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# DETERGENT COMPOSITIONS CONTAINING POLYMERIC QUATERNARY AMMONIUM SALTS

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U.S. Cl. 252—106

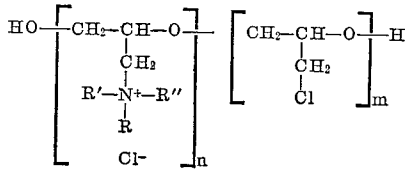
6 Claims

## ABSTRACT OF THE DISCLOSURE

Detergent compositions containing quaternary ammonium salts of polymerized epichlorohydrin are disclosed. These detergent compositions have effective antibacterial activity.

This application is a continuation-in-part of the copending application of George B. Walker and Cushman M. Cambre, Ser. No. 335,665, filed Jan. 3, 1964, now Patent No. 3,428,680.

This invention relates to antibacterial quaternary ammonium salts of polymerized epichlorohydrin and to a method of preparing the same. More particularly, this invention relates to salts having the following structural formula:



wherein R is an aliphatic group containing from 1 to about 24 carbon atoms, R′ and R″ each are aliphatic groups containing from 1 to about 4 carbon atoms. R′ and R″ can be different in the same compound. R, R′ and R″ have this definition throughout the description of this invention; they are preferably *n*-alkyls. $n+m$ ranges from 2 to 50; $n$ ranges from 1 to 50; $m$ ranges from 0 to 49. $n+m+$ the number of carbon atoms in R must be greater than 12. Preferably $n+m$ has a value of 4 to 15, $n$ a value of 1 to 15 and $m$ a value of 0 to 14. $n$, $m$ and $n+m$ are average values by the nature of the reaction forming the polymers; therefore, $n$, $m$ and $n+m$ can have fractional values.

Antibacterial quaternary ammonium chlorides are known to the art. Antibacterial compounds of the above structural formula, however, are not.

It is, therefore, an object of this invention to provide polyquaternary ammonium compounds having the above formula which are outstandingly active as antibacterial agents.

It is a further object of this invention to prepare such compounds by reacting acyclic tertiary amines with polyepichlorohydrin.

These and other objects will become apparent as the invention is hereafter described in more detail.

Anti-bacterial acyclic polyquaternary ammonium compounds, none of which are known to be described in the prior art and exemplary of those within the present invention, are set forth in Table I below wherein the tertiary amine, $m$ and $n$ are applied in the structural formula set forth above.

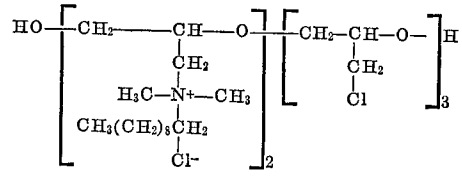


TABLE I

| Moles epichlorohydrin in polymer=$n+m$: | Acyclic tertiary amine $R'-N(R'')-R$ |
|---|---|
| 5 | Octyldimethyl. |
| 5 | Decyldimethyl. |
| 5 | Dodecyldimethyl. |
| 5 | Dodecyldiethyl. |
| 5 | Octadecyldimethyl. |
| 12.5 | Trimethyl. |
| 12.5 | Triethyl. |
| 12.5 | Tripropyl. |
| 12.5 | Methylethylpropyl. |
| 12.5 | Tributyl. |
| 12.5 | Hexyldimethyl. |
| 12.5 | Octyldimethyl. |
| 12.5 | Decyldimethyl. |
| 12.5 | Dodecyldimethyl. |
| 12.5 | Dodecyldiethyl. |
| 12.5 | Dodecylmethylethyl. |
| 12.5 | Dodecylethylbutyl. |
| 12.5 | Octadecyldimethyl. |
| 12.5 | Eicosyldimethyl. |
| 12.5 | Docosyldimethyl. |
| 25.0 | Trimethyl. |
| 25.0 | Triethyl. |
| 25.0 | Tripropyl. |
| 37.5 | Trimethyl. |
| 37.5 | Triethyl. |
| 37.5 | Tripropyl. |
| 37.5 | Octadecylmethylbutyl. |

In the above table the value of $m$ can be 0, 1 or range up to $n+m-1$.

