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PROCESS FOR RENDERING TEXTILES WATER-REPELLENT

Edgar Wolf, Krefeld, Germany, assignor to Heberlein Patent Corporation, New York, N. Y., a corporation of New York

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6 Claims. (Cl. 8—115.5)

This invention relates to processes for producing water-repellence in textile materials and to products therefrom. It also relates to processes for the production of chemicals for producing water-repellence and to products therefrom.

I have found, in accordance with my invention, that water-repellence may be produced in textile materials by suitable treatment of them with alpha-methyl-halide derivatives obtained from fatty acid or naphthenic acid amides or alkylamines which contain an aliphatic radical of at least 10 carbon atoms, formaldehyde or its polymers, a hydrogen halide, and a tertiary amine. As described more in detail below, the compounds are prepared by reacting one mol of amide with two mols of formaldehyde (two-thirds of a mol of trioxy-methylene may be employed, for example) in the presence of a hydrohalic acid. The compounds are then rendered water-soluble by subsequent treatment with a tertiary amine. Where the amide is a methylol amide, one mol of formaldehyde is used instead of two mols.

An object of the invention, accordingly, is to provide an improved process for producing water-repellence in textiles employing materials of the type mentioned and producing an improved series of water-repellent textiles thereby.

Another object is to provide a simple process for the manufacture of chemicals for producing such water-repellence and an improved series of such chemicals.

The invention, accordingly, consists in the novel products as well as the novel processes and steps of processes according to which such products are manufactured, the specific embodiments of which are described hereinafter by way of example and in accordance with which I now prefer to practice the invention.

In accordance with my invention, I have found that the alpha-methyl-halide derivatives mentioned above may be employed either in a non-aqueous solvent such as benzine or in water solution. In the latter case I prefer to employ the quaternary ammonium compounds mentioned above, produced by combining the alpha-methyl-halide derivatives with pyridine.

The process is applicable, not only to cellulose, such as cotton, or cellulose-derivative fiber material, such as the various forms of artificial silk, but may also be applied to wool.

In the treatment of artificial silk there is secured not only a water-repelling effect, but there also is effected a diminution of the capability of swelling in the presence of the swelling agents and an increase in resistance to wetting. The effects produced on textiles in accordance with my invention are resistant to dry cleaning and washing with soap. A remarkable feature in all the above-mentioned treatments or impregnations is the improvement which goes parallel therewith in the fastness, particularly in the fastness to washing, and the increase in wet tensile strength of artificial silk and an increase in the fastness of the dyes and in particular of the fastness to washing of the dyed fibres. These materials resist shrinking when subjected to mild shrinkage as in laundering and also more severe shrinkage by concentrated caustic alkali.

If aqueous solutions of the aforesaid compounds are employed, there may also be added to such compouds the water-soluble buffer salts of the alkalis or alkaline earths with weak acids, such as sodium acetate and similar compounds. By means of these additions, possible damage to the fiber, particularly at high temperatures, is avoided. When operating at higher temperatures, the action between the textile material and the alpha-methyl-halide derivatives is accelerated and may be satisfactorily completed for water-repellent purposes in a shorter time than where lower temperatures are employed.

In consequence of the water-solubility of the quaternary ammonium compounds of my invention, the treatment of the textile material for the purpose of increasing the resistance to wetting or water-repellence and diminution of swelling capacity can advantageously be combined with a treatment for increasing the resistance to wrinkling, which is ordinarily carried out also in an aqueous bath; thus, for the purpose of imparting water-repelling properties and wrinkle-resistance, a single aqueous bath may be employed containing not only the said quaternary ammonium compounds of my invention but also artificial resin or artificial resin initial condensation product or the formative components for the preparation of an artificial resin. Formaldehyde with ammonium chloride or other non-alkaline catalyst may be employed in place of the resin or resin components for producing wrinkle-resistance, and with this may be employed the quaternary ammonium compounds of my invention for producing water-repellence. The processes thus employed in combination will produce a textile material having both water-repellence and wrinkle-resistance.

The following are examples of my invention for producing water-repellence in textiles as I now prefer to practice it. The examples are illus-

trative and the invention is not to be considered as limited thereto except as indicated in the appended claims.

