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WATER-REPELLENT TEXTILE MATERIAL AND A PROCESS OF PREPARING IT

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15 Claims. (Cl. 117—143)

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

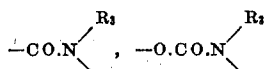
We have found that natural or artificial fibrous material of animal or vegetable origin and threads and fabrics made thereof may be rendered water-repellent by treating them with solutions or dispersions of quaternary ammonium salts obtainable by causing ester-like constituted compounds corresponding with one of the general formulae:



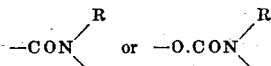
or



wherein R stands for an aliphatic, aliphatic-cycloaliphatic or araliphatic radical of at least 11 carbon atoms which may also be interrupted by hetero atoms; R₁ stands for an alkyl radical, X for oxygen or sulfur or one of the groups



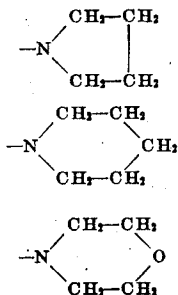
X_1 stands for one of the groups



R₃ stands for hydrogen or an alkyl radical, R₂ for a low molecular aliphatic hydrocarbon radical 30 which may, if desired, be substituted by halogen, Y stands for a readily exchangeable halogen atom or the group



R₄ and R₅ being aliphatic hydrocarbon radicals or R₄ and R₅ together standing for an alkylene radical with 4 or 5 carbon atoms or an alkylene radical with 4 carbon atoms, being interrupted by oxygen, for instance, Y may stand for the groups

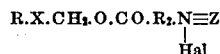


or

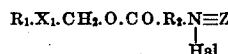
to react with a tertiary aliphatic or heterocyclic base or with a halogen alkyl compound, and then subjecting the impregnated fibrous material to a heat treatment at temperatures between 80° and 150° C.

The manufacture of the quaternary ammonium salts used for treating the fibrous materials by the process of the present invention is described in the copending U. S. patent application, Serial No. 273,042, filed May 11, 1939, by Gerhard Balle, Johann Rosenbach and Ludwig Orthner, for "Quaternary ammonium salts and process of preparing them."

The quaternary ammonium salts thus produced correspond with one of the general formulae:



20 or

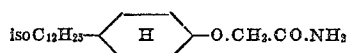


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wherein R, R₁, R₂, X, X₁ and R₃ have the above-indicated meaning, Hal means a halogen atom and Z means that at the pentavalent nitrogen atom three aliphatic hydrocarbon radicals are attached or that this nitrogen atom is a member of an unsaturated heterocyclic ring system or a member of a saturated heterocyclic ring system, in which latter case an aliphatic hydrocarbon radical is also bound to the nitrogen atom.

35 As compounds suitable for use in the present process there may, for instance, be named: The quaternary ammonium salts of pyridine with the ester-like condensation products from salts of chloracetic acid and the halogen-methyl derivatives of the following compounds: dodecylal-
40 cohoh, hexadecylalcohol, octadecylalcohol, oleyl-
alcohol, naphthene alcohols, montan alcohol, abietinols and the hydrogenation products there-
of, octadecane-diol, 9,10-dichloro-octadecanol,
45 octadecyl-monoglycol ether, para-butylphenyl-
butanol, octadecylphenylglycol ether, dodecyl-
mercaptan, octadecyl-mercaptan, lauric acid
amide, palmitic acid amide, stearic acid amide,
oleic acid amide, stearic acid methylamide, mon-
50 tanic acid amide, resinic acid amide, amides of
the carboxylic acids obtainable by oxidation of
paraffin with at least 12 carbon atoms, further-
more: dichlorostearic acid amide, ricinoleic
acid methylamide, acetic acid-N-octadecylamide,
55 iso-octylphenoxy acetic acid amide, isododecyl-

cyclohexyl-hydroxy-acetic acid amide corresponding with the formula:



tributylphenoxy-acetic acid butylamide.

