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PROCESS FOR IMPARTING WATER-REPELLANCY TO TEXTILES

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This invention relates to a method of treating textile materials, more particularly it concerns a process which allows of rendering textile materials or the like hydrophobic.

According to the present invention compounds of polyvalent metals are caused to act on such materials to be rendered water repellent as have been treated with waxes and/or paraffins as well as with compounds containing hydrocarbon radicals of higher molecular weight, which compounds when heated are capable of forming urea derivatives containing hydrocarbon radicals of higher molecular weight.

Compounds of polyvalent metals suitable for performing the process of the present invention are those which have already been used in other hydrophobing processes, for instance, aluminum compounds, such as aluminum formate, aluminum acetate or aluminum sols, zirconium compounds, such as zirconium formate, zirconium acetate, zirconium soaps or zirconium sols, zirconium lactic acid or its alkali salts and similar complex salts, zirconium oxynitrate and zirconium oxychloride, the last mentioned salts being preferably buffered by means of sodium acetate and acetic acid or the like in order to obviate destruction of the fibers, furthermore salts of rare earth metals, acid chromium salts and nickel salts. Colorless salts of aluminum and zirconium are preferred; of these compounds those are most advantageously used which when applied in a 0.1 to 1.0% aqueous solution—the suitable mode of application—do not tend to form insoluble hydrolysates on heating to 50 to 60° C. Suitable waxes and paraffins are montan wax, ketones of higher fatty acids, polyethylenes, hard paraffins and the paraffins obtainable by the process of synthesizing gasoline according to Fischer-Tropsch.

Agents which when heated are capable of forming urea derivatives containing hydrocarbon radicals of higher molecular weight include, for instance, aliphatic isocyanates containing a hydrocarbon radical of ten or more carbon atoms as such or in mixture with amines or polyamines, furthermore mixtures of polyisocyanates of hydrocarbons of lower molecular weight with amines or polyamines containing hydrocarbon radicals of higher molecular weight. These agents are preferably applied in the form of their water soluble derivatives, such as the addition products of bisulfite to the isocyanates and their reaction products with formaldehyde as well as the reaction products of the amines with formaldehyde and bisulfite.

The treatment of the materials with waxes or paraffins and the agents capable of forming urea derivatives containing hydrocarbon radicals of higher molecular weight may be carried out in any desired manner. A suitable procedure consists, for instance, in soaking the materials with aqueous emulsions of waxes or paraffins and with aqueous solutions of the aforedefined agents squeezing the materials and drying them at elevated temperature; if water soluble amines of higher molecular

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weight form part of the agents mentioned, they may simultaneously serve as emulsifying agents for preparing the wax or paraffin emulsion.

Further particulars of suitable modes of treating textiles or the like with waxes or paraffins and the agents mentioned are described in German Specification No. 818,189 and in my copending application Ser. No. 212,191, filed February 21, 1951. The action of the compounds of polyvalent metals proposed according to the present invention may take place at any moment after the materials have been treated with the agents containing the hydrocarbon radicals of higher molecular weight. The materials are preferably soaked with aqueous solutions of the metal compounds and after squeezing dried at elevated temperature, generally at temperature of about 100° C. In case the materials are not sufficiently wetted they should be briefly pretreated with suitable wetting agents such as soaps, alkyl arylsulfonates or the like, and well rinsed with water.

If the action of the compounds of polyvalent metals on the materials takes place immediately after the materials have been treated with the agents containing hydrocarbon radicals of higher molecular weight, it is possible to dry the materials in the treatment with the agents mentioned at lower temperatures than would be practicable without the subsequent reaction of the metal compounds since it is sufficient to fix the agents mentioned to the materials to such an extent that they are not removed during the following action of the metal compounds.

The process of the present invention allows the obtaining of excellent hydrophobing effects which are very fast even to hydrocarbon solvents.

The following examples serve to illustrate the present invention without, however, being restricted thereto. Temperatures are in degrees of centigrade.

