UNITED STATES PATENT OFFICE.

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ART OF PROTECTING AND FIREPROOFING WOOD AND OTHER MATERIALS.

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To all whom it may concern:

Be it known that we, ARTHUR ARENT and RUDOLPH A. KUEVER, citizens of the United States, residing at Badger, in the county of Webster and State of Iowa, and Iowa City, in the county of Johnson and State of Iowa, respectively, have invented certain new and useful Improvements in the Art of Protecting and Fireproofing Wood and other Materials; and we do hereby declare the following to be a full, clear, and exact description of the invention, such as will enable others skilled in the art to which it appertains to make and use the same.

This invention relates to the art of protecting and fireproofing wood and other materials; and it comprises a process in which wood, cloth, or other material to be fireproofed and protected against weather conditions, etc., is treated with a solution of a zinc compound of such character as to penetrate the material readily and to deposit therein a substantially insoluble compound of zinc without the aid of an auxiliary zinc precipitant.

The invention also comprises the treated product resulting from said process, as well as the treating solution employed therein.

It has been proposed heretofore to employ solutions of zinc salts, such as the chlorid and the sulfate, for fireproofing wood; but in these prior methods such of the zinc salt as is retained by the wood remains in soluble condition unless precipitated on the fiber by a second step of impregnation with a zinc precipitant.

An object of the present invention is to permanently fireproof and preserve materials of various kinds by a simple one-step impregnation process which can be carried out in practice with maximum convenience and at low cost. More particularly the invention contemplates impregnating or otherwise suitably treating materials with a zinc-containing solution of relatively high zinc content of such character that upon evaporation it will give a deposit of zinc oxid or an oxy-salt of zinc, or both, in the pores or on the fiber of the material, substantially no non-volatilizable matter, other than said zinc oxid or oxy-salt, being added to the wood by the treatment.

In the best form of the invention at present known to us, the treating solution is aqueous and is characterized by an alkaline reaction. This is in contradistinction to the ordinary aqueous treating solution of zinc chlorid, for example, which is somewhat acid in reaction, due to the fact that it is a salt of a strong acid and a weak base. Furthermore, in our treating solution as employed in practice, the zinc is most desirably present, at least in part, as a compound resulting from reaction between zinc chlorid and ammonium hydroxid. This compound acts like, and probably is, an ammonium zincate. It is rather readily decomposed either upon spontaneous evaporation or upon moderate heating, with formation of insoluble zinc oxid. The solution may also advantageously contain zinc in the form of a compound which upon evaporation, especially in the presence of a base such as ammonium hydroxid, will yield an insoluble basic salt or salts of zinc. In practice, a compound resulting from reaction between zinc chlorid and ammonium chlorid, probably in the nature of a double chlorid, is found to be highly useful for this purpose and is employed in conjunction with the first mentioned compound in somewhat ammoniacal aqueous solution.

For the purposes of this invention a solution such as that above described has special advantages in that the solution, upon evaporation, yields a mixture of insoluble zinc oxid and oxychlorids, or other basic salts.

In order to explain clearly the principles of the invention, a practical method of carrying it into effect will be described in detail. It is to be borne in mind, however, that this specific example is merely illustrative and that the ingredients, their proportions, and details of procedure, etc., may be varied within fairly wide limits while still realizing the benefits of the invention in some measure.

A strong solution of zinc chlorid containing about 50 per cent. zinc chlorid by weight (approximately 1.55 specific gravity), is prepared in any suitable way, as by dissolving zinc or zinc oxid in dilute hydrochloric acid. For convenience and accuracy in subsequently adding the other reagents it is desirable to have substantially no free hydrochloric acid present in the

zinc chlorid solution. If there be an excess of hydrochloric acid present, it may be neutralized by stirring an excess of zinc carbonate into the solution and filtering through mineral wool, the undissolved zinc carbonate coöperating with the mineral wool to provide an efficient filtering bed. This procedure is especially advantageous where the starting materials are relatively impure. In 300 liters of the zinc chlorid solution are dissolved 20 kilos of ammonium chlorid at ordinary temperature, and to the mixture are added gradually and with constant stirring, 350 liters of ammonium hydroxid (28 per cent. NH_3), the stirring being best continued until the solution has cooled from the temperature developed in the reaction to about 30° C. During the stirring sufficient water, about 340 liters, is added to make about 1000 liters of the solution at 30° C.

