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2,759,975

MIXED ALKYL-BENZYL-ALKYLOL QUATERNARY AMMONIUM SALTS

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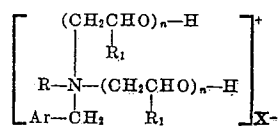
This invention relates to new quaternary compounds and particularly to a new class of a mixture of quaternary ammonium salts having valuable properties for many industrial applications.

A large variety of quaternary ammonium compounds have been prepared in which four of the nitrogen valences are connected to aliphatic and substituted aliphatic groups through carbon, and the fifth nitrogen valence is connected to an anion. While such compounds have found use as germicides, textile assistants, and in admixture with soap and soaplike products in various processes, not one of them is capable of general application. In other words, none of the quaternary compounds generally available is capable of being employed as emulsion breakers, collectors in froth flotation processes, wetting agents for pigments, corrosion and rust inhibitors, and the like. A particular quaternary compound may be an efficient germicide or biocide, but ineffective as an anti-static agent for plastics and various fibers or cannot be efficiently employed as an emulsion breaker or wetting agent. Each type has its own particular advantages not possessed by some other type.

It is an object of the present invention to provide a new class of a mixture of quaternary ammonium salts having a variety of industrial applications.

Other objects and advantages will become apparent from the following description.

The foregoing objects are accomplished by reacting a mixture of primary aliphatic amines in which the carbon atoms range from 7 to 18 carbon atoms with 2 to 50 mols of an alkylene oxide followed by a reaction with an alkyl halide. The mixture of compounds obtained by the foregoing reactions are characterized by the following general formula:



wherein R represents a mixture of alkyl radicals of from 7 to 18 carbon atoms, e. g., heptyl, octyl, nonyl, decyl, hendecyl, dodecyl, tetradecyl, hexadecyl, octadecyl, octadecenyl, octadecadienyl, and the like, or a mixture of said alkyl radicals, R₁ represents either hydrogen, methyl, ethyl, hydroxymethyl, and the like, Ar represents a phenyl, naphthyl, or a substituted phenyl, e. g., o- or m-tolyl, cumyl, xylyl, mesityl, o-chlorophenyl, m-chlorophenyl, p-chlorophenyl, 2,4-dichlorophenyl, 3,4-dichlorophenyl, 2,6-dichlorophenyl, 2,4,6-trichlorophenyl, and the corresponding bromo and iodo phenyls, o-, m-, and p-nitrophenyl, amylphenyl, propylphenyl, octylphenyl, dodecylphenyl, and the like, X represents an anion, such as chloride, bromide, or iodide, mono-, di-, or tribasic phosphate, acetate, lactate, gluconate, sulfate, nitrate, nitrite, alkylsulfate, alkyl and aryl sulfonates, e. g., dipropyl-naphthalenesulfonate, dibutyl-naphthalenesulfonate, methyl-, ethyl-, propyl-, butyl-, octyl-, or dodecylbenzene-

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sulfonate, and the like, and n represents a numeral ranging from 1 to 25.

It is to be noted that the anion of the foregoing quaternary ammonium compounds may be other than that specifically recited. Any inorganic or organic acid capable of forming a salt may be employed to yield the anionic group. The acid selected will determine the nature of the anionic group which may modify the solubility and other properties of the quaternary salt.

The mixture of quaternary ammonium salts characterized by the foregoing general formula are adaptable to an unusual number of applications. The most conspicuous property of these new salts is their great activity at surfaces and interfaces which promote their use in a large field of the technical arts. For instance, they can be used as wetting, frothing, or washing agents in the treating and refining of textiles; for converting liquid or solid substances which per se are insoluble in water (such as hydrocarbons, higher alcohols, oils, fats, waxes, fatty amines, resin amines, amine salts, and resins) into creamy emulsions, clear solutions or fine stable dispersions; for carbonizing; for dyeing; for the pasting of dyestuffs; for fulling, sizing, impregnating and bleaching treatments; as cleansing agents in hard water; in tanning and mordanting processes; for dyeing acetate with insoluble dyestuffs; for the preparation of dyestuffs in finely divided form; for producing foam in fire extinguishers; as a means for improving the absorptive power of fibrous bodies; and as an aid in softening baths for hides and skins.

