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3,510,248

TREATMENT OF CELLULOSIC FIBERS WITH CERTAIN CHLOROAMINES AND CHLOROQUATERNARIES

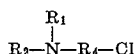
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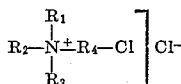
12 Claims

ABSTRACT OF THE DISCLOSURE

Cellulosic fibers are treated with chloroamines and chloroquaternaries to improve the softness and/or water repellency thereof, said chloramines and chloroquaternaries having the general formulae



and



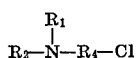
The present invention relates to the process of treating cellulosic fibers with certain chloroamines and chloroquaternaries and to the resulting treated fibers. More particularly, it relates to the method of improving the softness and/or water repellency of cellulosic fibers by treating same with certain chloroamines and chloroquaternaries.

A number of fatty compounds have been used in the past for textile softening purposes. One such compound in use at the present time is dimethyl difatty quaternary ammonium chloride, in which the fatty group is predominantly a C₁₈ saturated group—i.e. stearyl. While these compounds do soften textiles, particularly those derived from cellulosic fibers, such softening is far from permanent and thus the said quaternaries are ordinarily added to the textiles at each washing. It would be highly desirable to eliminate the need to add softening agents each and every time the fabric is washed.

It is, therefore, an object of our invention to provide a process of treating cellulosic fibers to improve the softness and/or water repellency thereof. It is a further object of the invention to provide a method of treating cellulosic fibers with certain chloramines and chloroquaternaries. Another object of the invention is to provide cellulosic fibers of improved softness and/or water repellency. These and other objects will become apparent from the following detailed description.

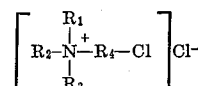
We have now discovered that cellulosic fibers can be treated with certain chloroamines or chloroquaternaries to yield treated fibers with improved and relatively permanent softness and/or water repellency. While we do not wish to be bound by the following theory, it is believed that the fatty groups of the chloroamines and chloroquaternaries employed provide the softening and water repellency and that such desirable improvements are made relatively permanent by the reaction of the hydroxy groups of the fibers and the chlorine groups of the chloroamines and chloroquaternaries. Thus the fatty amine moiety and the fatty quaternary moiety are attached to the fibers through ether linkages.

The chloroamines and chloroquaternaries useful in the practice of the present invention have the following idealized, general formulae:



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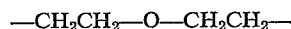
and



where R₁ is a saturated or mono or polyolefinically unsaturated aliphatic hydrocarbon group of from 8 to 24 carbon atoms, R₂ is an alkyl group of 1 to 4 carbon atoms or a saturated or mono or polyolefinically unsaturated aliphatic hydrocarbon group of from 8 to 24 carbon atoms, R₃ is an alkyl group of 1 to 4 carbon atoms and R₄ is a divalent alkylene or alkylene ether group containing from 2 to about 12 carbon atoms. Representative aliphatic hydrocarbon group (R₁, R₂) are octyl, octenyl, nonyl, decyl, decenyl, dodecyl, dodecenyl, ethyldodecyl, tridecyl, hexadecyl, octadecyl, methyloctadecyl, octadecenyl and the like. Representative alkyl groups (R₂, R₃) are methyl, ethyl, propyl, butyl, isobutyl and the like. Representative alkylene or alkylene ether groups (R₄) are —CH₂—, —CH₂CH₂—, —CH₂CH₂O—CH₂CH₂—, —CH₂CH₂CH₂—, —CH₂CH₂CH—O—CH₂CH₂CH₂—, —CH₂CH—CH₃

butylene, isobutylene, pentylene, heptylene, octylene, decylene, and the like.

It is preferred that the aliphatic hydrocarbon group (R₁) is a saturated, straight chained group of 12 to 24 carbon atoms, that the alkyl group (R₂, R₃) is methyl and that R₄ is an alkylene ether group—especially



It is also preferred that R₂ is a saturated, straight chained group of 12 to 24 carbon atoms. As the chain length of R₁ or R₂ is reduced to below 12 carbon atoms, the ability of the chloroamines and chloroquaternaries to provide softness and/or water repellency is also reduced somewhat. Thus compounds where R₁ or R₁ and R₂ are aliphatic hydrocarbon groups of 8 to 11 carbon atoms are less preferred treating agents. However, when fibers treated with such shorter chain length compounds are washed in a solution of an anionic detergent, the softness and/or water repellency is generally increased as is also the case with the longer chain length chloroamines and chloroquaternaries. Apparently, the anionic detergent complexes with the amine or quaternary moieties attached to the fibers and the resulting complex containing fibers have generally further improved softness and/or water repellency.

The chloroamines are prepared by reacting a secondary amine with an alkylene dichloride or an alkylene ether dichloride. The chloroquaternaries are prepared by reacting a tertiary amine with the alkylene dichloride or alkylene ether dichloride. Secondary and tertiary amines having the groups R₁, R₂ and R₃ defined above may be employed. The alkylene dichloride or alkylene ether dichloride employed is one providing the group R₄ defined above.

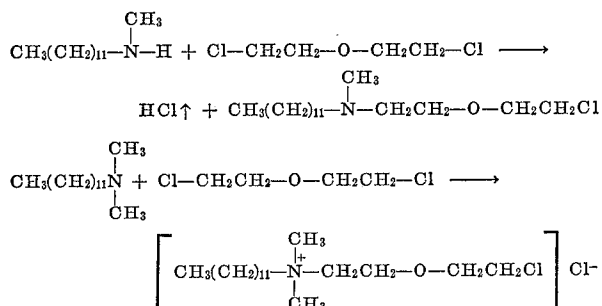
Representative secondary amines are methylstearyl, methyldecyl, methylloctyl, methyldecyl, ethylstearyl, ethyldecyl, ethyldodecyl, methylalanyl, methylmyristyl, methylpalmityl, methyloleyl, methylinoleyl, methyltallow, methyl(hydrogenated tallow), dioctyl, dioctenyl, didodecyl, didecyl, dihexadecyl, dilauryl, dimyristyl, dipalmityl, dioleyl, dilinoleyl, di(hydrogenated tallow) and the like.

Representative tertiary amines are dimethylstearyl, dimethyldecyl, dimethyldodecyl, diethylstearyl, diethyldecyl, diethyldodecyl, dimethyloctyl, dimethylalanyl, dimethylmyristyl, dimethylpalmityl, dimethyloleyl, dimethylinoleyl, dimethyltallow, dimethyl(hydrogenated tallow),

methyldioctyl, methyldioctenyl, ethyldioctyl, methyldidecyl, methyldidodecyl, ethyldidodecyl, methyldihexadecyl, methyldilauryl, methyldimyristyl, methyldipalmityl, methyldioleyl, methyldilinoleyl, methyldi(hydrogenated tallow) and the like. the term "tallow" wherever used refers to the mixture of hydrocarbon radicals derived from the mixture of fatty acids obtained from tallow. The term "hydrogenated tallow" refers to such mixtures of radicals which are essentially saturated and consist mainly of the stearyl and palmityl radicals.

Representative alkylene dichlorides and alkylene ether dichlorides are trimethylene dichloride, tetramethylene dichloride, 2,2'-dichlorodiethyl ether, dichloroisopropyl ether, decamethylene dichloride and the like.

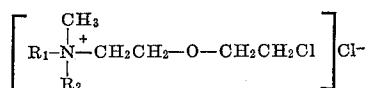
The described chloroamines and chloroquaternaries are prepared by slowly contacting the secondary or tertiary amine with an excess of the dichloride compounds. This reaction is preferably carried out at temperatures of about 100° C. to 150° C. After completion of the reaction the excess dichloride which also acts as the reaction solvent is removed such as by distillation or the like. The product can then be recrystallized from ethyl acetate if desired. The reactions can be illustrated as follows using 2,2'-dichlorodiethyl ether and methyldodecyl amine and dimethyldodecyl amine:



The preparation of the chloroamines and chloroquaternaries useful in the present invention is further illustrated by the following examples:

EXAMPLE A

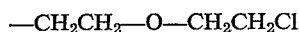
Two hundred eighty six grams (2 moles) of dichloroethyl ether and 16.8 g. (0.2 moles) NaHCO_3 were added to a reaction flask fitted with a stirrer and heated to 110° C. One hundred five grams (0.2 mole) di(hydrogenated tallow) methyl amine were then slowly added with stirring over a one half hour period. Heating and stirring was continued for about six hours during which time the highest temperature reached was 130° C. Excess dichloroethyl ether was removed and the product was recrystallized from ethyl acetate. There was obtained 94.3 g. of a solid white product which consisted essentially of the chloroquaternary having the formula:



where R_1 and R_2 are hydrogenated tallow.

EXAMPLE B

Example A is essentially repeated using methyl (hydrogenated tallow) amine. There is obtained the corresponding chloroamine containing the



group.

The chloroamines and chloroquaternaries are useful in treating cellulosic fibers or articles prepared from such fibers alone or in combination with noncellulosic fibers such as nylon, polyester fibers and the like. The invention is particularly applicable to the treatment of woven cellulosic textile materials. However, fibrous sheets, pads,

films and the like, laid down from cellulose fibers can be treated even though in a nonwoven form.

The cellulosic fibers can be treated with the chloroquaternaries and chloroamines by various methods. A preferred method is to immerse the fibers or articles (i.e. fabrics) derived therefrom in an aqueous solution or emulsion of the said chloroamines or chloroquaternaries. The saturated fibers or articles are then dried and cured at temperatures in the range of about 90° C. to about 140° C. Curing temperatures of 100° C. to 110° C. are preferred. The reaction between the cellulosic fibers and the chloroamines or chloroquaternaries is catalyzed by sodium hydroxide. The sodium hydroxide apparently reacts with the cellulosic hydroxyl groups to yield $-\text{ONa}$ groups. The latter groups then apparently react with the $\text{Cl}-\text{R}_4-$ groups to yield $-\text{O}-\text{R}_4-$ linkages and NaCl .

The sodium hydroxide can be added to the fiber, the aqueous treating solution or after the chloroamine or chloroquaternary has been brought into contact with the fiber. One preferred method is to pretreat the fibers with an aqueous solution of NaOH . Another preferred procedure is to add the NaOH to the aqueous solution or emulsion of the chloroamine or chloroquaternary and then immerse the fibers in such composite treating solution. The NaOH catalyst can be used in widely varying amounts such as from about 0.01 to 15% by weight and higher based on the dry weight of the cellulosic fibers or articles derived therefrom. The higher levels of NaOH are preferably used when the fibers are pretreated—i.e. the NaOH is added to the fibers prior to the addition of the chloroamine or chloroquaternary. The use of aqueous solutions or emulsions of the chloroamines or chloroquaternaries is preferred in order to obtain a fairly even distribution of the said compounds on the fibers or articles. In addition, the water is readily removed by drying, such as during the curing step.

The chloroamines and chloroquaternaries are used in an amount sufficient to improve the softness and/or water repellency of the cellulosic fibers. Preferably, the compounds are used in an amount of about 0.05 to 10% by weight based on the dry weight of the fibers. Amounts of about 0.5 to 2.5% by weight are especially preferred. At the higher levels, the fibers have increased softness levels, the fibers have increased softness and a considerable amount of water repellency. At the lower levels, the fibers have increased softness and a considerable amount of water repellency.

The following specific description further illustrates the present invention.

EXAMPLE 1

The chloroquaternary of Example A was dissolved in a 1.0% by weight aqueous NaOH solution at a level of 1% by weight. Birdseye cotton swatches (36" by 12") were immersed in an excess of the treating solution with agitation for one minute at room temperature and then wrung out to a 100% by weight wet pickup based on the dry weight of the cloth. The swatches were then dried and cured 15 minutes at 100° C. Following this curing step, the swatches were rinsed in water to remove NaOH and again dried. The specimens of cotton thus treated were very soft and water repellent as compared to an untreated control. Repeated washing of such treated swatches using the nonionic detergent "All" did not reduce the fine properties of the cloth. When the swatches were stained with bromphenol blue, a blue complex was formed with the quaternary moiety indicating the permanency of the treatment.

EXAMPLE 2

Example 1 was repeated except that no NaOH was included in the treating solution and the cotton swatches were pretreated with NaOH . Thus the swatches were immersed in an approximately 15% by weight aqueous NaOH solution for one minute at room temperature fol-

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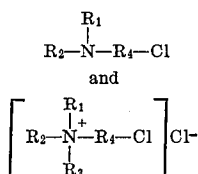
lowed by wringing out to about 200% wet pickup based on the dry weight of the cloth. The pretreated swatches were then immersed in chloroquaternary solution, dried and cured as in Example 1. The swatches had essentially the same fine properties as those prepared in Example 1. Repeated washing of such swatches using "All" did, however, lower the water repellency a small amount.

