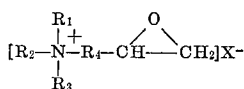


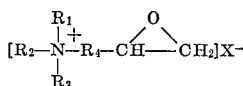
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No Drawing. Filed Feb. 8, 1967, Ser. No. 614,555
Int. Cl. D06m 13/34

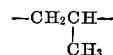
Cellulosic fibers are treated with glycidyl quaternaries to improve the softness and/or water repellency thereof, said glycidyl quaternaries having the general formula



The glycidyl quaternary ammonium compounds useful in the practice of the present invention have the following idealized, general formula:



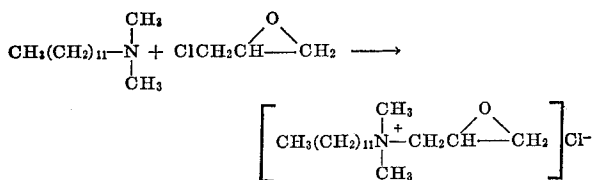
an alkyl group of 1 to 4 carbon atoms or a saturated or mono or polyolefinically unsaturated aliphatic hydrocarbon group of from 8 to 24 carbon atoms, R_3 is a saturated or mono or polyolefinically unsaturated aliphatic hydrocarbon group of from 8 to 24 carbon atoms, R_4 is a divalent alkylene group of from 1 to 3 carbon atoms and X^- is an anion. Representative alkyl groups (R_1 , R_2) are methyl, ethyl, propyl, butyl, isobutyl and the like. Representative aliphatic hydrocarbon groups (R_2 , R_3) are octyl, octenyl, nonyl, decyl, decenyl, dodecyl, dodecenyl, ethyldodecyl, tridecyl, hexadecyl, octadecyl, methyl octadecyl, octadecenyl and the like. Representative alkylene groups (R_4) are $-CH_2-$, $-CH_2CH_2-$, $-CH_2CH_2CH_2-$ and



The described glycidyl quaternary ammonium compounds are prepared by simply mixing substantially equimolar quantities of the tertiary amine and epihalohydrin in water and allowing the reaction to proceed preferably with agitation until formation of the product is complete. The water can be removed from the product by the use of a flash evaporator. It is also preferred to use a slight excess of the epihalohydrin (i.e. 5%). The reaction can be illus-

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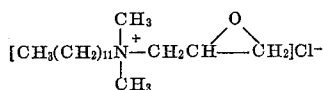
trated as follows using epichlorohydrin and dimethyl-dodecyl amine:



The preparation of the glycidyl quaternary ammonium compounds useful in the present invention is further illustrated by the following examples:

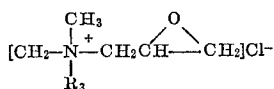
EXAMPLE A

Four hundred twenty six grams (2 mole) dodecyl-dimethyl amine, 194 g. (2.1 mole) epichlorohydrin and 2000 g. water were added to a reaction flask. The reaction mixture was agitated at room temperature for about two hours and then the pH was adjusted to 10.4 with hydrochloric acid to stabilize the epoxy group. The reaction mixture was agitated overnight and then warmed to 45–50° C. for two hours. It was then cooled to room temperature. The resulting product analyzed 23.1% by weight solids, the latter consisting of 81.8% by weight glycidyl quaternary of the formula



EXAMPLE B

Example A was repeated using 291 g. (1 mole) hydrogenated tallow dimethyl amine, 97 g. (1.05 mole) epichlorohydrin and 100 g. water. The resulting product analyzed 27.4% by weight solids, the latter consisting of 86.5% by weight glycidyl quaternary having the formula



where R_3 is hydrogenated tallow.

The glycidyl quaternary ammonium compounds 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 non-woven form.

