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NITROGEN-CONTAINING ORGANIC COMPOUNDS

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38 Claims. (Cl. 260—501)

This invention relates to new quaternary ammonium compounds, and more particularly refers to pentavalent nitrogen compounds wherein four of the nitrogen valences are connected to substituent groups through carbon, and wherein the fifth nitrogen valence is connected to an anion or is connected through oxygen to one of the other substituent groups.

It is an object of this invention to produce an entirely new class of quaternary ammonium derivatives. A further object is to produce pentavalent nitrogen compounds, many of which may be converted to their inner salts or anhydrides. A still further object is to produce a class of compounds which is related to betaine, but which differs therefrom in a manner to be described hereafter. A still further object is to produce wetting, detergent, emulsifying and dispersing agents. A still further object is to produce surface active materials which are particularly adapted for the production of self-emulsifying oils, etc. A still further object is to produce compounds which may be used in place of or in admixture with soap and soap-like products in the various processes wherein such products have previously been used or are capable of use. Additional objects will become apparent from a consideration of the following description and claims.

These objects are attained according to the herein described invention wherein nitrogenous compounds are reacted with hydrocarbon derivatives in order to produce pentavalent nitrogen compounds, four of the nitrogen valences of which are bound to substituent groups through carbon, and wherein one of the substituent groups contains at least six carbon atoms. In a more limited sense this invention pertains to pentavalent nitrogen compounds having the following general formula:



wherein X represents a non-hydrocarbon radical such as a halogen or hydroxyl group, R₁ represents a hydrocarbon radical containing at least six carbon atoms, and R₂, R₃ and R₄ represent hydrocarbon-containing substituents which are connected to the nitrogen atom through carbon, at least one of the substituents (R₁—R₂—R₃—R₄) being further substituted by at least one non-hydrocarbon radical. A non-hydrocarbon radical may be defined as a group which is not entirely composed of hydrogen and carbon atoms, as, for

example, hydroxyl, halogen, amino, carboxyl, sulfonic acid, etc., groups.

In its preferred embodiment this invention pertains to quaternary ammonium salts having the following general formula:



wherein X represents a halogen group, R₁ represents an aliphatic hydrocarbon radical containing from twelve to eighteen carbon atoms, R₂, R₃ and R₄ represent aliphatic hydrocarbon radicals each of which contains less than eight carbon atoms, and in addition, at least one of the groups represented by R₁, R₂, R₃ and R₄ has substituted thereon at least one group containing an acid hydrogen or a derivative thereof, particularly a single carboxyl or sulfonic acid group. This preferred embodiment is also intended to embrace inner salts or anhydrides of the aforementioned compounds wherein the halogen atom is removed from the nitrogen nucleus and wherein the hydrogen atom or its equivalent is removed from the salt-forming substituent, the resulting compounds having a nitrogen nucleus bound through oxygen to one of the substituents represented by R₁, R₂, R₃ and R₄.

The invention may be more readily understood by a consideration of the following illustrative examples, in which the quantities are stated in parts by weight:

Example 1

Into a pressure vessel provided with brine cooling were charged 300 parts by weight of liquid trimethylamine. To this were added 50 parts of alpha brom stearic acid (prepared as described by C. Hell and J. Sadomsky, Ber. 24, 2391 (1891)), and the vessel was closed and warmed to about 40° C. The brom stearic acid first dissolved in the trimethylamine and then as the quaternary ammonium derivative was formed, a solid deposits. The exact temperature was not important, the reaction proceeding more rapidly with increased temperature but at high temperatures decomposition of the product sets in. When the reaction had proceeded as far as it would, as indicated by the fact that no more solid was formed and that a representative sample showed no further increase in ionizable bromine, the trimethylamine was distilled off. This product may be used as such in certain applications but in general it was preferable to dissolve it in about 100 parts of warm alcohol and then add 5.5 parts of sodium

hydroxide dissolved in 100 parts of alcohol. The alcohol and trimethylamine were then distilled off. The product may be freed from sodium bromide by dissolving in a suitable solvent such as dry benzene and filtering.