Such a solution contains zinc, ammonium, and acid radicals or groups, and from simple calculations based on the data given, it will be seen that the amomnium radical is present in substantial excess over the proportion required to satisfy the acid radical, or the acid radicals where more than one acid is employed. The resultant alkalinity of the solution is such as to give a distinct basic reaction with phenolphthalein as well as with litmus. This condition is an important characteristic of our fireproofing solution in its most desirable form and it is due to this fact that the zinc is directly deposited as oxid or an oxysalt upon evaporation of the solution.

At 25° C. the solution has a specific gravity of 1.15, and when diluted with four volumes of water it precipitates a dense, voluminous, flocculent precipitate of zinc hydroxid and basic zinc chlorids. It contains substantially 10 per cent. of combined metallic zinc. Upon evaporation, the solution deposits the greater part of its zinc content as zinc oxid mixed with variable amounts of basic zinc chlorids or oxychlorids, the proportion of the latter depending largely upon the rapidity of evaporation.

It is to be understood that the proportions of the re-agents used can be varied considerably within the scope of the invention, but the content of combined zinc in the treating solution should amount to several per cent. by weight, ordinarily not less than about 5 per cent. The proportions recited in the above specific example have been found especially advantageous practically, however, because they give a solution of large zinc content and relatively low ammonium salt content. The presence of the ammonium salt enables the solution to hold much more zinc than it could otherwise; but too large an amount of the ammonium salt is undesirable.

The solution, prepared as described, is the finished fireproofing and preserving solution in a particularly desirable form; and it may be applied to wood, fabrics, etc., by dipping, spraying, or any other method which will insure the requisite degree of impregnation. By reason of its freedom from mucilaginous and gummy constituents, the solution is highly fluid or penetrating in character, in spite of its high content of combined zinc. In fireproofing wood, for example, combined vacuum and pressure treatment similar to that used in creosoting wood, may be effectively employed. Drying of the treated materials may or may not be hastened by application of heat. If rapid drying is resorted to, it should be carried out in a suitable drying chamber from which any ammonia and ammonium chlorid volatilized in the operation may be led away and recovered in well known ways for re-use.

While we do not desire to be limited to any particular theory as to what actually occurs in preparing the fireproofing solution or its conduct upon evaporation, as described in the foregoing specific example, it is probable that the general character of the reactions can be explained with approximate accuracy as follows:

Addition of ammonium chlorid to the zinc chlorid solution gives a double salt zinc and ammonium. This takes care of only a comparatively small proportion of the zinc chlorid present, however, the rest of the zinc chlorid forming, with the added ammonium hydroxid, a compound or compounds acting like zincates, such as ammonium orthozincate and perhaps some metazincate. In the example given a slight excess of ammonia is used so that the finished solution has a distinctly basic reaction toward phenolphthalein as well as toward litmus and a characteristic faintly ammoniacal odor.

Upon evaporation of the water from the impregnated wood or the like, the ammonium zincates, or the compounds resembling zincates in conduct, break up, depositing insoluble zinc oxid and setting free ammonia and water. At the same time the double salt of zinc and ammonium decomposes into its constituent chlorids, and the zinc chlorid, reacting with the ammonium hydroxid present, yields more or less complex mixtures of insoluble basic chlorids such as $Zn_2OCl_2ZnOHCl$, etc.

The advantages attained in the practice of this invention are important. Wood, for example, thoroughly saturated with this solution and dried retains within its pores a large amount of zinc oxid and some basic zinc chlorids, all of which are substantially insoluble in water and which therefore remain in the wood permanently even though it be exposed to severe weather conditions. The wood is uninflammable, merely charring slowly upon exposure to direct flame. If,

in drying, the wood be heated sufficiently to largely drive off ammonium compounds, the insoluble zinc oxid and oxychlorids are substantially the only non-volatile matter left in the wood by the treatment. On the other hand, if the wood is simply air dried, any persisting ammonium compounds constitute in themselves valuable fireproofing agents.

