POLYOXYALKYLENE-CONTAINING AMMONIUM COMPOUNDS

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7 Claims

ABSTRACT OF THE DISCLOSURE

Quaternary ammonium compounds, useful in fabric softeners, are prepared by quaternizing tertiary amines of the general formula R₁(R₂)N(R₃)OH, where R₁ and R₂ are aliphatic hydrocarbon radicals and R₃OH is a hetero polyoxyalkylene chain, with an alkyl halide, acid, or the like.

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5 Other objects will become apparent from the following disclosure and claims. The novel quaternary ammonium compounds of the present invention have the general formula:

\[ R_1 N^+ \left( R_2 O \right)_{n-1} \left( R_3 O \right) H^+ ] [ X^- \]

in which R₁ and R₂ are aliphatic hydrocarbon radicals of 12 to 20 carbon atoms, and where R₁R₂ and R₃OH can be the same or different radicals in each instance; R₃OH is a hetero polyoxyalkylene chain of randomly distributed oxyethylene and oxypropylene units, n is an integer equal to the total number of oxyalkylene units in the chain and is from 3 to 12, and preferably from 4 to 7, the ratio of oxyethylene to oxypropylene units in said chain varying from 1.5 to 4, and preferably from 2 to 3; R₄ is hydrogen or a lower alkyl (C₁-C₄) radical, and X is an anion.

The polyoxyalkylene-containing quaternary ammonium compounds of the present invention are obtained by the quaternization of tertiary amines produced by the condensation of a mixture of ethylene oxide and propylene oxide with a secondary amine containing two aliphatic hydrocarbon radicals. It is well recognized in the field of alkylene oxide chemistry that the oxyalkylation of a reactive hydrogen-containing compound with excess alkylene oxide results in the formation of a polymer of the alkylene oxide containing a terminal hydroxyl group. The reaction does not result in a single molecular compound having a definite number of oxyalkylene units, but rather one obtains a mixture of closely related homologs wherein the statistical average number of oxyalkylene groups equals the number of moles of the alkylene oxide employed per mole of reactive hydrogen compound and the individual members present in the mixture contain varying numbers of oxyalkylene groups. Where, as in this invention, different oxyalkylene groups are distributed randomly throughout the oxyalkylene chain, and thus, in addition to the varying lengths of the polyoxyalkylene chain, result in a varying structure of the oxyalkylene chain, it is conventional to characterize the chain as a hetero polyoxyalkylene chain. Nevertheless, the properties of the compounds containing such hetero polyoxyalkylene chains is characterized by the average length of the polyoxyalkylene chain and the average ratio of oxyethylene to oxypropylene units in the polyoxyalkylene chain.

The novel polyoxyalkylene-containing quaternary ammonium compounds of the present invention are produced by a process which comprises the quaternization of a tertiary amine having the general formula:

\[ R_1 N^+ \left( R_2 O \right)_{n-1} \left( R_3 O \right) H^+ ] [ X^- \]

in which R₁, R₂, and R₃OH have the above-indicated meaning. The tertiary amines employed in this process are obtained by the condensation of a secondary amine containing two aliphatic hydrocarbon radicals of 12 to 20 carbon atoms with a mixture of ethylene oxide and propylene oxide at temperatures of 150° F. to 280° F. in the presence of an ionic alkaline catalyst such as the salts or the hydroxides of the alkali metals or the alkaline earth metals and preferably in the presence of a lower alkyl (C₁-C₄) secondary alcohol such as isopropanol which acts as a color formation inhibitor. Since an essentially complete reaction between the secondary amine and the amine and the alkylene oxide is obtained, the average chain length of the polyoxyalkylene chain in the tertiary amine is readily controlled by the molar proportions of the alkylene oxides to the secondary amine reacted with each other. Similarly, the average oxyethylene-
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The preparation of the tertiary amines is described in greater detail in coiled copending application Ser. No. 555,265. The quaternization of the tertiary amine is carried out by reacting the tertiary amine with a compound having the formula R₂X wherein X is the anion desired in the quaternary ammonium salt, and R₂X is a lower alkyl radical or hydrogen at a temperature of about 150°F. to about 220°F. The preferred quaternizing agents are alkyl chlorides, alkyl bromides, dialkyl sulfates, dialkyl sulfonates, and alkyl aryl sulfonates in which the alkyl groups have from 1 to 4 carbon atoms and more preferably in which the alkyl groups are methyl. Other preferred quaternization agents include inorganic acids such as hydrochloric acid, sulfuric acid, and phosphoric acid, and monocarboxylic organic acids having from 1 to 3 carbon atoms.