Example 1

To a solution of 25 g. of the addition product of sodium bisulfite to stearyl isocyanate in half a liter of water of 85° to which 7.5 cc. of 33% formaldehyde had been mixed, 3 cc. of a 10% sodium carbonate solution and, after two minutes, 2 cc. of formic acid are added. Into the weakly acid solution are introduced while stirring 100 cc. of an emulsion which contains per liter 25 grams of a paste of 24% of paraffin, 4.25% of ceresine, 7.75% of montanic acid ester, 5.2% of sodium oleate and 2.5% of the sodium salt of oleylmethylaminoethanesulfonic acid. Hereafter the emulsion is made up to 1 liter by adding water of 40°.

A rain coat material of cotton poplin is soaked with the above emulsion, squeezed so that the increase in weight is 65%, dried at 100° and heated to 120° for 5 minutes.

The poplin is wetted by dipping it into a 0.1% sodium carbonate solution of 45° for one hour or into a 0.1% sodium carbonate solution of 80° for ten minutes or into a 0.2% solution of the sodium salt of isobutyl naphthalene sulfonic acid of 45° for five minutes or into a solution of 45° containing per liter 1 gram of soap and 1 gram of sodium carbonate for five minutes. After rinsing the material well with lukewarm and subsequently cold water, and squeezing a 0.5% solution of zirconium acetate is caused to act thereon for one minute whereupon the material is squeezed again and dried at 100°.

In each case a water repellent effect is obtained on the material which does not disappear even on repeated treatment with gasoline.

Example 2

A rain coat made of cotton poplin which had been

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treated with an emulsion prepared according to Example 1 is washed with a soap solution, thoroughly rinsed with warm and cold water and squeezed. The material is then put into a bath for some time, which contains 5 grams of zirconium acetate per liter, squeezed, dried by hanging in the air and ironed hot.

The coat treated with the zirconium salt as described above possesses a good water repellent effect which is retained even on treatment with hydrocarbon solvents. Materials not treated with the metal salt lose their water repellent effect in the second washing.

Example 3

A textile fabric of polyamide boiled in a 0.1% sodium carbonate solution is soaked with an emulsion prepared according to Example 1, but made up to 800 cc. only, squeezed so that the increase in weight is 50% and dried at 100°.

Thereafter the fabric is treated with a 0.3% soap solution of 45° C. for one minute, well rinsed with warm and cold water, squeezed again. Then the fabric is put in a 0.3% solution of zirconium acetate for one minute. After squeezing and drying at 100° the water repellent effect of the fabric is fast to hydrocarbon solvents.

The material thus treated absorbs 6.7% of water prior to the treatment with carbon tetrachloride, and 5.4% after treating five times with carbon tetrachloride, whereas the fabric soaked with the same emulsion, squeezed and dried at 120°, but not subjected to the action of the zirconium salt absorbs 17% and 20% of water respectively.

Example 4

A dyed twilled fabric of cotton is soaked with an emulsion prepared according to Example 1, but without the addition of formaldehyde; the material is then treated as described in Example 3. The resistance of the water repellent effect to hydrocarbon solvents is substantially improved by the zirconium salt. The material sprayed under equal conditions absorbs

	treatment with zirconium salt	
	without	with
	Percent	Percent
after washing once with carbon tetrachloride.....	13	7.8
after washing three times with carbon tetrachloride..	16.5	10.2
after washing five times with carbon tetrachloride..	16.3	10.3

Example 5

To an emulsion which has been prepared according to Example 1, but without the addition of formaldehyde and which has been made up to 800 cc., a solution of 1.475 grams of hexamethylene diamine in the form of the formaldehyde bisulfite compound is added, which has been prepared by heating to 70° one molecular proportion of hexamethylene diamine with two molecular proportions of a mixture of molecular parts of formaldehyde and sodium bisulfite in a concentrated solution.

After making up the emulsion to one liter rain coat material of cotton poplin is soaked therewith and squeezed so that the increase in weight amounts to 65%; the material is dried at 100° and for comparison a part thereof at 140° for a further six minutes.

