent at least to about three-fourths times the equivalents of acidic substance required to form a soluble zinc salt per equivalent basicity of the zinc chloride.

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