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PRESERVATIVE COMPOSITION AND METHOD OF PREPARING SAME

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This invention relates to a preservative composition, and method of production. More particularly, it is concerned with an improved preservative composition and to a method for its production.

Heretofore, it has been known that the life of many types of fabric, which are subject to microbiological attack or rotting in dampness or high humidity conditions may be prolonged if the fabric is treated with a preservative composition. Many fabrics when subjected to ordinary conditions of usage and given reasonable care require no preservative to give satisfactory service. However, when subjected to conditions highly unfavorable to the fabric, they soon rot. In peace times, for example, bags made of burlap and Osnaburg are used for storage and transportation. In war times, however, great quantities of these bags are filled with sand and constructed into revetments and barricades as a protection against blast and splinters caused by modern devastating aerial warfare. When used for this purpose public experience and research workers have proven the value of treating them with a preservative composition.

Now, in accordance with this invention, an improved preservative composition for fabrics has been prepared comprising the copper salts of rosin and rosin oil obtained by the destructive distillation of resin procured as a by-product in the refining of FF wood rosin to a pale grade of wood rosin. A fabric, such as burlap, Osnaburg and the like which has been impregnated with this composition possesses both fungicidal and bactericidal properties. The preservative composition, when impregnated in a fabric will not be leached out by rain and water, will not detract from the fibre strength, and provides a cheap, readily available and easily applied preservative composition. Thus, the process of this invention comprises impregnating a fabric with a composition comprising the copper salts of rosin and rosin oil obtained by the destructive distillation of resin procured as a by-product in the refining of FF wood rosin to a pale grade of wood rosin. The product of this invention is particularly adapted for impregnating Osnaburg and burlap fabric for use in sandbags.

Now, having indicated in a general way, the nature and purpose of this invention, the following examples will illustrate the method of preparing the improved preservative composition and the manner in which the principle of the invention has been applied. It is to be understood that these examples are used by way of illustration and not by way of limitation. In the examples, the ingredients are given in parts by weight unless otherwise indicated.

Example 1

Two hundred fifteen parts B wood rosin paste size (70% solids), one hundred fifty parts rosin oil and 45 parts of sodium hydroxide were dissolved in 790 parts of water at about 140° F. Three hundred parts of copper/ammonium complex, prepared by dissolving 20 parts of copper sulfate in 80 parts of water at about 140° F., and then adding 20 parts of ammonium hydroxide with stirring to form a solution, were slowly added to the mixture with stirring to form a solution in which the copper resinate did not precipitate. A sample of 6 oz. Osnaburg fabric was immersed in a bath containing the above solution. The excess solution was squeezed from the fabric and the fabric dried. The copper was precipitated in the fabric in the form of copper salts of the B rosin and rosin oil. The copper content of the fabric thus treated was 0.93%.

Example 2

A sample of 6 oz. Osnaburg fabric was immersed in a bath containing fifteen parts B wood rosin paste size (70% solids), ten parts of rosin oil, 0.7 part sodium hydroxide and 74.3 parts water. The impregnated cloth after removal of the excess solution by squeezing, was immersed in a second bath consisting of forty-five parts cupric acetate and 1455 parts water. The excess solution was squeezed from the fabric and the fabric dried. The copper was precipitated in the fabric in the form of copper salts of rosin and rosin oil.

Example 3

Fifty parts of N wood rosin and fifty parts of rosin oil were heated to 140° C. in 20 minutes. Seventeen and sixty-four hundredths parts cupric acetate was added over a period of 25 minutes, with constant stirring. The temperature of the mixture was then maintained at 140° C. with stirring for 30–40 minutes. To three hundred parts of copper resinate so prepared were added 1230 parts of Varsol. A sample of 6 oz. Osnaburg fabric was immersed in a bath containing the above prepared copper resinate solution. The excess solution was squeezed from the fabric and the fabric dried. The copper was precipitated in the fabric in the form of copper salts of rosin and rosin oil. The copper content of the fabric thus tested was 0.95%.

Example 4

A sample of 6 oz. Osnaburg fabric was im-

mersed for about 20 seconds in a bath containing fifteen parts B wood rosin paste size (70% solids), ten parts of rosin oil, three parts sodium hydroxide, one part pine oil and seventy-one parts water, maintained at a temperature of about 60° C. The impregnated cloth, after removal of the excess solution by squeezing, was immersed in a second bath consisting of three parts cupric acetate and ninety-seven parts water for 20 seconds, squeezed and the fabric dried. The copper was precipitated in the fabric in the form of copper salts of B wood rosin and rosin oil.

Example 5

A sample of 6 oz. Osnaburg fabric was treated with a solution prepared as in Example 1, except that seventeen and four-tenths parts cupric acetate were used in the cuprammonium complex in place of the copper sulfate. The copper content of the fabric thus treated was 0.89%.

Example 6

A sample of 6 oz. Osnaburg fabric was treated according to the method of Example 4, except that the first bath contained eight parts dry rosin size, made from K gum rosin, ten parts rosin oil, three parts ammonium hydroxide, one part pine oil and seventy-eight parts water. The copper content of the fabric thus treated was 1.25%.

