

UNITED STATES PATENT OFFICE

2,277,174

PROCESS FOR PRODUCING WATER-REPEL-
LENT TEXTILE MATERIALS AND PROD-
UCT THEREFROMErnst Waltmann, Krefeld, Germany, assignor to
Heberlein Patent Corporation, New York, N. Y.,
a corporation of New YorkNo Drawing. Application May 14, 1937, Serial
No. 142,623. In Germany May 19, 1936

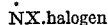
17 Claims. (Cl. 8—113)

This invention relates to processes for produc-
ing water-repellent textile materials and products
therefrom.

The principal object of the present invention is
to increase water-repellence in textile material by
a simple process; and to produce products having
improved characteristics thereby.

The invention accordingly comprises 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.

According to the present invention water-repel-
lence is accomplished by the impregnation of tex-
tile with water-soluble quaternary ammonium
compounds of methyl halogen ethers of higher
fatty alcohols having the general formula



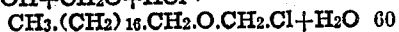
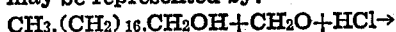
in which R is an aliphatic radical containing at
least 10 carbon atoms, and NX stands for a ter-
tiary amine, with subsequent heating.

As tertiary amines used for the formation of
the quaternary ammonium salts those tertiary
amines are used which are sufficiently volatile, in
order that they may volatilize off during the sub-
sequent treatment. There may be advantageously
employed the heterocyclic bases which contain
a tertiary nitrogen atom in the ring such as
pyridine, quinoline and isoquinoline or homo-
logues or substitution products thereof. There
may also be employed aliphatic tertiary amines
such as trimethylamine $(CH_3)_3N$ or triethylamine
 $(C_2H_5)_3N$.

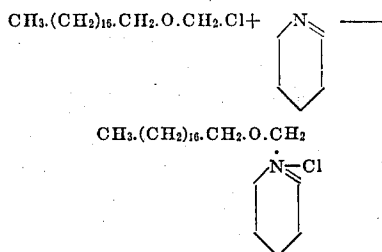
There may also be employed the quaternary
ammonium salts of methyl-halogen-thioethers of
higher fatty thioalcohols having the general
formula:



The quaternary ammonium salts of these ethers
are prepared as follows: The halogen ethers are
first prepared. For example methyl chloride ether
of octadecane is prepared as follows: Dry hydro-
chloric acid gas is introduced at ordinary tem-
perature into a mixture containing 270 parts of
octadecylalcohol, 810 parts of benzol, and 30 parts
of trioxymethylene, until the formation of the
octadecylchloromethylether occurs which can be
clearly recognized by the benzol solution becom-
ing clear. The water from the reaction which
accumulates at the bottom of the vessel is run off,
the benzol and the surplus hydrochloric acid are
removed in a vacuum. The reaction which occurs
may be represented by:



The quaternary ammonium salt of the ether,
for example with pyridine, is formed in the fol-
lowing manner: 319 parts of the octadecylchlor-
methylether are stirred with 80 parts of pyridine.
The mixture solidifies immediately and the
quaternary pyridinium salt of octadecylchlor-
methylether results:



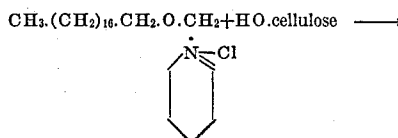
Other water-soluble quaternary ammonium
salts of these ethers may be obtained by similar
processes to that described above.

Instead of octadecanol: $CH_3.(CH_2)_{16}.CH_2OH$,
hexadecanol: $CH_3.(CH_2)_{14}.CH_2OH$, dodecanol:
 $CH_3.(CH_2)_{10}.CH_2OH$, octadecandiol:

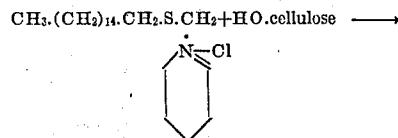
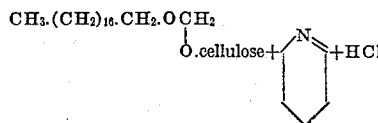


hexadecanthiol: $CH_3.(CH_2)_{14}.CH_2.SH$, octadecan-
thiol: $CH_3.(CH_2)_{16}.CH_2.SH$, cholesterol: $C_{27}H_{45}OH$
etc. can be used.