It is to be noted that although, in accordance with our process, a large percentage of zinc in insoluble form can be deposited in material to be protected, this is done without deleterious effect upon the fiber of the material. If it be attempted to treat wood or other cellulosic material with a zinc chlorid solution of a zinc content as high as that of the present treating solution, the fibers are thereby weakened, while in addition the residue left in the wood by a zinc chlorid solution is hygroscopic, a disadvantage which is overcome with our solution.

While the chlorids of zinc and ammonium are specified in the example given above, other salts may be used, although for most purposes they offer no advantage over the chlorids and are ordinarily less suitable. It is particularly desirable, however, that whatever acid radical is employed shall be volatilizable upon moderate heating. Thus the sulfate of zinc, though less advantageous, will serve instead of the chlorid; while the bromid, iodid, sulfate, etc., of ammonium may replace sal ammoniac.

What we claim is:

1. The process of protecting materials and decreasing their combustibility which comprises treating such a material with an ammoniacal solution containing a zinc compound but substantially free of other non-volatile constituents, said solution having an alkaline reaction toward phenolphthalein and its content of combined zinc being at least about 5 per cent.

2. The process of protecting materials and decreasing their combustibility which comprises treating such a material with a highly fluid ammoniacal solution of a zinc compound, said solution being alkaline to phenolphthalein, and containing several per cent. of zinc but being substantially free of other non-volatile constituents.

3. The process of protecting materials and decreasing their combustibility which comprises treating such a material with an aqueous solution containing a zinc and ammonium compound and ammonium hydroxid, said solution being alkaline to phenolphthalein, and drying the treated material to deposit a water-insoluble zinc compound therein or thereon, the zinc content of said solution amounting to several per cent.

4. The process of protecting materials and decreasing their combustibility which comprises treating such a material with a highly fluid solution having an alkaline reaction toward phenolphthalein and containing several per cent. of zinc in combination only with relatively volatile radicals.

5. The process of protecting materials and decreasing their combustibility which comprises treating such a material with an alkaline solution containing an ammonium zincate and a salt of zinc, the zinc content of the solution being relatively high.

6. The process of protecting materials and decreasing their combustibility which comprises treating such a material with an alkaline solution containing an ammonium zincate, a salt of zinc, and another ammonium salt.

7. The process of protecting materials and decreasing their combustibility which comprises treating such a material with an alkaline solution containing an ammonium zincate, zinc chlorid and ammonium chlorid.

8. The process of fireproofing wood which comprises impregnating wood with an alkaline-to-phenolphthalein solution of a zinc compound, the zinc content of the solution amounting to several per cent., drying the wood and thereby depositing within the wood a water-insoluble zinc compound having fire-retarding properties.

9. The process of fireproofing wood which comprises impregnating wood with an alkaline-to-phenolphthalein ammoniacal solution of a heavy metal compound, the metal content of the solution amounting to at least about 5 per cent., drying the wood and thereby depositing within the wood a water-insoluble heavy metal compound having fire-retarding properties.

10. The process of treating wood and the like which comprises impregnating wood or other material with a solution containing a zinc compound and an ammonium compound and having an alkaline reaction toward phenolphthalein, the zinc content of the solution amounting to at least about 5 per cent.

11. The process of protecting materials and decreasing their combustibility which comprises treating such a material with an alkaline solution containing zinc, ammonium, and acid radicals, the proportion of the ammonium radical present being in substantial excess of that required to satisfy said acid radical or radicals and the content of combined zinc amounting to several per cent.

12. The process of protectively treating fibrous material which comprises impregnating such material with an ammoniacal aqueous solution containing approximately ten per cent. of combined zinc, and drying the treated material.

13. The process of protectively treating fibrous material which comprises impregnating such material with an aqueous solution

containing a zinc compound and an ammonium compound, said solution containing approximately ten per cent. of combined zinc, and drying the treated material.

14. As a new article of manufacture, fireproofed or uninflammable material containing distributed therethrough a non-hygroscopic mixture of zinc oxid and a zinc oxy-salt of a relatively volatile acid radical, said material being substantially free of added water-soluble non-volatilizable compounds.

15. As a new article of manufacture, fireproofed or uninflammable material containing distributed therethrough a non-hygroscopic mixture of zinc oxid and a basic chlorid of zinc, said material being substantially free of added water-soluble non-volatilizable compounds.

In testimony whereof we hereunto affix our signatures.

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