Examples

1. A cloak fabric which consists of spun rayon in warp and weft is impregnated in an aqueous solution which contains, per liter, 15 grams of the quaternary pyridinium compound of the methyl chloride derivative prepared from stearic acid amide $C_{17}H_{35}.CO.NH_2$ trioxymethylene (CH_2O) x and dry hydrogen chloride, as more specifically described hereinafter. The temperature of the bath is about 40° C. (104° F.). After the impregnation the material is dried and is then subjected for approximately six hours to a heat treatment in a drying chamber at about 90° C. (194° F.).

2. To an aqueous solution of 15 grams per liter of the quaternary pyridinium salt in accordance with Example 1 there are added 4 grams per liter of sodium acetate. An acetate satin having a warp of acetate salt and a weft of viscose crepe is impregnated in this solution, dried, and exposed for about 5 minutes to a temperature of about 120° C. (248° F.).

3. A dress material, having a warp of dull-spun viscose and a weft of cellulose crepe, is impregnated in an aqueous solution which contains, per liter, 15 grams of the quaternary pyridinium compound of the methyl chloride derivative prepared from stearic acid methylol amide,

$$C_{17}H_{35}\cdot CO\cdot NH\cdot CH_2OH$$

trioxymethylene, and dry hydrogen chloride, as more specifically described hereinafter. The temperature of the bath is about 40° C. (104° F.). After the impregnation the material is dried and then subjected for about six hours to a heat treatment at about 90° C. (194° F.) in a drying chamber.

4. Undyed, unbrightened, loose spun rayon is introduced into an aqueous bath heated to about 40° C. containing per liter 15 grams of the montanyl compound described below in Example 11. The spun rayon remains for about 5 minutes in this bath, is then removed, centrifuged and dried at 90° C. After the drying has taken place the spun rayon is preferably heated for several hours at 90° C. The spun rayon which has been treated in this way shows a water-repellence which resists washing with soap and water and also resists dry-cleaning by benzine. In the presence of soap or other wetting agents the water-repellent material so produced may be dyed hot; after thorough rinsing of the wetting agent or soap the water-repellent effect reappears.

5. In an aqueous solution which contains 15 grms. per liter of the same compound as in Example 1 and 5 grams per liter of sodium acetate a raincoat material consisting of mercerised cotton is treated at a temperature of about 50° C. Following the impregnation it is wrung out, dried, and subjected for few hours to a temperature of 90° C. The material thus treated is permanently water-repellent.

6. A cloak fabric of pure wool is impregnated in an aqueous solution which contains 15 grms. per liter of the same compound as in Example 1. Following the impregnation it is wrung out, dried, and subjected for a few hours to a temperature of 90° C. The material thus treated is permanently water-repellent.

7. A fabric, suitable for rucksacks, consisting of linen and cotton is impregnated in an aqueous solution which contains, per liter 15 grams of the quarternary pyridinium compound of the methylchloride derivative prepared from a mixture of bicyclic naphthenic acid amides of high molecular weight trioxymethylene, and dry hydrogen chloride, as more specifically described hereinafter. There are added 4 grams per liter of sodium acetate. The temperature of the bath is about 40° C. (104° F.) After the impregnation the material is dried and then subjected for about six hours to a heat treatment at about 90° C. (194° F.) in a drying chamber.

8. A plush fabric, consisting of cotton in warp and weft and artificial silk spun fiber in the pile, is passed through an aqueous bath which contains, per liter, 250 grams of a formaldehyde-urea condensation product which is on the market under the name "Kaurit," 6 grams of primary sodium phosphate, 6 grams of secondary sodium phosphate, 2 grams of tartaric acid, and 15 grams of the quaternary pyridinium salt obtained by double decomposition of pyridine with the methyl chloride compound formed from montanic acid, amide, $C_{28}H_{57}\cdot CONH_2$ trioxymethylene, and dry hydrochloric acid, as more specifically described hereinafter.

After the impregnation the material is squeezed out, brushed, and treated for about 5 minutes at about 140° C. (284° F.). In this manner the fabric receives a water-repelling and wrinkle-resistant finish, in which connection the water-repelling effect is proof to dry-cleaning and washing with soap.

