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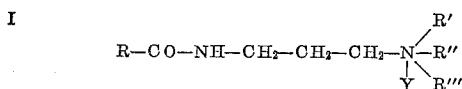
3,082,227

METHOD OF PREPARING A QUATERNARY AMMONIUM COMPOUND

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7 Claims. (Cl. 260-404.5)

This invention relates to a method of preparing a quaternary ammonium compound and, more particularly, a quaternary ammonium compound represented by the general formula



In the above formula R is a member of the group consisting of aliphatic and alicyclic radicals containing at least 7 carbon atoms, R' and R'' are members of the group consisting of alkyl radicals having from 1 to 3 carbon atoms, inclusive, and monohydroxyalkyl radicals having from 2 to 3 carbon atoms, inclusive, R''' is a monohydroxyalkyl radical having from 2 to 3 carbon atoms, inclusive, and Y is the anion of an acid.

Illustrative examples of radicals represented by R in Formula I are heptyl, octyl, nonyl, decyl, undecyl, tridecyl, heptadecyl, the residue of abietic acid, etc.; illustrative examples of radicals represented by R' and R'' are methyl, ethyl, propyl, isopropyl, hydroxyethyl, hydroxypropyl, hydroxyisopropyl, etc.; illustrative examples of radicals represented by R''' are hydroxyethyl, hydroxypropyl and hydroxyisopropyl; illustrative examples of anions represented by Y are the halide ions (that is, Y can represent halogen, more particularly chlorine, bromine, fluorine or iodine), sulfate, sulfonate, phosphate, borate, cyanide, carbonate, hydrocarbonate, thiocyanate, thiosulfate, isocyanate, sulfite, bisulfite, nitrate, nitrite, oxalate, silicate, sulfide, cyanate, acetate and the other common inorganic anions.

Quaternary ammonium compounds of the kind prepared by the method of this invention are claimed, both broadly and specifically, as new compounds in Cook and Moss U.S. Patent No. 2,589,674 dated March 18, 1952.

With further reference to the definition of R and as stated in the aforementioned Cook et al. Patent 2,589,674, R may be any aliphatic or alicyclic radical containing a sufficient number of carbon atoms to provide a hydrophobic radical which will provide orientation of the compounds at an oil-water surface. Thus, R can be a radical derived from a wide variety of monocarboxylic acids including caproic, decanoic, lauric, myristic, palmitic, stearic, arachidic, oleic, and other more highly unsaturated fatty acids having from 14 to 18 carbon atoms and which are obtained from vegetable and animal oils and fats, e.g., soyabean oil, cottonseed oil, coconut oil, linseed oil, castor oil, dehydrated castor oil and the like, or from other commercial sources such as tall oil. Additionally, R can be a radical derived from an alicyclic monocarboxylic acid including petroleum naphthenic acids of 7-14 carbon atoms having boiling points within the range of 215°-310° C., as described in Ellis "Chemistry of Petroleum Derivatives," (1934 edition), pages 1062-1082, or abietic acid and the like.

The number of carbon atoms in the aliphatic or alicyclic radical represented by R is largely dependent upon the particular use to which the quaternized compound is to be placed. Thus, for some uses of the compound it

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may be desirable that R represented a radical containing in excess of 20 carbon atoms. However, for most wetting, emulsifying, antistatic and similar uses, it is generally more desirable that R represent a radical containing not more than about 20 carbon atoms and preferably, for most ready dispersibility in aqueous media, not more than 19 carbon atoms.