There may further be used in the present process the products of reaction of pyridine with the condensation products from sodium chloracetate and the halogen-methyl derivatives of carbamic acid dodecyl ester, carbamic acid-hexadecyl ester, carbamic acid octadecyl ester, N-methylcarbamic acid octadecyl ester and carbamic acid-isododecylphenyl ester.

There may further be named the products of reaction of pyridine with the products of reaction of salts of chloroacetic acid and halogen-methyl derivatives from compounds of high molecular weight containing a nitrilo-group and formaldehyde, in the presence of hydrogen halides, such as, for instance, contained in the condensation product from heptadecyl-nitrile and formaldehyde in the presence of hydrochloric acid.

There may also be used in this invention compounds obtainable by causing the above-named chloromethyl compounds to react, in an analogous manner, with salts of other halogen-carboxylic acids containing an easily exchangeable halogen atom, for instance the salts of dichloroacetic acid, bromoacetic acid and chloropropionic acid.

Instead of the above-mentioned pyridinium salts there may likewise be used ammonium salts which are formed when the pyridine is exchanged for another tertiary base, such as, for instance, the homologues of pyridine, quinoline, trimethylamine, dimethylaminoacetic acid methyl ester, N-methylmorpholine, tetramethylethylenediamine.

The process consists in impregnating the textile material with a solution or dispersion of the hydrophobing agent, removing the excess of the treating liquid by squeezing or centrifuging the material and exposing the material thus treated for some time to a temperature of 80° C. to 150° C. (ripening). The degree of the ripening temperature required for obtaining the desired effect depends upon the kind of the hydrophobing agent used. In some cases, it may be preferable first to pre-dry the impregnated material at a low temperature and subsequently to heat it at a higher temperature.

A special advantage is obtained, in some cases, by impregnating the textile material in the presence of agents having a feebly acid action, such as lactic acid, tartaric acid, glycolic acid, boric acid or the like. Frequently it is possible, thereby, to shorten the subsequent heat treatment or to obtain a sufficient effect though applying a considerably lower ripening temperature. The treatment of the textile material with agents having an acid action may also be performed before or after the impregnation.

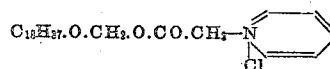
It is, in many cases, of advantage, to use the above-named compounds in admixture with other hydrophobing agents, such as paraffin, aluminium salts, zirconium salts, the methylolamides of acids of high molecular weight, isocyanates of high-molecular weight or the addition compounds of halogen-methyl ethers or halogen-methyl amides of high-molecular weight to tertiary bases, and the ester-like condensation products of salts of the halogen-carboxylic acids with halogen-methyl derivatives of alcohols, 75

amides and the like of high-molecular weight, which have already been mentioned above as intermediate products for the manufacture of the treating agents used in this invention.

It has, furthermore, been found that in some cases the water-proofing action of the products used in the present process may be increased by simultaneously using for the impregnation condensation products of the series of the so-called condensation resins, such as condensation products from urea, thio-urea, phenol, aniline, melamine, dicyanidiamide and the like with aldehydes, especially with formaldehyde and glyoxal. In this case, the fibrous material acquires a considerable resistance to creasing in addition to the improved waterproofing.

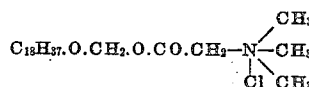
The following examples serve to illustrate the invention but they are not intended to limit it thereto:

1. A viscose artificial silk fabric is impregnated with an aqueous solution of 1 per cent strength of the compound:



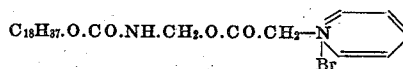
The material is then freed, by centrifuging, from the excess solution and heated, for half an hour, at a temperature of 105° C. to 110° C. By this treatment, the fabric becomes, to a high degree, impermeable to water and immediately repels water dropped thereon. This effect is not changed, even when the material has been washed several times.

2. A cotton fabric is treated, for 10 minutes, with an aqueous solution of 1 per cent strength of the compound:



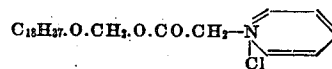
The material is then squeezed and heated, for half an hour, at 135° C. to 140° C. After this treatment, the material is very water-repellent.