In the quaternization of the tertiary amine with an R₂X compound wherein R₂ is a shorter alkyl group of 1 to 4 carbon atoms, the quaternization is conducted by charging the tertiary amine to a reactor without any diluent added or with sufficient diluent added to result in a liquid solution having the desired activity in the application of the resulting quaternary ammonium compound. In addition to the diluent, there is charged a neutralizing agent to neutralize the base formed as a result of the reaction. The mixture is heated to the desired temperature at which the reaction proceeds at a desired rapid rate without decomposition of the quaternary product (which desired temperature will generally be within the range of 150°F. to 220°F.) and the quaternizing agent, which is normally gaseous at the reaction condition, is charged to the reaction mixture at pressures ranging from autogenous to 200 p.s.i.g., although such pressure is not critical. The quaternizing agent is charged in excess of 50 to 100% of the stoichiometric quantity required to form the quaternary ammonium compound and can be added as a single charge or in increments as desired. With certain quaternizing agents, some decomposition of the quaternizing agent can occur during the reaction and it may, therefore, be desirable to repeatedly vent and recharge the reaction vessel with the quaternizing agent until no further reaction occurs, as established by pressure drop. In the quaternization of the tertiary amines with an inorganic base of the type described above, some of the base, as determined by titration of a sample of the tertiary amine, is added to the tertiary amine. The acid can be employed in concentrated or diluted form. The tertiary amine reagent employed in the quaternization can be employed without purification when formed by the above-described process, or, if desired, can be employed in pure form. The optionally employed diluents are water, water-miscible organic solvents such as lower alkanols and mixtures of water and such organic solvents. The diluent, where used, can be from 15 to 50 weight percent, or higher, based on the final total reaction mixture. Where such diluent is used, the resulting quaternary ammonium product is obtained as a normally liquid material (with freezing point below 65°F.) which can be employed as a concentrate to make fabric softener formulations. If desired, the concentrate can be filtered to remove organic salt residue. If desirable, a base can be added to adjust the pH of the product to within a range of 6 to 8. In instances where a diluent is not used in the preparation of the quaternary ammonium product, the latter will be a solid or soft paste at room temperature, and it is preferred to add said diluent in order to obtain a liquid product. For reasons discussed above, a liquid product is preferred in preparing fabric softener formulations.

The quaternary ammonium compounds of the present invention are surface-active agents which exhibit a particular combination of properties making them eminently suitable as active components in fabric softener formulations. In liquid fabric softener formulations (the preferred utility of the quaternary product of this invention), the active component will be from 3 to 10 weight percent of the formulation, and preferably about 5 weight percent. However, said quaternary compounds can be admixed with inert solid diluents, such as sodium sulfite, sodium chloride, urea, etc., to form solid or particulate fabric softener formulations, having for example 15 to 20 weight percent of active component.