In addition, these products are valuable emulsifiers for insecticide compositions and agricultural sprays, such as DDT, 2,4-D, (Toxaphene), (Chlordane), dormant or mineral oil sprays, nicotine sulfate, isomers and mixed isomers of hexachlorocyclohexane, and the like.

They are also valuable for use as additives to petroleum products, as additives to fuel oils, hydraulic fluids, lubricating oils, cutting oils, greases, and as additives to water or brine used for oil recovery from oil-bearing strata by flooding techniques.

Other valuable uses are in metal cleaning compositions, dry cleaning compositions, additives for rubber latices, foam inhibitors for synthetic rubber latex emulsions, froth flotation agents, additives for road building materials, as air entraining agents for concrete or cement; additives to asphalt compositions, plasticizers and modifiers for vinyl plastics, alkyl resins phenol-formaldehyde resins, and other type of polymeric type plastic materials; for incorporation into adhesives, paint, linoleum; for use in bonding agents used in various insulating and building materials; as refining aids in wood digesters to prepare pulp; as additives to pulp slurries in beating operations to prevent foaming and also to aid the beating operation in paper-making.

These salts are very valuable as emulsifiers for emulsion polymerization, as mercerizing assistants, wetting agents, rewetting agents, dispersing agents, detergents, penetrating agents, softening agents, cutting oils, lime soaps dispersants, dishwashing agents, anti-static agents, disinfectants, insecticides, mothproofing agents, bactericides, fungicides, and biocides.

They are particularly useful as anti-fogging agents for application to glass and other surfaces where the accumulation of an aqueous fog is detrimental. They are useful in the rayon industry as additives to the dope or to the spinning bath and as aids in clarifying viscose rayon. They are also of value in hydraulic fluids to improve viscosity characteristics.

These salts are especially useful in breaking petroleum emulsions. They may be used to break emulsions of crude petroleum and salt water as obtained from oil wells, or to prevent water-in-oil emulsions resulting from acidi-

zation of oil wells by introducing the agent into the well, or to break or prevent emulsions which would result from a water flooding process for recovering oil from oil-bearing strata. They may also be used to break emulsions encountered in a petroleum refining process. They are useful as corrosion inhibitors, as rust inhibitors, in the protection of metals especially ferrous metals, in acid pickling baths, in acid cleaning compositions, and in electro-plating baths.

Other valuable uses are as solvents, as cleaning agents for paint brushes, as additives for paints, lacquers, and varnishes, as lubricants, as greases, and stuffing agents.

These salts are valuable in the preparation of skin creams, lotions, salves, and other cosmetic preparations, such as home hairwave sets, shampoos, toothpastes, etc. They may also be of value in food products as foaming agents, emulsifying agents, and softening agents.

It has been found that the reason the foregoing quaternary ammonium salts are capable of general utilization as pointed out above is due to the presence of at least two ethenoxy or substituted ethenoxy groups, and the position of the Ar group in the molecule of the quaternary ammonium salt structure. These two features together with the presence of a mixture of alkyl radicals represented by R and a variety of anionic radicals contribute to the new and unexpected properties conferred by the quaternary ammonium salts.

In preparing the base material for the quaternary ammonium salts, a 2-liter stainless steel Blaw-Knox autoclave was employed. A molar proportion of a mixture of primary aliphatic amines containing from 7 to 18 carbon atoms was charged into the autoclave and the mixture heated to a reaction temperature of 100° to 120° C., preferably to 110° C. Two to 50 molecular proportions of an alkylene oxide were admitted portionwise from a special reservoir. The reaction pressure was regulated at 20 to 35 lb. p. s. i. The reaction was complete after 3 to 4 hours. The polyalkyloxylated mixture of amines was then discharged from the autoclave.

