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PROCESS FOR IMPARTING WATER REPELLENCE AND PRODUCTS THEREOF

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ABSTRACT OF THE DISCLOSURE

A fabric having thereon a substantially continuous, hydrophobic layer of a fatty acid-hydrous zirconia adsorbate is produced by alterntaely immersing said fabric in an aqueous soap solution and in an aqueous solution of ammonium zirconyl carbonate, which may also contain tetrammine zinc, tetrammine copper, and/or phenylmercury ions, drying after the second immersion, repeating such treatment, and drying said fabric at a temperature of at least 70° C. and preferably 90° C. The adsorbate layer is resistant to washing and dry cleaning solvents; and also where the other mentioned metal ions are included in the metal salt solution imparts resistance to attack by microorganisms.

BACKGROUND OF THE INVENTION

This invention is concerned with the treatment of surfaces to impart thereto water repellence and other desired properties, such as protection against the action of microorganisms.

Many attempts have previously been made to produce water-repellent textiles and to impart water repellence to other types of surfaces. High levels of water repellence have hitherto been obtained only with wax emulsions, organic resins, or silicone compounds and protection against microorganisms has been accomplished by the use of solutions of toxic salts, for example, salts of copper or mercury, or of toxic organic compounds such as pentachlorophenol.

The materials mentioned have, in many cases, not been satisfactory because of poor durability, undesirable alterations of physical properties, and/or excessive cost of application.

Water-insoluble metallic soaps have been employed as water repellents. They have not, however, been fully satisfactory since they generally are effective to produce a high level of water repellence only when used in conjunction with waxes or resins and these adjuncts are rapidly dissolved and removed by dry cleaning solvents.

SUMMARY OF THE INVENTION

According to the present invention, durable water-repellent surfaces are secured on fibrous and other materials by producing thereon successive deposits of fatty acid-hydrous zirconia adsorbates. Such adsorbates in conjunction with compounds of certain metals also impart to such surfaces resistance to attack by microorganisms. These results are accomplished without the use of waxes or organic resins. It is to be noted that the fatty acid-hydrous zirconia adsorbates are formed on the surfaces being treated and cannot be applied in solution as are the soaps of the prior art.

As stated above, the present invention is concerned with fatty acid-hydrous zirconia adsorbates and their application on surfaces. These adsorbates are different from and not to be confused with zirconium soaps of fatty acids. The latter are formed, for example, when a zirconium salt such as zirconium tetrachloride ($ZrCl_4$) reacts in a suitable solvent medium with a fatty acid. Such zirconium soaps are molecular compounds of zirconium with the chemical equivalent of the fatty acid and have the generalized formula

$$(CH_3\cdot(CH_2)_xCOO)_4Zr$$

When, however, hydrous zirconia ($ZrO_2\cdot xH_2O$) is treated with, or precipitated in the presence of, a fatty acid or a soluble salt of a fatty acid, some, but not all, of the chemisorbed water of the hydrate particles is replaced by chemisorbed fatty acid or fatty acid anions. It is such products which are both chemically and physically different from common soaps to which the term "fatty acid-hydrous zirconia adsorbates" is herein applied. The fatty acids which are of interest in the present invention and which are meant to be included in the above-mentioned term are those having from 14 to 18 carbon atoms. The fatty acid-hydrous zirconia adsorbates form as extremely small, discrete, insoluble particles.

By forming particles of such fatty acid-hydrous zirconia adsorbates on surfaces such as those of textiles, paper, and siliceous materials, such as glass, in deposits of sufficient thickness as to produce a substantially continous layer thereon, it is possible to provide the surfaces with a high order of water repellence. This may be done by repeated treatments of the surface to produce these adsorbate particles thereon. Although several successive treatments can be used, two treatments are usually sufficient to achieve the desired result since the adsorbate particles formed in the second treatment fill in any spaces remaining between the adsorbate particles formed in the first treatment, and the layer thus formed is firmly bonded to the surface.

DESCRIPTION OF THE INVENTION

The following examples illustrate the treatment of textiles according to the present invention to provide water repellence and resistance to attack by microorganisms. In each case, the textile material is given a preliminary treatment to remove any sizing, oil, or other foreign material thereon. For cellulosic textiles preliminary treatment with a hot solution of sodium carbonate followed by washing is generally satisfactory although special treatment may be required for textiles that have been coated with certain types of sizing, such, for example, as polyvinyl acetate.

