

## UNITED STATES PATENT OFFICE

2,380,133

PROCESS FOR RENDERING TEXTILES  
WATER-REPELLENT

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7 Claims. (Cl. 8—116.2)

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. Applicant Serial No. 533,102, filed April 27, 1944, covers such processes and products.

In the copending application of Edgar Wolf, Serial No. 177,054, filed November 29, 1937, now Pat. No. 2,294,435, there is described the preparation of compounds from alpha-methyl halide derivatives obtained from higher fatty acid or naphthenic acid amides or their methylol compounds, or higher alkyl amines with formaldehyde or its polymers and a halogen or hydrogen halide; and the use of these materials for combining with textile materials.

We have found in accordance with the herein-described invention that the above-described reaction can be extended to an additional series of nitrogenous derivatives of the higher fatty acids having at least ten carbon atoms and that these materials can be employed for combination under suitable conditions with textile materials. We prefer to employ these materials in water-soluble form and this may be effected by employing them as their quaternary ammonium compounds.

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 to produce 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. Other objects will be in part obvious and in part pointed out hereinafter.

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

We have found suitable for our purpose in carrying out the treatment of textiles, the nitrogenous derivatives of higher fatty acids which con-

tain a removable hydrogen atom linked to nitrogen or oxygen. Further there can be employed the nitrogenous derivatives of carbon dioxide which contain an aliphatic radical of at least ten carbon atoms. Accordingly for example hydroxamic acids, amidines, urethanes, hydrazides, derivatives of urea or dimethylol-urea which are acylated unilaterally with higher fatty acid chlorides, or which are acylated unilaterally with higher fatty chlorocarbonic acid esters may be employed. The aforesaid compounds are converted preferably by combining the derivatives just mentioned with trioxymethylene or formaldehyde or other polymer with a halogen material such as hydrochloric acid gas, thereby converting into methyl chloride compounds, and the latter are converted by double decomposition with tertiary bases into water soluble quaternary ammonium compounds. As methyl chloride compounds they are particularly suitable for the etherification of cellulose or cellulose derivative fibrous material.

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 be also applied to animal fibers such as 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 our invention are resistant to dry cleaning and washing with soap. A remarkable feature in all the treatments or impregnations made in accordance with our invention is the increase in wet tensile strength of artificial silk and an increase in the fastness of the dyes on all textiles, and particularly the fastness to washing of dyed textiles of various types including cotton, artificial silk and animal fibers. These materials resist shrinking when subjected to mild shrinking 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 compounds 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 reaction 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.

The following examples are illustrative and the invention is not to be considered as limited thereto except as indicated in the appended claims.

#### Examples for textile treatment

1. A fabric for wearing apparel made of spun rayon (viscose) is passed through an aqueous solution which contains 20 grams per liter of a quaternary pyridinium compound of the methyl chloride derivative prepared from carbamic ester of octadecylalcohol  $C_{18}H_{37}O.CO.NH_2$  trioxymethylene  $(CH_2O)_x$  and dry hydrogen chloride, as more specifically described hereinafter. The said fabric is passed through the said aqueous solution while the latter is at about 35° C. Thereafter the impregnated material is dried and thereupon subjected to heat treatment in a drying chamber at about 95° C. for 5 hours.

2. Dyed cotton yarn is introduced at 50° C. into an aqueous solution of 15 grams per liter of the quaternary pyridine compound of the methyl chloride derivative prepared from stearyl urea  $C_{17}H_{35}.CO.NH.CO.NH_2$  trioxymethylene  $(CH_2O)_x$  and dry hydrogen chloride, as more specifically described hereinafter. The bath also contains 4 grams per liter of sodium acetate. After the impregnation the yarn is centrifuged, dried and thereupon subjected to heat treatment in a drying chamber at about 95° C. for 5 hours.

3. Bleached wool gabardine is passed through an aqueous solution which contains 20 grams per liter of a quaternary pyridinium compound of the methyl chloride derivative prepared from allophanic ester  $C_{18}H_{37}O.CO.NH.CO.NH_2$  trioxymethylene  $(CH_2O)_x$  and dry hydrogen chloride, as more specifically described hereinafter. The said fabric is passed through the said aqueous solution while the latter is at about 40° C. Thereafter the impregnated material is dried and thereupon subjected to heat treatment in a drying chamber at about 85° C. for 6 hours.

4. Cotton calico is passed through an aqueous solution which contains 15 grams per liter of a quaternary pyridinium compound of the methyl chloride derivative prepared from stearic acid hydrazide  $C_{17}H_{35}.CO.NH.NH_2$  trioxymethylene  $(CH_2O)_x$  and dry hydrogen chloride; as more specifically described hereinafter. The said fabric is passed through the said aqueous solution while the latter is at about 40° C. Thereafter the impregnated material is dried and thereupon subjected to heat treatment in a drying chamber at about 85° C. for 6 hours.