One of the important and rapidly growing uses of quaternary ammonium compounds of the kind embraced by Formula I is as an antistatic agent, e.g., as a component of or in the surface treatment of various plastic and textile materials. Examples of such materials are those comprised or consisting essentially of polyvinyl chloride, polystyrene, poly-(methyl methacrylate), polyethylene, polypropylene, copolymers of vinyl chloride and vinyl acetate, and the like. Examples of textile materials to which the aforesaid antistatic agents can be applied are those composed of or containing fibers or filaments of wool, silk, cellulose esters (e.g., cellulose formate, cellulose acetate, cellulose propionate, cellulose butyrate, etc.), cellulose ethers (e.g., ethyl cellulose, benzyl cellulose etc.), viscose rayons, nylon, polyesters, vinyl resins (e.g., vinyl chloride polymers and copolymers, acrylonitrile polymers and copolymers, etc.), polypropylene, and other natural and synthetic textiles in the form of continuous-filament yarn, staple fiber, tow, roving, knitted, woven or felted fabrics, or in other form.

Prior to the present invention the common method of preparing quaternary compounds embraced by Formula I has been to effect the reaction between the aliphatic- or alicyclic-amidopropyl amine and an alkylene oxide, e.g., ethylene oxide, in an aqueous or aqueous ethanol solution, the latter being usually a 50-50 mixture by volume of water and alcohol. An acid is added to the solution, the anion of which corresponds to the anion represented by Y in Formula I, either prior to, during or after the addition of the alkylene oxide.

The foregoing method of preparation has several disadvantages. For example, if the reaction is carried out in 100% water, the reaction does not proceed with optimum efficiency and lower yields of product are obtained. Furthermore, when the reaction is carried out in 100% water or in a liquid reaction medium comprising water and an organic solvent, there is the additional time and expense incurred in drying the quaternary compound if one wants to market a dried product.

The present invention is based on my discovery that optimum yields of product can be obtained and the foregoing difficulties can be obviated by carrying out the reaction between the aliphatic- or alicyclic-amido-propyl amine in a liquid reaction medium of a limited class or group and which is critical in practicing the present invention. More particularly, the liquid reaction medium used in carrying the instant invention into effect consists essentially of at least one member of the group consisting of dioxane, ethylene glycol, ethylene glycol monoethyl ether, acetone and chloroform. The reaction medium is essentially anhydrous and, depending upon the acid used, may be almost completely anhydrous. In any case, only such water is added to the reaction mixture as may be present in the concentrated acid employed or in the commercially available solvent of the kind used in practicing this invention.

The foregoing results were all the more surprising and unobvious when it is considered that they were obtained without adversely affecting the useful properties of the quaternary ammonium compound, more particularly as an antistatic agent. For example, when

gamma-stearamidopropyl dimethyl beta'-hydroxyethyl ammonium nitrate was made using ethylene glycol as the liquid reaction medium and then was tested as an antistatic agent as described more fully hereinafter, the antistatic value (electrostatic locator reading determined as hereafter described) was between 1.5 and 0. In marked contrast, when the same compound made using absolute ethyl alcohol as a liquid reaction medium was similarly prepared and tested, the antistatic value was 60. It may here be mentioned that an electrostatic locator reading of from 0 through 10 is generally considered to indicate static-free conditions; a value of from 11 through 100 indicates no static control; while a value over 100 indicates no static control. From this

ethylene glycol monoethyl ether, ethylene glycol, acetone, trile, acetone and chloroform in the individual example) and 100 g. (0.272 mole) of gamma-stearamidopropyl dimethyl amine are placed in an autoclave. The temperature is raised to 75–80° C. with accompanying increase in pressure ranging from 6–30 p.s.i., and ethylene oxide (15 g., 0.34 mole) is added over a period of from 2 to 6 hours. Upon completion of the ethylene oxide addition, the reaction mass is cooled. Its pH ranges between 9.2 and 10.8 in the individual case. Concentrated (70%) nitric acid is added to lower the pH to between 5.6 and 7.8 in the individual example, the amount of 70% HNO₃ required to do this ranging between 10 and 25 g. The results are summarized in Table I.