The preferred compound within the scope of the invention is:



Compounds similar to those of the present invention but with R′ and/or R″ containing more than about 4 carbon atoms apparently cannot be formed in a reasonable amount of time.

The degree of polymerization ($n+m$) is arbitrarily limited to 50 because of difficulty in producing compounds with $n+m$ greater than 50. If a tertiary amine is reacted with epichlorohydrin, the tertiary amine catalyzes polymerization, and the monomer apparently cannot be formed. If $n+m+$ the number of carbon atoms in R is not greater than 12, compounds similar to those of the present invention can be formed. However, such compounds do not have anti-bacterial properties. Thus, for anti-bacterial properties in polymers having a low degree of polymerization, a long chain length R is necessary.

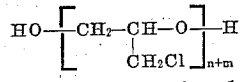
The degree of quaternization or $n$ must at least be 1. No increase in anti-bacterial efficacy is apparent over $n=1$ as the value of $n$ is raised. The precise value of $m$ within the above stated ranges is not critical.

These anti-bacterial acyclic polyquaternary ammonium compounds can be produced by a variety of methods. It is preferable to start with polymerized epichlorohydrin. The polymerized epichlorohydrin is reacted with an acyclic tertiary amine, either in the presence of a solvent or with no solvent present, together with a suitable quaternization catalyst. If a solvent is present, the reaction can be carried out at the reflux temperature of the solvent.

If no solvent is present, the boiling point of the acyclic tertiary amine is the limiting reaction temperature.. Mixtures of acyclic tertiary amines can be employed or different amines meeting the limitations herein can be added sequentially. Generally, reaction temperatures range from 60° F. to 300° F.

Examples of acyclic tertiary amines that can be used to produce compositions within the scope of the present invention are trimethylamine, triethylamine, tripropylamine, methylethylpropylamine, tributylamine, hexyldimethylamine, octyldimethylamine, decyldimethylamine, dodecyldimethylamine, dodecylmethylethylamine, dodecyldiethylamine, dodecylethylbutylamine, octadecyldimethylamine, octadecylmethylbutylamine, eicosyldimethylamine and docosyldimethylamine.

The polymerized epichlorohydrin referred to above has the following structure:

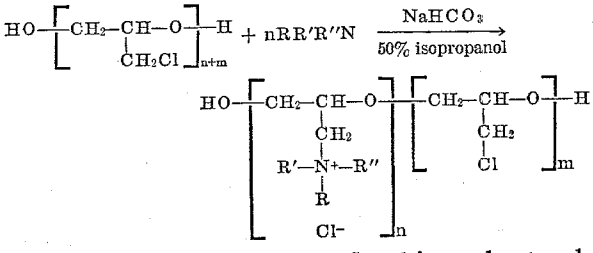


wherein $n+m$ is the degree of polymerization. The $-CH_2Cl$ group in the polyepichlorohydrin structure will hereafter be referred to as a pendent chloromethyl group and the —Cl atom in the polyepichlorohydrin structure as a pendent chlorine atom.

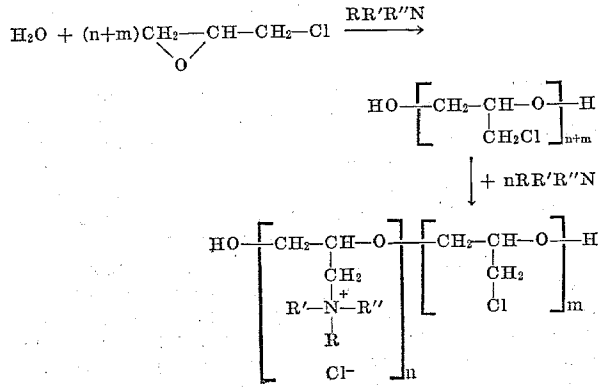
Examples of catalysts that can be used in a process to produce the compounds of the present invention are alkaline substances such as sodium bicarbonate, sodium hydroxide, potassium bicarbonate, potassium hydroxide and mixtures of these. The amount of catalyst to be used ranges from 0.1 to 6% by weight of polyepichlorohydrin.

