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CHEMICALS FOR WATER REPELLENCE

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11 Claims. (Cl. 260—237)

This invention relates to water-repellent textiles, chemicals for producing water-repellence, and processes for manufacturing such textiles and chemicals.

This invention may also be said to relate to alternative or improved water-repellents and the processes for making same, useful in a manner generally similar to the water-repellent compounds and treatments disclosed in my copending application Ser. No. 177,054, filed November 29, 1937, reference to which is hereby made.

I have found that in general the compounds derived from substituted ammonia-formaldehyde-condensation products can be converted with acyl 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 acid chlorides with hexamethylenetetramine and subsequent treatment of the reaction product with tertiary bases such as pyridine and others hereinafter mentioned, one may produce water-soluble quaternary compounds. Such compounds comprise highly desirable products for the treatment of textile materials for water-repellence upon properly combining such materials with such products under reaction conditions.

The objects of the invention accordingly include the provision of improved water-repellent textiles treated with compounds of the above indicated character, and the production of the novel chemical compounds, and provision of improved processes for making such chemicals adapted for use in producing such water-repellent textile materials, among other possible uses.

Further and more specific objects, features and advantages of the invention will more fully appear 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 chemical and textile products are manufactured, specific embodiments thereof being described hereinafter by way of various examples according to which I now prefer to practice the invention.

In accordance with the present invention the acyl halides above mentioned may have the general formula R. Co halide, in which R is an aliphatic or aliphatic-aromatic radical in which the aliphatic portion has at least ten carbon atoms. The conversion of such acyl halides with hexamethylenetetramine [$(CH_2)_6N_4$] is preferably effected 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 moles of the acid halide to one mole of the hexamethylenetetramine. The resulting conversion products obtained in this manner may then be converted as by the use of pyridine, 2-methyl-pyridine, triethyl-amine, or equivalent tertiary bases, into quaternary ammonium compounds. Such compounds are remarkably effective in imparting water-repelling properties to textile material when properly applied thereto, in a manner generally similar to the application of the water-repellent chemicals to the textiles as disclosed by said copending application. That is, 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 washing of the substantive dyestuffs of the treated textile material 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 compounds are also suitable for addition to baths serving for imparting crease- or wrinkle-resistant properties to textiles.

In cases where the acyl halides, for example, are converted by the use of substituted ammonia-formaldehyde condensation products, a compound of the general formula $R'.X.NH_2$ is first converted with formaldehyde or trioxymethylene. The converted product is treated with the acyl chloride. In the formula $R'.X.NH_2$, as herein used, R' represents an alkyl radical (such for example as $C_{17}H_{35}$), a cycloalkyl radical for example cyclohexylamine $C_6H_{11}.NH_2$, or an aralkyl radical ($C_{16}H_{33}$.phenyl for example), and X indicates methylen or the C=O or SO_2 group. In place of the fatty acid chlorides, one may also use the corresponding chlorocarbonic acid

(R.OCOCl)

or carbamic acid ester chlorides (carbamido chlorides), such as $C_{18}H_{37}NHCOCl$, for example. As the tertiary bases to be used in such cases, one may for example use the volatile tertiary bases such as pyridine and its homologs, or trimethylamine, triethylamine etc. The resulting products may be used for the same purposes with substantially the same results above specified 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, 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.

Examples

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° C. (with splitting off of formaldehyde).

2. 1208 parts of stearic 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° C.

3. 140 parts of hexamethylenetetramine are dissolved in 1400 parts of chloroform; thereupon, 1768 parts of montanic 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 waxlike compound obtained has a melting point of about 110° C.

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

5. 1350 grams of the conversion product obtained in accordance with Example 1 from stearic chloride and hexamethylenetetramine are mixed while stirring, with 372 grams of 2-methyl-pyridine. The quaternary ammonium 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 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 chlorocarbonic-acid-octadecyl-ester $C_{18}H_{37}.OCOCl$ 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° 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

$C_{17}H_{35}.CONH_2$

are melted with 85 grams of trioxymethylene $(CH_2O)_3$ at a temperature of 110–120° 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

($C_{17}H_{35}.CO.O.phenyl.COCl$)

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.