The weight of the product obtained minus the weight of the mixture of amines charged into the autoclave equals the amount of alkylene oxide which reacted. These weights were substituted in the following formula:

$$\frac{\text{Weight of alkylene oxide reacted} \times \text{molecular weight of mixed amines}}{\text{Weight of mixture of amines charged} \times \text{molecular weight of alkylene oxide}} = \text{mol ratio}$$

A molecular proportion of the polyalkyloxylated mixture of amines is mixed with a small amount of a lower alkyl alcohol, such as methyl, ethyl, propyl, or butyl alcohol to reduce viscosity and a small quantity of an alkali metal halide catalyst, such as sodium, potassium, or lithium iodide. The weight of the latter was equivalent in weight to about 1% of the total charge. The mixture was then heated to about 65–80° C., preferably to 70° C., in a constant temperature bath and a molecular proportion in slight excess of an alkyl halide, preferably benzyl or a substituted benzyl halide was added in one portion. During the heating there was a moderate heat of reaction which requires slight cooling for a short time to keep the temperature below 80° C. After a period of time ranging from 10 to 15 hours at about 70° C., the quaternary salt was discharged from the reaction vessel. If a longer reaction time is not objectionable, the solvent and catalyst can be omitted.

The amine and amine halide content of the quaternization reaction mixture was determined at intervals by removing a small sample and titrating it with standard acid and then with standard base.

The quaternary ammonium salts of the present invention can also be prepared by the foregoing procedure by replacing the molecular proportions of mixed amines by an equivalent proportion of a primary substituted or unsubstituted benzylamine and conducting the reaction in the same manner with 2 to 50 mols of an alkylene oxide.

The quaternization of the polyalkyloxylated benzylamine is also conducted in the same manner with the exception that the benzyl halide is replaced by a mixture of alkyl halides containing 7 to 18 carbon atoms.

As examples of primary aliphatic mono amines which may be employed either alone or in admixture, the following may be mentioned:

- n-Heptylamine
- 8-Methylhexylamine
- 1-octylamine
- Isooctylamine
- ε-Methylheptylamine
- Nonylamine
- n-Decylamine
- η-Methylnonylamine
- Undecylamine
- θ-Methyldecylamine
- Dodecylamine
- Tridecylamine
- Tetradecylamine
- Pentadecylamine
- Hexadecylamine
- Octadecylamine
- Octadecenylamine
- Octadecadienylamine

Other amines which may be used include branched chain alkyl amines prepared from ammonia and oxo alcohols as described in Sundberg et al Application Serial No. 263,976, filed on December 28, 1951, and entitled "Branched Chain Alcohol Derivatives."

For practical purposes, I have found that mixtures of the following amines designated as A, B, and C to be very useful and to yield quaternary ammonium salts in accordance with the process described above having the new and unexpected properties:

A		Per cent
Octylamine	-----	8
Decylamine	-----	8
Dodecylamine	-----	47
Tetradecylamine	-----	18
Hexadecylamine	-----	8
Octadecylamine	-----	5
Octadecenylamine	-----	5
B		
Hexadecylamine	-----	10
Octadecylamine	-----	10
Octadecenylamine	-----	35
Octadecadienylamine	-----	45
C		
Hexadecylamine	-----	30
Octadecylamine	-----	25
Octadecenylamine	-----	45

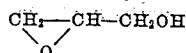
As examples of benzyl halides and substituted benzyl halides, the following are employed in the foregoing process:

- o-Chlorobenzyl chloride
- p-Chlorobenzyl chloride
- 2,4-dichlorobenzyl chloride
- 3,4-dichlorobenzyl chloride
- 2,6-dichlorobenzyl chloride
- 2,4,6-trichlorobenzyl chloride
- 1- or 2-chloromethylnaphthalene
- Nitrobenzyl chloride
- Alkylated benzyl chloride, such as
- Amylbenzyl chloride
- Propylbenzyl chloride
- Octylbenzyl chloride
- Dodecylbenzyl chloride,

and the corresponding bromides and iodides of the preceding chlorides.