The cellulosic fibers can be treated with the glycidyl quaternary ammonium compound 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 glycidyl quaternary ammonium compound. 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 glycidyl quaternary ammonium compound is also preferably carried out in the presence of a catalyst. The catalyst may be an acid or base. Representative acid type catalysts are zinc perchlorate and zinc fluoroborate. A preferred basic catalyst is sodium hydroxide. The catalyst can be added to the fiber, the aqueous treating solution or after the glycidyl quaternary ammonium compound 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 glycidyl quaternary ammonium compound and then immerse the fibers in such composite treating solution. The 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

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derived therefrom. When NaOH is used, the concentration thereof in the aqueous solution should not exceed about 15% by weight. Also, such fairly concentrated solutions are preferably used to pretreat the fibers—i.e. the NaOH is added to the fibers prior to the addition of the glycidyl quaternary ammonium compound. The use of aqueous solutions or emulsions of the glycidyl quaternary ammonium compound are preferred in order to obtain a fairly even distribution of the said compound on the fibers or articles. In addition, the water is readily removed by drying, such as during the curing step.

The glycidyl quaternary ammonium compounds 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 but greatly increased water repellency. At the lower levels, the fibers have increased softness and a considerable amount of water repellency.

As indicated above, washing of the treated cellulose fibers in aqueous solutions of anionic detergents tends to increase both softness and water repellency. It is believed that this is due to the formation of a complex between the anionic detergent and cationic moiety of the quaternary compound.

The following specific description further illustrates the present invention.

EXAMPLE 1

The glycidyl quaternaries as prepared in Examples A and B and Aliquat H226 (a dimethyl difatty quaternary ammonium chloride wherein the fatty groups are mainly stearyl) were each dissolved in 0.5% by weight aqueous NaOH solutions at a level of 1% by weight. Birdseye cotton swatches (36" by 12") were immersed in an excess of treating solutions 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 then subjected, along with an untreated control, to a softness test by a panel of women. The treated cloth and the control were placed in normal 8-pound wash loads and washed using water at 140° F. and either "Fels" soap or "Tide" detergent at the recommended levels of usage. The samples were also coded prior to being subjected to the panel. The numbers in the following table indicate the number of times the indicated sample of each pair was chosen as being softer out of 24 tests. The smaller numbers in parenthesis indicate the statistical significance level of the test (the smaller the number, the more highly significant the result—N.S. means not significant).

TABLE I

1 Wash ¹	6 Washes
"Fels" Soap Washed	
A-18 vs. D-6 (0.025).....	A-22 vs. D-2 (0.01).
A-17 vs. C-7 (0.05).....	A-11 vs. C-13 (N.S.).
B-21 vs. D-3 (0.01).....	B-24 vs. D-0 (0.01).
B-23 vs. C-1 (0.01).....	B-18 vs. C-6 (0.025).
"Tide" Washed	
A-21 vs. D-3 (0.01).....	A-23 vs. D-1 (0.01).
A-24 vs. C-0 (0.01).....	A-22 vs. C-2 (0.01).
B-23 vs. D-1 (0.01).....	B-22 vs. D-2 (0.01).
B-24 vs. C-0 (0.01).....	B-20 vs. C-4 (0.01).

¹ A = cloth treated with the glycidyl quaternary ammonium compound of Example A; B = cloth treated with the glycidyl quaternary ammonium compound of Example B; C = cloth treated with Aliquat H226; D = untreated cloth.

The above data show that cotton fabric treated with the glycidyl quaternaries is very significantly softened. In addition it shows that the treatment according to the pres-

ent invention is generally more permanent than treatment with the well known softener Aliquat H226.

EXAMPLE 2

Swatches of Birdseye cotton cloth were treated as in Example 1 with the glycidyl quaternary ammonium compounds of Examples A and B and Aliquat H226. Additional swatches were pretreated in approximately 15% by weight NaOH aqueous solutions for five minutes at room temperature followed by wringing out to about 200% wet pickup based on the dry weight of the cloth. These pretreated swatches were then immersed in solutions of the glycidyl quaternaries of Examples A and B and cured as in Example 1. The various swatches were then tested for water absorption before washing and after washing as in Example 1. In the following table, the figures represent the percent of water absorbed based on the amount of water absorbed by a pre-washed control, washed once in a non-ionic detergent. The lower the value, the more repellent the sample is.