A solution of this material in water, containing 0.075% of the active ingredient, showed remarkable detergent power in the washing of badly soiled mixed wool and cotton fabric. It was particularly valuable for this purpose because of its insensitivity toward hard water. Excellent emulsions can be prepared by the use of one or two per cent of this material based on the weight of the dispersed phase.

Example 2

A mixture of 50 parts by weight of alpha brom stearic acid and 35 parts of dimethyl cyclohexylamine was warmed gently until a clear liquid was obtained. This was maintained at 60° until no further increase in ionizable bromine occurred. The product was dissolved in 150 parts alcohol and a solution of 5.5 parts of sodium hydroxide in 100 parts of alcohol was added. The alcohol and amine were removed at 50° under reduced pressure.

Example 3

757 parts of octadecylene chloresulfonate (obtained, for example, by addition of chloresulfonic acid to octadecylene) were added to 4500 parts of liquid trimethylamine, cooled to prevent loss of the latter. The mixture was kept under pressure at 30-50° until no more solid was deposited. The amine was evaporated and the product dissolved in 1000 parts of alcohol. A solution of 50 parts of sodium in 1000 parts of alcohol was then added and the sodium chloride filtered out. The alcohol was removed under reduced pressure.

Example 4

A mixture of 95 parts sodium chloracetate, 297 parts of dimethyl octadecylamine and 5000 parts of alcohol was kept at 40-50° for 12 hours and the temperature then raised to 70-80° until the reaction was complete as shown by the fact that a sample was wholly soluble in dilute alkali. The product was filtered and the alcohol removed under reduced pressure.

Example 5

To a solution of 757 parts of octadecylene chlor-sulfonate in 2500 parts of ethylene dichloride were added 750 parts of triethanolamine. The mixture was maintained at 60-70° for 48 hours and 1500 parts of alcohol were added. Hydrogen chloride was then passed through the mixture until in excess to precipitate the excess triethanolamine. The hydrochloride was filtered out and the excess hydrogen chloride removed under reduced pressure. The alcohol may be removed under reduced pressure and the product used as it is or it may be neutralized to Brilliant Yellow before drying.

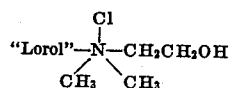
Example 6

A mixture of 211 parts of brom ethane sodium sulfonate and 297 parts of dimethyl octadecylamine in 5000 parts of alcohol was heated at 70° until no further increase in ionizable halogen occurred. The product was filtered and the alcohol removed under reduced pressure.

Example 7

21.8 parts of ethylene chlorhydrine (10% excess) and 31 parts of "lorol" dimethylamine were heated together under an air condenser at 95-100° C. for 24 hours or until a test drop showed com-

plete solubility in water. (Note: By "lorol" is meant a mixture of C₁₀, C₁₂, C₁₄, C₁₆ and C₁₈ carbon length chains with the C₁₂ chain predominating. The "lorol" dimethylamine was made from lorol chloride and dimethylamine.) The product, the quaternary ammonium salt of "lorol" dimethylamine and ethylene chlorhydrine, was a white waxy solid and had the following formula:



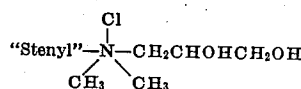
In place of relatively dry ethylene chlorhydrine, an aqueous solution of ethylene chlorhydrine has been found to work equally well.

In place of the "lorol" dimethylamine, 39 parts of "stenyl" dimethylamine have been used. (Note: By "stenyl" is meant a mixture of essentially C₁₆ and C₁₈ carbon length chains with some C₁₂, C₁₄ and C₂₀ carbon length chains also being present. The "stenyl" dimethylamine was made from "stenyl" chloride and dimethylamine.) In this case the mixture was heated at 125-150° C. for 16 hours to effect complete solubility in water. The product of this reaction was the quaternary ammonium salt of "stenyl" dimethylamine and ethylene chlorhydrine.

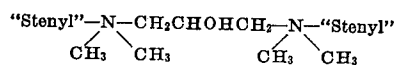
In place of "lorol" dimethylamine, 42 parts of octadecyl dimethylamine have been used. In this case, the mixture was heated at 120-135° C. for 20 hours to effect complete solubility in water. This gave as a product the quaternary ammonium salt of octadecyl dimethylamine and ethylene chlorhydrine. The "stenyl" and octadecyl derivatives possessed properties which were similar to those of the "lorol" derivative.