As examples of suitable alkylene oxides which may be condensed with the mixture of primary aliphatic amines,

we prefer to employ ethylene oxide, 1,2-propylene oxide, 1,2-butylene oxide, and hydroxylated-alkylene oxides, such as glycidol, having the following formula:



and the like.

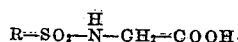
The following are illustrated examples of the substituted and unsubstituted benzylamines which may be employed in lieu of the mixture of primary aliphatic amines:

Benzylamine
 α -Methylbenzylamine
 α -Ethylbenzylamine
 α -Aminocumene (α,α -dimethylbenzylamine)
 p-Chlorobenzylamine
 2,4-dichlorobenzylamine
 4-nitrobenzylamine
 4-methylbenzylamine
 Amylbenzylamine.

Compounds which may be effectively employed to convert the quaternary ammonium hydroxides into salts having other anionic groups are as follows:

Phosphoric acid
 Phosphorus acid
 Acetic acid
 Hexylbenzenesulfonic acid
 Nonylbenzenesulfonic acid
 Lactic acid
 Gluconic acid
 Sulfuric acid
 Ethyl hydrogen sulfate
 Dodecyl hydrogen sulfate
 Dinonylbenzenesulfonic acid
 Diamylbenzenesulfonic acid
 Dodecylbenzenesulfonic acid
 Dibutyl-naphthalenesulfonic acid
 Dodecyl-naphthalenesulfonic acid
 Octylsulfonic acid
 Dodecylsulfonic acid
 Sulfoacetic acid
 Sulfolauric acid
 Sulfostearic acid
 Propionic acid
 Formic acid.

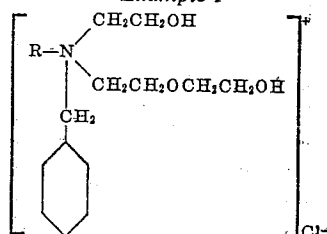
In lieu of the foregoing, a mixture of alkylsulfonamido-acetic acids obtained by chlorosulfonation of mineral oils or kerosene by the "Reed-Horn Process" followed by conversion to the amide with ammonia and then treated with chloroacetic acid to form:



may be employed.

The following examples will illustrate in complete detail the mode of preparing the quaternary ammonium salts of the present invention. It is to be understood that these examples are merely illustrative and are not to be construed as being limitative. All parts are by weight unless otherwise stated.

Example I



R represents a mixture of alkyl radicals having 16 to 18 carbon atoms

542 grams (2 mols) of the mixture of amines designated above by C were charged into an autoclave and

the mixture heated to a reaction temperature of approximately 110° C. The autoclave, as mentioned above, was equipped with a special alkylene oxide reservoir to deliver the alkylene oxide into the autoclave. Into this autoclave there were introduced portionwise 264 grams (6 mols) of ethylene oxide over a period of 3¼ hours. The interior pressure of the autoclave was regulated at 25 to 35 lb. p. s. i. by the addition of alkylene oxide. After 10 to 20 minutes, there was a heat of reaction which, although not severe, required the use of cooling. The product was discharged at 60° C. and the total yield was 799.2 grams. The product had an amber color and a solidification point of 20–21° C. The pH of a 2½% aqueous solution of the product in water was about 10.7. By employing the foregoing formula, the mol ratio was 2.92.

The quaternization of the foregoing product was conducted in a 2-liter, 4-necked flask equipped with stirrer, thermometer, condenser, and constant temperature bath. The condenser was fitted with a calcium chloride tube to exclude atmospheric moisture. 599.4 grams (1.5 mols) of the polyethoxylated amine, prepared as above, 62.5 grams of isopropyl alcohol, and 7.9 grams of potassium iodide were heated to 70° C. in a constant temperature bath, and 192.4 grams (1.52 mols) of benzyl chloride added in one portion. There was a moderate heat of reaction that required slight cooling for a short time in order to maintain the temperature below 78° C. After approximately 14½ hours at 70° C., the quaternary salt was discharged.

The amine and amine hydrochloride content of the reaction mixture was determined at intervals by removing a small sample and titrating it with standard acid and then with standard base. The results are given in Table 1.