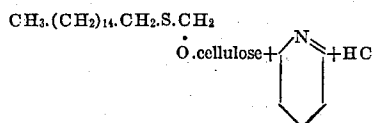
The compounds falling under the general for-
mula appears to react with cellulose with the
formation of mixed acetals, according to the
equation:



Quaternary pyridinium salt of octadecylmethyl chloride ether



Quaternary pyridinium salt of hexadecylmethylchloride thioether



The pyridine formed in the above reaction is

volatilized as above stated during the heating to which the textile materials are subjected after reaction, as given for instance in the examples below.

It has been found that textiles, particularly natural or regenerated cellulose, can be rendered water-repellent by treatment with these quaternary ammonium salts of the halogen ethers. The materials herein described are all soluble in water and the treatment may be accordingly carried out in this medium, thereby avoiding the use of expensive organic solvents and recovery apparatus therefor.

The pyridine and other tertiary amines liberated by the reaction of the chemicals on the textile materials treated by the above examples is volatilized when the textile is heated at the temperatures therein mentioned.

Where the context permits the expression "ethers" as used in the appended claims designates either an ordinary ether or thioether.

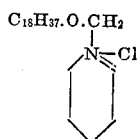
The process is also applicable to textiles of animal origin such as wool and silk, etc. as shown for instance in the examples below.

The impregnation of the textile material by the products set forth can be effected in any desired manner, by immersion of the material to be treated or by spraying it or other like procedure. The impregnation is preferably accomplished at a temperature slightly above that of room temperature, and thereafter upon drying the material is usually heated at a temperature above the drying temperature and in the neighborhood of 100° C. to affect water-repellence.

The following are examples of the invention as I now prefer to practice it. It is to be understood that these examples are illustrative and that the invention is not limited thereto except as indicated in the appended claims:

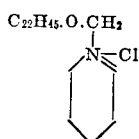
Examples

1. Undyed, unbrightened, loose spun viscose rayon is introduced into an aqueous bath heated to about 40° C. containing per liter 15 grams of octadecoxymethyl pyridinium chloride.



The spun rayon remains for about 15 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 benzene. 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.

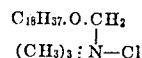
2. A dyed dress material having a warp of cotton and a filling of viscose silk is treated in an aqueous solution of 20 grams per liter of docosoxymethyl pyridinium chloride



at a temperature of about 45° C. It is then re-

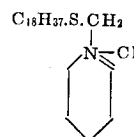
moved, squeezed and dried at about 80° C. After the drying it is preferably heated for several hours at about 100° C. in a drying chamber. The treated material shows water-repellence which is resistant to dry-cleaning as by benzene and washing with soap.

3. A dyed cloak material made of spun cuprammonium rayon is treated in an aqueous solution of 15 grams per liter of trimethyl octadecoxymethyl ammonium chloride



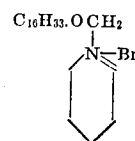
at a temperature of about 45° C. It is then removed, squeezed and dried at about 90° C. and after drying is preferably exposed for several hours at a temperature of about 100° C. The resulting material has substantially the same properties as described for materials in Examples 1 and 2.

4. A popelin from mercerized cotton, suitable for rain-proof overcoats is treated in an aqueous solution of 15 grams per liter of quaternary pyridinium salt of octadecylmethylchloride thioether



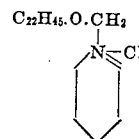
at a temperature of about 45° C. It is then removed, squeezed and dried at about 90° C. and after drying is preferably exposed for several hours at a temperature of about 100° C. The resulting material has substantially the same properties as described for materials in Examples 1 and 2.