3. Woollen piece goods are impregnated with an aqueous solution of 2 per cent strength of the product:



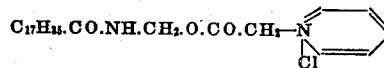
The fabric is then freed, by centrifuging, from the excess of the adhering solvent and heated, for one hour, at 90° C. to 100° C.

4. Muslin-delaine is introduced into an aqueous solution containing per litre 15 grams of the compound:



After squeezing, the material is heated, for one hour, at 80° C. to 90° C.

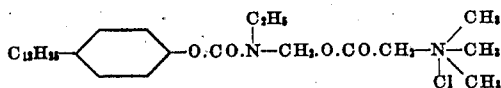
5. Viscose artificial silk is treated, for a short time, with an aqueous solution of 1 per cent strength of the product:



The silk is freed, by centrifuging, from the excess of solvent and exposed, for half an hour, to a temperature of 120° C. After this treatment, the fabric is very water-repellent. It does not lose this property even when washed.

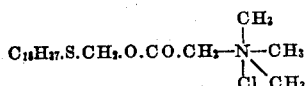
6. A fabric from cuprammonium artificial silk

is impregnated with a solution of 2 per cent strength of the compound:



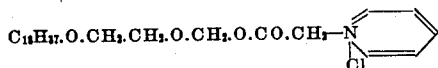
and heated, after squeezing, for one hour at 130° C.

7. A linen fabric is impregnated with an aqueous solution of 1 per cent strength of the product:



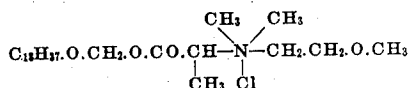
After centrifuging, it is heated, for half an hour, at a temperature of 125° C.

8. A mixed fabric consisting of wool and staple fiber (50:50) is treated with an aqueous solution containing per liter 15 grams of the product:



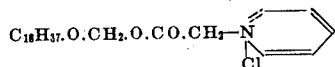
The material is then squeezed and exposed, for one hour, to a temperature of 105° C.

9. A fabric from cuprammonium artificial silk is impregnated with an aqueous solution of 2 per cent strength of the compound:



After removal of the excess solvent, the fabric is exposed, for one hour, to a temperature of 120° C.

10. Viscose artificial silk is treated, at 60° C. to 70° C., with an aqueous dispersion of 1 per cent strength of a mixture consisting of equal parts of stearic acid methylol amide and the compound:

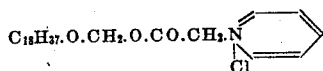


After centrifuging, the fabric is heated, for one hour, at 120° C.

11. Viscose artificial silk is impregnated with an aqueous dispersion of 1 per cent strength of a mixture consisting of equal parts of the compounds:

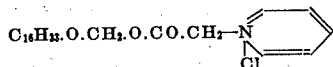


and



The material is freed, by squeezing, from the excess solution and then heated, for half an hour, at 105° C. to 110° C.

12. A fabric made from viscose staple fiber is passed through a bath containing per liter 10 grams of the compound:



5 grams of tartaric acid and 100 grams of dimethylolurea. After centrifuging, the fabric is heated, for one hour, at 140° C.

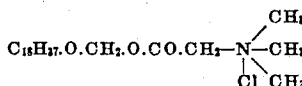
13. Viscose artificial silk crepe is impregnated with an aqueous solution containing per liter 5 grams of melamine, 5 grams of lactic acid, 30 cc.

of a formaldehyde solution of 35 per cent strength and 10 grams of the product:



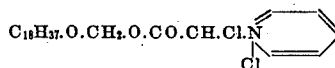
The fabric is then centrifuged and heated, for half an hour, at 135° C.

14. A fabric made from viscose staple fiber is treated, at 20° C. to 25° C., with an aqueous dispersion containing per liter 3 grams of sodium carbonate, 16.5 grams of crystallized sodium acetate, 24 grams of zirconium-hydroxy chloride and 10 grams of the compound:



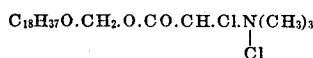
After squeezing, the material is exposed, for half an hour, to a temperature of 135° C. to 140° C.