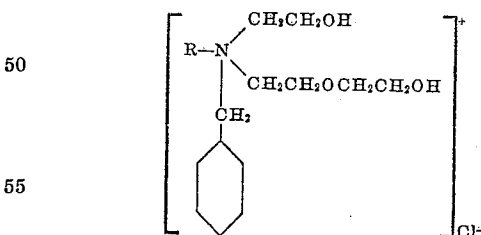
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TABLE 1

Total Hours Reaction Time	Mols of Amine per Gram Sample	Mols of Amine Hydrochloride Per Gram Sample	Percent Amine Consumed
2	.0001746	.000058	69.4
5	.0002257	.000052	86.7
10	.0001208	.0000558	89.8
14½	.0000812	.0000547	92.2

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Example II



R represents a mixture of alkyl radicals having 8 to 18 carbon atoms

The general procedure of Example I was utilized with the exception that 542 grams (2 mols) of the amine mixture designated as C were replaced by 822 grams (3 mols) of the mixture of amines designated as A, and 264 grams (6 mols) of ethylene oxide were replaced by 400 grams (9.09 mols) of ethylene oxide. The reaction was carried out at 90° C. for 6 hours. At the end of this time, most of the ethylene oxide had reacted. The addition of ethylene oxide was portionwise. The temperature was then raised to 120° C. for ½ hour to insure complete reaction of the small remainder of ethylene oxide. The weight of the discharged product which amounted to 1213 grams indicated that 391 grams of ethylene oxide had reacted (mol ratio of the product=2.96).

800.8 grams of the product obtained as above, 117

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grams of isopropyl alcohol, and 11.7 grams of potassium iodide were heated to about 70° C. in a constant temperature bath and 258.1 grams of benzyl chloride added in one portion. The reaction mixture was stirred at 70° C. for 10 hours. Analysis of a small sample by titration showed 0.000139 mol of amine per gram and 0.000188 mol of amine hydrochloride per gram were present in the product. This represents a consumption of 80% of the starting amine mixture. The reaction mixture was stirred for an additional 3 hours at 70° C. Titration showed 88% disappearance of amine.

Example III

Example I was again repeated with the exception that 660 grams (3.21 mols) of the amine mixture designated as A were allowed to react with 434 grams (9.86 mols) of ethylene oxide at 100° C. and at a pressure of 25–32 lbs. p. s. i. The condensation reaction was complete in about 2 hours. The product weighed 1089.8 grams and had a calculated mol ratio of 3.0. The color of the product was amber and the solidification point below –4° C. The pH of a 10% aqueous solution was 11.7.

Analysis for primary amine showed less than 0.2% by the salicylaldehyde method. The neutral equivalent was 349 (theory 344) and 0.00025 mol of secondary amine per gram was detected. The foregoing product was quaternized with benzyl chloride as above, except that the catalyst and solvent were omitted.

Into a 300 cc. round-bottom, 3-necked flask equipped with a stirrer, thermometer, and condenser, and heated by means of a constant temperature oil bath, 68.2 grams of the foregoing product were heated to 80° C. with stirring. 25.3 grams of benzyl chloride were then added in one portion and the temperature of the mixture kept at 80° C. + or –1° C. for 22 hours and 15 minutes. The product was stirred continuously and samples removed at intervals and titrated for remaining amine and amine hydrochloride.

Phenol coefficients of the final product were determined and the results obtained are shown in Table 2.

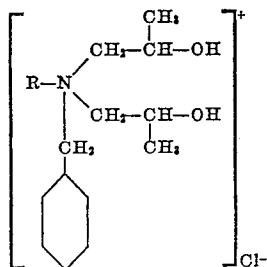
TABLE 2

Total Hours Reaction Time	Mols of Amine Per Gram Sample	Mols of Amine Hydrochloride Per Gram Sample	Percent Amine Consumed	Phenol Coefficient
3	4.02×10^{-4}	0.79×10^{-4}	77.5	213
6	1.89×10^{-4}	1.40×10^{-4}	84.6	264
22½	0.80×10^{-4}	1.80×10^{-4}	87.8	325

Example IV

A molecular equivalent of the amine mixture designated as A was polyoxyethylated with 5 mols of ethylene oxide. 43.5 grams of this product were mixed with 12 grams of benzyl chloride and placed in an oven at 69–70° C. for 96 hours. The product contained 13.6% of unreacted free amine and 7% of amine hydrochloride. The phenol coefficient against *E. typhosa* at 20° C. was 154.