EXAMPLE 1

A woven cotton fabric is first dipped in a dilute soap solution containing about 2 g. of sodium stearate per liter of water and thereafter is wrung out by passing it between tightly pressed rubber rollers. The still wet textile, containing about its own weight of soap solution, is then dipped in an aqueous solution of ammonium zirconyl carbonate ($(NH_4)_3ZrOH(CO_3)_3\cdot 2H_2O$) assaying approximately 7.5 g. of Zr per liter and is wrung out a second time to about the same degree of wetness. It is then dried in hot air at about 90° C.

After the drying the foregoing steps are repeated with the result that the fabric after the second drying step has a layer of stearic acid-hydrous zirconia adsorbate on the fibers of the fabric which is so water-repellent that the fabric has a water repellence rating of 100 by A.S.T.M. Spray Test Procedure D583–63.

It is believed that the good results are explained by the fact that during the drying steps the ammonium zirconyl carbonate decomposes to form hydrous zirconia which reacts with the stearate ions present to form the hydrous zirconia-stearic acid adsorbate. It also appears that at least some of the zirconium atoms of the zirconia particles that are in contact with the surface being treated bond with the oxygen of the surface hydroxyl groups of the textile fabric, thus improving adhesion of the adsorbate layer and rendering it very durable.

In the event that it is desired to impart resistance to attack by microorganisms to the surface being treated, for example that of cotton cloth, a metal compound having bactericidal and/or fungicidal properties is used in conjunction with the fatty acid-hydrous zirconia adsorbate. This is illustrated in the following examples:

EXAMPLE 2

A cotton fabric is first dipped in a dilute sodium stearate solution containing about 2 g. of the soap per liter of water and is then wrung out, as in Example 1, so as to retain about its own weight of soap solution. While still wet from wringing, the fabric is dipped into a treating bath consisting essentially of an aqueous solution of ammonium zirconyl carbonate which contains tetrammine zinc compound in the hydrophobic layer formed on the to about the same liquid content and dried at about 90° C.

After the drying, the above-described steps are repeated with the result that the fabric after the second drying step, with an A.S.T.M. Spray Test rating of 100, is highly water repellent. It is, additionally, found to show some resistance to decomposition by microorganisms present in soil as a result of the presence of an insoluble zinc compound in the hydrophobic layer formed on the fibers.

The treating bath is conveniently prepared by adding 32 g. of zinc oxide (ZnO) to 1 kg. of an aqueous ammonium zirconyl carbonate solution and 90 g. of ammonium hydroxide (0.9 sp. gr.). The mixture is stirred until the zinc oxide dissolves and is then diluted with water to make 10 liters. The resulting solution contains about 7.5 g./l. of Zr and 2.5 g./l. of Zn.

EXAMPLE 3

Repeating the treating procedure of Example 2 but using an ammonium zirconyl carbonate bath containing instead of tetramminezinc ions, tetramminecopper ions gives a cotton fabric having a fatty acid-hydrous zirconia adsorbate layer containing an insoluble copper compound which not only produces an A.S.T.M. Spray Rating of 100 but also a very high resistance to attack by microorganisms.

The treating bath is conveniently made by adding 49 g. of basic cupric carbonate ($2\ CuCO_3 \cdot Cu(OH)_2$) to 1 kg. of an aqueous solution of ammonium zirconyl carbonate assaying 7.5 g. of zirconium per 100 g. and 54 g. of 0.9 sp. gr. ammonium hydroxide and stirring until the copper carbonate dissolves. Water is then added to make 10 liters of solution. The solution obtained contains about 7.5 g. of Zr and 2.7 g. of Cu per liter.

EXAMPLE 4

Repeating the treating procedure of Example 2 but using, instead of the tetramminezinc ions, phenylmercury ions, a cotton fabric is obtained which is also highly resistant to attack by microorganisms and has an A.S.T.M. Spray Rating of 100 as a result of the presence of an insoluble mercury compound in the hydrophobic adsorbate layer produced on the textile fibers. The treating bath is conveniently produced by adding phenylmercury propionate to a concentrated ammonium zirconyl carbonate solution in which it is dissolved. The concentrated solution is then diluted for use in the textile treatment. Enough phenylmercury propionate is employed to give a bath containing about 7.5 g. of Zr and 10 g. of Hg per liter of solution.

If desired, additional protection against attack by microorganisms may be given textiles by employing a treatment in which two or more of the metals zinc, copper, and mercury are applied to the fabric along with the ammonium zirconyl carbonate. This is illustrated in the following example.

EXAMPLE 5

Cotton fabric having an excellent resistance to attack by microorganisms and so water repellent that in the spray test the drops of water fall off the fabric is obtained by having in the second bath employed in the procedure set forth in Example 2 both tetramminezinc ions and tetramminecopper ions, each in an amount equivalent to about 2.5 g./l. of the metal, the ammonium zirconyl carbonate being present in an amount equivalent to about 7.5 g. of Zr per liter of solution.