Suitable solvents for such a process include water, acetone, benzene and lower primary alcohols such as methyl, ethyl, propyl, isopropyl, butyl and iso-butyl alcohols.

In the preferred method, polyepichlorohydrin, e.g. where $n+m=12.5$, is refluxed in aqueous isopropanol in the presence of $NaHCO_3$ catalyst with sufficient molar quantities of an acyclic tertiary amine, e.g. trimethylamine, to quaternize from 1 to $m+n$ of the pendent chlorine atoms in the pendent chloromethyl groups. This is shown in the following representative equation:



Also epichlorohydrin can be refluxed in a solvent such as benzene with an acyclic tertiary amine, e.g. trimethylamine, as a polymerization catalyst followed by the quaternization of the polyepichlorohydrin thus formed by the same amine. This is shown in the following representative equation, e.g. wherein $n+m=12.5$:





The following specific examples are illustrative of the present invention, but are not limitive thereof:

## EXAMPLE I

A mixture of 100 parts (0.087 mole) of polyepichlorohydrin with an average molecular weight of 1150, equivalent to 12.5 moles epichlorohydrin monomer in the polymer or $n+m=12.5$ (Dow Chemical Co., Polyglycol 166–1150), 78.4 parts of 25% aqueous trimethylamine solution (equivalent to 0.335 mole of anhydrous trimethylamine), and 178.4 parts of isopropyl alcohol, together with 6 parts sodium bicarbonate (6% by weight, based on polyepichlorohydrin) was refluxed for a total of seven hours. The reaction mixture was cooled to room temperature and $NaHCO_3$ removed by filtration. Removal of isopropyl alcohol under aspirator vacuum yielded a tan waxy material that was completely water soluble and ether insoluble. Ionizable chloride content: actual 9.4%; theory, 10.2%; this indicates a high degree of quaternization of 92.0%. The formed compound had the general structural formula set forth above with $n+m=12.5$, $n=4$, and the tertiary amine=trimethylamine; it is effective as an antibacterial agent.

## EXAMPLE II

A mixture of 100 parts (0.087 mole) of polyepichlorohydrin similar to that used in Example I was refluxed with 33.90 parts (0.335 mole) of triethylamine together with 133.9 parts of isopropyl alcohol and 6 parts of sodium bicarbonate for a total of seven hours. The product obtained after removal of the sodium bicarbonate by filtration at room temperature, and the isopropyl alcohol by evaporation, was a light tan waxy solid that was water soluble and either insoluble. The ionizable chloride content was 8.25% while the theoretical content was 9.10%, indicating a quaternization of 90.5%. The formed compound had the general structural formula set forth above with $n+m=12.5$, $n=4$, and the tertiary amine= triethylamine; it is effective as an anti-bacterial agent.

## EXAMPLE III

One hundred parts (0.22 mole) of polyepichlorohydrin (Dow Chemical Company Polyglycol 166–450, average molecular weight=450, equivalent to 5 moles of epichlorohydrin in the polymer or $n+m=5$), 141 parts of dodecyldimethylamine (0.66 mole) and 6 parts of sodium bicarbonate were heated together under a nitrogen atmosphere for a total time of five hours between the temperatures of 150 and 160° C. The reaction mixture was freed from sodium bicarbonate by filtration and was soluble in isopropanol and in water but was ether insoluble. Ionizable chloride content of 8.25% compared to the theoretical value of 9.75% indicated that a quaternization completeness of 84.5% was obtained. The formed compound had the general structural formula set forth above with $n+m=5$, $n=3$ and the tertiary amine=dodecyldimethylamine; it is effective as an antibacterial agent.

## EXAMPLE IV

One hundred parts of polyepichlorohydrin (0.22 mole) as in Example III, 46.86 parts (0.22 mole) dodecyldimethylamine, 147 parts isopropyl alcohol, and 6 parts of sodium bicarbonate were refluxed together for seven hours. The product of this reaction was freed from sodium bicarbonate by filtration when cool and the alcohol was removed under vacuum. The resulting material was water soluble and ether insoluble. The ionizable chloride content of 3.58% compared with the theoretical value of 5.35% indicated that quaternization to the extent of 67% had occurred. The formed compound had the general structural formula set forth above with $n+m=5$, $n=1$ and the tertiary amine=dodecyldimethylamine; it is effective as an antibacterial agent.