Example V



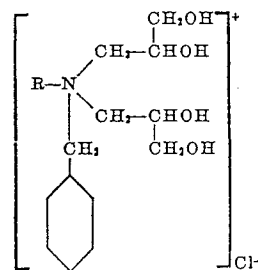
R represents a mixture of alkyl radicals having from 8 to 18 carbon atoms

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618 grams of the amine mixture designated as A were treated with 364.5 grams of propylene oxide according to the procedure of Example 1. The reaction was carried out at 120° C. and required 5½ hours for completion. The product contained no unreacted primary amine. There was 0.00045 mol/gram of secondary amine in the product.

327 grams (1 mol) of this product were mixed with 126.6 grams (1 mol) of benzyl chloride, 45.4 grams of isopropanol, and 4.5 grams of potassium iodide. The reaction mixture was stirred at 75° C. for 55 hours. The product contained a total of 20.5% of the original amount of amine and amine hydrochloride. The phenol coefficient against *E. typhosa* was 156.

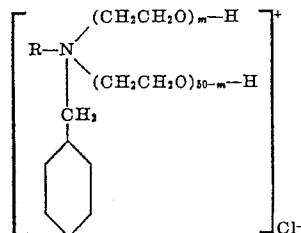
Example VI



R represents a mixture of alkyl radicals having from 8 to 18 carbon atoms

The procedure of Example V was followed except that 400 grams of glycidol were used in place of 364.5 grams of propylene oxide. 354.2 grams (1 mol) of the product were benzylated with benzyl chloride (126.6 grams; 1 mol) as in Example V.

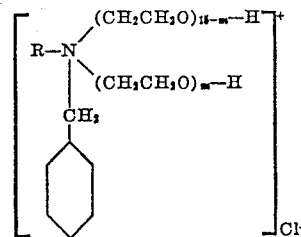
Example VII



R represents a mixture of alkyl radicals having from 8 to 18 carbon atoms

240.6 grams (0.1 mol) of the reaction product of 1 mol of the amine mixture A with 50 mols of ethylene oxide were treated with 12.6 grams (0.1 mol) of benzyl chloride in the presence of 25.3 grams of isopropanol and 253 grams of potassium iodide at 75° C. for 10 hours. Titration of the reaction mixture showed 71% conversion of amino nitrogen to quaternary nitrogen.

Example VIII



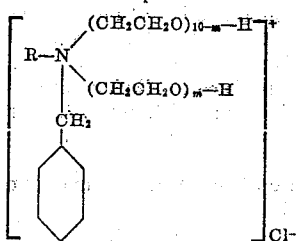
R represents a mixture of alkyl radicals having from 8 to 18 carbon atoms

87.9 grams (0.1 mol) of one mole of the reaction product of the amine mixture A with 15 mols of ethylene oxide were treated with 12.6 grams (0.1 mol) of benzyl chloride in the presence of 10 grams of isopropanol and 1 gram of potassium iodide. Titration showed 82% conversion of amino nitrogen to quaternary nitrogen.

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The product of the foregoing example is useful in the acidizing of oil wells and as an inhibitor in pickling baths for steel.