TABLE I

Ex. No.	Solvent	Approximate		Amount 70% HNO ₃ added (g.)	pH after acid addition	Theoretical			Remarks
		Reaction time (hrs.)	pH at end of reaction			Yield of product, percent	Water, percent	Solvent, percent	
1.	Dioxane.....	2	10.6	25	5.9	39.0	2.2	58.8	Product is a heavy, viscous liquid. Solvent removal gave a waxy solid containing 80% solids.
2.	Ethylene glycol monoethyl ether.....	2½	10.2	24	5.85	38.8	2.1	59.1	Product dark brown, quite fluid liquid.
3.	Ethylene glycol.....	1½	9.2	23	5.6	38.8	*2.4	58.8	*Karl Fischer determination indicates 2.5% water.
4.	Acetonitrile.....	4	-----	10	7.8	36.3	0.9	62.8	Pale, yellow solid precipitated after addition of 10 g. acid. pH lowered to 5.4 with conc. HNO ₃ before use.
5.	Acetone.....	3	10.8	24	5.8	38.9	2.1	59.0	Most of solvent had evaporated in 2 days.
6.	Chloroform.....	4	9.6	23	5.7	38.8	2.0	59.2	Clear, reddish brown solution.

it will be seen the differences between an antistatic rating of 1.5–0 and 60 are not merely differences in degree but are differences in kind which were wholly unobvious and in no way could have been predicted by those skilled in the art.

In general, the quaternary ammonium compounds embraced by Formula I are prepared in accordance with the methods previously used in the art with the exception that a different liquid reaction medium is employed. For more detailed information on the prior-art technique, see the aforementioned Cook et al. U.S. Patent No. 2,589,674 and, also, Patent No. 2,459,062, dated January 11, 1949, to which reference is made in col. 2, lines 49–52, of Patent 2,589,674.

In practicing the present invention the reaction between the aliphatic- or alicyclic-amidopropyl amine and the alkylene oxide is effected at a temperature ranging from about 35° C. up to the boiling temperature of the reaction mass or at higher temperatures under super-atmospheric pressure, e.g., up to about 200° C. As hereinbefore stated, the acid corresponding to the salt of the quaternary ammonium compound can be added either prior to, during or after the addition of the ethylene oxide or throughout all of such stages, as desired or as conditions may require. The reaction between the amidopropyl amine reactant and the alkylene oxide can be partly or wholly completed in the presence or absence of an acid. However, if insufficient or no acid has been added to the liquid reaction medium prior to the time when the addition of the alkylene oxide has been completed, then the required amount of acid to form the salt is added after completing the addition of the alkylene oxide.

In order that those skilled in the art may better understand how the present invention can be carried into effect the following examples are given by way of illustration and not by way of limitation.

EXAMPLES 1–6

Preparation of Gamma-Stearamidopropyl Dimethyl Beta-Hydroxyethyl Ammonium Nitrate

In these examples 200 g. of the solvent (dioxane, 75

EXAMPLE 7

A 0.05% (solids basis) aqueous solution, using de-ionized water, is made of each of the quaternary compounds of Examples 1 through 6, adding HNO₃, when necessary, to adjust the pH to within the range of about 4.5 to 6.0. A woven cloth of polyacrylonitrile fibers is dipped into the solution, excess treating agent is removed by squeezing between two rollers, and the resulting impregnated cloth is dried in an oven at 200° F. for 5 minutes. The dried, treated polyacrylonitrile cloth is rubbed against a woolen cloth, then held to a Simco Electrostatic Locator, and a reading is recorded. The average of at least five such readings is taken as a measure of the antistatic rating of the individual specimen of polyacrylonitrile cloth. The electrostatic readings are taken under substantially the same temperature and humidity conditions and, in nearly all cases, on the same day.

The interpretation of readings from 0 through 10, from 11 through 100, and over 100 has been given hereinbefore. The results are given in Table II.