## EXAMPLE V

One hundred parts (0.22 mole) of polyepichlorohydrin as in Example III, 140.58 parts (0.66 mole) of dodecyldimethylamine (mole ratio amine to polyepichlorohydrin—3/1), 240 parts of isopropyl alcohol and 6 parts of sodium bicarbonate were refluxed together for a total time of five hours. The polyepichlorohydrin was added in two portions; one-half at the start of reflux and one-half after two hours had elapsed. After working up the reaction product as described in previous example, a tan waxy gum was obtained that dissolved in water or isopropanol but was ether insoluble. The ionizable chloride content of 8.40% indicated a quaternization completeness of 86%. The formed compound had the general structural formula set forth above with $n+m=5$, $n=3$ and the tertiary amine=dodecyldimethylamine; it is effective as an anti-bacterial agent.

## EXAMPLE VI

Epichlorohydrin, 115.6 parts (1.25 moles), was dissolved in 275.6 parts of benzene and the mixture was brought to the reflux temperature. 106.5 parts (0.5 mole) of dodecyldimethylamine was added slowly to the refluxing mixture. After a total reflux time of 7 hours, the product was freed from benzene in a rotary evaporator under vacuum and the orange waxy residue thus obtained was water soluble and ether insoluble and contained 1.9% oxirane oxygen compared to the initial value of 8.3% indicating 77% utilization of the epichlorohydrin. The molecular weight (ebullioscopic) was 890 indicating that approximately two dodecyldimethylamine molecules were attached to a polyepichlorohydrin molecule containing five monomer units. The formed compound had the general structural formula set forth above with $n+m=5$; $n=2$ and the tertiary amine=dodecyldimethylamine; it is an effective anti-bacterial agent.

Effective agents are also obtained by substituting in the foregoing examples various other previously described acyclic tertiary amines for the amines there employed. Similar results are also achieved by replacing the solvent and the catalyst of the preceding examples with other solvents and catalysts of the character hereinbefore indicated.

## EXAMPLE VII

As indicated previously, the polyquaternary ammonium compounds described herein have been discovered to be valuable anti-bacterial agents. The anti-bacterial activity of these compounds was determined by conducting "Standard Tube Dilution Tests." Such tests are conducted in vitro and consist essentially of preparing test tubes of a standardized broth medium containing serial dilutions (diminishing concentrations) of a compound being tested, inoculating each tube with a preselected micro-organism and after an incubation period, determining the growth of bacteria in each tube.

The broth medium employed in these asay tests was an FDA phenol coefficient test nutrient broth. Stock solutions of the test product were then prepared in sterile distilled water. Serial dilutions were prepared of the test stock solution and then placed into the tubes containing the nutrient broth.

The broth tubes were inoculated with a bacterial suspension prepared in the following manner. A 24 hour broth culture of gram-positive *Staphylococcus aureus* FDA 209 was prepared. One-tenth milliliter quantities of the broth culture were added per each previously prepared broth tube containing the test materials. Gram-negative *Escherichia coli* ATCC 10536 cultures were prepared as inoculum in a similar manner.

Treatment tubes were incubated for 48 hours at 37° C. and then observed for the presence or absence of growth. The smallest concentration of test material completely inhibiting growth is the end point. This concentration (parts per million of bacteriostatic agent) is called the bacteriostatic breakpoint. Appropriate sterility and inoculum controls were incorporated.

In order to allow for a comparison of the relative bacteiostatic effectiveness of the novel acyclic polyquaternary ammonium compounds, similar in vitro tests were run on heterocyclic polyquaternary ammonium compounds prepared as shown in Wittcoff, U.S. Letters Patent 2,483,749, granted Feb. 24, 1948.

Such heterocyclic compounds were prepared using pyridine and quinoline tertiary amines.

The results of the in vitro tests described above are tabulated in Table II.