The part dried only at 100° is wetted with a 0.3 soap solution of 45° and well rinsed with warm and cold water. A solution of 50° which contains per liter 10 grams of zirconium oxychloride, 6 cc. of glacial acetic acid and 2.5 grams of sodium carbonate is caused to act on the material which is still wet. After squeezing the material is dried at 100° for ten minutes.

The material possesses a water repellent effect which is very fast to organic solvents. When subjected to sprav-

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ing it absorbs 9% of water before it has been treated with carbon tetrachloride and 12% and 13% respectively after it has been treated once or five times with carbon tetrachloride whereas that part of the material which had been heated to 140° but not aftertreated with the zirconium salt absorbs under the same conditions 8% before and 18% of water after treating with carbon tetrachloride.

Example 6

3 cc. of a 10% sodium carbonate solution and after two minutes 2 cc. of formic acid are added to a solution of 25 grams of the addition product of sodium bisulfite to stearyl isocyanate in half a liter of water of 85°. To the solution 100 cc. of an emulsion of 80° are added while stirring, which contains per liter 25 grams of a paste containing 32% of paraffin, 4% of ceresine, 4% of montan wax and 7.5% of an emulsifying agent obtained by the addition of three molecular proportions of the sodium salt of hydroxymethanesulfonic acid to one molecular proportion of stearyl dipropylene triamine. The emulsion is then made up to 1 liter by adding lukewarm water.

Raincoat material of cotton poplin is soaked with this emulsion, squeezed so that the increase in weight amounts to 65% and dried at 100°. The material is then wetted with a 45° hot 0.3% soap solution, well rinsed with warm and cold water, squeezed and passed through a 0.5% solution of zirconium acetate. After squeezing the material is dried at 100°. The poplin fabric possesses excellent water repellent properties which are even fast to organic solvents.

Example 7

A fabric of cotton poplin is soaked with the emulsion described in Example 1 and dried at 90 to 100°. Then the material is treated on the padding machine with an emulsion of 75°, which has been prepared by stirring a solution of 5 grams of curd soap in 100 cc. of water of 80° into a solution of 10 grams of zirconium oxychloride in 200 cc. of water of 70°, buffing the solution with 6 cc. of glacial acetic acid and 25 cc. of 10% sodium carbonate solution and making the mixture up to one liter. The material is wetted at once; it is then squeezed and dried at 100° for ten minutes. The fabric shows a very good water repellent effect; its fastness to hydrocarbon solvents is equal to that achieved according to Example 1.

Example 8

A fabric of cotton poplin is soaked with an emulsion containing 2.56% of paraffin, 0.32% of ceresine, 0.32% of montanic acid ester, 0.32% of stearyl dipropylene triamine in the form of the formaldehyde-bisulfite addition product and 1.2% of the addition product of two molecular proportions of bisulfite to one molecular proportion of hexamethylene diisocyanate. After squeezing the material so that the increase in weight amounts to 65% it is dried at 100° and one part of the material heated to 140° for a further six minutes.

The material dried at 100° is treated on the padding machine with an aqueous solution of 45° which contains per liter 5 grams of zirconium oxychloride, 6.5 cc. of 60% acetic acid and 1.25 grams of sodium carbonate. After drying on the stretching frame at about 100° the material shows the same good water repellent effect as the material which had been subjected to further heating at 140° but not to the action of the zirconium salt; the effect obtained on the material treated with the zirconium salt is, however, considerably faster to soap washings as well as to the usual hydrocarbon solvents.

A coat manufactured from the material heated to 140° may be subjected to such an action of zirconium salts even after a usual household washing. For this purpose the material is well rinsed with warm and cold water after the soap washing and before it is subjected to the action of the zirconium salt in the manner indicated; it is not necessary that the coat is dry. Then the material is dried

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by hanging in the air and ironed hot. A coat which occasionally after soap washings is treated with zirconium salts in the herein described manner is rain proof and shows an excellent water repellent effect.