TABLE II

Antistatic evaluation of quaternary ammonium compound of example	Approx. pH of treating soln.	Electrostatic locator reading
None.....	-----	700
1.....	4.6	15-0
2.....	4.6	11.5-0
3.....	4.6	17-0
4.....	5.3	2
5.....	5.9	3
6.....	4.6	10

¹ In each case the reading varied from the higher value given to 0 in a few seconds.

EXAMPLES 8–11

These examples illustrate the preparation of gamma-stearamidopropyl dimethyl beta'-hydroxyethyl ammonium nitrate using, as the liquid reaction medium, representative solvents that yield a product having an unsatisfactory antistatic rating, viz., absolute ethyl alcohol, benzene, carbon tetrachloride and heptane. The results are summarized in Table III.

TABLE III

Ex. No.	Solvent	Approximate		Amount 70% HNO ₃ added (g.)	pH after acid addition	Theoretical			Remarks
		Reaction time (hrs.)	pH at end of reaction			Yield of product, percent	Water, percent	Solvent, percent	
8-----	Absolute ethyl alcohol-----	3½	9.1	25	5.7	39	2.2	58.8	Clear tannish solution obtained. After 2 weeks standing, mixture had pH of 4.8. Material separated into a clear, upper layer and an orange-brown lower layer. Light brown solid began to form after addition of 6 ml. HNO ₃ .
9-----	Benzene-----	6	10.1	23	5.7	38.8	2.0	59.2	
10-----	Carbon tetrachloride-----	4	9.2	6	7.0	37.0	0.6	62.4	
11-----	Heptane-----	4	10.0	21	6.0	38.6	1.9	59.5	

EXAMPLE 12

Same as in Example 7 with the exception that the products of Examples 8 through 11 are evaluated as antistatic agents. The results are given in Table IV.

TABLE IV

Antistatic evaluation of quaternary ammonium compound of example	Approx. pH of treating soln.	Electrostatic locator reading
None-----	-----	700
8-----	4.5	60
9-----	4.6	80
10-----	4.5	70
11-----	4.5	80

EXAMPLE 13

Essentially the same procedure is followed as described above with reference to Example 1 with the exception that instead of ethylene oxide there is used an equivalent amount of propylene oxide thereby obtaining gamma-stearamidopropyl dimethyl gamma'-hydroxypropyl ammonium nitrate. Similar results are obtained when this compound is tested for its antistatic characteristics as described under Example 7.

EXAMPLES 14-19

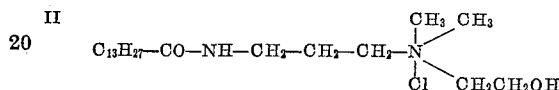
Examples 1 through 6 are repeated exactly with the exception that the specified amount (see Table I) of concentrated (70%) aqueous nitric acid is added to the solvent solution of the gamma-stearamidopropyl dimethyl amine prior to the addition of the ethylene oxide thereto. When the resulting quaternary ammonium salt is evaluated for its antistatic effectiveness as described in Example 7, the ratings on the treated polyacrylonitrile cloth are of the same general order as those given in column 3 of Table II with respect to the evaluation of the quaternary ammonium salts of Examples 1 through 6.

Instead of adding all of the nitric acid prior to the addition of the ethylene oxide as described above, one can add it to the reaction mass concurrently with the addition of the ethylene oxide; or part of the nitric acid may be added to the reaction mass prior to starting the addition of the ethylene oxide and the remainder during and/or after completing the ethylene oxide addition; or part of the nitric acid may be added concurrently with the addition of the ethylene oxide and the remainder after all of the ethylene oxide has been added.

EXAMPLE 20

Two hundred and sixty-six (266) g. (0.852) mole of gamma-myristamidopropyl dimethyl amine is dissolved in 590 g. p-dioxane, and to the resulting solution is added 90.5 ml. (1.1 mole) of concentrated hydrochloric acid. In an autoclave containing the foregoing solution is passed ethylene oxide (40 g.; 0.9 mole), and the reaction is continued for 3 hours at 80° C. The p-dioxane solvent is removed by distillation under reduced pressure. The product is gamma-myristamidopropyl dimethyl beta'-

hydroxyethyl ammonium chloride, the formula for which is



This quaternary ammonium compound likewise shows excellent antistatic characteristics when tested as described under Example 7.