Softening and/or water repellency is also obtained by treating the cellulosic fibers as in Examples 1 and 2 with various of the other described chloroamines and chloroquaternaries such as those compounds obtained by reacting hexamethylene dichloride or 2,2'-dichloroethyl ether with methyldodecyl amine, methyl(hydrogenated talow) amine, methyldidodecyl amine and the like.

While specific examples of the invention have been described, it will be evident that other variations of the invention are possible within the scope of the following claims.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process of treating cellulose fibers which comprises contacting said fibers with a compound selected from chloroamines and chloroquaternaries in an amount sufficient to improve the softness and/or water repellency of the fibers and curing the fibers, said chloroamines and chloroquaternaries having the formulae:



where R_1 is an aliphatic hydrocarbon group of from 8 to 24 carbon atoms, R_2 is an alkyl group of 1 to 4 carbon atoms or an aliphatic hydrocarbon group of from 8 to 24 carbon atoms, R_3 is an alkyl group of 1 to 4 carbon atoms and R_4 is an alkylene or alkylene ether group containing from 2 to about 12 carbon atoms.

2. The process of claim 1 wherein the cellulosic fibers are in the form of a woven fabric.

3. The process of claim 1 wherein the cellulosic fibers are contacted with the compound by immersing the former in an aqueous solution or emulsion of the latter.

4. The process of claim 1 wherein the compound is used in amount of about 0.05 to 10% by weight based on the dry weight of the cellulosic fibers.

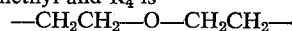
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5. The process of claim 1 wherein the curing of the fiber-compound is carried out at temperatures of about 90° C. to 140° C.

6. The process of claim 1 wherein R_2 is an aliphatic hydrocarbon group of 8 to 24 carbon atoms.

7. The process of claim 1 wherein R_1 and R_2 are aliphatic hydrocarbon group of 12 to 24 carbon atoms.

8. The process of claim 1 wherein the compound is a chloroquaternary and wherein R_1 and R_2 are saturated, straight chain hydrocarbon groups of 12 to 24 carbon atoms, R_3 is methyl and R_4 is



9. The process of claim 7 wherein the compound is a chloroamine.

10. The process of claim 1 wherein the cellulosic fibers are in the form of a woven fabric, the contacting is carried out by immersing the fabric in an aqueous solution of the compound, the aqueous solution contains NaOH as a catalyst, the compound is a chloroquaternary, the chloroquaternary is used in an amount of about 0.05 to 10% by weight based on the dry weight of the fabric, the curing is carried out at a temperature of about 90° C. to 140° C., and R_1 and R_2 are aliphatic hydrocarbon groups of 12 to 24 carbon atoms.

11. The process of claim 10 wherein R_3 and R_4 is $-CH_2CH_2-O-CH_2CH_2-$.

12. The treated cellulosic fibers prepared by the process of claim 1.

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GEORGE F. LESMES, Primary Examiner

J. R. MILLER, Assistant Examiner

U.S. Cl. X.R.

260-563, 567.6

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,510,248

Dated May 5, 1970

Inventor(s) Jean B. Thielen, James L. Keen and Lyle F. Elmquist

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 49 "chloramines" should read --chloroamines--.
Column 2, line 14 "group" should read --groups--; line 20 insert a comma --,-- after last formula; line 21 "-CH₂CH₂CH-O" should read -- -CH₂CH₂CH₂-O --; line 21 insert a comma --,-- after last formula. Column 3, line 5 "like. the term" should read --like. The term--. Column 4, lines 44 and 45 cancel "levels, the fibers have increased softness and a considerable amount of" and insert --but greatly increased--; line 61 "speciments" should read --specimens--. Column 5, line 22 "cellulose" should read --cellulosic--. Column 6, line 2 after "compound" insert --combination--; line 25 after "R₃" insert --is methyl--.

SIGNED AND
SEALED
MAR 2 1971

(SEAL)

Attest:

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Attesting Officer

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Commissioner of Patents