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 materials in benzine 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 pyridine 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 one hour to a heat treatment in a drying chamber at about 120° 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 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 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 pyridine compound prepared according to Example 1, from hexamethyl-

enetetramine, 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 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 pyridine 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 pyridine 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 homogenously 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 and other salts and glucose at a temperature of 40° C. The temperature and rate of spinning are substantially the same as those practised 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.

The expression "ammonia-formaldehyde compound" as used in the appended claims, is intended to cover compounds of formaldehyde and ammonia and substituted ammonia such as herein described.

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. A process for the production of quaternary ammonium compounds, which comprises reacting hexamethylenetetramine in the presence of heat and an inert solvent, with a fatty acid chloride having an aliphatic radical of at least ten carbon atoms, the amount of such acid chloride used being in the neighborhood of three to four times the amount of hexamethylenetetramine by molar ratio, and treating the resulting conversion product with a tertiary base to convert such product to a quaternary ammonium compound.

2. A process for the production of quaternary ammonium compounds, which comprises reacting hexamethylenetetramine, in the presence of heat and an inert solvent with an acyl chloride having an aliphatic radical of at least ten carbon atoms, and treating the resulting conversion product with a pyridine to convert such product to a quaternary ammonium compound.

3. A process for the production of quaternary ammonium compounds, which comprises reacting hexamethylenetetramine in the presence of heat and an inert solvent with a chlorocarbonic acid ester halide having an aliphatic radical of at least ten carbon atoms, and treating the resulting conversion product with a pyridine to convert such product to a quaternary ammonium compound.

4. A process for the production of quaternary ammonium compounds, which comprises reacting hexamethylenetetramine in the presence of heat and an inert solvent with a carbamic acid halide having an aliphatic radical of at least ten carbon atoms, and treating the resulting conversion product with a pyridine to convert such product to a quaternary ammonium compound.

5. A process of the character described, which comprises: reacting hexamethylenetetramine in the presence of heat and an inert solvent with a compound having the linkage—C:O. halide selected from the group consisting of fatty acid halides, carbonic ester halides and carbamic acid halides.

6. A process for the production of quaternary ammonium compounds, which comprises: reacting hexamethylenetetramine in the presence of heat and an inert solvent with a compound having the linkage—C:O.halide selected from the group consisting of fatty acid halides, carbonic ester halides and carbamic acid halides, and treating the reaction product with a tertiary amine.

7. A condensation product prepared by reacting hexamethylenetetramine, under conditions such that decomposition of the latter does not take place, with a fatty acid halide containing at least ten carbon atoms, and with a tertiary amine.

8. A condensation product prepared by reacting hexamethylenetetramine, under conditions such that decomposition of the latter does not take place, with a carbonic ester halide containing at least ten carbon atoms, and with a tertiary amine.

9. A condensation product prepared by reacting hexamethylenetetramine, under conditions such that decomposition of the latter does not take place, with a carbamic acid halide containing at least ten carbon atoms, and with a tertiary amine.

10. A condensation product prepared by reacting hexamethylenetetramine, under conditions such that decomposition of the latter does not take place, with a compound containing at least ten carbon atoms and selected from the group consisting of fatty acid halides, carbonic ester halides and carbamic acid halides.

11. A condensation product prepared by reacting hexamethylenetetramine, under conditions such that decomposition of the latter does not take place, with a compound containing at least ten carbon atoms and selected from the group consisting of fatty acid halides, carbonic ester halides and carbamic acid halides, combined with a tertiary amine.

EDGAR WOLF.

CERTIFICATE OF CORRECTION.

Patent No. 2,242,565. May 20, 1941.

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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 49, for "R.Co" read --R.CO--; same page, second column, line 40, strike out the word "ester" and insert the same after "acid" in line 37; 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 8th day of July, A. D. 1941.

(Seal)

Henry Van Arsdale,
Acting Commissioner of Patents.

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