EXAMPLE 21

Example 20 is repeated exactly with the exception that instead of concentrated hydrochloric acid there is used an equivalent amount of concentrated phosphoric acid containing about 98% H₃PO₄ thereby to obtain gamma-myristamidopropyl dimethyl beta'-hydroxyethyl ammonium phosphate (dihydrogen phosphate).

Similarly one can make gamma-stearamidopropyl dimethyl beta'-hydroxyethyl ammonium phosphate by using an equivalent amount of gamma-stearamidopropyl dimethyl amine as a starting reactant in place of gamma-myristamidopropyl diethyl amine.

EXAMPLE 22

To 460 g. acetonitrile in an autoclave is added 250 g. (1.1 mole) of caprylamidopropyl dimethyl amine, and to the resulting solution is added 90.5 ml. (1.1 mole) of concentrated hydrochloric acid. To this solution at 50° C. is then added 53 g. (1.2 mole) of ethylene oxide over a period of 3 hours. Thereafter the acetonitrile is removed under reduced pressure. A yield of about 350 g. of gamma-caprylamidopropyl dimethyl beta'-hydroxyethyl ammonium chloride is obtained. It shows excellent antistatic characteristics when tested as described under Example 7.

In a similar manner the corresponding gamma'-hydroxypropyl ammonium chloride can be obtained by using an equivalent amount of propylene oxide instead of ethylene oxide.

The corresponding sulfate salts of both the aforementioned beta'-hydroxyethyl and gamma'-hydroxypropyl derivatives are obtained by using an equivalent amount of concentrated (about 95%) sulfuric acid in place of concentrated hydrochloric acid.

EXAMPLE 23

One hundred and eighty-six (186) grams (0.48 mole) of gamma-abietamidopropyl dimethyl amine is dissolved in an equal weight of acetone, and to the resulting solution is added 40 ml. (0.48 mole) of concentrated hydrochloric acid. About 24 g. (0.54 mole) of ethylene oxide is passed into the resulting solution. The reaction mass that results is allowed to stand for about 16 hours at about 45° C. The resulting quaternary ammonium compound, gamma-abietamidopropyl dimethyl beta'-hydroxyethyl ammonium chloride, shows excellent antistatic characteristics when tested as described under Example 7.

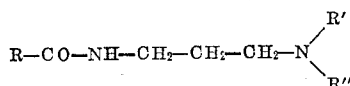
The corresponding diethyl and dipropyl ammonium

chlorides are prepared by using equivalent amounts of gamma-stearamidopropyl diethyl amine and gamma-stearamidopropyl dipropyl amine as starting reactants in place of gamma abietamidopropyl dimethyl amine.

The corresponding gamma-heptamidopropyl methyl ethyl beta'-hydroxyethyl ammonium chloride and lauramidopropyl ethyl propyl ammonium chloride are prepared by using equivalent amounts of heptamidopropyl methyl ethyl amine and of lauramidopropyl ethyl propyl amine, respectively, as starting reactants instead of gamma-abietamidopropyl dimethyl amine.

It will be understood, of course, by those skilled in the art that my invention is not limited (other than as to the liquid reaction medium comprising the specified organic solvent or mixture of two or more of them) to the specific ingredients or to the specific conditions of reaction that have been given in the foregoing examples solely by way of illustration. Thus, there can be used any amine corresponding to the general formula

