Patented July 7, 1942

2,289,275

UNITED STATES PATENT OFFICE

2,289,275

PROCESS OF WATERPROOFING TEXTILES

Ludwig Orthner and Gerhard Balle, Frankfort-on-the-Main, Johann Rosenbach, Wiesbaden, and Kurt Bonstedt, Frankfort-on-the-Main, Germany, assignors, by mesne assignments, to General Aniline & Film Corporation, New York, N. Y., a corporation of Delaware

No Drawing. Application March 25, 1939, Serial No. 264,176. In Germany April 2, 1938

4 Claims. (Cl. 8—120)

The present invention relates to water-proof textile material and to a process of preparing it.

We have found that natural or artificial fibrous materials of animal or vegetable origin as well as products made therefrom may be rendered water-repellent by treating them with a solution or a dispersion of a condensation product of betaine-like structure substituted at the betaine nitrogen by the group

$$R—X—CH_2—$$

and subjecting the material thus impregated to a heat treatment between 80° C. and 150° C.

In the above formula R means a hydrocarbon radical with at least 12 carbon atoms which may be interrupted by hetero-atoms, for instance oxygen or sulfur and X means oxygen or sulfur. The compounds which are to be used in the process may be prepared as described in our co-pending application Serial No. 261,760, Patent No. 2,217,846. Compounds suitable for treating the fibrous materials are, for instance, condensation products of betaine-like structure prepared from aminocarboxylic acids disubstituted at the nitrogen atom and for instance the following halogen methyl compounds: dodecyl chloromethyl ether, octadecyl chloromethyl ether, dodecyl - bromomethyl ether, octylcyclo - hexyl chloromethyl ether, the chloromethyl ethers of iso-octylphenol-monoglycol ether, dodecyldiglycol ether, dodecylhydroxy ethyl sulfide, montan-alcohol, abietinol and di-hydroabietinol. There are, likewise, suitable the corresponding condensation products from thio-ethers such as, for instance, dodecyl chloromethylsulfide and octadecyl chloromethyl sulfide.

From the amino-carboxylic acids having tertiary nitrogen, whose products of reaction with the above mentioned compounds are suitable for rendering textiles water-repellent, there may be mentioned, for instance, dimethylamino-acetic acid, dibutylamino-acetic acid, piperidino-acetic acid, morpholino-acetic acid, alpha-dimethyl-amino-propionic acid and gamma-diethylamino-butyric acid.

The textile material is impregnated with a solution or dispersion of the condensation product of betaine-like structure which is to be used as water-proofing agent, the excess of the solution is removed by squeezing or centrifuging and the material thus treated is then exposed for some time to a temperature of 80° C. to 150° C. The degree of temperature necessary for obtaining a satisfactory effect depends upon the kind of the waterproofing agent used. In some cases it may be advantageous first to dry the impregnated material at low temperature and then to heat to a higher temperature.

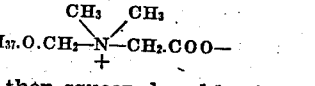
An alternative method of manufacturing water-repellent textile materials by means of the condensation products of betaine-like constitution here in question consists in adding one of the condensation products of betaine-like constitution above described to the spinning solution which is to serve as the parent material for making artificial threads.

It is often of special advantage to impregnate the textile material in the presence of agents of feebly acid action, such as lactic acid, tartaric acid, glycolic acid, boric acid or the like. It is possible thereby to reduce the duration of the subsequent heat treatment or to obtain a satisfactory effect even at essentially lower ripening temperature. The textile material may be treated with the acid agents also before or after the impregnation proper.

The condensation products of betaine-like structure may also be used in admixture with other water-proofing agents, for instance, with the methylol-amides of acids of high molecular weight, isocyanates of high molecular weight or the addition products of halogen methylethers or halogen methylamides of high molecular weight with tertiary bases. Furthermore, it is possible to enhance the waterproofing effect of the condensation products used in the present invention by adding to the impregnation liquors resin-like condensation products or the pre-condensation products thereof, for instance, condensates of urea, thiourea, aniline, melamine, dicyandiamide, phenyliminodiacetic acid-diamide or the like with aldehydes, especially formaldehyde and glyoxal. In this case not only the water-repellent property of the fibrous material may be enhanced but the material acquires a considerable fastness to creasing. The treatment may also be combined with other processes, for instance, by adding to the above described baths softening agents, delustering agents, agents known to enhance resistance to creasing, filling and dressing agents and other agents usually applied in the finishing of textiles. Various special effects may be obtained which are not diminished even by several washing operations.