15. A viscose artificial silk fabric is impregnated with a solution of 1 per cent strength of the compound:



After the material has been freed by centrifuging from the excess of the solution it is dried at 40° C. to 50° C. and then heated, for 10 minutes, at a temperature of 135° C. to 140° C. By this treatment, the fabric becomes, to a high degree, impermeable to water and immediately repels water dropped thereon. This effect is not changed, even when the material has been washed several times.

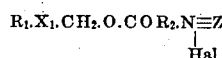
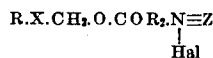
16. A cotton fabric is impregnated with a solution of 1 per cent strength of the compound:



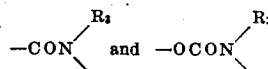
After the fabric has been freed, by centrifuging, from the excess of solution, it is dried at 40° C. to 50° C. and thereupon heated, for 30 minutes, at a temperature of 135° C. to 140° C. By this treatment, the fabric becomes, to a high degree, impermeable to water and immediately repels water dropped thereon. This effect is not changed, even when the material has been washed several times.

We claim:

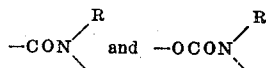
1. The process of manufacturing water-repellent textile material which comprises impregnating the textile material with a liquor containing a quaternary ammonium salt of one of the general formulae of the group consisting of



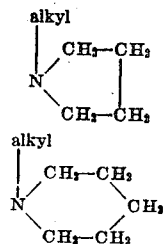
where R stands for a radical of at least 11 carbon atoms selected from the group consisting of aliphatic, aliphatic-cycloaliphatic and araliphatic radicals and aliphatic, aliphatic-cycloaliphatic and araliphatic radicals containing hetero-atoms as members of their carbon structure; R₁ stands for an alkyl radical; X stands for a member of the group consisting of oxygen, sulfur,



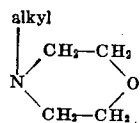
X₁ stands for a member of the group consisting of



R₃ stands for a member of the group consisting of hydrogen and alkyl radicals; R₂ stands for a member of the group consisting of low molecular aliphatic hydrocarbon radicals and low molecular aliphatic hydrocarbon radicals substituted by halogen; Hal means halogen; N≡Z stands for a member of the group consisting of tertiary aliphatic amines, tertiary heterocyclic bases



and

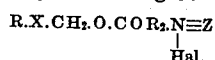


and drying said impregnated textile material.

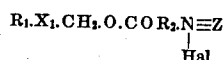
2. A modification of the process described in claim 1 which consists in treating the textile material with an acid agent before impregnating it with the liquor containing the quaternary ammonium salt.

3. A modification of the process described in claim 1 which consists in treating the textile material with an acid agent after impregnating it with the liquor containing the quaternary ammonium salt.

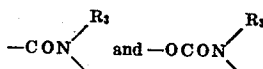
4. Water-repellent textile material obtained by impregnating a textile material with a quaternary ammonium salt of one of the general formulae of the group consisting of



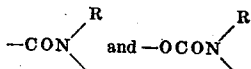
and



wherein R stands for a radical of at least 11 carbon atoms selected from the group consisting of aliphatic, aliphatic-cycloaliphatic and araliphatic radicals and aliphatic, aliphatic-cycloaliphatic and araliphatic radicals containing hetero-atoms as members of their carbon structure; R₁ stand for an alkyl radical; X stands for a member of the group consisting of oxygen, sulfur,

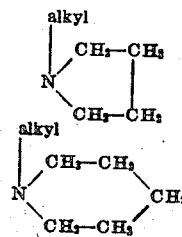


X₁ stands for a member of the group consisting of

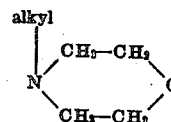


R₃ stands for a member of the group consisting of hydrogen and alkyl radicals; R₂ stands for a member of the group consisting of low molecular aliphatic hydrocarbon radicals and low molecular aliphatic hydrocarbon radicals substituted by halogen; Hal means halogen; N≡Z stands for a

member of the group consisting of tertiary aliphatic amines, tertiary heterocyclic bases,



and



5. Water-repellent textile material obtained by impregnating a textile material with an acid agent and a quaternary ammonium salt as defined in claim 4.