9. A sample of transparent velvet comprising a silk backing and viscose rayon pile is passed through an aqueous bath at 40° C. for 2 seconds which contains per liter:

400 cc. of formaldehyde 40% solution
5 grams of ammonium chloride and
15 grams of the quaternary pyridinium salt obtained by double decomposition of pyridine with the methyl-chloride compound formed from stearic acid amide, trioxylmethylene, and hydrochloric acid, as more specifically described hereinafter.

After the impregnation the material is squeezed out, brushed, and heated for about 5 minutes at about 140° C. (284° F.). In this manner the fabric receives a water-repelling and wrinkle-resistant finish, in which connection the water-repelling effect is proof even to dry-cleaning and washing with soap.

In order to remove a slight odor of pyridine remaining on the fabric in all the above examples, the impregnated and dried fabric is passed for 5–10 minutes through an aqueous bath containing 1 gram per liter of soap or ammonia at about 50° C. Then the fabric is rinsed and dried.

In accordance with my invention, I have also devised a process for producing chemicals which may be employed for water-repellence, and I will now describe this part of my invention.

It is known to prepare condensation products by reaction of fatty acid amides with aldehydes in the presence of acids or salts having an acid reaction, as, for example, as set forth in French Patent No. 792,589. However, the products obtained by this process are insoluble in water and cannot be brought into water-soluble form, even with the aid of tertiary amines. The melting point of the finished compounds lies substantially higher than that of the fatty acid amide which is employed. Furthermore, the condensation

products which are obtained are difficult to dissolve or insoluble in organic solvents.

In contradistinction to the condensation products prepared by the process of the said French patent, the methyl-halide derivatives produced in accordance with my invention have a melting point which is generally still substantially below that of the starting material. These methyl-halide derivatives are easily soluble in organic solvents. Their quaternary ammonium compounds are soluble in water.

I have discovered, in accordance with my invention, that hydrogen halide or halogen may be combined with fatty acid amides or alkylamines in the presence of formaldehyde or its polymeric form, such as trioxymethylene, to produce methyl-halide derivatives of the fatty acid amides or alkylamines, which differ from the above-mentioned products of the French patent and may be employed in the above processes for producing water-repellence.

In place of the fatty acid amides given, the methylol compounds of the fatty acid amides may also be employed. In the case of the employment of the last-mentioned compounds, the methyl chloride compound, for example, can be obtained with and without the addition of trioxymethylene. Instead of fatty acid amides, I may employ naphthenic acid amides, but in either group only such amides are to be employed as have a saturated alkyl radical of at least 10 carbon atoms. By alkylamines only such alkylamines are to be understood as have a saturated alkyl radical of at least 10 carbon atoms.

These methyl-halide derivatives may be converted with the aid of tertiary amines into water-soluble compounds which can be employed to impregnate textiles.

The following are examples of methods for producing the reaction products of my invention as I now prefer to practice it. These examples are illustrative and the invention is not to be restricted thereto except as indicated in the appended claims.

Examples

10. Into a mixture, at a temperature of about 40° C. (104° F.), of 284 grams of stearic acid amide, 1500 grams of benzene, and 60 grams of trioxymethylene, dry hydrochloric acid gas is introduced until the formation of the methyl chloride compound takes place, which is recognizable purely externally by the clearing-up of the benzene solution. The reaction water collected at the bottom of the vessel is drained off, the benzene and the excess hydrochloric acid are driven off in a vacuum, and the methyl chloride compound obtained. It has a melting point of about 55° C. (131° F.). The product so obtained may be used as such or may be combined with a tertiary amine to produce a water-soluble product. For this purpose, it is stirred with 90 grams of pyridine at about 100° C., whereupon the pyridine compound is formed, which is soluble in water.

11. Into a mixture, at a temperature of 45° C. (113° F.), of 422 grams of montanic acid amide, 2000 grams of benzene, and 60 grams of trioxymethylene, dry hydrochloric acid gas is introduced until the formation of the methyl chloride compound takes place. The latter is treated as stated in Example 10 and is stirred with 90 grams of pyridine.