The following examples serve to illustrate the invention but they are not intended to limit it thereto:

(1) Artificial silk crepe is impregnated at 60° C. with an aqueous solution of 1 per cent strength of octadecyloxybetaine of the formula



The material is then squeezed and heated for ½ hour at 135° C. to 140° C. Thereby, the material becomes very water-repellent.

(2) Artificial silk fabric is impregnated for 10 minutes at 50° C. with a bath containing per litre of water 10 grams of octadecyloxybetaine (which has likewise been applied in Example 1) and 6 cc. of lactic acid of 75 per cent strength. The fabric is then squeezed and subjected for ½ hour to 105° C. to 110° C. After this treatment the material becomes very water-proof and water poured thereon immediately runs off in drops. The effect remains undiminished even after several washing operations.

(3) Artificial silk crepe is impregnated with an alcoholic solution containing per litre 6 cc. of lactic acid and 10 grams of octadecyloxybetaine. The fabric is then freed from the excess of the adherent solvent by centrifuging and heated for 30 minutes at 120° C.

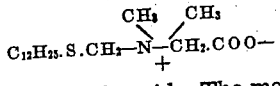
(4) Wool piece goods are treated with an aqueous solution of the octadecyloxybetaine of the formula:

$$C_{18}H_{37}.O.CH_2.\overset{+}{\underset{}{}}.CH_2.COO-$$

containing per litre 15 grams of the waterproofing agent and 8 grams of tartaric acid. After squeezing, the textile material is exposed for 40 minutes to 105° C.

(5) Loose viscose artificial silk fibre is impregnated for a short time with an aqueous solution of 1 per cent strength of the product obtained by saponification of the condensation product from alpha-dimethyl-amino-propionic acid methyl ester and dodecyl chloromethyl ether. After centrifuging, the textile material is first pre-dried at 50° C. and then heated for 1 hour at 130° C.

(6) A mixed fabric made from equal parts of wool and artificial silk staple fibre is treated for 10 minutes with an aqueous solution containing per litre 20 grams of the betaine

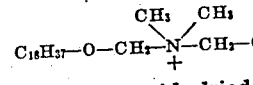


and 8 grams of lactic acid. The material is then squeezed and heated for 1 hour at 105° C.

(7) Artificial silk fabric is impregnated for a short time with an aqueous dispersion of 1 per cent strength of a mixture consisting of equal parts of octadecyloxybetaine (cf. Example 1) and stearic acid methylolamide. The material is then squeezed and heated for ½ hour at 135° C.

(8) Fabric from artificial silk staple fibre is impregnated with an aqueous solution containing per litre 100 grams of dimethylol urea, 5 grams of tartaric acid and 10 grams of octadecyloxybetaine (cf. Example 1). The excess of the impregnating liquor is then removed by centrifuging and the material exposed to a temperature of 135° C. to 140° C.

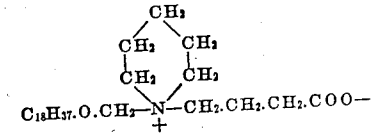
(9) A fabric from viscose staple fiber is impregnated on the foulard with carbon tetrachloride containing per litre 10 grams of an interpolymerization product from maleic acid anhydride and vinyloctadecyl ether in the dissolved state. The fabric is then further impregnated, likewise on the foulard, in a second bath containing per litre of water 20 grams of octadecyloxybetaine of the formula:



and 5 grams of lactic acid, dried and heated for 10 minutes at 150° C. A fabric is obtained which is very water-repellent, even being resistant to a boiling soap-treatment.

