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WATER-REPELLENT TEXTILES, AND
PROCESS FOR MAKING SAME

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

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11 Claims. (Cl. 8—116)

This invention relates to water-repellent tex-
tiles and processes for manufacturing such tex-
tiles.

This application comprises a division of my co-
pending application Ser. No. 195,600, filed March 12,
1938, Patent No. 2,242,565.

This invention may also be said to relate to al-
ternative improved water-repellent material and
processes for making same, in a manner gener-
ally similar to the use of the water-repellent
compounds and treatments disclosed in my co-
pending application Ser. No. 177,054, filed No-
vember 29, 1937, Patent No. 2,294,435, reference
to which is hereby made.

I have found that in general the compounds
derived from substituted ammonia-formalde-
hyde-condensation products can be converted
with acid halides, and thereafter transformed
by the addition of the tertiary bases into water-
soluble compounds.

In accordance with this, I have also found that
by the conversion of higher fatty chlorides with
hexamethylenetetramine and subsequent treat-
ment of the reaction product with tertiary bases
such as pyridine and others hereinafter men-
tioned, one may produce water-soluble quater-
nary compounds. I have also found in accord-
ance with my invention that such compounds
comprise highly desirable products for the treat-
ment of textile materials for water-repellence
upon properly combining such materials with
such products under reaction conditions.

The objects of the invention accordingly in-
clude the provision of improved textiles rendered
water-repellent by treatment with compounds of
the above indicated character, and provision of
improved processes for using the above-men-
tioned chemicals in producing such water-repel-
lent textile materials, among other possible uses.

Further and more specific objects, features and
advantages of the invention will more fully ap-
pear from the following specification.

The invention consists in the novel products as
well as the novel processes and steps of processes
according to which such textile products are
manufactured, specific embodiments thereof be-
ing described hereinafter by way of various ex-
amples according to which I now prefer to prac-
tice the invention.

In accordance with the present invention the
acid halides above mentioned may have the gen-
eral formula $R.CO$ halide, in which R is an ali-
phatic or aliphatic-aromatic radical in which the
aliphatic portion has at least ten carbon atoms.
The conversion of such acid halides with hexa-

methylenetetramine $[(CH_2)_6N_4]$ is preferably ef-
fected with a molar ratio of four parts of acid
halide to one part of hexamethylenetetramine.
The quantity of hexamethylenetetramine used,
however, may also be increased for example to a
ratio in the neighborhood of three mols of the
acid halide to one mol of the hexamethylenetetra-
mine. The resulting conversion products ob-
tained in this manner may then be converted as
by the use of pyridine, 2-methyl-pyridine, tri-
ethyl-amine, or equivalent tertiary bases, into
quaternary ammonium compounds. Such com-
pounds are remarkably effective in imparting
water-repelling properties to textile material
when properly applied thereto, in a manner gen-
erally similar to the application of the water-re-
pellent chemicals to the textiles as disclosed by
said copending application. The water-repelling
effect is fast to washing or laundering with soap
solutions and to dry cleaning with benzine for
example. Furthermore, the fastness to wash-
ing of substantive dyestuffs where employed with
the textile material so treated is substantially
improved. And in connection with rayon fabrics
produced from cellulose, it is possible by means
of the process to effectively increase the fastness
of such dyestuffs both against deterioration by
moisture and under dry conditions. Such com-
pounds are also suitable for addition to baths
serving for imparting crease- or wrinkle-resist-
ant properties to textiles.

I may employ other substituted ammonia-
formaldehyde condensation products, instead of
hexamethylenetetramine, for instance, a com-
pound of the general formula $R'.X.NH_2$ is first
converted with formaldehyde or trioxymethylene.
The converted product is treated with the acid
halide. In the formula $R'.X.NH_2$, as herein used,
 R' represents an alkyl radical (such for exam-
ple as $C_{17}H_{35}$), a cycloalkyl radical for example
cyclohexylamine $C_6H_{11}.NH_2$, or an aralkyl radical
($C_{10}H_7$, phenyl for example), and X indicates
methylene or the $C=O$ or SO_2 group. In place
of the fatty acid chlorides, one may also use
the corresponding chlorocarbonic acid ester
($R.OCOCl$) or carbamic acid chlorides (carba-
mido chlorides), such as $C_{18}H_{37}NHCOC$, for ex-
ample. As the tertiary bases to be used in such
cases, one may for example use the volatile ter-
tiary bases such as pyridine and its homologs,
trimethylamine, triethylamine, etc. The result-
ing products may be used for the same purposes
with substantially the same results above speci-
fied in connection with the previous embodiments
of the invention.