TABLE II

	No. of Washes		
	0	1	6
"Fels" Soap Washed:			
Control, percent.....	100(±10)	107	110
Aliquat H226.....	28	82	100
A ¹	97	85	110
B.....	88	20	30
A-Pre.....	87	75	10
B-Pre.....	45	10	8
"Tide" Washed:			
Control, percent.....	100(±10)	88	92
Aliquat H226.....	28	95	85
A.....	97	62	65
B.....	88	12	20
A-Pre.....	87	(²)	100
B-Pre.....	45	(²)	12

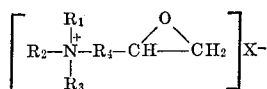
¹ A—Cloth treated with the glycidyl quaternary of Example A as in Example 1; B—Cloth treated with the glycidyl quaternary of Example B as in Example 1; A-Pre.—Cloth treated with the glycidyl quaternary of Example A using the NaOH pretreatment; B-Pre.—Cloth treated with the glycidyl quaternary of Example B using the NaOH pretreatment.
² Not tested.

The data of this example show that the glycidyl quaternaries improve the water repellency of the cotton cloth and that such improvement is generally heightened by washing of the cloth in anionic detergent solutions. The glycidyl quaternaries also generally give more permanent water repellency to the cloth than the conventional and known Aliquat H226 softener.

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 cellulosic fibers which comprises contacting said fibers with a glycidyl quaternary ammonium compound in an amount sufficient to improve the softness and/or water repellency of the fibers and curing the fibers, said glycidyl quaternary ammonium compound having the formula:



where R₁ is an alkyl group of 1 to 4 carbon atoms, R₂ is an alkyl group of 1 to 4 carbon atoms or an aliphatic

hydrocarbon group of from 8 to 24 carbon atoms, R₃ is an aliphatic hydrocarbon group of from 8 to 24 carbon atoms, R₄ is an alkylene group of 1 to 3 carbon atoms, and X⁻ is an anion.

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 glycidyl quaternary ammonium compound by immersing the former in an aqueous solution or emulsion of the latter.

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

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

6. The process of claim 1 wherein R₂ is an alkyl group of 1 to 4 carbon atoms.

7. The process of claim 1 wherein R₃ is an aliphatic hydrocarbon group of 12 to 24 carbon atoms.

8. The process of claim 1 wherein R₁ is methyl, R₂ is methyl, R₃ is a saturated, straight chain hydrocarbon group of 12 to 24 carbon atoms, R₄ is —CH₂— and X⁻ is Cl⁻.

9. The process of claim 8 wherein R₃ is dodecyl.

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 glycidyl quaternary ammonium compound, the aqueous solution contains a catalyst, the glycidyl quaternary ammonium compound 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 R₂ is an alkyl group of 1 to 4 carbon atoms.

11. The process of claim 10 wherein the catalyst is sodium hydroxide, R₁ and R₂ are methyl, R₃ is dodecyl, R₄ is —CH₂— and X⁻ is Cl⁻.

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

13. The process of claim 1 including the step of treating the cellulosic fibers with an aqueous solution of sodium hydroxide prior to contacting the fibers with the glycidyl quaternary ammonium compound.

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GEORGE F. LESMES, Primary Examiner
 J. R. MILLER, Assistant Examiner

U.S. Cl. X.R.

260—348, 567.6

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,510,246 Dated May 5, 1970

Inventor(s) 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 2, line 4, "hydrcarbon" should read --hydrocarbon--.
Column 3, line 39 of the formula " $\overline{\text{CH}_2}$ -" should read -- $\overline{\text{CH}_3}$ - --.
Column 6, line 24 "mehtyl" should read --methyl--.

SIGNED AND
SEALED
JAN 5 1971

(SEAL)

Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents