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QUATERNARY AMMONIUM XANTHATES

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This invention relates to quaternary ammonium alkyl and alkenyl xanthates and to methods for their preparation and more particularly pertains to quaternary ammonium lower alkyl and alkenyl xanthates in which the xanthate radical is attached to the compounds by a nitrogen to sulfur linkage, and to methods for their preparation.

An object of the invention is the provision of new and useful quaternary ammonium alkyl and alkenyl xanthates.

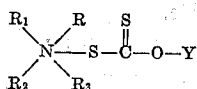
Another object is the provision of quaternary ammonium lower alkyl and alkenyl xanthates which have high degrees of biological activity.

Still another object is the provision of quaternary ammonium compounds in which the anion is a lower alkyl or alkenyl xanthate radical.

Yet another object is the provision of a method for preparing quaternary ammonium lower alkyl and alkenyl xanthates by reacting a quaternary ammonium halide with an alkali metal lower alkyl or alkenyl xanthate.

The quaternary ammonium xanthates of this invention have unique biological properties which make them useful as bacteriostatic or bactericidal agents, as fungicides, herbicides, algicides, insecticides and as preservatives for cellulosic materials.

The compounds have the generic structure



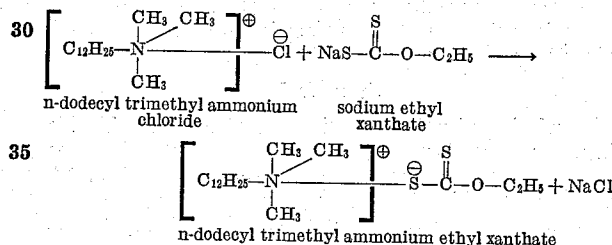
where R and R₁ each represents a methyl group and one valence of the hydrocarbon residue of a pyridine nucleus, R₂ represents a methyl, a benzyl hydrocarbon group and one valence of the hydrocarbon residue of a pyridine nucleus, and R₃ represents an aliphatic hydrocarbon group having from 1 to 20 carbon atoms, an aryl group, and an alkaryl group, and Y represents a lower alkyl or lower alkylene group having from 1 to 4 carbon atoms.

Typical compounds of the type described are tetramethyl ammonium methyl, ethyl, propyl, isopropyl, butyl, isobutyl and allyl xanthates; butyl trimethyl ammonium methyl, ethyl, propyl, isopropyl, butyl, isobutyl and allyl xanthates, octyl trimethyl ammonium, methyl, ethyl, propyl, isopropyl, butyl, isobutyl and allyl xanthates; decyl trimethyl ammonium methyl, ethyl, propyl, isopropyl, butyl, isobutyl and allyl xanthates; dodecyl trimethyl ammonium methyl, ethyl, propyl, isopropyl, butyl, isobutyl and allyl xanthates; tetradecyl trimethyl ammonium methyl, ethyl, propyl, isopropyl, butyl, isobutyl and allyl xanthates; octadecyl trimethyl ammonium methyl, ethyl, propyl, isopropyl, butyl, isobutyl and allyl xanthates; octadecenyl trimethyl ammonium methyl, ethyl, propyl, isopropyl, butyl, isobutyl and allyl xanthates; p-diisobutylphenoxyethoxyethyl dimethyl benzyl ammonium methyl, ethyl, propyl, isopropyl, butyl, isobutyl and allyl xanthates; phenyl trimethyl ammonium methyl, ethyl, propyl, isopropyl,

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butyl, isobutyl, and allyl xanthates; benzyl trimethyl ammonium methyl, ethyl, propyl, isopropyl, butyl, isobutyl and allyl xanthates; cetyl dimethyl benzyl ammonium methyl, ethyl, propyl, isopropyl, butyl, isobutyl and allyl xanthates; methyl pyridinium methyl, ethyl, propyl, isopropyl, butyl, isobutyl and allyl xanthates; butyl pyridinium methyl, ethyl, propyl, isopropyl, butyl, isobutyl and allyl xanthates; octyl pyridinium methyl, ethyl, propyl, isopropyl, butyl, isobutyl and allyl xanthates; decyl pyridinium methyl, ethyl, propyl, isopropyl, butyl, isobutyl, and allyl xanthates; dodecyl pyridinium methyl, ethyl, propyl, isopropyl, butyl, isobutyl and allyl xanthates; octadecyl pyridinium methyl, ethyl, propyl, isopropyl, butyl, isobutyl and allyl xanthates; octadecenyl pyridinium methyl, ethyl, propyl, isopropyl, butyl, isobutyl, and allyl xanthates, and benzyl pyridinium methyl, ethyl, propyl, isopropyl, butyl, isobutyl, and allyl xanthates. The preferred compounds are those which have an aryl group or an alkyl group having at least 12 carbon atoms or those prepared from pyridines in which the hydrocarbon portion of the pyridine residue is attached directly to the quaternary nitrogen atom.

These compounds are prepared by dissolving a quaternary ammonium halide in water, adding an alkali metal salt of a lower alkyl or lower alkenyl xanthate. A chemical reaction occurs, whereby the halide of the quaternary ammonium compound is replaced by a xanthate radical, in accordance with the following equation.



If a quaternary ammonium xanthate free of a metal halide is desired it can be prepared by the use of a diluent in which the quaternary ammonium halide and alkali metal xanthate are soluble, but in which the alkali metal halide is insoluble. One specific procedure is to prepare a solution of a quaternary ammonium halide in an alcohol, such as isopropanol, add the requisite amount of the appropriate alkali metal xanthate, such as sodium xanthate, cool the mixture to permit crystallization of the sodium halide, and filter the solution of quaternary ammonium xanthate to remove the sodium halide. Numerous other inert diluents having the above-described characteristics can be employed in place of isopropanol.

It is to be understood that other quaternary ammonium halides will react with other alkyl or alkenyl xanthates in the same manner as that described above.

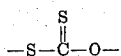
The quaternary ammonium xanthates are soluble in benzene and other liquid aromatic hydrocarbon solvents and can therefore be easily separated from the reaction mixture. If desired, however, the quaternary ammonium xanthates can be left in the reaction mixture, and the concentration can be adjusted by dilution or evaporation of the water, and used without prior separation. The quaternary ammonium xanthates which contain a benzyl radical in the anion are only slightly soluble in water and may require an additional dispersing agent to maintain concentration substantially greater than about 1% in water.

For biological purposes the quaternary ammonium xanthates can be employed as dilute solutions in water, as emulsion concentrates, as solutions in benzene, xylene, or other liquid, inert, aromatic organic solvents, or as dusts admixed with talc, kieselgur, clay, chalk or other

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solid, inert fluent carriers. An adhesive ingredient such as a rubber or synthetic resin latex, fish or vegetable oil, heavy mineral oil or other adhesive material can be added to the liquid compositions containing the quaternary ammonium xanthates to permit as long a contact time as possible in order that the complete affect of the biological activity of the compounds can be exerted on the treated materials.

The quaternary ammonium xanthates will vary somewhat in their biological activity depending in part on the structure of the cationic portion of the molecule and in part on the anionic portion. In general a long chain alkyl or alkenyl hydrocarbon group with about 12 carbon atoms or more as the cation broadens the spectrum of biological activity. The compounds with a phenyl or benzyl group in the cation are of intermediate activity and those which have only the lower alkyl groups, such as the tetramethyl ammonium xanthates are less active. The difference in activity due to the length of the carbon chain in the anion are not as pronounced as those of the cation. However, the presence of the



group in the molecule increases the activity greatly over the quaternary ammonium halides with the same cationic moiety.

Some of the compounds of this invention are crystalline solids at room temperature, others are amorphous solids and those with a long hydrocarbon chain in the cationic portion of the molecule are viscous liquids.

The specific examples which follow are intended to illustrate the invention and are not to be considered as limitations thereon. The proportions of ingredients are given in parts by weight, unless otherwise specified.

Example I

A solution of n-dodecyl trimethyl ammonium chloride in water containing 33% by weight of the chemical was prepared, and 79.5 parts were warmed to 50–60° C. A solution containing 18 parts of sodium isopropyl xanthate in 100 parts of water was added with stirring to the warmed quaternary ammonium halide solution. Two liquid phases resulted, the top being a viscous, oily organic layer. The aqueous phase was extracted with benzene and then combined with the organic liquid layer, and the solution was then dried with anhydrous sodium sulfate and the solvent distilled under vacuum to yield 36.1 parts of residue, which yield is quantitative. An analysis of the compound showed the following results.

	Percent C	Percent H	Percent N
Calculated for $\text{C}_{19}\text{H}_{41}\text{NOS}_2$	62.80	11.29	3.85
Found.....	62.59	11.71	3.83
	62.41	11.51	3.82

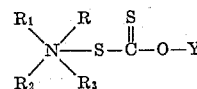
In a biological assay wherein this new compound was compared directly with n-dodecyltrimethyl ammonium chloride at the same concentration by weight it was found that at 100 p. p. m. both prevented the germination of spores of *A. oleracea*. The chloride left a clear zone 4.5 cm. in diameter and the xanthate a 6–8 cm. zone when tested against *S. fruticola* by the filter paper disc method. Cotton duck treated with the chloride in a soil burial test retained 24% of its original strength, whereas the duck treated with the xanthate retained 77% of its original strength. In addition the xanthate is a better herbicide than the chloride.

Example II

A quaternary ammonium chloride having three methyl groups and the hydrocarbon chains of coconut oil was used as one reactant in water with a slight excess of iso-

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propyl xanthate as the second reactant. The reaction conditions were substantially the same as those described in Example I. The quaternary ammonium xanthate that formed, was a viscous liquid with a density less than that of the aqueous phase of the reacted mixture. The R_3 group of the generic structure



in the quaternary ammonium xanthate contained aliphatic carbon chains with a length of from 8 to 18 carbon atoms, the major proportion being C_{12} .

The biological activity of this quaternary ammonium xanthate was compared directly with the quaternary ammonium chloride which was used as one reactant in the preparation of the xanthate. The sterile zone in the filter paper disc test against *S. fruticola* for the xanthate was more than 7 cm. in diameter, as compared with a zone of 4.5 cm. for the chloride. In the cotton duck burial test, the cloth treated with the xanthate did not lose any of its strength, but the cloth treated with the chloride had only 60% of its strength at the end of the same period of time. Kraft paper was also protected from deterioration in soil to a vastly greater degree by the xanthate when compared with the chloride, and the xanthate was also a better herbicide than the chloride.

Example III

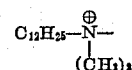
A quaternary ammonium xanthate was prepared from a quaternary ammonium chloride, which had three methyl groups and the hydrocarbon residue of amines made from soya oil. The soya-amine moiety had a carbon length of from 8 to 18 carbon atoms.

A slight excess of sodium isopropyl xanthate was used. The procedure was similar to that of Example I. This end product was an oil which was purified by solution in benzene and distillation of the solvent.

The quaternary ammonium xanthate was outstanding in its ability to protect cotton duck and paper from deterioration by soil microorganisms, whereas the quaternary ammonium chloride was only fair in this respect, and the herbicidal activity of the xanthate was superior to that of the chloride.

Example IV

A series of other alkali metal xanthates, namely, sodium ethyl, allyl and isobutyl xanthates, was used in preparing derivatives of n-dodecyltrimethyl ammonium chloride. The anion in the end product corresponded to that of the alkali metal xanthate used in the reaction, and the cation in each instance had the following structure



The method used was the same as that previously described. Each of these quaternary ammonium xanthates is a viscous liquid at room temperature, and each is a good fungicide, bactericide and herbicide. The xanthates are all good protective agents for cotton duck, and much superior to the chloride. n-Dodecyl trimethyl ammonium allyl xanthate is a very powerful broad spectrum bactericide.

Example V

Phenyl trimethyl ammonium isopropyl xanthate was prepared by reacting a slight excess of potassium isopropyl xanthate with phenyl trimethyl ammonium chloride in aqueous media at a temperature of approximately 50 to 60° C. This quaternary ammonium xanthate was a very good protective agent against the decomposition of kraft paper and cotton duck in soil burial tests. The herbicidal activity, however, was not as high as the dodecyl

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derivatives described above. The compound is crystalline with a melting point of 119–121° C. and is slightly soluble in water and quite soluble in benzene, which property makes it possible to purify and recrystallize the compound.

Example VI

A series of lower alkyl xanthate derivatives were prepared by reacting sodium alkyl xanthates with lauryl pyridinium chloride (technical) in water at a slightly elevated temperature, usually not higher than about 60° C. The xanthates that were reacted included sodium ethyl xanthate, sodium n-propyl xanthate, sodium isopropyl xanthate, sodium allyl xanthate, sodium n-butyl xanthate and sodium isobutyl xanthate. In all instances the xanthate salt of the quaternary amine was a viscous liquid which formed a supernatant layer in the aqueous reaction system. Separation was made by dissolving the quaternary ammonium xanthate in benzene and washing with saturated salt solution while maintaining the temperature at about 50° C. The benzene solution was dried with anhydrous sodium sulfate and the solvent was distilled off under vacuum. The residue of the lauryl pyridinium isopropyl xanthate when weighed amounted to a quantitative yield. This was dried under vacuum and analyzed for carbon, hydrogen and sulfur. The results of this analysis are as follows:

	C	H	S
Calculated for $C_{21}H_{37}NOS_2$ (C_{21} av. chain length).....	65.8	9.67	16.7
Found.....	65.46	9.97	15.6
	65.26	9.81	15.41

The yields for the other xanthates are also substantially quantitative. When tested for bactericidal activity by the filter paper disc method against *S. aureus* the ethyl xanthate derivative yielded a clear zone of 5.6 cm.; propyl xanthate 7 cm.; the isopropyl xanthate 5.3 cm.; the allyl xanthate 5.6 cm.; the butyl xanthate 4.8 cm.; and the isobutyl xanthate 5.8 cm. The original quaternary ammonium chloride used in preparing the xanthate derivatives had a clear zone of 3.8 cm. The ethyl xanthate, isopropyl xanthate, butyl xanthate and isobutyl xanthate quaternary ammonium salts were excellent protective agents against the deterioration of cotton duck by soil microorganism and each piece of duck treated with xanthate salts retained a minimum of 83% of its strength whereas the quaternary ammonium chloride treated duck retained only 60% of its strength. The ethyl xanthate quaternary ammonium salts are also excellent protectants for kraft paper, but the chloride is relatively poor. The herbicidal activity is quite superior to that of the chlorides.

Example VII

Tetramethyl ammonium isopropyl xanthate was prepared by the procedures described above. This compound was crystalline and had lower fungicidal, bactericidal and herbicidal activity when compared with the corresponding xanthates in which one methyl group is replaced by a phenyl, a dodecyl, a lauryl pyridinium or a C_{18} group. It, nevertheless, can act as a mild germicide where plants need some protection from certain specific organisms. The melting point of this compound was 138–140° C.

	C	H	N
Calculated for $C_8H_{19}NOS_2$	45.9	9.1	9.1
Found.....	45.81	9.08	9.08

Example VIII

Cetyl dimethyl benzyl ammonium isopropyl xanthate was prepared by dissolving the quaternary ammonium chloride in water and adding sodium isopropyl xanthate to

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the solution. The oily quaternary ammonium xanthate was separate from the aqueous layer and the latter was extracted with benzene and then recovered by distillation of the benzene. The quaternary ammonium xanthate was then washed thoroughly with water to remove the traces of halide salt.

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Analysis	C	H
Calculated for $C_{19}H_{33}NOS_2$	70.3	10.7
Found.....	69.80	10.48
	69.95	10.36

The xanthate derivative was much more effective in killing *S. aureus* when compared directly with the parent quaternary ammonium halide.

Example IX

A solution of 5 parts of p-diisobutylphenoxyethoxyethyl dimethylbenzyl ammonium chloride (also known by the trade name Hyamine 1622) in excess isopropanol was heated to 50° C., and 2.5 parts of sodium isopropyl xanthate were added. The mixture was held at 40–50° C. for about an hour and it was then cooled to ice bath temperature. The sodium chloride precipitated and was removed by filtration. The oil residue from the alcohol solution was dissolved in benzene and washed thoroughly with water. Thereafter the benzene was distilled to yield 6 parts of an oil. This was analyzed, and the following results were obtained:

Analysis	C	H
Calculated for $C_{31}H_{49}NO_3S_2$	68.0	8.85
Found.....	67.93	9.05
	68.29	9.08

The original quaternary ammonium chloride did not prevent the growth of algae at 10 p. p. m. concentration in water, but the xanthate derivative completely prevented growth under identical incubation conditions and at the same concentration. Also, the bactericidal activity of the xanthate quaternary against *S. aureus* was superior to the chloride. When tested by the filter paper disc method the clear zone with the xanthate was 2.9 cm. and that of the chloride was 1.9 cm.