III

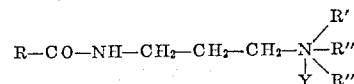


where R, R' and R'' have the same meanings as given hereinbefore with reference to Formula I. Any organic or inorganic acid can be used such, for example, as acids the anions of which correspond to those hereinbefore given as illustrative of anions represented by Y in Formula I. Alkylene oxides containing either 2 or 3 carbon atoms, specifically ethylene oxide and propylene oxide, can be employed. Approximately equal molar proportions of amine, alkylene oxide and acid can be used. Generally, it is advantageous to employ a slight excess of the alkylene oxide reactant, for example from 0.1 mole percent to 10 mole percent in excess. An excess of the acid, particularly at the end of the reaction, so that the quaternary ammonium compound has a pH below about 6.5, e.g., about 4.5-6.0, also is usually advantageous. This is particularly true when the quaternary compound is to be used as an antistatic agent.

The quaternary compounds prepared in accordance with the method of this invention are suitable for direct use as, for example, antistatic agents; or they may be diluted with a wide variety of solvents for such use. The invention makes it possible to prepare antistatic agents containing very minor amounts of water for use where water creates problems in rendering materials antistatic. Examples of such uses of antistatic agents include the incorporation of an antistatic agent into a molding (moldable) composition comprising a thermoplastic or thermosetting resin or polymer, which is then shaped as by molding, extruding, calendering, etc., and where appreciable amounts of water normally cause or tend to cause blistering, discoloration, decomposition, etc.

I claim:

1. The method of preparing a quaternary ammonium compound represented by the formula



wherein R is a member of the group consisting of aliphatic and alicyclic radicals containing at least 7 carbon atoms and up to about 20 carbon atoms, R' and R'' are members of the group consisting of alkyl radicals having from 1 to 3 carbon atoms, inclusive, and monohydroxyalkyl radicals having from 2 to 3 carbon atoms, inclusive, R''' is a monohydroxyalkyl radical having from 2 to 3 carbon atoms, inclusive, and Y is the anion of an inorganic acid, said method comprising effecting reaction between (1) the corresponding amidopropylamine, (2) an alkylene oxide containing from 2 to 3 carbon atoms, inclusive, and (3) an acid the anion of which corresponds to Y in the above formula, said reaction being effected at a temperature ranging from about 35° C. up to the boiling temperature of the reaction mass and in a liquid reaction medium consisting essentially of at least one member selected from the group consisting of dioxane, ethylene glycol, ethylene glycol monoethyl ether, acetonitrile, acetone and chloroform.

2. A method as in claim 1 wherein R represents a heptadecyl radical, R' and R'' each represent a methyl radical, R''' represents a beta'-hydroxyethyl radical, and the alkylene oxide is ethylene oxide.

3. A method as in claim 1 wherein R represents a heptadecyl radical, R' and R'' each represent a methyl radical, R''' represents a beta'-hydroxyethyl radical, Y represents a nitrate anion, the amidopropylamine is gamma-stearamidopropyl dimethyl amine, the alkylene oxide is ethylene oxide and the acid is nitric acid.

4. A method as in claim 1 wherein at least part of the acid is incorporated in the reaction mass not later than concurrently with the completion of the addition of all of the alkylene oxide to the reaction mass.

5. A method as in claim 1 wherein all of the acid is added to the reaction mass prior to the completion of the addition of all of the alkylene oxide to the reaction mass.

6. A method as in claim 1 wherein all of the acid is added to the admixture of solvent and amidopropylamine prior to starting the addition of the alkylene oxide to the reaction mass.

7. A method as in claim 1 wherein all of the acid is added to the reaction mass after completing the addition of all of the alkylene oxide to the reaction mass.

References Cited in the file of this patent

UNITED STATES PATENTS

2,459,062	Cook et al.	Jan. 11, 1949
2,459,088	Moss et al.	Jan. 11, 1949
2,589,674	Cook et al.	Mar. 18, 1952

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,082,227

March 19, 1963

Allan E. Sherr

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, line 13, for "no" read -- poor --; column 6, line 38, for "diethyl amine" read -- dimethyl amine --.

Signed and sealed this 8th day of October 1963.

(SEAL)

Attest:

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