5. A plush fabric, consisting of cotton in warp and weft an 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 pyridine salt obtained by double decomposition of pyridine with the methyl chloride compound formed from carbamic ester of octadecylalcohol  $C_{18}H_{37}O.CO.NH_2$  trioxymethylene  $(CH_2O)_x$  and dry hydrogen chloride, as more specifically described hereinafter. The said fabric is passed through the said aqueous solution while the latter is about 35° C. Thereafter the impregnated material is squeezed out, brushed, and dried. The material is subjected

to a heat treatment in a drying chamber at about 120° C. for 2 hours, then.

#### Examples for chemicals

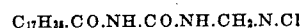
6. Into a mixture at a temperature of about 20° C. of 313 grams of carbamic ester of octadecylalcohol  $C_{18}H_{37}O.CO.NH_2$  1500 grams of benzene, and 60 grams of trioxymethylene, dry hydrochloric acid gas is introduced until the formation of the methyl chloride compound takes place. The reaction water which has 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 which is obtained is stirred with 100 grams of pyridine at room temperature. The quaternary pyridinium salt of the methyl chloride derivative of carbamic ester of octadecylalcohol is formed having the formula:



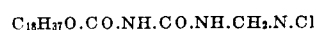
7. Into a mixture, at a temperature of about 20° C., of 327 grams of stearyl urea



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. This compound is treated as stated in Example 6 and is stirred with 100 grams of pyridine at room temperature. The quaternary pyridinium salt of the methyl chloride derivative of stearyl urea is formed having the formula:



8. Into a mixture, at a temperature of about 20° C. of 356 grams of allophanic octadecylester  $C_{18}H_{37}O.CO.NH.CO.NH_2$  (Liebig's Annalen der Chemie 244, 41), 2000 grams of benzene, and 60 grams trioxymethylene, dry hydrochloric acid gas is introduced until the formation of the methyl chloride compound takes place. This compound is treated as stated in Example 6 and is stirred with 100 grams of pyridine at room temperature. The quaternary pyridinium salt of the methyl chloride derivative of allophanic octadecylester is formed having the formula:



The above methyl chloride compounds without pyridine may be employed in benzene or like solvent to treat textiles in a manner similar to that set forth in Examples 1 to 5. The conversion of the other materials given below for the production of chemicals and the use of such chemicals in the form of their alpha methyl halide compounds is effected in the same manner as given in the above examples. The other substances referred to are as follows:

stearo-hydroxamic acid



and derivatives of urea, thiourea, or dimethylol-

urea which contain an aliphatic radical of at least ten carbon atoms, for example:

N-n-heptadecyl-urea



or stearoyl-thiourea



or allophanic ester thiourea, for example



The amount of the reaction product deposited when uncombined with a tertiary amine in Examples 1 to 5 on the textile material will naturally vary with the weight of the material and its reactivity. 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 1-2 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. The fibers of the textiles have a superficial etherification. They show improved properties with respect to known textiles treated with fatty acid anhydrides including greater durability towards dry-cleaning with benzene and soap washing. The feel and hang of the material having water-repellence as produced above is not substantially altered. In addition, the artificial silks have resistance to swelling agents and wetting agents.

The tertiary amines used for the formation of the quaternary ammonium compounds can be either heterocyclic or aliphatic, for instance, pyridine, picoline or the other pyridine homologue, or quinoline, or an N-alkyl-piperidine or N-benzyl-piperidine, trimethylamine, triethylamine or dialkylcyclohexylamine.

The process for producing these improved 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.

The expression "textile material" used herein 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 animal fiber such as for example wool.

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 inven-

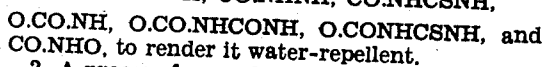
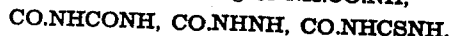
tion, that changes and modifications may be made therein without departing from the spirit or scope of the invention, and it is intended in the appended claims to cover all such changes and modifications.

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

1. A process for rendering textile material water-repellent which comprises heating the material with a compound of the formula



where R is an aliphatic radical containing at least 10 carbon atoms and Y is a radical selected from the group consisting of  $NH.CO.NH$ ,



2. A process for rendering textile material water-repellent which comprises impregnating the material with a compound of the formula



where R is an aliphatic radical containing at least 10 carbon atoms, and then heating the impregnated material in the absence of moisture until it becomes water-repellent.

3. A process for rendering textile material water-repellent which comprises impregnating the material with a compound of the formula



where R is an aliphatic radical containing at least 10 carbon atoms, and then heating the impregnated material in the absence of moisture until it becomes water-repellent.

4. A process for rendering textile material water-repellent which comprises impregnating the material with a compound of the formula



where R is an aliphatic radical containing at least 10 carbon atoms, and then heating the impregnated material in the absence of moisture until it becomes water-repellent.

5. A process according to claim 2 in which the compound employed for impregnation has the formula



6. A process according to claim 3 in which the compound employed for impregnation has the formula



7. A process according to claim 4 in which the compound employed for impregnation has the formula



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