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COMPOSITION FOR WATERPROOFING TEXTILES AND METHOD OF PREPARATION

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1

This invention relates to new compositions of matter and to the rendering of textile materials water repellent or water resistant therewith. More particularly, it relates to such compositions containing zirconyl soaps.

It has been suggested to employ zirconyl soaps (zirconyl salts of fatty acids) as agents for rendering textile fibers or fabrics water repellent or water resistant. Several methods of incorporating such soaps in textile materials have been suggested, but most of these methods have one or more disadvantages. Thus, the textile material may be impregnated with a solution of a zirconyl soap in an organic solvent and the solvent then evaporated. The difficulty with this method is that few satisfactory solvents are available and for those that are available an elaborate solvent recovery system is desirable for economical reasons. A second method is to impregnate the textile with an aqueous solution of a water soluble zirconyl salt, and then to precipitate the zirconyl soap by treating with a water soluble soap or salt of a fatty acid. Zirconyl salts of the strong acids, such as hydrochloric, nitric and sulfuric acids, tend to hydrolyze and, because of their acid character, cause loss of tensile strength in the fibers of the material treated. Zirconyl salts of the weak acids, such as zirconyl acetate, also tend to hydrolyze and precipitate zirconium hydroxide from the solution. To prevent such hydrolysis and consequent precipitation, an excess of free acid must be added to the solution which is harmful to the textile as in the case of the strong acids. In either case, if such solutions are used in conjunction with various soap solutions for the impregnation of cloth to produce water repellent properties, there is produced, in addition to the formation and precipitation of zirconium salts of the fatty acids, a precipitate of some of the free fatty acid. While the presence of such free fatty acid does give water repellent properties to the material so treated, such properties are in a large measure only temporary, since the free fatty acid portion of the impregnation may be subject to oxidation by the air, and attack by microorganisms. Such action may also be harmful to the fabric so treated. In addition, the water repellent properties due to the presence of the free fatty acid are lost if the fabric is dry cleaned, since the fatty acid is soluble in the organic solvents usually used for this purpose and is consequently dissolved out of the treated material.

It is therefore an object of this invention to provide a new composition of matter containing a

2

zirconyl soap and suitable for rendering textile materials water repellent or water resistant. It is another object to provide such a composition which will not result in the precipitation of free fatty acid in the textile material. It is a further object to provide such a composition which will not cause the textile to be subject to attack by acids. A still further object is to provide a method for rendering textile materials water repellent or water resistant. Other objects will appear hereinafter.

These objects are accomplished by means of a composition comprising a colloidal suspension of a zirconyl soap. A textile material is impregnated with such a composition, and the zirconyl soap then precipitated by means of an electrolyte or a weak acid.

In accordance with this invention, an aqueous solution of a water soluble zirconium or zirconyl salt, such as the chloride, sulfate or nitrate, is first prepared. Such a solution is added to an aqueous solution of a carbonate or bicarbonate of an alkali metal or of ammonium or ammonium carbonate-carbamate (commonly called ammonium carbonate). In effecting this addition it is important that the zirconyl salt solution be added to the alkaline solution, and not vice versa, in order to prevent the formation and precipitation of zirconium hydroxide. The combined solutions must be maintained distinctly alkaline, in order to prevent the precipitation of certain zirconium salts which become insoluble if the pH is lowered much below a value of 8.

The alkaline solution of a zirconyl salt and alkali metal or ammonium carbonate or bicarbonate is then mixed with an aqueous solution of a water-soluble soap, to form a colloidal suspension of a zirconyl soap, from which the zirconium salt of the fatty acid of the soap is not precipitated. Of the water soluble soaps which may be used, the sodium, potassium or ammonium soaps of stearic, oleic or palmitic acids, or the acids obtained from linseed or tung oil, or those obtained from other animal or vegetable fats or oils, may be mentioned. In addition, soaps of organic bases may be used, for example, the soaps obtained by the interaction of an organic base such as triethanolamine, $N(CH_2—CH_2OH)_3$, with any of the fatty acids such as are mentioned above. The concentrations of such soap solutions which are mixed with the zirconium salt solutions may be varied within certain limits. The relative quantities of zirconyl salt and water soluble soap used should preferably be the stoichiometric quantities necessary to form the cor-