TABLE II

| Moles epichlorohydrin in polymer=n+m | Tertiary amine | Moles amine per mole of polymer=n | Bacteriostatic breakpoints (parts per million) | |
|---|---|---|---|---|
| | | | Gram positive micro-organism [1] | Gram negativ-micro organism |
| 5 | Octyldimethyl | 2 | >0.9<1 | >4<6 |
| 5 | Decyldimethyl | 2 | >0.5<.6 | <2 |
| 5 | Dodecyldimethyl | 1 | <1 | >3<5 |
| 5 | do | 3 | <1 | <3 |
| 5 | do | 5 | <1 | <3 |
| 12.5 | Trimethyl | 4 | >15<50 | >500 |
| 12.5 | do | 6.25 | >10<25 | >500 |
| 12.5 | do | 12.5 | >25<50 | >500 |
| 12.5 | Triethyl | 4 | >1<2 | >20 |
| 12.5 | Octyldimethyl | 4 | >.8<.9 | >4<6 |
| 12.5 | Decyldimethyl | 4 | >1<2 | >6<8 |
| 12.5 | Dodecyldimethyl | 4 | 50 | >100 |
| 12.5 | do | 6.25 | >25<50 | >100 |
| 12.5 | do | 12.5 | >25<25 | >100 |
| | do | | 5 | 20 |
| | Roccal [3] | | 0.5 | 12.5 |
| 5 | Pyridine [4] | 3 | >1,000 | >1,000 |
| 5 | Quinoline [4] | 3 | >1,000 | >1,000 |

[1] *Staphylococcus aureus* FDA 209.
[2] *Escherichia coli* ATCC 10536.
[3] Roccal is a registered trademark of an alkyl-dimethyl-benzyl ammonium chloride wherein the alkyl group is $C_8$ to $C_{18}$ and is made by Sterwin Chemicals, Inc., a subsidiary of Sterling Drugs, Inc.
[4] These were made according to examples in U.S. 2,483,749.

Similar anti-bacterial results to those displayed by the compounds within the scope of the invention and listed in Table II are displayed by compounds with the previously described structural formula and wherein $n+m$ equals 37.5, $n$ equals 1 and the tertiary amines are dodecylmethylbutylamine, octadecylmethylbutylamine, eicosyldimethyl amine and docosyldimethylamine.

As can be seen from Table II, the acyclic polyquarternary ammonium compounds described above have su-

perior bacteriostatic properties to the heterocyclic polyquaternary ammonium compounds of U.S. 2,483,749. This is especially true in the case of the polymers produced by reacting the polyepichlorohydrin of molecular weight 450 ($n+m=5$) with octyldimethylamine, decyldimethylamine and dodecyldimethylamine where the bacteriostatic breakpoints are less than 1 p.p.m. as compared with greater than 1,000 p.p.m. in the case of the quinoline and pyridine compounds made according to U.S. 2,483,749. In fact, the above-mentioned polymers of the present invention compare favorably with Roccal, a ($C_8$–$C_{18}$) alkyl-dimethyl-benzyl ammonium chloride made by Sterwin Chemicals, Inc., and which is an effective germicidal agent.

There is thus provided by this invention a class of new compounds which are effective anti-bacterial agents. These compounds can be dissolved in water in the range of about 500 to about 1,000 p.p.m. and the solution used as antibacterial compositions. The water can contain a nonionic or other surfactants if desired.

These new compounds further unexpectedly retain their anti-bacterial properties when combined with certain detergent compositions. Thus, an effective anti-bacterial detergent composition can be formulated which consists essentially by weight of from about 0.1% to about 10% of an acyclic polyquarternary ammonium compound of the present invention, from about 5% to about 50% of a compatible detergent selected from the group consisting of nonionic, zwitterionic, and ampholytic synthetic detergents, and from about 5% to about 95% of a builder material selected from the group consisting of water-soluble inorganic alkaline builder salts, water-soluble organic alkaline sequestrant builder salts, and mixtures thereof. The balance of the detergent composition can be water, diluents such as sodium sulfate and other compatible additives and adjuvants. The weight ratio of detergent active to builder material in these compositions ranges from about 4:1 to about 1:20.