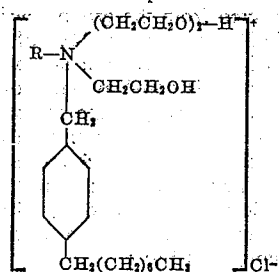
Example IX



R represents a mixture of alkyl radicals having 16 to 18 carbon atoms

The procedure of Example I was repeated with the exception that 880 grams (20 mols) of ethylene oxide were used in place of 264 grams (6 mols) to yield a product containing 10 mols of ethylene oxide per mol of amine

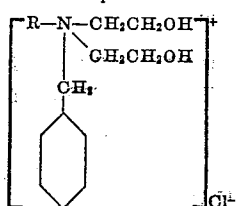
Example X



R represents a mixture of alkyl radicals having 16 to 18 carbon atoms

The procedure of Example I was repeated with the exception that 358 grams of octylbenzyl chloride were used in place of 192.4 grams of benzyl chloride. Titration of the unreacted amine and amine hydrochloride showed that there was a conversion of 83% of amino nitrogen to quaternary nitrogen.

Example XI



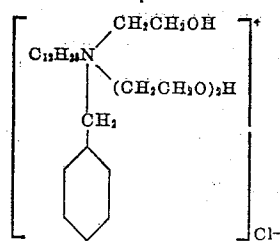
R represents a mixture of alkyl radicals having 8 to 18 carbon atoms

The general procedure of Example I was utilized with the exception that 542 grams (2 moles) of the amine mixture designated as C were replaced by 660 grams (3.2 moles) of amines designated as A, and 264 grams (6 moles) of ethylene oxide were replaced by 310 grams (7 moles) of ethylene oxide. The reaction was carried out at 90° C. for 7½ hours. The addition of ethylene oxide was portionwise. The weight of the discharged product was 966.5 grams, indicating that 306.5 grams of ethylene oxide had reacted. (The mole ratio of the product was 2.17.)

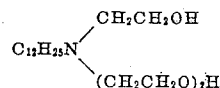
The product had a neutral equivalent of 307 by titration and contained less than 1% of unreacted primary amine. 60.3 grams (0.2 mole) of the product obtained above and 25.3 grams (0.2 mole) of benzyl chloride were well mixed and placed in an oven at 70° C. for 10 days. At the end of this time the product contained 83% of quaternary nitrogen and had a phenol coefficient of 375 against *E. typhosa* at 20° C.

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Example XII

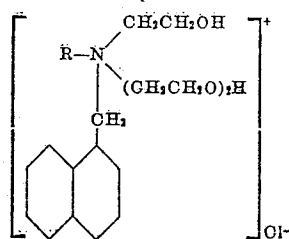


The general procedure of Example II was carried out except that the mixture of amines designated by A was substituted by n-dodecylamine. The reaction of the tertiary amines



with benzyl chloride was carried out in the same manner and molar quantities as described in Example II to yield a water soluble product which gave copious foam in water.

Example XIII



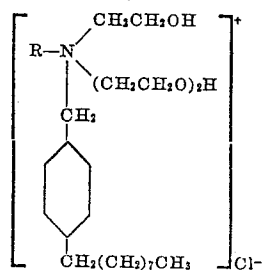
R represents a mixture of alkyl radicals having 8 to 18 carbon atoms.

To 70 grams (0.2 mole) of tertiary amines prepared by the reaction of the amine mixture A with 3 mole equivalents of ethylene oxide as described in Example II were added 35.3 grams (0.2 mol) of chloromethyl naphthalene, 21 grams of isopropanol, and 1 gram of potassium iodide. The mixture was heated at 75° C. for 10 hours. The product contained 81% of quaternary nitrogen and had a phenol coefficient of 330 against *E. typhosa* at 20° C.

The product was also very effective in preventing the attack of 10% hydrochloric acid on steel. A 0.2 of one per cent concentration of the above product in 10% hydrochloric acid showed a weight loss of a steel panel corresponding to 0.010 lb. per sq. ft. per day. A control using no inhibitor resulted in a weight loss of 1.358 lbs. per sq. ft. per day.

The chloromethyl naphthalene employed in the foregoing example was prepared by the reaction of para-formaldehyde and concentrated hydrochloric acid with naphthalene in the presence of phosphoric acid. The product is predominantly α-substituted and has a boiling point of 141–146° C. at 8 mm.

