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BIOCIDAL UNSYMMETRICAL DI-HIGHER ALKYL DIMETHYL AMMONIUM COMPOUNDS

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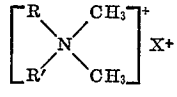
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ABSTRACT OF THE DISCLOSURE

Water-soluble unsymmetrical di-higher alkyl dimethyl ammonium salts having the structure:



wherein R and R′ are either straight chain or predominantly straight chain but dissimilar alkyls, each ranging from 7 to 15 carbons, and at least one of which has an odd number of carbons, the sum of the carbon atoms in R and R′ being in the range of from 20 to 22 carbons; and wherein X is a biocidally acceptable anion preferably derived from a halogen such as bromine or chlorine, or which may be methosulfate. These compounds have effective biocidal activity even in hard water, unlike other quaternary ammonium compounds which are inhibited in their biocidal activity by hard water. They are highly effective for the sanitization of all types of surfaces as well as eggs, fruits, vegetables and similar products.

This is a division of co-pending application Ser. No. 782,439, filed Dec. 9, 1968.

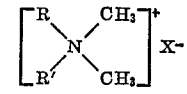
This invention relates to the biocidal use of certain water-soluble unsymmetrical di-higher alkyl dimethyl ammonium salts.

Although many compounds, including a wide variety of quaternary ammonium salts having higher alkyl groups, have very effective biocidal activities, it has been found that, in general, such biocidal activities are substantially inhibited or sometimes even totally suppressed when such compounds are used in hard water.

The term "hard water" is generally used to describe water having an appreciable amount of carbonates, bicarbonates, sulfates and chlorides of calcium and magnesium, and sometimes also of iron. The term "hard water" also includes the possible presence of alkaline earths and heavy metal ions in general. By "appreciable amount" is meant at least about 75 p.p.m. to about 500 p.p.m. Very hard water is that which contains over 1,000 p.p.m.

It is particularly important that such hard water resistant quaternaries be employed where the time of contact is short, as in the sanitization of utensils, for example in the dairy industry, restaurants and bars, and in the washing of eggs, fruits and vegetables in order to prevent the spread of infection. In general, these compounds are effective for sanitization of surfaces wherever they can feasibly be used.

In accordance with the present invention, it has now been discovered that certain unsymmetrical di-higher alkyl dimethyl ammonium salts which are water-soluble, and particularly their bromides and chlorides and, to some extent, their methosulfates, remain biocidally effective even in very hard water, where the content of the contaminants is above 750 p.p.m. On the other hand, other closely related homologs show little biocidal effectiveness in hard water even where the amount of the contaminants is considerably lower. These salts have the structure:



wherein R and R′ are either straight chain or predominantly straight chain but dissimliar alkyls, each ranging from 7 to 15 carbons, and at least one of which has an odd number of carbons, the sum of the carbon atoms in R and R′ being in the range of 20 to 22 carbons; and wherein X is a biocidally acceptable anion preferably derived from a halogen such as bromine or chlorine. It is also possible to use methosulfate, although much less preferable since the results are not as effective and the compounds are somewhat more difficult to make.

It is possible to use, as the straight chain or predominantly straight chain alcohols such as may be obtained by the oxo-reaction of alpha-olefins. For example, an oxo-drived alcohol containing about 20% by weight C_{12}, 30% by weight C_{13}, 30% by weight C_{14} and 20% by weight C_{15} may be converted to a tertiary amine and quaternized. Decene-1 may be converted to a C_{11} amine via the C_{11} oxo-alcohol.

The biocides of the present invention are effective in very hard water in a concentration of the biocide of between about 100 to 1,000 p.p.m. The preferred and most effective range is about 200 to 400 p.p.m.

The present compounds are all easily prepared in various manners. The following examples are illustrative of their preparation.

EXAMPLE 1

Equimolecular amounts of dodecyl dimethyl amine and nonyl bromide were mixed with an amount of 99% isopropanol equal to about the weight of the mixture of the amine and the bromide. The mixture was then heated at the reflux temperature (about 88° to 90° C.) and at atmospheric pressure for a period of about eight hours, or until the reaction appeared to be complete. It was determined by argentometric titration that the yield was about 90% complete after five hours, and essentially complete (about 98–99%) overnight on the steam bath. The product was then cooled to room temperature and the concentration adjusted to 50 weight percent by the addition of 99% isopropanol.

EXAMPLE 2

In the same manner as in Example 1, dodecyl bromide was reacted with nonyl dimethyl amine, to yield the same product as that of Example 1.

EXAMPLE 3

In a similar manner to Examples 1 and 2, the corresponding alkyl chlorides were substituted for the corresponding alkyl bromides in each instance, and the reactions were carried essentially to completion to yield nonyl dodecyl ammonium chloride in each instance.

EXAMPLE 4

Using the same procedure as in Examples 1, 2 and 3, and using the same reaction conditions, the di-higher alkyl dimethyl ammonium bromides shown in Table I hereinafter, as well as the corresponding chlorides, were prepared from the corresponding alkyl dimethyl amines and alkyl bromides and chlorides.