Water-soluble inorganic alkaline builder salts which can be used in this invention alone or in admixture are alkali metal carbonates, borates, phosphates, polyphosphates, bicarbonates and silicates. Ammonium or substituted ammonium, e.g., triethanol ammonium, salts of these materials can also be used. Specific examples of suitable salts are sodium tripolyphosphate, sodium carbonate, sodium tetraborate, sodium and potassium pyrophosphate, sodium and ammonium bicarbonate, potassium tripolyphosphate, sodium hexaphosphate, sodium sesquicarbonate, sodium orthophosphate, and potassium bicarbonate. The preferred inorganic alkaline builders according to this invention are alkali metal tripolyphosphates for built liquid compositions. Potassium is the preferred alkali metal used in liquid compositions and sodium finds best application for granular or tablet compositions.

Examples of suitable organic alkaline sequestrant builder salts used in this invention alone or in admixture are alkali metal, ammonium or substituted ammonium, aminocarboxylates, e.g., sodium and potassium ethylenediaminetetraacetate, sodium and potassium N-(2-hydroxyethyl)-nitrilodiacetates, sodium and potassium nitrilotriacetates. Mixed salts of these polycarboxylates are also suitable. The alkali metal salts of phytic acid, e.g., sodium phytate are also suitable as organic alkaline sequestrant builder salts (see U.S. Patent 2,739,942). Also suitable as organic alkaline sequestrant builder salts are the water-soluble salts of polycarboxylate polymers and copolymers as described in the copending application of Francis L. Diehl, Ser. No. 269,359, filed Apr. 1, 1963, now Patent No. 3,308,067 (e.g., polymers of itaconic acid, aconitic acid, maleic acid, mesaconic acid, fumaric acid, methylene malonic acid, and citraconic acid and copolymers with themselves and other compatible monomers such as ethylene).

Polyphosphates are also valuable builders in terms of the present invention, including specifically sodium and potassium salts of ethane-1-hydroxy-1,1-diphosphonic acid, sodium and potassium salts of methylene diphosphonic acid, and sodium and potassium salts of ethylene diphosphonic acid, and sodium and potassium salts of ethane-1,1,2-triphosphonic acid. Other examples includes the alkali metal salts of ethane-2-carboxy-1,1-diphosphonic acid, hydroxymethanediphosphonic acid, carbonyldiphosphonic acid, ethane-1-hydroxy-1,1,2-triphosphonic acid, ethane-2-hydroxy-1,1,2-triphosphonic acid, propane-1,1,3,3-tetraphosphonic acid, propane-1,1,2,3-tetraphosphonic acid, and propane-1,2,2,3-tetraphosphonic acid.

Examples of nonionic organic detergents which can be used in the compositions of this invention are: polyethylene oxide condensates of alkylphenols wherein the alkyl group contains from 8 to 15 carbon atoms (e.g., t-octylphenol) and the ethylene oxide is present in a molar ratio of ethylene oxide to alkylphenol in the range of 8:1 to 20:1; condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylene diamine wherein the molecular weight of the condensation products ranges from 5,000 to 11,000; the condensation products of from about 5 to 30 moles of ethylene oxide with one mole of a straight or branched chain aliphatic alcohol containing from 8 to 18 carbon atoms, e.g., condensation product of 6 moles of ethylene oxide with one mole of lauryl alcohol; higher alkyl dilower alkyl amine or phosphine oxides, e.g., dodecyldimethylamine oxide or dodecyldimethyl phosphine oxide; alkyl methyl sulfoxides such as dodecyl methyl sulfoxide.

Ampholytic synthetic detergents can be broadly described as derivatives of aliphatic secondary and tertiary amines in which the aliphatic radical can be straight chain or branched and wherein one of the aliphatic substituents contains from about 10 to about 20 carbon atoms and one contains an anionic water solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, phosphinate, or phosphonate. Examples of compounds falling within this definition are sodium 3-dodecylaminopropionate, sodium 3-(N-methyl-N-hexadecylamino)-2-hydroxypropane-1-sulfonate and its dodecyl homolog, sodium 3-dodecylaminopropane-1-sulfonate, sodium dodecyl-beta-alanine, sodium N-alkyltaurines such as the one prepared by reacting dodecylamine with sodium isethionate according to the teaching of United States Letters Patent No. 2,658,072, N-higher alkyl aspartic acids such as those produced according to the teaching of United States Letters Patent No. 2,438,091, and the products sold under the trade name "Miranol" and described in United States Letters Patent No. 2,528,378.