Example XIV

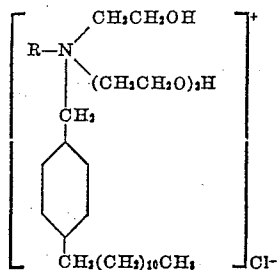


R represents a mixture of alkyl radicals having 8 to 18 carbon atoms.

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The general procedure and materials described in Example II were utilized except that 258.1 grams of benzyl chloride were replaced by an equivalent weight, 516 grams, of nonylbenzyl chloride prepared by chloromethylation of nonyl benzene with formaldehyde and hydrogen chloride. The nonyl benzene was prepared by the reaction of tripropylene with benzene in the presence of an acid catalyst. The resulting product had pronounced surface active properties.

Example XV



R is a mixture of alkyl radicals having 8 to 18 carbon atoms

The general procedure and materials utilized in Example II were utilized except that 258.1 grams of benzyl chloride were replaced by an equivalent weight, 600 grams, of dodecylbenzyl chloride. The dodecylbenzyl chloride was prepared by reaction of tetrapropylene with benzene using an acid catalyst and then with formaldehyde and hydrogen chloride. The resulting product foamed in water.

The quaternary ammonium salts prepared as above not only possess strong germicidal power which makes them particularly useful in various sanitizing and cleansing compositions, but they are also stable and effective in nonionic surface active compositions. Moreover, they have beneficial surface active properties which enable them to be highly efficient for many purposes.

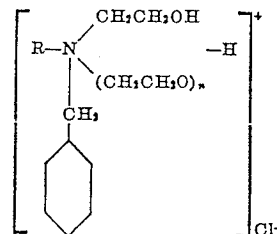
From the formulae of Examples VII to IX, it is to be noted that the molecular amount of alkylene oxide is represented by an average numerical value of 50, 15, and 10, respectively and m represents an average numerical value which is one-half of the total number of moles of alkylene oxide consumed by the reaction. From these formulae, it is clearly obvious that $m+(50-m)$, $m+(15-m)$, and $m+(10-m)$ are equal to 50, 15, and 10 moles, respectively, of alkylene oxide utilized during the reaction per mole of the amine mixture. The reason for so designating these values becomes manifest when one considers the reaction between the amine mixture and alkylene oxide. In the mono amine mixture there are two replaceable hydrogens in each of the amines. The addition of alkylene oxide to each of the replaceable hydrogens of the amine and of the alcohol produced is a matter of chance

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so that the increase in the length of one particular chain may not proceed at the same rate as the increase in the length of the other in one individual molecule. However, in a statistical consideration of all the molecules produced, a substantial number will have two polyalkyleneoxy chains of approximately equal length. This number will increase as n is decreased toward 1. The distribution of chain lengths produced in alkylene oxide reactions is discussed in detail in an article by P. J. Flory in Journal of American Chemical Society, 62, 1561.

We claim:

1. A mixture of quaternary ammonium chlorides having the formula:



said mixture selected from the group consisting of (A) a mixture wherein R represents in 24% of the compounds equal amounts of octyl, decyl and hexadecyl radicals, in 10% of the compounds equal amounts of octadecyl and octadecenyl radicals, in 47% of the compounds a dodecyl radical and in 18% of the compounds a tetradecyl radical, and (B) a mixture wherein R represents in 30% of the compounds a hexadecyl radical, in 25% of the compounds an octadecyl radical and in 45% of the compounds an octadecenyl radical, and n represents a positive integer ranging from 1 to 2.

2. A mixture of quaternary ammonium chlorides as defined in claim 1 wherein R represents in 24% of the compounds equal amounts of octyl, decyl, and hexadecyl radicals, in 10% of the compounds equal amounts of octadecyl and octadecenyl radicals, in 47% of the compounds a dodecyl radical and in 18% of the compounds a tetradecyl radical.

3. A mixture of quaternary ammonium chlorides as defined in claim 1 wherein R represents in 30% of the compounds a hexadecyl radical, in 25% of the compounds an octadecyl radical, and in 45% of the compounds an octadecenyl radical.

References Cited in the file of this patent

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