The aforesaid unsymmetrical quaternary ammonium compounds may also be prepared by a two-stage process whereby an unsymmetrical di-higher alkyl monomethyl amine is first prepared by the interaction of an alkyl halide, such as chloride or bromide, and an alkyl monomethyl amine. Then after liberating the tertiary amine, by treatment with a caustic, from its hydrohalide salt,

the tertiary amine is quaternized by reaction with an alkylating agent. This is illustrated in Examples 5 and 6 as follows:

EXAMPLE 5

Equimolecular amounts of dodecyl monomethyl amine and nonyl bromide were mixed with an amount of 99% isopropanol equal to about the combined weight of the amine and the bromide. The mixture was then heated at about 90° C., under agitation, and under reflux, at atmospheric pressure, for a period of hours until the reaction was essentially complete as indicated by argentometric titration of the bromide ion. The solution was then mixed with about twice its volume of water plus about 1 to 1.2 molecular equivalent of NaOH. The liberated tertiary amine (nonyl dodecyl monomethyl amine) was then separated in a separatory funnel, washed with water, and dried.

EXAMPLE 6

The tertiary amine of Example 5 was quaternized by reaction with methyl chloride, in an agitated pressure vessel at about 90° C., in a medium of 99% isopropanol, along with about 3% of water and 0.5% of sodium bicarbonate as an acid acceptor. Methyl chloride was then passed into the vessel at such a rate as to maintain a pressure of less than 30 p.s.i. in the reactor, the addition of the methyl chloride being continued until no further reaction occurred, as indicated by failure of the pressure to fall when the methyl chloride supply was cut off.

About midway in the addition of the methyl chloride, an additional 0.5% of sodium bicarbonate was added, to take up any traces of HCL that might have been formed.

Agitation and heating were then continued for about two hours longer, after which the reaction mass was cooled to about 50° C., and was then filtered to remove the salts. The concentration was then adjusted to 50% by the addition of 99% isopropanol, the resulting product being nonyl dodecyl dimethyl ammonium chloride.

The corresponding bromide was prepared in a similar manner by reacting the tertiary amine with methyl bromide at about 50–55° C., at about atmospheric pressure.

EXAMPLE 7

A process similar to Example 6 was used to obtain the corresponding methosulfate, except that the reaction was conducted at about 60° C. and a stoichiometric amount of dimethyl sulfate was used as the reactant.

It is also within the scope of the present invention to react an alcohol, either straight or branched chain, such as those obtained by oxo reactions of alpha-olefins, with a suitable halogenating agent, by methods known to the art, to form the corresponding alkyl halide, either straight or branched chain, or mixtures thereof. Such alkyl halide may then be employed as a quaternizing agent for the tertiary amines, or it may be reacted with either monomethyl amine or dimethyl amine to form the corresponding higher alkyl monomethyl amine or higher alkyl dimethyl amine. It may theretafter be reacted according to the foregoing examples to yield the unsymmetrical di-higher alkyl dimethyl ammonium quaternary salts of this invention. This type of reaction is shown by the following example:

EXAMPLE 8

The alcohol derived by the oxo reaction from decene-1, which yields a mixture of n-undecanol and alpha-methyl decanol, was halogenated by reaction with hydrogen chloride to yield the undecyl chloride. This chloride was then reacted with dodecyl monomethyl amine in the manner described in Example 5 to form undecyl dodecyl monomethyl amine. This was quaternized by reaction with methyl chloride in the same manner described in Example 6, to yield the unsymmetrical di-higher alkyl dimethyl ammonium salt.

In all the above examples, any desirable alcohol other than isopropanol may be used, or any other feasible solvent may be substituted.

The unexpectedly high biocidal activity in very hard water of these unsymmetrical di-higher alkyl dimethyl ammonium salts having at least one odd-carbon chain and a sum total of from 20 to 22 carbons in the said alkyls is illustrated by the following table, in which their performance is compared with the closest homologous symmetrical dialkyl dimethyl ammonium salts, as well as certain unsymmetrical homologs of different carbon ranges. The test method used was the Methods of Analysis of the Association of Official Analytical Chemists, 10th Edition" published by that organization in 1965, and contained in pages 87–89, a copy of which is enclosed.

The organism used was *Escherichia coli,* the inoculum containing a concentration of the organism in the order of 100,000,000 per milliliter.

In each case, the compound used was the bromide salt.

TABLE I

[Hard Water Tolerance in p.p.m. (at 200 p.p.m. quaternary) Unsymmetrical Dialkyl Dimethyl Quaternaries]

	Carbons in other alkyl				
	6	7	8	9	10
Carbons in one alkyl:					
11	<300	<300	550	1,400	1,300
12	<300	900	1,200	1,300	750
13	750	900	800	900	<300
14	550	700	750	500	<300
16	400	<300	<300	----------	----------
18	400	<300	<300	----------	----------

The product of this invention may be used for the disinfection or sanitization of hard surfaces; for the sanitization of textile and other fabrics; as topical antiseptics; in water treatment; and for other bactericidal, fungicidal and algacidal purposes where quaternary ammonium compounds are compatible.

When mixed with an equal amount of a non-ionic surfactant, such as alkyl phenol ethoxylate, the products retain a substantial proportion of their efficacy. They also remain substantially potent in the presence of small amounts of anionic surfactants of the protein.

The invention claimed is:

1. Nonyl undecyl dimethyl ammonium chloride.
2. Nonyl undecyl dimethyl ammonium bromide.

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