Fabrics provided with fatty acid-hydrous zirconia adsorbate layers in accordance with the present invention retain water repellent surfaces after laundering and even after treatment with dry cleaning solvents such as benzene, trichloroethylene, and perchloroethylene. Products resulting from the procedure of Example 1 retain a rating of at least 80 in the A.S.T.M. spray test after 1 and sometimes 2 launderings with soap and water or washings with such solvents. The products obtained by the procedure of Example 2 are quite resistant to loss of water repellence, often showing a spray test rating of at least 80 after as many as 3 launderings or 5 washings with trichloroethylene.

The process of the present invention is applicable to fabrics made from both natural and synthetic organic fibers. Among the fibers that have been treated to render them water resistant are silk, rayon, nylon, polyester (e.g. "Dacron" a trademark of E. I. du Pont de Nemours & Co.), cotton and linen. The amount of fatty acid-hydrous zirconia adsorbate found on the different fabrics after treatment according to the invention will, of course, vary with the type of fabric, as well as the solution concentrations and other process variables. However, in general, good results may be obtained with as little as about 1%. Ordinarily, amounts greater than about 3–5% will not be desirable since the flexibility and appearance of the fabric are unfavorably affected if an excessive amount of adsorbate is present. It should be noted in any case that all of the tested fabrics are rendered sufficiently water resistant by a double application as to warrant a spray test rating of 100. It is important, however, in carrying out the present process to remove from the fabric or textile, before subjecting it to the described procedure, any interfering sizing or other material that has been applied to the fabric or the yarns thereof. This can be done by any convenient method.

In carrying out the process of the invention, it may be preferred to use deionized water in making up the treating baths. Such use will prevent the precipitation of the soap in the first bath that may occur when hard water is employed as well as the formation of undesirable complexes with the zirconia. However, quite satisfactory results will usually be obtained if only the divalent cations are removed from the water and in most cases water regarded as soft can be used without further deionization with satisfactory results.

Although in carrying out the process of the present invention the fabric may be dipped first into either the soap solution or the ammonium zirconyl carbonate solution, the former is preferred. This ensures that all of the soap has reacted so that residual soap will not counteract the water-repellent effect. With the procedure described in the foregoing examples, the baths may be used for prolonged periods.

Since ammonium zirconyl carbonate in solution decomposes rather rapidly above about 50° C., it is expedient to hold the salt solution bath at a temperature below that point. Preferably, a bath temperature of about 20° C.–25° C. is employed. The soap solution may be used at any temperature up to boiling. For convenience, it is usually maintained at about 20° C.–25° C., although in some cases somewhat better results are obtained if the soap solution is maintained at about 50° C. The drying temperature employed after the first immersion in the salt solution is not critical, air drying, although slow, being satisfactory so far as imparting water repellence is concerned. On the other hand, the treated fabric after the second immersion in the salt bath must be dried at a temperature of at least 70° C. The drying temperature in this step is not critical, except as high temperatures may damage the coated textile, and may be as high as about 140° C., but a temperature of about 90° C. is preferred.

A rather wide variety of soaps may be used in preparing the treating bath for carrying out the present invention. Not only may sodium stearate be used, but also potassium and ammonium stearates as well as the sodium, potassium, and ammonium soaps derived from the 14 to 18 carbon fatty acids. For example, it has been demonstrated that water-soluble soaps of such fatty acids as myristic, palmitic, oleic, and linoleic acids, and the mixture of fatty acids found in tallow give quite satisfactory results. Very good results have also been obtained using a relatively pure commercial soap ("Ivy," a trademark of Procter & Gamble Co.), formed from a mixture of fatty acids. The concentration of the soap in the bath may range from about 1 g./l. to about 20 g./l., although from about 2 g./l. to 5 g./l. is preferred.

Although in the foregoing examples the zinc, copper, and mercury compounds employed are formed in situ in the solution of ammonium zirconyl carbonate, it will be understood that if desired they may be prepared separately and added to the ammonium zirconyl carbonate bath. The concentration of the ammonium zirconyl carbonate (calculated as Zr) is preferably maintained between about 3.5 g./l. and 7.5 g./l. but may be between about 1.5 g./l. and 30.0 g./l. The concentration of the zinc, copper, or mercury compound (calculated as the metal) may range from about 1.0 g./l. to about 20 g./l., but from about 2.5 g./l. to 5.0 g./l. is preferred. Preferably, when they are used, a ratio of Zn, Cu, or Hg to Zr of from about 1:10 to 1:1 is maintained. It is also preferred to maintain the pH of the salt bath at least as high as 8.5 since below that pH there is a tendency for solids to be deposited therein. A pH as high as 10.0 can be employed. The pH of the soap solution is commonly and preferably about 8.0.