responding zirconyl soap of the formula $ZrOX_2$, wherein X represents a monobasic fatty acid radical. If the water soluble soap is present in excess of this, undesirable free fatty acid may be formed under certain conditions, as disclosed in U. S. Patent No. 2,221,975. On the other hand, the presence of excess zirconyl salt is not particularly harmful, and under certain conditions may be desirable.

Substances of a waxy nature, such as paraffin, may also be incorporated in the colloidal suspension. This can conveniently be accomplished by adding the waxy material to the solution of the water soluble soap (before mixing with the zirconyl salt solution), to form an emulsion of the waxy material. The waxy material serves to increase the water repellent properties of the textile material being treated.

The colloidal suspension of a zirconyl soap is then impregnated in the desired textile material. The zirconyl soap is precipitated on the textile materials by treating with an aqueous solution of an electrolyte, or by neutralizing with a weak acid. The most suitable electrolyte is sodium chloride, because of its cheapness and abundance, but other electrolytes may also be used, such as the soluble alkali or alkaline earth chlorides, sulfates or nitrates. Among suitable weak acids are boric or acetic.

The invention having been described generally, the following examples are now given:

Example 1

6.0 grams of ammonium carbonate-carbamate are ground to a powder and dissolved in approximately 75 ml. of water, 5.0 grams of hydrated zirconyl chloride (containing 40% ZrO_2 by weight) are dissolved in approximately 75 ml. of water. The zirconyl chloride solution is poured slowly into the ammonium carbonate solution with stirring. Some carbon dioxide is evolved and a slight amount of precipitate at first formed quickly redissolves. 5.0 grams of sodium stearate are added to approximately 100 ml. of water and heated until the solution is clear (approximately to 75° C.). The solution is then cooled to 40° C. The solution containing the ammonium carbonate and zirconyl chloride is then added, with stirring, to the soap solution and water is then added to bring the total volume up to 300 ml. The temperature of the resulting colloidal solution is raised to 60° C. and maintained at that point.

The fabric to be treated is immersed in the colloidal solution for two minutes, removed from the solution and the excess liquid removed by squeezing between rollers or by centrifuging. The piece is then immersed for two minutes in a solution containing approximately 30 grams of sodium chloride per 100 ml. at a temperature of from 90 to 95° C. during which time the zirconium soap is precipitated in the fiber. The fabric is then washed and dried.

Example 2

6.0 grams of anhydrous sodium carbonate (or its equivalent of the hydrated form) are dissolved in approximately 75 ml. of water. 5.0 grams of zirconyl chloride (40% ZrO_2) is dissolved in 75 ml. of water and the resulting solution added slowly, with stirring, to the solution of sodium carbonate. 10.0 grams of sodium stearate is added to approximately 100 ml. of water, dissolved by heating, and cooled to 40° C. The sodium carbonate-zirconyl chloride solution is then added with stirring to the soap solution. Since this solution is strongly alkaline, the solution is adjusted to a pH of approximately 8 by the addition of the necessary quantity of a weak acid. Water is added to bring the volume up to 300 ml. The temperature of the solution is raised to 75° C. and maintained at that point. The fabric to be treated is immersed in this solution for two minutes, removed from the solution, and excess liquid removed by squeezing between rollers or by centrifuging. The precipitation of the zirconium soap can then be effected by immersing the fabric for two minutes in a solution containing 7.0 grams of boric acid dissolved in 100 ml. of water at 90 to 95° C. The fabric is then washed and dried.