12. Into a mixture, at a temperature of 45° C. (113° F.), of 314 grams of stearic acid methyol amide, 1500 grams of benzene, and 30 grams of trioxymethylene, dry hydrochloric acid gas is introduced until the formation of the methyl choride compound takes place. The latter is treated as stated in Example 10 and is stirred with 90 grams of pyridine.

13. Into a mixture, at a temperature of 45° C. (113° C.), of 314 grams of stearic acid methylol amide, 1500 grams of benzene, dry hydrochloric acid gas is introduced until the formation of the methyl chloride compound takes place. The latter is treated as stated in Example 10 and is stirred with 90 grams of pyridine.

14. Into a mixture, at a temperature of about 40° C. (104 F.), of 284 grams of stearic acid amide, 1500 grams of benzene, and 60 grams of trioxymethylene, chlorine gas is introduced until the formation of the methyl chloride compound takes place, which is recognizable purely externally by the clearing-up of the benzene solution. The reaction water collected at the bottom of the vessel is drained off, the benzene and the excess chlorine are driven off, in a vacuum, and the methyl chloride compound obtained. It has a melting point of about 55° C. (131° F.) The product so obtained may be used as such or may be combined with a tertiary amine to produce a water-soluble product. For this purpose, it is stirred with 90 grams of pyridine at about 100° C., whereupon the pyridine compound is formed which is soluble in water.

15. Into a mixture, at a temperature of about 40° C. (104° F.), 1500 grams of benzene, and 260 grams of bicyclic naphthenic acid amides of high molecular weight, and 60 grams of trioxymethylene dry hydrochloric acid gas is introduced until the formation of the methyl chloride compound takes place, which is recognizable purely externally by the clearing-up of the benzene solution. The reaction water collected at the bottom of the vessel is drained off, the benzene and the excess hydrochloric acid are driven off in a vacuum, and the methyl chloride compound obtained. It has a melting point of about 55° C. The latter is treated as stated in Example 10 and is stirred with 90 grams of pyridine.

16. Into a mixture, at a temperature of about 40° C. (104° F.), of 269 grams of octadecylamine $C_{18}H_{37}NH_2$, 1500 grams of benzene, and 60 grams of trioxymethylene, dry hydrochloric acid gas is introduced until the formation of the methyl chloride compound takes place. The latter is treated as stated in Example 10 and is stirred with 90 grams of pyridine.

The pyridinium products produced in accordance with the above examples are all water-soluble. When the process is conducted employing one mol of amide to two-thirds of a mol of trioxymethylene (or its equivalent, two mols of formaldehyde), and the process is conducted in two stages, the first of which is the production of the compound of the amide with the formaldehyde and acid compound followed by the second stage, namely, combination with the tertiary amine, the products obtained form thinly fluid water solutions which do not readily gelatinize on standing.

Both the fatty acid amide compounds disclosed, for instance, in Examples 1, 2, 10 and 11, and the fatty acid methylol amide compounds disclosed, for instance, in Examples 3, 12, and 13, function to give approximately the same results and I regard them as substantial equivalents.

The amount of the reaction product deposited when uncombined with a tertiary amine in Examples 1 to 8 on the textile material will natur-

ally vary with the weight of the material and its other characteristics. I have found that, ordinarily, an amount equal to 0.5-1.5 per cent of the material is sufficient to give the effect. When combined to form a quaternary ammonium salt, approximately 1 to 2 per cent, based on the weight of the material, will give the desired effect.

The textiles produced in accordance with the above examples show a high degree of water-repellence. They show improved properties with respect to known textiles treated with fatty acid chlorides and fatty acid anhydrides, including greater durability towards dry-cleaning with benzine and soap washing. The feel and hang of the materials having water-repellence as produced above is not substantially altered. In addition, the artificial silks have resistance to swelling agents and wetting agents. The materials produced in accordance with my invention which show both water-repellence and wrinkle-resistance also have similar improved water-repellent characteristics along with their resistance to wrinkling, and the feel and hang of these materials is also not substantially altered.

The process for producing these water-repellent and wrinkle-resistant textiles may be carried out with simple apparatus and in a relatively short time.