The following are specific examples of the above described chemical products as made according to the invention and to the treatment of textiles therewith, carried out in various ways now preferred. It is to be understood that the invention is not limited to any of these particular examples or others as hereinafter given, except as indicated in the appended claims.

In the following examples the reaction between the fatty acid halide, carbonic ester halide, and carbamic acid halide with hexamethylenetetramine is conducted so that no decomposition of the hexamethylenetetramine into formaldehyde and ammonia occurs.

Examples for making the chemicals

1. 140 parts of hexamethylenetetramine are dissolved in 1400 parts of chloroform; 1208 parts of stearic acid chloride ($C_{17}H_{35}COCl$) are added and the whole is heated for one hour in a reflux condenser. The chloroform is thereupon drawn off by suction in vacuum and the conversion product is stirred with 320 parts of pyridine. There occurs the formation of the quaternary pyridinium compound with the simultaneous development of heat. The white wax-like mass obtained is now soluble in hot water; its melting point after recrystallization from petroleum ether is about $115^{\circ}C$. (with splitting off of formaldehyde).

2. 1208 parts of stearic acid chloride are diluted with about the same quantity of benzol or carbon tetrachloride and 140 parts of finely pulverized hexamethylenetetramine are added. After heating for two hours on a boiling water bath, the solvent is drawn off by suction in vacuum and the conversion product is stirred with 320 parts of pyridine. The wax-like resulting product is water-soluble. Its melting point is about $115^{\circ}C$.

3. 140 parts of hexamethylenetetramine are dissolved in 1400 parts of chloroform; thereupon, 1768 parts of montanic acid chloride $C_{27}H_{55}COCl$ are added, and the whole is heated for one hour in the reflux condenser. The benzol is thereupon drawn off by suction in vacuum and 320 parts of pyridine are stirred with the reaction product. The water-soluble wax-like compound obtained has a melting point of about $110^{\circ}C$.

4. 140 parts of finely pulverized hexamethylenetetramine are stirred with 1208 parts of stearic acid chloride and heated, while stirring constantly, for one hour, at about $110^{\circ}C$. Thereupon, 320 parts of pyridine are added, while stirring. The wax-like water-soluble product has a melting point of about $115^{\circ}C$.

5. 1350 grams of the conversion product obtained in accordance with Example 1 from stearic acid chloride and hexamethylenetetramine are mixed while stirring, with 372 grams of 2-methyl-pyridine. The quaternary pyridinium compound of 2-methyl-pyridine is produced with development of heat. The product is water-soluble.

6. 1350 grams of the conversion product obtained in accordance with Example 1, from stearic acid chloride and hexamethylenetetramine are stirred with 404 grams of triethylamine. The quaternary ammonium compound of triethylamine is produced with simultaneous development of heat. The product is water-soluble.

7. 140 parts of finely pulverized (powdered) hexamethylenetetramine are dissolved in 1400 parts of chloroform and 1340 parts of chloro-carbonic-acid-octadecyl-ester (octadecyl chlor-

carbonate) $C_{18}H_{37}OCOC$ are added; the whole is heated for one hour in the reflux condenser, the solvent is drawn off by suction in vacuum and to the residue, 320 parts of pyridine are added, while stirring. The product is water-soluble.

8. 850 grams of para-toluol sulfonamide $CH_3.C_6H_4.SO_2NH_2$ are melted with 300 grams of trioxymethylene $(CH_2O)_3$ at a temperature of $110-120^{\circ}C$. until the condensation product is formed. Thereupon 1500 grams of stearyl chloride are added, the whole is well stirred and 400 grams of pyridine are added. The product is water-soluble.

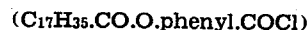
9. 400 grams of stearic-acid-amide



are melted with 85 grams of trioxymethylene $(CH_2O)_3$ at a temperature of $110-120^{\circ}C$. until the condensation product is formed. Thereupon 350 grams of stearyl chloride are added and 150 grams of pyridine are added to the paste. The product is water-soluble.

10. 140 parts of hexamethylenetetramine are dissolved in 1400 parts of chloroform; 906 parts of stearic acid chloride ($C_{17}H_{35}COCl$) are added and the whole is heated for one hour in a reflux condenser. The chloroform is thereupon drawn off by suction in vacuum and the conversion product is stirred with 240 parts of pyridine. There occurs the formation of the quaternary pyridinium compound with the simultaneous development of heat. The white wax-like mass obtained is now soluble in hot water.