The novel process of the present invention may also be employed for the treatment of inorganic textiles such as those produced from glass, asbestos, and refractory oxides. This is illustrated in the following example.

EXAMPLE 6

A woven glass fabric, such, for example, as one used for window curtains, after being heated to about 600° C. to remove the sizing material thereon, is subjected to the repeated dipping and drying treatment described in Example 1. When subjected thereafter to the A.S.T.M. Spray Test, the fabric has a rating of 100. This water repellence is maintained even after laundering with soap and water or cleaning with a solvent such as trichloroethylene. Variations from the treatment described in Example 1 such as those described in the other preceding examples may be employed if desired.

Glass surfaces on which a layer of fatty acid-hydrous zirconia adsorbate has been deposited and dried exhibit, in addition to water repellence, a resistance to scratching or galling when in contact with other glass surfaces and an improved adherence to many organic materials such as resins and adhesives. The treatment of glass fabrics by the process of the present invention consequently permits better bonding when such fabrics are used as reinforcing materials with resins.

It will be understood that the process of the present invention may be used in the treatment of textile yarns, both staple and monofilament, and non-woven fabrics, as well as in treating woven textiles.

Percentages and ratios as specified in the foregoing description and the appended claims are by weight except as otherwise specified.

We claim:

1. A textile having on the surface thereof a substantially continuous hydrophobic layer of fatty acid-hydrous zirconia adsorbate, said fatty acid containing from 14 to 18 carbon atoms, and characterized by a high degree of water repellence which is resistant to destruction by laundering with soap and water and washing with dry cleaning solvents, said adsorbate being present in amounts of from 1% to 5%, said layer of adsorbate including at least one compound of a metal selected from the group of zinc, copper, and mercury, the concentration of said metal in said textile ranging from a ratio of about 1:10 to 1:1 with respect to zirconium.

2. A textile as set forth in claim **1** in which said compound is a zinc compound.

3. A textile as set forth in claim **1** in which said adsorbate includes a mixture of fatty acids.

4. A textile as set forth in claim **1** in which said compound is a copper compound.

5. A textile as set forth in claim **1** in which said layer includes compounds of zinc and copper.

6. A textile as set forth in claim **3** in which said compound is a copper compound.

7. A textile as set forth in claim **3** in which said layer includes compounds of zinc and copper.

8. A process for producing a textile having on the surface thereof a substantially continuous hydrophobic layer of a fatty acid-hydrous zirconia adsorbate and characterized by a high degree of water repellence which is resistant to destruction by laundering with soap and water and washing with dry cleaning solvents, said process comprising the steps of (a) immersing a fabric in a first bath of an aqueous soap solution, the concentration of soap therein ranging from about 1 g./l. to about 20 g./l.; (b) wringing said fabric; (c) then immersing said fabric in a second bath comprising an aqueous solution of ammonium zirconyl carbonate, the cencentration of ammonium zirconyl carbonate (calculated as Zr) therein being between 1.5 g./l. and 30 g./l.; (d) wringing said fabric; (e) drying said fabric; then repeating steps (a), (b), (c), and (d), and finally (f), drying said fabric at a temperature of at least 70° C., said soap being a water-soluble soap of a fatty acid containing from 14 to 18 carbon atoms and the concentrations of said solutions being such as to impart a high degree of water repellence to said fabric.

9. A process as set forth in claim **8** in which the concentration of soap in said first bath ranges from about 2 g./l. to about 5 g./l. and the concentration of ammonium zirconyl carbonate (calculated as Zr) in said second bath is between about 3.5 g./l. and 7.5 g./l.

10. A process as set forth in claim **8** in which the final drying step is carried out at about 90° C.

11. A process as set forth in claim **8** in which said second bath also contains metal-including ions selected from the group tetramminezinc, tetramminecopper, and phenylmercury.

12. A process as set forth in claim **8** in which said second bath contains tetramminezinc ions.

13. A process as set forth in claim **8** in which second second bath contains tetramminecopper.

14. A process as set forth in claim **9** in which said second bath also contains metal-including ions selected from the group tetramminezinc, tetramminecopper, and phenylmercury.

15. A process as set forth in claim **9** in which said second bath contains tetramminezinc ions.

16. A process as set forth in claim **12** in which the ratio of zinc to zirconium in said second bath is from 1:10 to 1:1.

17. A textile as set forth in claim **3** in which said compound is a zinc compound.

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