5. A wool muslin is treated in an aqueous solution of 15 grams per liter of hexadecoxymethyl pyridinium bromide



at a temperature of about 45° C. It is then removed, squeezed and dried at about 90° C. and after drying is preferably exposed for several hours at a temperature of about 100° C. The resulting material has substantially the same properties as described for materials in Examples 1 and 2.

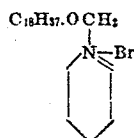
6. A velvet weave consisting of a real silk warp and weft and a viscose pile is passed through a bath which contains per liter 20 grams of docosoxymethyl pyridinium chloride



at a temperature of about 45° C. It is then squeezed and dried at about 80° C. After the drying it is preferably heated for several hours at about 100° C. in a drying chamber. The velvet material shows water-repellence which is resistant to dry-cleaning as by benzene and washing with soap.

7. A velvet weave consisting of real silk in the

warp and weft and having a viscose pile is passed through a bath which consists per liter 20 grams of octadecoxymethyl pyridine bromide



at a temperature of about 45° C. It is then squeezed and dried at about 80° C. After the drying it is preferably heated for several hours at about 100° C. in a drying chamber. The velvet material shows water-repellence which is resistant to dry-cleaning as by benzine and washing with soap.

The term "halogen" as used in the appended claims is intended to designate one of the three elements—chlorine, bromine, iodine.

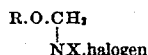
The process of the invention, particularly as set forth in the specific embodiments, may be carried out with simple apparatus at relatively small expense and in a relatively short time. The products show an improved appearance, their feel as compared with similar untreated material is not substantially altered, and they have a high degree of water-repellence which does not rapidly disappear upon cleansing by laundering or otherwise of the materials produced.

The term "textiles" as herein employed is intended to include wool, silk and other animal fiber, as well as cellulose-containing material. The expression "cellulose-containing material" as herein employed is intended to cover fibers, yarns, 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. The fibers of animal origin may be employed in various similar forms.

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.

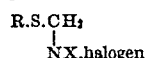
What is claimed as new and desired to be secured by Letters Patent is:

1. A process for treating textiles which comprises subjecting a textile material of animal origin to a water-soluble quaternary ammonium compound of methyl halogen ether of a higher fatty alcohol having the general formula



in which R is an aliphatic radical containing at least 10 carbon atoms, and NX stands for a tertiary amine, and heating the so treated textile material to increase the water-repellence thereof.

2. A process for treating textiles which comprises subjecting a textile material to a water-soluble quaternary ammonium compound of methyl halogen thioether of a higher fatty thioalcohol having the general formula



in which R is an aliphatic radical containing at least 10 carbon atoms, and NX stands for a

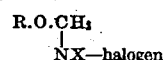
tertiary amine, and heating the so treated textile material to increase the water-repellence thereof.

3. A process for treating textiles which comprises subjecting a textile material of animal origin to a water-soluble pyridinium methyl chloride ether of a higher fatty alcohol containing an aliphatic radical of at least 10 carbon atoms, and heating the so treated textile material to increase the water-repellence thereof.

4. A process for treating textiles which comprises subjecting a textile material to a water-soluble pyridinium methyl chloride thioether of a higher fatty thioalcohol containing an aliphatic radical of at least 10 carbon atoms, and heating the so treated textile material to increase the water-repellence thereof.

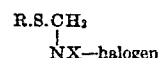
5. A process for treatment of cellulose-containing material which comprises subjecting the cellulose-containing material to a water solution of the quaternary pyridinium salt of octadecyl methyl chloride thioether, drying the treated cellulose-containing material and heating it to about 100° C. to produce a water-repellence in said cellulose-containing material.

6. A textile material of animal origin treated with a water-soluble ammonium compound of the methyl halogen ether of a higher fatty alcohol having the general formula



in which R is an aliphatic radical containing at least 10 carbon atoms, and NX stands for a tertiary amine, said material having a water-repellent property but its appearance and feel being substantially the same as similar material untreated, said property also being capable of withstanding ordinary house laundering and dry cleaning being the product of a process as defined in claim 1.