Tests were made on the fabrics prepared in the above examples to determine their resistance to rotting when buried in mushroom soil (pH 7). Samples of the fabric were cut into 3 x 6" strips and buried about 4½" deep in the mushroom soil. The samples and soil were wet periodically with a garden sprinkler to maintain a rather high moisture content in the soil. The moisture content as well as the temperature were determined at intervals. Ten strips were buried in different locations in the box. The following table illustrates their resistance to rotting when compared with an untreated sample of identical Osnaburg fabric which was buried and tested under the same conditions:

Impregnation Table

	Moisture	Temperature	Water added	Untreated	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6
	Per cent	*° C.*	*Gallons*							
Beginning	31.4	25	1	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent.
1st day		25	1	do	do	do	do	do	do	Do.
4th day	35.0	25	1	Poor	do	do	do	do	do	Do.
6th day		25	1	Rotted	do	do	do	do	do	Do.
8th day					do	do	Poor	do	do	Do.
10th day	35.5	25	1		do	do	do	do	do	Do.
11th day					do	do	Rotted	do	do	Do.
12th day					Poor	Poor		do	do	Do.
14th day					Rotted	Rotted		Rotted	Rotted	Do.
16th day	34.0	24	1							Do.
18th day										Rotted.

While grège Osnaburg fabric was used in the examples, Osnaburg fabric that has been kiered and bleached may be used, if desired. Other similar fabrics such as burlap may also be employed.

The rosin which may be used in accordance with this invention may be those derived from any of the various grades of wood or gum rosin, or the rosin acids contained therein, as abietic acid, pimaric acid, sapinic acid, etc.

As illustrated in the examples, rosin paste or dry size may be employed in carrying out the process of this invention. Neutralization of the rosin may be carried out in a number of ways. Thus, paste sizes are conveniently prepared by adding the rosin in the solid or molten state to a hot aqueous alkali such as sodium carbonate, sodium hydroxide and the like, and continuing the heating until the reaction is complete. The concentration of the aqueous alkali solution is usually adjusted so that upon completion of the reaction, sufficient water is present to form a paste size of desired consistency and solids content. The proportion of alkali employed varies with the particular alkali employed as well as with the type of size desired. In preparing neutral size, for example, sufficient alkali is employed to react with all of the rosin acids in the rosin whereas in preparing high free rosin size wherein the rosin is only partially neutralized, a smaller amount of alkali is used, the exact proportions depending upon the proportion of free rosin desired in the size. The reaction may also be carried out in the cold, employing a variety of alkalies and special procedures adapted to modify certain properties and characteristics of the size. Other variables will readily occur to those skilled in the art.

Dry rosin size may be prepared by a number of methods, the most convenient of which is that described in U. S. Patent 2,134,911. Such method essentially comprises introducing a concentrated aqueous alkali into molten rosin contained in an autoclave and heated to a temperature of about 275° F. after which the mixture is heated at 275° F. to 375° F. and under autogenous pressure of the mixture until the neutralization reaction is complete. The mixture is then discharged into a drying atmosphere under its own pressure whereby it is instantly desiccated to a dry, finely divided powder.

The rosin oil employed in carrying out this invention is obtained by the destructive distillation of resin procured as a by-product in the refining of FF wood rosin to a pale grade of wood rosin. Thus, the resin may be, more specifically, the dark-colored resin obtained as a by-product when FF wood rosin is dissolved in a low boiling petroleum hydrocarbon and refined to pale grades of wood rosin by treatment with furfural. Other refining agents such as, for example, fuller's earth, phenol, sulfur dioxide, chlorohydrin, furfuryl alcohol, resorcinol, etc. may be used. The resin may also be obtained as the distillation residue in the distillation of FF wood rosin to produce pale grades of wood rosin. The by-product resin will have the following approximate analysis:

Acid number		105–140
Saponification number		150–170
M. P. (Hercules drop method)	°F.	175–210
Unsaponifiable	per cent	10–20
Gasoline—insoluble	do	30–80
Petroleum ether—insoluble	do	30–80

The rosin oil is a complex mixture of volatile components and decomposition products obtained by the destructive distillation of the above de-

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scribed resin by-product resin at relatively high temperatures, e. g. 300°–400° C. The distillation operation may be carried out in any desirable manner, for example, by distilling the by-product resin under vacuum or at atmospheric pressure. Alternatively, the distillation may be carried out in the presence of a decarboxylation catalyst such as fuller's earth, sodium acid sulfate, phosphoric acid, etc., and may be effected either by the use of superheated steam or by direct firing. If desired, an inert gas, such as carbon dioxide or nitrogen, may be passed through the still as the distillation proceeds in order to sweep out the more volatile components before complete decomposition takes place. Any of the other well-known variations in destructive distillation processes may likewise be employed.