6. Water-repellent textile material obtained by impregnating a textile material with an acid agent, a condensation product from an aldehyde and a member of the group consisting of urea, thiourea, phenol, aniline, melamine, dicyandiamide and a quaternary ammonium salt as defined in claim 4.

7. Water-repellent material comprising a textile material impregnated with an acid agent, a condensation product from an aldehyde and a member of the group consisting of urea, thiourea, phenol, aniline, melamine, dicyandiamide and a quaternary ammonium salt as defined in claim 4.

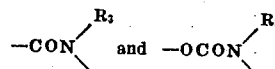
8. The process of manufacturing water-repellent textile material which comprises impregnating the textile material with a liquor containing a quaternary ammonium salt which has been prepared from ester-like constituted compounds corresponding with one of the general formulae of the group consisting of



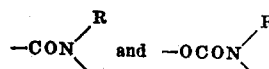
45 and



wherein R stands for a radical of at least 11 carbon atoms selected from the group consisting of aliphatic, aliphatic-cycloaliphatic and araliphatic radicals and aliphatic, aliphatic-cycloaliphatic and araliphatic radicals containing hetero-atoms as members of their carbon structure; R₁ stands for an alkyl radical; X stands for a member of the group consisting of oxygen, sulfur,



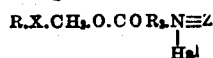
60 X₁ stands for a member of the group consisting of



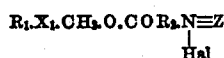
R₃ stands for a member of the group consisting of hydrogen and alkyl radicals; R₂ stands for a member of the group consisting of low molecular aliphatic hydrocarbon radicals and low molecular aliphatic hydrocarbon radicals substituted by halogen, by reacting them with an organic tertiary base of the group consisting of aliphatic and heterocyclic bases, removing the excess of the liquor from the textile material and expos-

ing the textile material to a temperature between about 80° C. and about 150° C.

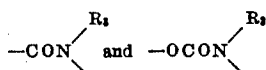
9. The process of manufacturing water-repellent textile material which comprises impregnating the textile material with a liquor containing an acid agent and a quaternary ammonium salt of one of the general formulae of the group consisting of



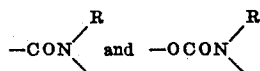
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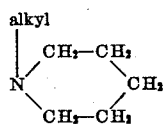
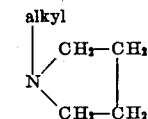
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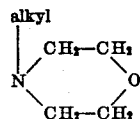
X₁ stands for a member of the group consisting of



R₃ stands for a member of the group consisting of hydrogen and alkyl radicals; R₂ stands for a member of the group consisting of low molecular aliphatic hydrocarbon radicals substituted by halogen; Hal means halogen; N≡Z stands for a member of the group consisting of tertiary aliphatic amines, tertiary heterocyclic bases,

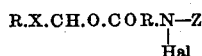


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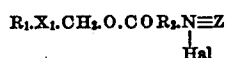


and drying said impregnated textile material.

10. The process of manufacturing water-repellent textile material which comprises impregnating the textile material with a liquor containing a condensation product from an aldehyde and a member of the group consisting of urea, thiourea, phenol, aniline, melamine, dicyandiamide and a quaternary ammonium salt of one of the general formulae of the group consisting of

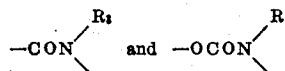


and



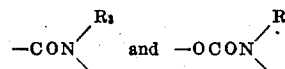
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ing of aliphatic, aliphatic-cycloaliphatic and araliphatic radicals and aliphatic, aliphatic-cycloaliphatic and araliphatic radicals containing hetero-atoms as members of their carbon structure; R₁ stands for an alkyl radical; X stands for a member of the group consisting of oxygen, sulfur,