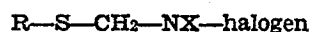
7. A textile material treated with a water-soluble ammonium compound of methyl halogen thioether of a higher fatty thioalcohol having the general formula



in which R is an aliphatic radical containing at least 10 carbon atoms, and NX stands for a tertiary amine, said material having a water-repellent property but its appearance and feel being substantially the same as similar material untreated, said property also being capable of withstanding ordinary house laundering and dry cleaning being the product of a process as defined in claim 2.

8. A cellulose-containing material treated with a water-soluble pyridinium methyl chloride thioether of a higher fatty thioalcohol containing an aliphatic radical of at least 10 carbon atoms, having a water-repellent property but its appearance and feel being substantially the same as similar material untreated, said property also being capable of withstanding ordinary house laundering and dry cleaning, being the product of a process as defined in claim 4.

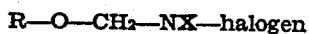
9. A process for rendering cellulose textile material water-repellent which comprises impregnating the material with a quaternary ammonium compound having the formula



in which R stands for an aliphatic radical containing at least twelve carbon atoms and NX for

a tertiary amine, and then heating the impregnated material in the absence of moisture at a temperature sufficient to decompose the quaternary ammonium compound with the liberation of the free amine.

10. A process for rendering textile material of animal origin water-repellent which comprises impregnating the material with an alkoxy methylene quaternary ammonium compound having the formula



in which R stands for an aliphatic radical containing at least twelve carbon atoms and NX for a tertiary amine, and then heating the impregnated material in the absence of moisture at a temperature sufficient to decompose the quaternary ammonium compound with the liberation of the free amine.

11. A process for rendering textile material of animal origin water-repellent which comprises impregnating the material with a quaternary ammonium compound having the formula



in which R stands for an aliphatic radical containing at least twelve carbon atoms and NX for a tertiary amine, and then heating the material in the absence of moisture at a temperature sufficient to decompose the quaternary ammonium compound with the liberation of the free amine.

12. A process for treatment of textiles which comprises subjecting a textile material of animal

origin to octadecoxymethyl pyridinium halide and then heating the treated material in the absence of moisture at a temperature sufficient to decompose the compound with the liberation of the free amine.

13. A cellulose-containing material treated with a quaternary pyridinium salt of octadecyl methyl chloride thioether, having a water-repellent property capable of withstanding ordinary house laundering and dry cleaning but having an appearance and feel substantially the same as similar material untreated, being the product of a process as defined in claim 5.

14. A process for treatment of textile material of animal origin which comprises impregnating the material with a water solution of hexadecoxymethyl pyridinium halide and heating the dried material to a temperature of the order of 100° C. to produce water-repellence therein.

15. A process for treatment of textile material of animal origin which comprises impregnating the material with a water solution of octadecoxymethyl pyridinium halide and heating the dried material to a temperature of the order of 100° C. to produce water-repellence therein.

16. A textile material of animal origin having water-repellent properties and being the product of a process as defined in claim 14.

17. A textile material of animal origin having water-repellent properties and being the product of a process as defined in claim 15.

ERNST WALTMANN.

CERTIFICATE OF CORRECTION.

Patent No. 2,277,174.

March 24, 1942.

ERNST WALTMANN.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, first column, line 16-17, for the word "textile" read --textiles--; and second column, line 31, for "appears" read --appear--; page 2, first column, lines 14 to 21 inclusive, strike out the following paragraphs and insert the same after "soap." on page 3, first column, line 16 -

The pyridine and other tertiary amines liberated by the reaction of the chemicals on the textile materials treated by the above examples is volatilized when the textile is heated at the temperatures therein mentioned.

Where the context permits the expression "ethers" as used in the appended claims designates either an ordinary ether or thioether.--

page 2, second column, line 21, for "popelin" read --poplin--; line 23, before "quaternary" insert --the--; page 3, first column, line 2, for "consists" read --contains--; 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 2nd day of June, A. D. 1942.

(Seal)

Henry Van Arsedale,
Acting Commissioner of Patents.