Example X

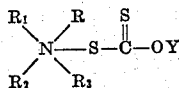
4.84 parts of n-dodecyl dimethyl methylcarboxyethyl ammonium iodide in 10 parts of water were treated with 2.3 parts of sodium isopropyl xanthate dihydrate at 40 to 50° C. The reaction mixture was extracted with benzene and the benzene layer was dried with anhydrous sodium sulfate. The benzene was then removed by vacuum distillation to yield 5 parts of a waxy solid with a melting point of 120 to 130° C. The xanthate derivative was superior to the iodide when compared directly for bactericidal activity against *S. aureus* in that a clear zone of 6 centimeters was present in the test involving the iodide and a clear zone of 8 centimeters was present with the xanthate.

The remaining quaternary ammonium xanthates disclosed herein are also more effective as bactericidal, fungicidal, insecticidal and herbicidal agents than are the parent quaternary ammonium chlorides, and any of the quaternary ammonium xanthates mentioned herein can be prepared by reacting the quaternary ammonium halide with an alkali metal lower alkyl or alkylene xanthate.

Although I have described my invention by specific examples, they are intended to be illustrative only and not limiting, except as defined by the appended claims, as it will be obvious to those skilled in the art that various substitutions of ingredients and proportions can be made without departing from the spirit and scope of the invention.

I claim:

1. A compound having the generic structure



in which R and R₁ each is a methyl group, R₂ is selected from the class consisting of methyl, phenyl and benzyl hydrocarbon groups and R, R₁ and R₂ collectively represent the hydrocarbon residue of a pyridine nucleus, and R₃ is selected from the class consisting of an aliphatic hydrocarbon group having from 1 to 20 carbon atoms, a lower alkyl carboxyethyl group, a monocyclic aryl group, a monocyclic aryalkyl hydrocarbon group and a p-diisobutylphenoxyethoxyethyl group, and Y is selected from the class consisting of lower alkyl and alkenyl hydrocarbon groups having from 1 to 4 carbon atoms.

2. Trimethyl soya oil hydrocarbon ammonium lower alkyl xanthate having from 1 to 4 carbon atoms in the alkyl group.

3. Trimethyl coconut oil hydrocarbon ammonium lower alkyl xanthate having from 1 to 4 carbon atoms in the alkyl group.

4. Trimethyl phenyl ammonium lower alkyl xanthate having from 1 to 4 carbon atoms in the alkyl group.

5. Dimethyl cetyl benzyl ammonium lower alkyl xanthate having from 1 to 4 carbon atoms in the alkyl group.

6. Lauryl pyridinium lower alkyl xanthate having from 1 to 4 carbon atoms in the alkyl group.

7. Trimethyl soya oil hydrocarbon ammonium isopropyl xanthate.

8. Trimethyl coconut oil hydrocarbon ammonium isopropyl xanthate.

9. The method which comprises reacting a quaternary ammonium halide of the formula



in which R and R₁ each is a methyl group, R₂ is selected from the class consisting of methyl, phenyl and benzyl hydrocarbon and collectively said R, R₁ and R₂ represent the hydrocarbon residue of a pyridine nucleus, and

- 5 R₃ is selected from the class consisting of aliphatic hydrocarbon groups having from 1 to 20 carbon atoms, a lower alkyl carboxy lower alkyl group, a monocyclic aryl group, a monocyclic aralkyl hydrocarbon group, and a p-diisobutylphenoxyethoxyethyl group, with a member selected from the class consisting of lower alkyl and alkenyl alkali metal xanthates having from 1 to 4 carbon atoms in a reaction medium selected from the class consisting of water and a liquid alkanol at a temperature up to about 70° C. to thereby form a quaternary ammonium xanthate.

- 10 10. The method of claim 9 in which the xanthate is isopropyl xanthate and the quaternary ammonium compound is a trimethyl soya oil hydrocarbon ammonium halide.

- 20 11. The method of claim 9 in which the xanthate is isopropyl xanthate and the quaternary ammonium compound is a trimethyl coconut oil hydrocarbon ammonium halide.

- 25 12. The method of claim 9 in which the xanthate is isopropyl xanthate and the quaternary ammonium compound is a trimethyl n-dodecyl quaternary ammonium halide.

13. The method of claim 9 in which the xanthate is isopropyl xanthate and the quaternary ammonium compound is a dimethyl cetyl benzyl ammonium halide.

- 30 pound is a dimethyl cetyl benzyl ammonium halide.

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