The process of the invention for the manufacture of the chemicals may be carried out with simple apparatus at relatively small expense.

The term "halogen" as used in the appended claims is intended to include halogen elements, such as chlorine, or bromine, as well as hydrochloric, hydrobromic and hydriodic acid.

The expression "textile material" is intended to cover fibers, yarns, fabrics including velvets and other pile fabrics or other forms of cotton, jute, linen, hemp or rayon, including viscose, cuprammonium or other precipitated cellulose or derivatives of cellulose such as acetyl cellulose and wool.

Subject matter described but not herein claimed is claimed in my copending application Serial No. 279,659, filed June 17, 1939.

While the invention has been described in detail according to the preferred manner of carrying out the process, it will be obvious to those skilled in the art, after understanding the invention, that changes and modifications may be made therein without departing from the spirit or scope of the invention, and it is intended in the appended claims to cover all such changes and modifications.

What is claimed as new and desired to be secured by Letters Patent is:

1. A process for ennobling textile material which comprises impregnating the material with the reaction product of stearic acid amide, two-thirds of a mol of trioxymethylene for each mol of amide, and hydrochloric acid, rendered water-soluble by subsequent treatment with pyridine, and heating the impregnated textile so treated to a temperature above about 90° C. for a sufficient time to drive off said pyridine and hydrochloric acid, thereby producing water-repellence in said textile material.

2. A process for ennobling textile material which comprises impregnating the material with the reaction product of stearic acid methylol amide, one-third of a mol of trioxymethylene for each mol of the amide, and hydrochloric acid, rendered water-soluble by subsequent treatment with pyridine, and heating the impregnated textile so treated to a temperature above about 90° C. for a sufficient time to drive off said pyridine and hydrochloric acid, thereby producing water-repellence in said textile material.

3. A process for ennobling textile material which comprises impregnating the material with a reaction product formed by combining an amide containing a naphthenic radical having an alkyl radical of at least 10 carbon atoms with two-thirds of a mol of trioxymethylene for each mol of the amide, and a hydrohalic acid, rendered water-soluble by subsequent treatment with a tertiary amine, and then heating the impregnated material in the absence of moisture thereby producing water-repellence in said textile material.

4. A process for ennobling textile material which comprises impregnating the material with a reaction product of a fatty acid methylol amide containing at least 10 carbon atoms in the fatty acid radical, one-third of a mol of trioxymethylene for each mol of amide used, and a hydrohalic acid, rendered water-soluble by subsequent treatment with a tertiary amine, and then heating the impregnated material in the absence of moisture, thereby producing water-repellence in said textile material.

5. A process for ennobling textile material which comprises impregnating the material with an aqueous solution of a reaction product prepared by combining an amide having an aliphatic radical of at least 10 carbon atoms with two-thirds of a mol of trioxymethylene for each mol of amide and a hydrohalic acid, rendered water-soluble by subsequent treatment with a tertiary amine, and then heating the impregnated material in the absence of moisture to produce water-repellence therein.

6. A process for ennobling textile material which comprises impregnating the material with a reaction product of an amide selected from the group consisting of: a fatty acid amide and a fatty acid methylol amide, said amide containing at least ten carbon atoms in the fatty acid radical, trioxymethylene in the proportion of two-thirds of a mol thereof for each mol of fatty acid amide and one-third of a mol thereof for each mol of fatty acid methylol amide, and a hydrohalic acid, rendered water-soluble by subsequent treatment with a tertiary amine, and then heating the impregnated material in the absence of moisture, to produce water-repellence in said textile material.

EDGAR WOLF.

CERTIFICATE OF CORRECTION.

Patent No. 2,294,435. September 1, 1942.

EDGAR WOLF.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, first column, line 23, Example 2, for "acetate salt" read --acetate silk--; page 3, second column, line 7, Example 13, for "113° C." read --113° F.--; line 14, Example 14, for "104 F." read --104° F.--; line 75, for the numeral "8" read --9--; for the claims now numbered 1, 2, 3, 4, 5 and 6 read 4, 5, 6, 3, 1 and 2 respectively; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 6th day of October, A. D. 1942.

(Seal)

Henry Van Arsdale,
Acting Commissioner of Patents.