Although quaternary ammonium compounds containing two aliphatic hydrocarbon radicals of 12 to 20 carbon atoms are known to have superior fabric-softening properties, the solubility and physical characteristics of the compounds have adversely affected their usefulness as fabric softeners. It was surprisingly found that by incorporating a polyoxyalkylene chain of particular configuration into the quaternary ammonium compound the disadvantages of prior art quaternary ammonium compounds in their utility as fabric softeners could be reduced or eliminated. Thus, quaternary ammonium compounds containing a hetero polyoxyalkylene chain of 3 to 12 and preferably of 4 to 7 randomly distributed oxyethylene and oxypropylene units wherein the average oxyethylene-to-oxpropylene ratio is from 1.5 to 4 and preferably from 2 to 3, are liquid in concentrates containing 85% or less of the quaternary ammonium compound. The compounds do not exhibit their concentrate dissolve or collooidally disperse readily in water, even in cold water. The compounds significantly improve the hand and feel of fabrics on washing and drying with automatic equipment. Fabrics softened with these compounds have improved rewettability properties and liquid fabric softener formulations based on these compounds have superior freeze-thaw stability as compared to such known liquid fabric softener formulations based on dimethyl-di(hydrogenated tallow) ammonium chloride. The particular structure of the polyoxyalkylene chain is critical in achieving the described improved properties. Thus, both an increase or a decrease in the average chain length of the polyoxyalkylene causes increased tendency to solidify at the required concentrate levels. Both ethylene oxide and propylene oxide are necessary, as is the randomness of the distribution of the alkylene oxide units in the polymer chain. The use of only ethylene oxide results in products which are largely solids or mixtures of liquid and solid phases. The use of only propylene oxide causes the product to have less solubility. Block copolymer analyses are undesirable since quaternary ammonium compounds containing such reflect the properties attributable to a polyoxyethylene chain and a polyoxypropylene chain which, as explained above, are undesirable, rather than a novel combination of properties obtainable by random copolymerization. It will be apparent that optimum combinations of properties desirable in a fabric softener will also vary with the nature of the aliphatic hydrocarbon radical having from 12 to 20 carbon atoms, and that such can be compensated for by adjusting the average length of the polyoxyalkylene chain and/or the average oxyethylene-to-oxpropylene ratio within the operative ranges set forth hereinabove. The solubility is, additionally, affected by the radical attached to the nitrogen atom as a result of the quaternization. In general, the solubility of the quaternary ammonium compound decreases as the number of carbon atoms in the added radical is increased and hence it is preferred that the radical added through quaternization is either hydrogen or methyl. It is to be understood, however, that the utility of the quaternary ammonium compound of the present invention is not limited to the described fabric softeners and that in view of their surface activity, the quaternary ammonium compounds of the present invention can be employed in a wide variety of detergent applications.

The aliphatic hydrocarbon radicals attached to the nitrogen of the quaternary ammonium compounds are aliphatic hydrocarbon radicals of 12 to 20 and preferably...
of 14 to 18 carbon atoms, which are preferably free of ethylenic unsaturation. The hydrocarbon radical need not be the same in each molecule and can also vary from molecule to molecule within the described range. A particularly preferred hydrocarbon radical is the hydrogenated tallow radical, which itself is a mixture of C₁₀ to C₁₈ fatty radicals. When preparing quaternary ammonium compounds based on di(hydrogenated tallow)amine, the optimum properties for a fabric softener are realized with polyoxyalkylene chains of about 7 oxyalkylene units at a oxyethyleno-to-oxypropylene ratio of 4:1.5.

The invention is further illustrated by the following examples in which, unless otherwise stated, all units of quantity are by weight.

**EXAMPLE 1**

Into a stainless steel autoclave is charged 653 g. of a di(hydrogenated tallow)oxyalkylene amine containing an average of 4 ethylene oxide and propylene oxide units in the polyoxyalkylene chain, the average oxyethyleno-to-oxypropylene ratio in the chain being 3:1, 235 g. of an isopropanol water mixture containing 4 parts of isopropanol and 1 part of water, and 60 g. of sodium bicarbonate. The reaction mixture is heated to a temperature of 212° F. and pressurized to 40 to 60 p.s.i.g. with methyl chloride. On reaching equilibrium conditions, the reaction gases are vented. Reaching and venting of the reaction mixture is repeated until no further methyl chloride is absorbed by the reaction mixture. The resulting product is filtered and a solution containing 75% of the resulting quaternary ammonium compound, di(hydrogenated tallow)-polyoxo(ethylene-propylene) methyl ammonium chloride, is obtained.

**EXAMPLE 2**

The procedure of Example 1 is repeated employing ethyl bromide in place of the methyl chloride and upon filtering a liquid solution containing 75% of di(hydrogenated tallow)-polyoxo(ethylene-propylene) ethyl ammonium bromide is obtained.

**EXAMPLE 3**

The procedure of Example 1 is repeated except that a 100% excess, based on the stoichiometric quantity of quaternizing agent required for the amine, of methyl chloride is charged to the reaction vessel initially and the reaction vessel is agitated at autogenous pressure for a period of three hours at 100° F. On filtering, there is obtained at 75% liquid concentrate of di(hydrogenated tallow)-polyoxo(ethylenepropylene) methyl ammonium chloride.