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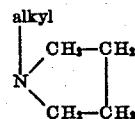
X₁ stands for a member of the group consisting of



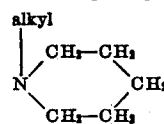
15

R₃ stands for a member of the group consisting of hydrogen and alkyl radicals; R₂ stands for a member of the group consisting of low molecular aliphatic hydrocarbon radicals and low molecular aliphatic hydrocarbon radicals substituted by halogen; Hal means halogen; N≡Z stands for a member of the group consisting of tertiary aliphatic amines, tertiary heterocyclic bases,

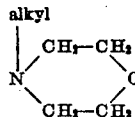
25



30



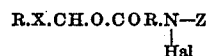
35 and



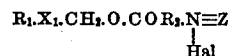
40

and drying said impregnated textile material.

11. The process of manufacturing water-repellent textile material which comprises impregnating the textile material with a liquor containing an acid agent, a condensation product from an aldehyde and a member of the group consisting of urea, thiourea, phenol, aniline, melamine, dicyandiamide, and a quaternary ammonium salt of one of the general formulae of the group consisting of

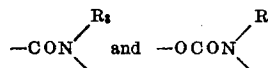


and

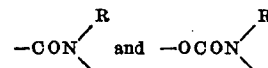


55

wherein R stands for a radical of at least 11 carbon atoms selected from the group consisting of aliphatic, aliphatic-cycloaliphatic and araliphatic radicals and aliphatic, aliphatic-cycloaliphatic and araliphatic radicals containing hetero-atoms as members of their carbon structure; R₁ stands for an alkyl radical; X stands for a member of the group consisting of oxygen, sulfur,

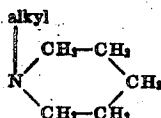
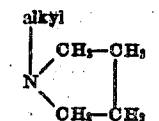


70 X₁ stands for a member of the group consisting of

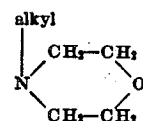


75 R₃ stands for a member of the group consist-

ing of hydrogen and alkyl radicals; R_2 stands for a member of the group consisting of low molecular aliphatic hydrocarbon radicals and low molecular aliphatic hydrocarbon radicals substituted by halogen; Hal means halogen; $N \equiv Z$ stands for a member of the group consisting of tertiary aliphatic amines, tertiary heterocyclic bases,

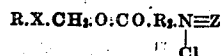


and

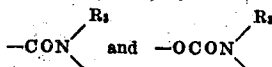


and drying said impregnated textile material.

12. Water-repellent textile material obtained by impregnating a textile material with a quaternary ammonium salt of the general formula:

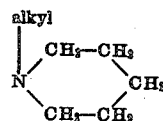
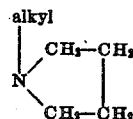


wherein R stands for an aliphatic radical of at least 12 carbon atoms, X stands for a member of the group consisting of oxygen, sulfur,

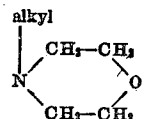


R_3 stands for a member of the group consisting of hydrogen and alkyl radicals, R_2 stands for a member of the group consisting of low molecular aliphatic hydrocarbon radicals and low molecular aliphatic hydrocarbon radicals sub-

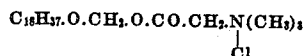
stituted by halogen, $N \equiv Z$ stands for a member of the group consisting of tertiary aliphatic amines, tertiary heterocyclic bases,



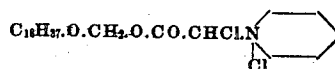
and



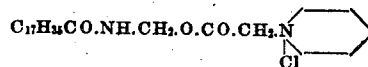
13. Water-repellent textile material obtained by impregnating a textile material with the product of the formula:



14. Water-repellent textile material obtained by impregnating a textile material with the product of the formula:



15. Water-repellent textile material obtained by impregnating a textile material with the product of the formula:



GERHARD BALLE.
JOHANN ROSENBACH.
LUDWIG ORTHNER.