Instead of the zirconium oxychloride the other metal compounds mentioned above may likewise be applied with similar success. For the action on dark colored poplin, for instance, a 0.2% solution of a basic complex salt of the Werner type containing stearic acid as described in U. S. specification 2,273,040 is suited, the solution being buffered by the addition of formic acid, sodium formate and urea.

Example 9

A fabric of acetate rayon is rinsed with a hot 0.1% sodium carbonate solution soaked on the padding machine with an emulsion prepared according to Example 8, squeezed so that the increase in weight is 50% and dried at 100° for five minutes.

The material is then wetted with a solution of 55° containing per liter 5 grams of zirconium oxychloride, 10 cc. of 30% acetic acid and 1.25 grams of sodium carbonate and dried again at 100°. The fabric possesses now a water repellent effect which is completely fast to washing, a result which cannot be achieved without the action of the metal salt.

Example 10

A rain coat material made from staple rayon is soaked with an emulsion prepared according to Example 8, squeezed so that the increase in weight amounts to 90%, dried at 100° and heated to 130° for 6 minutes. Then the fabric is soaked with a solution of zirconium oxychloride as used in Example 9, squeezed and dried at 100°.

The material shows an excellent water repellent effect which is fast to washing. Without the action of the zirconium oxychloride the fastness to washing of the water repellent effect is inferior.

I claim:

1. A process for imparting water repellency to textile materials which comprises contacting said textile materials with water-soluble salts of metals which are at least trivalent, subsequent to treatment with a mixture of (I) at least one wax and (II) compounds of the group consisting of (1) addition products of sodium bisulfite to an aliphatic isocyanate containing a hydrocarbon radical of at least 10 carbon atoms, (2) reaction products of formaldehyde with the addition product of sodium bisulfite to an aliphatic isocyanate containing a hydrocarbon radical of at least 10 carbon atoms, (3) addition products of sodium bisulfite to an aliphatic isocyanate containing a hydrocarbon radical of at least 10 carbon

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atoms, in mixture with an aliphatic amine of molecular weight in the form of its formaldehyde-bisulfite-compound, and (4) diisocyanates containing a hydrocarbon radical of less than 10 carbon atoms, in mixture with an aliphatic amine containing a hydrocarbon radical of at least 10 carbon atoms which amine is present in the form of its formaldehyde-bisulfite-addition product; heating and drying the materials contacted.

2. A process for imparting water repellency to textile materials which comprises contacting said textile materials with at least one wax and (II) compounds of the group consisting of (1) addition products of sodium bisulfite to an aliphatic isocyanate containing a hydrocarbon radical of at least 10 carbon atoms, (2) reaction products of formaldehyde with the addition product of sodium bisulfite to an aliphatic isocyanate containing a hydrocarbon radical of at least 10 carbon atoms, (3) addition products of sodium bisulfite to an aliphatic isocyanate containing a hydrocarbon radical of at least 10 carbon atoms, in mixture with an aliphatic amine of molecular weight in the form of its formaldehyde-bisulfite-compound, and (4) diisocyanates containing a hydrocarbon radical of less than 10 carbon atoms, in mixture with an aliphatic amine containing a hydrocarbon radical of at least 10 carbon atoms with amine is present in the form of its formaldehyde-bisulfite-addition product, heating and drying the contacted materials, then contacting said dried materials with water-soluble salts of metals which are at least trivalent and reheating.

3. Process according to claim 1 wherein zirconium compounds are used as polyvalent metal compounds.

4. Process according to claim 1 wherein zirconium acetate is used as polyvalent metal compound.

5. Process according to claim 1 wherein zirconium oxychloride in an aqueous medium buffered by means of sodium acetate and acetic acid is used as polyvalent metal compound.

6. Process according to claim 1 wherein reaction products of formaldehyde with the addition product of sodium bisulfite to an aliphatic isocyanate containing a hydrocarbon radical of at least 10 carbon atoms are used.

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