**EXAMPLES 4-7**

A number of di(hydrogenated tallow)-polyoxo(ethylenepropylene) methyl ammonium chloride compositions having in the polyoxy(ethylene-propylene) chain the average chain lengths and oxyethyleno-to-oxypropylene ratios indicated in the following table are prepared by the procedure of Example 1. The characteristic properties and impurities of the compositions are set forth in the table.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Impurities</th>
<th>Percent Diluents based on mixture</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ex.</td>
<td>Number of oxyethylene units</td>
<td>EO/PO ratio</td>
<td>Percent</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Acid II</td>
</tr>
<tr>
<td>1</td>
<td>4</td>
<td>3</td>
<td>Trace</td>
</tr>
<tr>
<td>2</td>
<td>4.5</td>
<td>2</td>
<td>2.67</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>2.67</td>
<td>2.67</td>
</tr>
<tr>
<td>4</td>
<td>5.5</td>
<td>2.67</td>
<td>2.67</td>
</tr>
</tbody>
</table>

1 Amino hydrochloride resulting from quaternization of unreacted secondary amines.
2 Unreacted secondary and tertiary amine.

In the following table, the use of some of the quaternary ammonium compounds described in Table 1 as fabric softeners is illustrated. The samples were employed at the concentration indicated in the rinse water of a standard automatic washing and drying cycle using towels to establish the effectiveness of the fabric softener. The softness of the towels was measured on an arbitrary scale of 1 to 5 in which 5 is the softness obtained by washing and drying the towels by the standard cycle in the absence of any fabric softener and 1 is the softness of the unwashed towels employed in the test. The softness rating is based on an average of 6 measurements of each of five different persons having no knowledge of the washing and drying history of the towels. The re-wettability is established by measuring the time required for the towel to absorb a given weight of water and is based on an average of four readings. The table below shows the fabric softeners of the present invention to have a superior combination of properties.

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Fabric Softener</th>
<th>Use level, percent oxyethylene to oxypropylene ratio</th>
<th>Softness rating</th>
<th>Treatment</th>
<th>Rewettability in seconds</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control (no fabric softener)</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Example 4</td>
<td>0.1</td>
<td>1.6</td>
<td>1.7</td>
<td>2.0</td>
<td>0.8</td>
</tr>
<tr>
<td>Example 5</td>
<td>0.1</td>
<td>1.7</td>
<td>1.7</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Example 6</td>
<td>0.07</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
</tr>
<tr>
<td>Commercially available quaternary ammonium compound</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
</tbody>
</table>

1 Based on weight of fabric.

The foregoing examples have illustrated the preparation, properties, and utility of the novel quaternary ammonium compounds of the present invention. As will be apparent from these examples, other tertiary amines falling within the scope of the invention and other alkyl compounds and acids can be employed in the specific procedures illustrated to produce the described quaternary ammonium compounds. Various modifications and alterations of this invention will become apparent to those skilled in the art without departing from the scope and spirit of this invention, and it should, therefore be understood that the foregoing description and examples are not to be construed as limiting. What is claimed is:

1. A compound having the formula:

   \[ R_1 \quad (R_2-O)^n \quad H^+ \quad [X]^- \quad R_4 \]

   wherein \( R_1 \) and \( R_2 \) are alkyls of 12 to 20 carbon atoms, said alkyls being the same or different; \( R_2 \) is a heteric polyoxyalkylene chain of randomly distributed oxyethylene and oxypropylene units, said chain having from 3 to 12 units, the ratio of oxyethylene to oxypropylene units being from 1.5/1 to 4/1; \( R_4 \) is hydrogen or an alkyl group of 1 to 4 carbon atoms; and \( X \) is an anion selected from the group consisting of chloride, bromide, sulfide, phosphate, alkanoate of from 1 to 3 carbon atoms, methyl sulfate and sulfonate.

2. The compound of claim 1, wherein the chain has from 4 to 7 units and the ratio of oxyethylene to oxypropylene is from 2 to 3.
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3. The compound of claim 1, wherein R₄ is methyl.

4. The compound of claim 1, wherein X is chlorine, bromine, methyl sulfate, or alkanoate of from 1 to 3 carbon atoms.

5. The compound of claim 1, wherein R₁ and R₂ are dihydrogenated tallow radicals.

6. The compound of claim 5, wherein the polyoxyalkylene chain contains from 3 to 7 units, the ratio of oxyethylene to oxypropylene is from 2 to 3, and R₄ is methyl.

7. The compound of claim 1 where R₁ and R₂ are dihydrogenated tallow radicals, R₄ is methyl, X is chloride, and R₃O is a polyoxyalkylene chain having 3 to 7 units, the ratio of oxyethylene to oxypropylene being from 2/1 to 3/1.

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