Zwitterionic synthetic detergents can be broadly described as derivatives of aliphatic quarternary ammonium, phosphonium, and sulfonium compounds, in which the aliphatic radical may be straight chain or branched, and wherein one of the aliphatic substituents contains from about 10 to about 20 carbon atoms and one contains an anionic water solubilization group, e.g., carboxy, sulfonate, sulfate, phosphate, phosphinate, or phosphonate. Examples of compounds falling within this definition are: 3-(N,N-dimethyl-N-hexadecylammonio)-2-hydroxypropane-1-sulfonate and the corresponding dodecyl and tetradecyl homologs and 3-(N,N-dimethyl-N-dodecylammonio)-propane-1-sulfonate and the corresponding hexadecyl and tetradecyl homologs.

The compatibility of the acyclic polyquaternary ammonium compounds of the present invention with detergent compositions containing the above-stated amounts of detergent active and alkaline builder is shown in the following example:

## EXAMPLE VIII

"Standard Tube Dilution Tests" similar to those in Example VII were conducted; however, 50 p.p.m. of a detergent composition containing 5% diethanolamide of coconut oil fatty acid, 7% potassium toluene sulfonate,

12% potassium pyrophosphate and 76% water was added to the nutrient broth. The acyclic polyquaternary ammonium compound tested for compatibility was one with $n+m=5$, $n=2$ and the tertiary amine=decyldimethylamine. The bacteriostatic breakpoint for *Staphylococcus aureus* FDA 209 was about 0.6 p.p.m. and for *Escherichia coli* ATCC 10536 was less than 5 p.p.m. These breakponits are substantially the same as those in Table II where no detergent composition was added and such similar results show the compatibility of the acyclic polyquaternary ammonium compounds of the present inventions with detergent compositions containing alkaline builders.

The following examples illustrate heavy-duty detergent compositions which contain as antibacterial agents the novel acyclic polyquaternary ammonium compounds of this invention. These compositions can be used, for example, under conditions of ordinary usage to clean soiled clothing and dishes and to inhibit the growth of bacteria on these articles. All percentages herein are by weight.

### EXAMPLE IX

Solid—granules

| | Percent |
|---|---|
| Polyquaternary ammonium compound of Example I | 2 |
| Tallow alcohol ethoxylated with 10 moles of ethylene oxide per mole of alcohol | 15 |
| Sodium tripolyphosphate | 50 |
| Sodium sulfate | 33 |

### EXAMPLE X

Solid—granules

| | Percent |
|---|---|
| Polyquaternary ammonium compound of Example II | 7 |
| Coconut alcohol (2%-$C_{10}$, 66%-$C_{12}$, 23%-$C_{14}$, 9%-$C_{16}$) ethoxylated with 6 moles of ethylene oxide per mole of alcohol | 12 |
| Sodium nitrilo triacetate | 81 |

### EXAMPLE XI

Solid—granules

| | Percent |
|---|---|
| Polyquaternary ammonium compound of Example III | 1 |
| Nonylphenol condensed with 12 moles of ethylene oxide per mole of phenol | 20 |
| Trisodium ethane-1-hydroxy-1,1-diphosphonate | 50 |
| Sodium tripolyphosphate | 10 |
| Sodium sulfate | 19 |

### EXAMPLE XII

Solid—granules

| | Percent |
|---|---|
| Polyquaternary ammonium compound of Example IV | 8 |
| Pluronic L-68 | 15 |
| Trisodium methylene diphosphonate | 50 |
| Sodium sulfate | 27 |

### EXAMPLE XIII

Liquid

| | Percent |
|---|---|
| Polyquaternary ammonium compound of Example V | 2 |
| Dimethyldodecylamine oxide | 20 |
| Tetrapotassium pyrophosphate | 30 |
| Sodium toluene sulfonate | 8 |
| Ethanol | 10 |
| Water | 30 |

### EXAMPLE XIV

Solid—granules

| | Percent |
|---|---|
| Polyquaternary ammonium compound of Example VI | 5 |
| Dimethyldodecylphosphine oxide | 15 |
| Pentasodium ethane-1-hydroxy-1,1,2-triphosphonate | 60 |
| Sodium sulfate | 20 |