Example 3

8 grams of sodium oleate are prepared by the addition of 10.5 ml. of 10% caustic soda solution to 7.5 grams of oleic acid with heating until saponification is complete. The resulting soap is dissolved in 100 ml. of hot water and then cooled to 40° C. To this soap solution is added a zirconyl chloride-sodium carbonate mixture prepared as directed in Example 2. The solution is adjusted to a pH of approximately 8 and the volume made up to 300 ml. The fabric to be treated is immersed in this solution at 75° C. for two minutes, excess solution is removed, and precipitation of the zirconyl oleate produced by immersion in a hot sodium chloride or boric acid solution as in Example 1 or 2.

Example 4

The zirconyl chloride-sodium carbonate solution is prepared as described in Example 2. The soap solution is also prepared as described in Example 2, except that during the heating to bring about solution of the soap, 0.5 gram of paraffin is added and the emulsion stirred briskly. The solution is cooled to between 55° and 60° C. and the zirconyl chloride-sodium carbonate mixture added. The fabric to be treated is immersed in this solution at 75° C. for two minutes, excess solution is removed as previously directed, and precipitation of the zirconium soap produced by immersion of the sample in either hot sodium chloride or boric acid solution as previously directed.

Example 5

1.65 grams of triethanolamine,

$N(CH_2.CH_2.OH)_3$

are mixed with 100 ml. of water. To this solution is added 9.25 grams of oleic acid. The mixture is heated until saponification is completed and then cooled to 40° C. To this solution of triethanolamine oleate is added a zirconyl chloride-sodium carbonate mixture prepared as described in Example 2. The resulting colloidal suspension, either with or without the addition of wax, may be used for impregnating the sample of fabric and precipitation of the zirconyl soap may be accomplished as directed in the previous examples.

Example 6

Five grams of hydrated zirconium sulfate ($Zr(SO_4)_2.4H_2O$) are added to a solution of 6.0 grams of anhydrous sodium carbonate in approximately 100 ml. of water. The solution may be heated slightly to effect solution of the zirconium sulfate. The resulting zirconium sulfate-sodium carbonate solution may be added to solutions of the different soaps previously mentioned, and of

various concentrations to produce a colloidal suspension which may be used for the impregnation of fabric as previously described herein. The precipitation of the zirconyl soap is likewise accomplished by the methods described in the previous examples.

The expressions "zirconyl salts" and "zirconyl soaps" are used throughout the present specification and claims, instead of "zirconium salts" and "zirconium soaps." The best scientific evidence points to the fact that tetravalent zirconium salts such as $ZrCl_4$, do not exist in aqueous media, or exist only in negligible quantities. They hydrolyze to form oxy-salts, such as $ZrOCl_2$, commonly called zirconyl salts. In other words, the ion Zr^{****}(tetravalent) does not exist in aqueous solution but only the ion ZrO^{**}(divalent). Thus, although the use of "zirconium" sulfate is described in the present specification, the best evidence points to the fact that this material actually exists as $ZrOSO_4.H_2SO_4.3H_2O$ or

$$ZrOH_2(SO_4)_2.3H_2O$$

in aqueous media, and should be termed "zirconyl hydrogen sulfate." As the present invention deals throughout with the use of aqueous media it will be understood that the terms "zirconyl salts" and "zirconyl soaps" in the present specification and claims contemplate the use of materials which are often designated as zirconium salts or zirconium soaps.

As many variations are possible within the scope of this invention, it is not intended to be limited except as defined by the appended claims.

I claim:

1. As a new composition of matter for rendering textiles water repellent, an aqueous colloidal suspension of a zirconyl soap.

2. As a new composition of matter for rendering textiles water repellent, an aqueous alkaline colloidal suspension of a zirconyl soap.

3. As a new composition of matter for rendering textiles water repellent, an aqueous alkaline colloidal suspension of a zirconyl soap, said suspension containing paraffin.

4. The method of preparing a composition for waterproofing textiles which comprises adding an aqueous solution of a zirconyl salt to an aqueous solution of a substance taken from the class consisting of the carbonates, bicarbonates and carbonate-carbamate of the alkali metals and ammonium, to form an alkaline solution, and mixing said alkaline solution with an aqueous solution of a water soluble soap, to form an aqueous colloidal suspension of a zirconyl soap.

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