11. 140 parts of hexamethylenetetramine are dissolved in 1400 parts of chloroform; 1692 grams of p-stearyl-oxy-benzoic-acid chloride



are added and the whole is heated for one hour in a reflux condenser. The chloroform is thereupon drawn off by suction in vacuum and the conversion product is stirred with 320 parts of pyridine. There occurs the formation of the quaternary pyridinium compound with the simultaneous development of heat. The white wax-like mass obtained is now soluble in hot water.

Although I have described the chemical compounds above as quaternary ammonium salts made with a tertiary amine, it will be understood that I may employ the compounds without such addition of tertiary amine, or other water-solubilizing agent. If such material is omitted from the various compounds above, they are nevertheless useful for treatment of textiles in a similar manner to that herein described, but the treatment is preferably carried out by dissolving the compounds in benzene or similar solvent. An example of such treatment is given below.

The following comprise specific examples of methods now preferred for treating various textile materials according to the invention.

12. 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 prepared according to Example 1, from hexamethylenetetramine, stearic acid chloride and pyridine. The bath also contains 5 grams per liter of sodium acetate. The temperature of the bath is about $40^{\circ}C$. After the impregnation the material is dried and is then subjected for approximately one hour to a heat treatment in a drying chamber at about $120^{\circ}C$.

13. Cotton calico is passed through an aqueous

solution which contains 15 grams per liter of a quaternary pyridinium compound prepared according to Example 3 from hexamethylenetetramine, montanic acid chloride and pyridine. The bath also contains 5 grams per liter of sodium acetate. The said fabric is passed through 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 120° C. for 2 hours.

14. Bleached wool gabardine is passed through an aqueous solution which contains 20 grams per liter of a quaternary pyridinium compound as described in Example 12. The impregnated material is dried and thereupon subjected to heat treatment in a drying chamber at about 90° C. for 4 hours.

15. A crepe de chine fabric which consists of real silk in warp and weft is impregnated in an aqueous solution which contains per liter 15 grams of the quaternary pyridinium compound prepared according to Example 1, from hexamethylenetetramine, stearic acid chloride and pyridine. The bath also contains 5 grams per liter of sodium acetate. The temperature of the bath is about 40° C. After the impregnation the material is dried and is then subjected for approximately two hours to a heat treatment in a drying chamber at about 110° C.

16. A clothing material of spun viscose rayon is impregnated in an aqueous solution of 5 grams per liter of sodium acetate, following the impregnation it is wrung out, dried, and passed through a 1% solution of the conversion product of hexamethylenetetramine and stearic acid chloride (Example 1 without pyridine) in carbon tetrachloride. The solvent is evaporated and the material is subjected for five minutes to a temperature of 110° C.

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 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.

17. 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 prepared according to Example 3 from hexamethylenetetramine, montanic acid chloride and pyridine. After

the impregnation the material is squeezed out, brushed, dried and treated for about 60 minutes at about 110° C. 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.

18. 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:

Formaldehyde 40% solution	cc	400
Ammonium chloride	grams	5
The quaternary pyridinium salt	do	15

such as employed in Example 17.

After impregnation the material is squeezed out, rolled up and remains untreated for 20 minutes. The velvet is then stretched upon a stenter frame and dried at a temperature of about 100° C. During the drying process the velvet pile is brushed. After drying the velvet is further treated 60 minutes at a temperature of about 110° C.

The new compounds described above can also be added to the spinning solutions of viscose and cuprammonium cellulose to produce a filament having water-repellent properties.

19. 20 parts of the quaternary ammonium compound obtained in accordance with Example 6 from stearic acid chloride, hexamethylenetetramine and trimethylamine are stirred to a paste with 40 parts of hot water, and are added to 1000 parts of a viscose solution having 5% of cellulose; the whole is homogeneously mixed and is spun in well-known fashion. The precipitating bath which I prefer to employ contains sulphuric acid (8-10%) with the addition of ammonium sulphate or any other salts and glucose at a temperature of 40° C. The temperature and rate of spinning are substantially the same as those practiced commercially. The spun filament is dried and then heated to 90° C. for 60 minutes. The completed thread manifests water-repellent properties and is of extraordinary softness.

While the invention has been described in detail with respect to various preferred products and preferred methods of making the same, it will be obvious to those skilled in the art after understanding the invention, that further 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. Process for imparting permanent water-repellence to cellulosic fabrics, which comprises: impregnating with a solution of a compound containing an aliphatic radical of at least ten carbon atoms, and comprising the product obtained by reacting a member of the group consisting of fatty acid halide, carbonic ester halide and carbamic acid halide, with hexamethylenetetramine, in the presence of heat and an inert solvent; drying the fabric so impregnated; and heating to a sufficiently high temperature to impart said water-repellence.

2. Process for imparting permanent water-repellence to cellulosic fabrics, which comprises: impregnating with an aqueous solution of a compound containing an aliphatic radical of at least ten carbon atoms, and comprising a tertiary amine combined with the product obtained by

reacting a fatty acid halide with hexamethylenetetramine in the presence of heat and an inert solvent; drying the fabric so impregnated; and heating to a sufficiently high temperature to impart said water-repellence.

3. Process for imparting permanent water-repellence to cellulosic fabrics, which comprises: impregnating with an aqueous solution of a compound containing an aliphatic radical of at least ten carbon atoms, and comprising a tertiary amine combined with the product obtained by reacting a carbamic acid halide with hexamethylenetetramine in the presence of heat and an inert solvent; drying the fabric so impregnated; and heating to a sufficiently high temperature to impart said water-repellence.

4. Process for imparting permanent water-repellence to cellulosic fabrics, which comprises: impregnating with an aqueous solution of a compound containing an aliphatic radical of at least ten carbon atoms, and comprising a tertiary amine combined with the product obtained by reacting a carbamic acid halide with hexamethylenetetramine in the presence of heat and an inert solvent; drying the fabric so impregnated; and heating to a sufficiently high temperature to impart said water-repellence.

5. A permanently water-repellent cellulosic fabric, having its fibers chemically treated by heating after impregnation with an aqueous solution of a compound containing an aliphatic radical of at least ten carbon atoms, and comprising a tertiary amine combined with the product obtained by reacting a member of the group consisting of fatty acid halide, a carbonic ester halide and carbamic acid halide, with hexamethylenetetramine, under conditions such that decomposition of the latter does not occur.

6. A permanently water-repellent cellulosic fabric having its fibers chemically treated by heating after impregnation with a compound containing an aliphatic radical of at least ten carbon atoms, and comprising a tertiary amine combined with the product obtained by reacting a fatty acid halide with hexamethylenetetramine, under conditions such that decomposition of the latter does not occur.

7. A permanently water-repellent cellulosic fabric having its fibers chemically treated by heating after impregnation with a compound containing an aliphatic radical of at least ten

carbon atoms, and comprising a tertiary amine combined with the product obtained by reacting a carbonic ester halide with hexamethylenetetramine, under conditions such that decomposition of the latter does not occur.

8. A permanently water-repellent cellulosic fabric having its fibers chemically treated by heating after impregnation with a compound containing an aliphatic radical of at least ten carbon atoms, and comprising a tertiary amine combined with the product obtained by reacting a carbamic acid halide with hexamethylenetetramine, under conditions such that decomposition of the latter does not occur.

9. Process for imparting permanent water-repellence to cellulosic fabrics, which comprises: impregnating with an aqueous solution of a compound containing an aliphatic radical of at least ten carbon atoms and comprising a tertiary amine combined with the product obtained by reacting a member of the group consisting of fatty acid halide, carbonic ester halide and carbamic acid halide, with hexamethylenetetramine, under conditions such that decomposition of the latter does not occur; drying the fabric so impregnated; and heating at a sufficiently high temperature to impart said water-repellence.

10. Process for imparting permanent water-repellence to cellulosic fabrics, which comprises: impregnating with an aqueous solution of a compound containing an aliphatic radical of at least ten carbon atoms, and comprising a tertiary amine combined with the product obtained by reacting a member of the group consisting of fatty acid halide, carbonic ester halide and carbamic acid halide, with hexamethylenetetramine in the presence of heat and an inert solvent; drying the fabric so impregnated; and heating to a sufficiently high temperature to impart said water-repellence.

11. A permanently water-repellent cellulosic fabric having its fibers chemically treated by heating after impregnation with a solution of a compound containing an aliphatic radical of at least ten carbon atoms, and comprising the product obtained by reacting a member of the group consisting of fatty acid halide, carbonic ester halide and carbamic acid halide, with hexamethylenetetramine, under conditions such that decomposition of the latter does not occur.

EDGAR WOLF.