### EXAMPLE XV

Solid—granules

| | Percent |
|---|---|
| Polyquaternary ammonium compound of Example I | 5 |
| Dimethylcoconut (2%-$C_{10}$, 66%-$C_{12}$, 23%-$C_{14}$, 9%-$C_{16}$) alkylammonia hydroxypropane sulfonate | 20 |
| Trisodium ethylidene diphosphonate | 30 |
| Sodium sulfate | 45 |

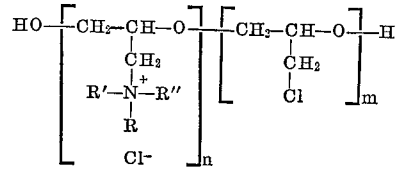
Other polyquaternary ammonium salts can be substituted for the polyquaternary ammonium compounds of Examples IX–XV to provide effective antibacterial detergent compositions. For example, any of the polyquaternary ammonium salts in Table I hereinbefore can replace all or part of the polyquaternary ammonium compounds of the compositions in these examples. Moreover, other compatible detergents can replace the detergent actives in the compositions of Examples IX–XV to provide effective antibacterial detergent compositions. For example, various ampholytic detergents, e.g., dodecyl-beta-alanine, the sodium salt of N-dodecyl taurine, or disodium N-dodecyl aspartate can replace all or part of the amine oxide in Example XIII. Moreover, other builders can be substituted for the builders of Examples IX–XV to provide effective antibacterial detergent compositions. For example, the following builders can be substituted for all or part of those employed in the examples: sodium ethylenediaminetetraacetate; sodium N-(2-hydroxyethyl)-nitrilodiacetates; phytates; polycarboxylate polymers; other polyphosphonates.

The polyquaternary ammonium compounds of the present invention are further useful as antistatic agents, emulsifying agents and dispersing assistants.

The foregoing description of the invention has been presented describing certain operable and preferred embodiments. It is not intended that the invention should be so limited since variations and modifications thereof will be obvious to those skilled in the art, all of which are within the spirit and scope of the invention.

What is claimed is:

1. An antibacterial detergent composition consisting essentially of from about 5% to about 50% of a detergent selected from the group consisting of nonionic, zwitterionic, and ampholytic synthetic detergents, from about 5% to about 95% of a builder material selected from the group consisting of water-soluble inorganic alkaline builder salts, water-soluble organic alkaline sequestrant builder salts, and mixtures thereof, and from about 0.1% to about 10% of a polyquaternary ammonium salt having the following unit structure:



wherein R is an alkyl group having 1 to 24 carbon atoms, R′ and R″ are each alkyl groups containing from 1 to 4 carbon atoms, $n$ plus $m$ ranges from 2 to 50, $m$ ranges from 0 to 49, and $n$ ranges from 1 to 50 and wherein $n$ plus $m$ plus the number of carbon atoms in R is greater than 12.

2. The antibacterial detergent composition according to claim 1 wherein the polyquaternary ammonium salt has a unit structure wherein R is an octyl group, R′ and R″ are each methyl groups, and *n* plus *m* is equal to 5.

3. The antibacterial detergent composition according to claim 1 wherein the polyquaternary ammonium salt has a unit structure wherein R is an octyl group, R′ and R″ are each methyl groups, and *n* plus *m* is equal to 12.5.

4. The antibacterial detergent composition according to claim 1 wherein the polyquaternary ammonium salt has a unit structure wherein R is a decyl group, R′ and R″ are each methyl groups, and *n* plus *m* has a value ranging from 4 to 15.

5. The antibacterial detergent composition according to claim 1 wherein the polyquaternary ammonium salt has a unit structure wherein R is a dodecyl group, R′ and R″ are each methyl groups, and *n* plus *m* has a value ranging from 4 to 15.



6. The antibacterial detergent composition according to claim 4 wherein the polyquaternary ammonium salt has a unit structure wherein R is a decyl group, R′ and R″ are each methyl groups, *n* is equal to 2 and *m* is equal to 3.

**References Cited**

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