Example 8

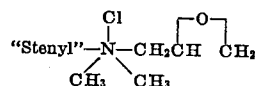
100 parts of "stenyl" dimethylamine (see Example 7) and 42 parts of glycerol-mono-chlorhydrine (10% excess) were heated under an air condenser at 140-155° C. for 12 hours or until a test drop showed complete solubility in water. This reaction gave the quaternary ammonium salt of "stenyl" dimethylamine and mono-chlorhydrine, a waxy solid and had the formula:



In place of glycerol-mono-chlorhydrine, 25 parts of glycerol-di-chlorhydrine (10% excess) has been used. The product, the di-quaternary ammonium salt of "stenyl" dimethylamine and glycerol-di-chlorhydrine, a waxy solid, has the formula:



Also in place of glycerol-mono-chlorhydrine, 35 parts of epichlorhydrine (10% excess) has been used. The reaction was exothermic but was heated at 145-155° C. for 7 hours. The product, the quaternary ammonium salt of "stenyl" dimethylamine and epichlorhydrine, a semi-hard waxy solid, has the formula:

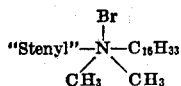


The quaternary ammonium compounds in Examples 7 and 8 that possess an hydroxyl group in a side chain may be sulfated with the usual re-

agents to give detergent bodies of interest and for other uses as surface active bodies.

Example 9

- 5 91 parts of hexadecyl bromide and 86 parts of "stenyl" dimethylamine (see Example 7) were heated under an air condenser at 125-150° C. for 7 hours. The product, the quaternary ammonium salt of "stenyl" dimethylamine and hexadecyl bromide, was a semi-hard waxy solid, and had the formula:



- 15 In place of hexadecyl bromide, 83 parts of "stenyl" chloride or 97 parts of "stenyl" bromide or 111 parts of "stenyl" iodide have each been heated with 86 parts of "stenyl" dimethylamine at temperatures of 95-175° C. for 12 to 24 hours to form the corresponding quaternary ammonium salts. They were all waxy solids.

Example 10

- 25 50 parts of "stenyl" dimethylamine (see Example 7) and 45 parts of chloropropanol sulfonate sodium salt in 100 parts of water were refluxed for 6 hours or until the amine has gone completely into solution. The aqueous solution of the product was almost water white.

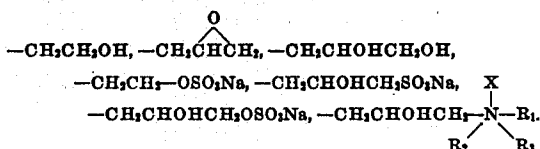
- 30 It is to be understood that the aforementioned examples are illustrative merely of a representative few of the many means of carrying into practical operation the present invention. The processes utilized, the reactants entering into such processes, the proportions of reactants, and the conditions of reaction, may be varied widely without departing from the scope of this invention. In general, it may be stated that the desired pentavalent compounds may conveniently be obtained by reacting a tertiary amine with a hydrocarbon containing a replaceable anion. Where one of the substituents also contains an acid hydrogen or a derivative thereof the resulting pentavalent nitrogen compounds may ordinarily be converted to inner salts or anhydrides, for example, by treatment with an alkali.

- 40 The majority of compounds comprised within the scope of this invention, in their uncondensed form, may be represented by the following general formula:



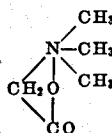
- 55 wherein X represents a non-hydrocarbon radical such as chlorine, bromine, iodine or hydroxyl groups, and R₁, R₂, R₃ and R₄ represent hydrocarbon groups or derivatives thereof connected to the nitrogen nucleus through carbon, at least one of said groups containing at least six carbon atoms. One or more of the aforementioned hydrocarbon groups may have substituted thereon one or more non-hydrocarbon radicals, as, for instance, hydroxyl, halogen, amino, benzoylamino, trifluormethyl, carboxyl, acetyl, borate, alkoxo, sulfonic acid, sulfuric acid, phosphoric acid, etc. groups. The hydrocarbon radicals represented by R₁, R₂, R₃ and R₄ may be of open chain or cyclic derivation and may be saturated or unsaturated. For example, they may be derived from hydrocarbons of the aliphatic, aralkyl, aromatic, or cycloaliphatic series. A few of the radicals coming within this category are methyl, ethyl, propyl, isopropyl, butyl, isobutyl, secondary

butyl, amyl, hexyl, octyl, decyl, lauryl, myristyl, cetyl, stearyl, oleyl, ricinoleyl, linoleyl,