In most cases, the distillate obtained comprises an oily material, a considerable amount of water, and small amounts of low-boiling materials. The oil may vary somewhat in composition depending upon the particular distillation process employed, but, in general, is characterized by the following approximate analysis:

Saponification number	30–55
Acid number	25–45
Boiling range °C	165–395
Specific gravity at 15.6° C	1.02–1.035

The above defined oily material is referred to herein and in the appended claims as procured as a by-product in the refining of FF wood rosin to a pale grade of wood rosin. Rosin oil is obtained by the destructive distillation of resin.

The amount of rosin and rosin oil may vary. Generally speaking, however, a ratio of rosin to rosin oil of from about 4:1 to about 1:4, and preferably from about 1:1 to 2:1 should be used. If a higher ratio of rosin to rosin oil than about 4:1 is used, the fabric will lose its pliability and become stiff and unsuitable for use. If a lower ratio of rosin to rosin oil than about 1:4 is used, less copper will be deposited on the fabric than needed to satisfactorily impregnate the fabric.

A convenient method of carrying out the process of this invention, fabric, for example, such as burlap, Osnaburg, and the like, is immersed in a bath containing an aqueous emulsion of an alkali-metal salt of rosin, for example, B wood rosin paste size (70% solids) and rosin oil. If desired, a small amount of pine oil may be added. The impregnated fabric is then freed of excess solution by means of squeeze rolls, and immersed in a second bath consisting of an aqueous solution of, for example, copper sulfate, cupric acetate and the like. The excess composition is squeezed from the fabric and the fabric dried. As a result, the copper is precipitated in the fabric in the form of the copper salts of rosin and rosin oil.

Alternately, if desired, rosin and rosin oil may be heated together at a temperature of about 140° C. for a short period, for example, twenty minutes. A copper salt, such as cupric acetate, may then be slowly added, with agitation, at a temperature of about 140° C. The stirring may then be continued for a period of about 30–40 minutes while the temperature is maintained at 140° C. The copper resinate may then be dissolved in any suitable solvent, such as Varsol, Solvesso No. 2, xylene, toluene, benzene, V. M. & P. naphtha and the like. The fabric may then be immerged in a bath containing this impregnating solution and the fabric dried.

Other modes of applying the principle of my invention may be employed instead of those explained, change being made as regards the ingredients or methods employed, provided the product stated by any of the following claims, or the equivalent of such stated product be obtained.

While the preserving composition is adaptable for use generally with fabrics which are subject to micro-biological attack or rotting in dampness or high humidity conditions, it is particularly suitable for use for rotproofing Osnaburg or burlap used in sandbags. It provides an economical, readily available and easily applied efficient and effective preservative.

What I claim and desire to protect by Letters Patent is:

1. A preservative composition for fabric comprising the copper salts of rosin and rosin oil, said rosin oil being obtained by the destructive distillation of resin procured as a by-product in the refining of FF wood rosin to a pale grade of wood rosin, said rosin and rosin oil being present in a ratio of rosin to rosin oil of from about 4:1 to about 1:4.

2. A preservative composition for fabric comprising the copper salts of rosin and rosin oil, said rosin oil being obtained by the destructive distillation of resin procured as a by-product in the refining of FF wood rosin to a pale grade of wood rosin, said rosin and rosin oil being present in a ratio of rosin to rosin oil of from about 1:1 to about 2:1.

3. A treated fabric comprising fabric which has been impregnated with the copper salts of rosin and rosin oil, said rosin oil being obtained by the destructive distillation of resin procured as a by-product in the refining of FF wood rosin to a pale grade of wood rosin said rosin and rosin oil being present in a ratio of rosin to rosin oil of from about 4:1 to about 1:4.

4. A treated fabric comprising Osnaburg which has been impregnated with the copper salts of rosin and rosin oil, said rosin oil being obtained by the destructive distillation of resin procured as a by-product in the refining of FF wood rosin to a pale grade of wood rosin, said rosin and rosin oil being present in a ratio of rosin to rosin oil of from about 4:1 to about 1:4.

5. A treated fabric comprising burlap which has been impregnated with the copper salts of rosin and rosin oil, said rosin oil being obtained by the destructive distillation of resin procured as a by-product in the refining of FF wood rosin to a pale grade of wood rosin, said rosin and rosin oil being present in a ratio of rosin to rosin oil of from about 4:1 to about 1:4.

6. A method of impregnating a fabric comprising treating said fabric with a composition containing the copper salts of rosin and rosin oil, said rosin oil being obtained by the destructive distillation of resin procured as a by-product in the refining of FF wood rosin to a pale grade of wood rosin said rosin and rosin oil being present in a ratio of rosin to rosin oil of from about 4:1 to about 1:4.

7. A method of impregnating a fabric comprising treating said fabric in a bath containing an alkali-metal salt of rosin and rosin oil, said rosin oil being obtained by the destructive distillation of resin procured as a by-product in the refining of FF wood rosin to a pale grade of wood rosin, then immersing said fabric in a bath containing copper sulfate said rosin and rosin oil being present in a ratio of rosin to rosin oil of from about 4:1 to about 1:4.

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