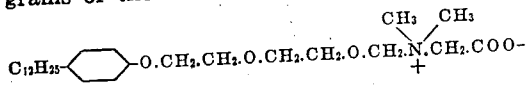
(10) A fabric prepared from viscose artificial silk and artificial silk staple fiber made according to the viscose process is treated for a short time at 50° C. to 60° C. with an aqueous solution containing per litre 10 grams of octadecyloxybetaine and 6 cc. of lactic acid of 75 per cent strength. The material is then squeezed, pre-dried for 1 hour at 60° C. and then heated for 20 minutes at 140° C.

(11) Cotton fabric is impregnated with an aqueous solution heated to 60° C. containing per litre 6 cc. of lactic acid of 75 per cent strength and 10 grams of the betaine of the following constitution



The material is then centrifuged, pre-dried at 50° C. and heated for ½ hour at 135° C. to 140° C.

(12) Viscose artificial silk crepe is impregnated with an aqueous solution containing per litre 10 cc. of lactic acid of 75 per cent strength and 15 grams of the betaine of the following formula



The material is squeezed and heated for 1 hour at 140° C.

(13) 11.2 grams of the compound made by saponifying the reaction product from octadecyl-chloromethyl ether and piperidino-acetic acid-methyl ester are added in the form of an aqueous solution of 20 per cent strength to 5 kilograms of a viscose solution ready for spinning containing 7.5 per cent of cellulose and 6.5 per cent of alkali and the solution is spun in the usual manner, for instance according to the two-bath-process. The fiber is washed until neutral, dipped into a lactic acid bath of 0.3 per cent strength, dried and subjected for 45 minutes at 110° C. to a ripening process.

(14) 10 grams of the compound made by saponifying the reaction product from octadecyl-chloromethyl ether and dimethylamino-acetic acid-methyl ester are added in the form of an aqueous solution of 10 per cent strength to 5 kilograms of a viscose solution ready for spinning containing 7.5 per cent of cellulose and 6.5 per cent of alkali and the solution is spun in the usual manner, for instance according to the two-bath-process. The fiber is washed until neutral, dipped into a lactic acid bath of 0.3 per cent strength, dried and subjected for 45 minutes at 110° C. to a ripening process.

(15) 11.2 grams of the compound made by saponifying the reaction product from octadecyl-chloromethyl ether and piperidino-acetic acid methyl ester are added in a cyclohexanone solution of 10 per cent strength to 5 kilograms of a viscose solution ready for spinning containing 7.5 per cent of cellulose and 6.5 per cent of alkali and the solution is spun in the usual manner in a Müller-bath. The desulfurized and acidified fiber is washed until neutral, dipped into a solution of tartaric acid of 0.3 per cent strength and heated for 1 hour at 100° C.

We claim:

1. The process of manufacturing water repellent textile material which comprises impregnating the textile material with a liquor containing a condensation product of betaine-like constitution substituted at the betaine nitrogen atom by the group

R. X. CH_2—

wherein R stands for a member of the group consisting of hydrocarbon radicals and hydrocarbon radicals containing hetero atoms as members of their carbon structure the radicals having at least 12 carbon atoms, X stands for a member of the group consisting of oxygen and sulfur, removing the excess of the liquor from the textile material and exposing the textile material to a temperature between about 80° C. and about 150° C.

2. The process of manufacturing water repellent textile material which comprises impregnating the textile material with a liquor containing a weak acid and a condensation product of betaine-like constitution substituted at the betaine nitrogen atom by the group

R. X. CH_2—

wherein R stands for a member of the group consisting of hydrocarbon radicals and hydrocarbon radicals containing hetero atoms as members of their carbon structure the radicals having at least 12 carbon atoms, X stands for a member of the group consisting of oxygen and sulfur, removing the excess of the liquor from the textile material and exposing the textile material to a temperature between about 80° C. and about 150° C.

3. A modification of the process described in claim 1 which consists in treating the textile material with a weak acid before impregnating it with the liquor containing the condensation product of betaine-like constitution.

4. A modification of the process described in claim 1 which consists in treating the textile material with a weak acid after impregnating it with the liquor containing the condensation product of betaine-like constitution.

LUDWIG ORTHNER.
GERHARD BALLE.
JOHANN ROSENBACH.
KURT BONSTEDT.