The aforementioned and related groups may be used as such, or may be further substituted with non-hydrocarbon radicals such as those mentioned previously, substitution taking place either before or after preparation of the quaternary ammonium compounds. Moreover, these radicals may be externally joined in such manner that the nitrogen nucleus becomes an integral portion of a heterocyclic ring. In other words, the nitrogen nucleus may be a component of a heterocyclic compound of the pyridine, piperidine, quinoline, acridine, etc. series. It is to be understood that the aforementioned hydrocarbon radicals or derivatives thereof may be the same or dissimilar to one another, and one or more should contain at least six carbon atoms.

Since this invention is particularly directed to compounds of the betaine type it is to be understood that the following instructions which pertain to such compounds are the preferred embodiment thereof. As is well known, betaine is a trimethyl-amino-acetic acid inner salt. It has the following configuration:



In accordance with the present invention it has been found that an entirely new class of compounds may be obtained by substituting for a hydrogen atom of the CH₂ group or for the CH₂ group itself, in the above identified betaine formula, a hydrocarbon group or derivative containing at least six and preferably from twelve to eighteen carbon atoms. It is also contemplated that the aforementioned higher hydrocarbon group may be substituted for one or more of the methyl groups, rather than for the CH₂ group. Furthermore, in place of one or more of the methyl groups, shown in said formula, other substituents, as, for instance, other alkyl groups or aralkyl, aryl or cycloaliphatic groups may be substituted. In the same manner, the nitrogen nucleus may form an integral part of a heterocyclic ring, such as a pyridine or piperidine ring. Likewise, the carbonyl group may be the residue of other salt-forming groups than the carboxyl group. For instance, it may be the residue of a sulfonic acid, a sulfuric acid ester, a phosphoric acid or a phosphoric acid ester group. This carbonyl group, or other salt-forming group, may, moreover, be substituted on some other substituent of the compound rather than upon the substituent which contains, or is, a long chain hydrocarbon group. In other words, the salt-forming group may be substituted on one of the methyl groups, referred to in the above formula, or it may be substituted on the group which replaces such methyl group or which is substituted thereon. The aforementioned compounds are herein designated as inner salts or anhydrides. It should be borne in mind, however, that the quaternary ammonium derivatives which give rise to such inner salts or anhydrides are themselves of considerable merit in the industrial arts.

"Betaine type" compounds referred to herein may conveniently be produced by reacting a hydrocarbon derivative of at least six carbon atoms, which in addition contains both an acid hydrogen or its equivalent and a replaceable anion, with a tertiary amine. Hydrocarbon derivatives which are well adapted for use in this connection may be obtained from a variety of compounds, both naturally occurring and synthetic, for example, from petroleum or vegetable and animal oils, fats and waxes. Such derivatives, as is clear from the preceding description, are higher hydrocarbons which preferably contain from twelve to eighteen carbon atoms. Hydrocarbons of open chain series, and in particular straight chain hydrocarbons, are of optimum value for use herein under a wide variety of conditions. These hydrocarbons may be derived from heptane, octadecane, octane, decane, tetradecane, hexadecane, dodecane and the intermediate homologues thereof. Moreover, they may be unsaturated members of the aforementioned series, such as hexylene, octylene, decylene, tetradecylene, dodecylene, hexadecylene, octadecylene and didecylene, etc. Salt-forming groups which may be substituted thereon prior to use herein are, for example, carboxyl, sulfonic acid, sulfuric acid ester, phosphoric acid, phosphoric acid ester, and the like. Replaceable anions which may also be substituted thereon prior to use herein are acid residues such as chlorine, bromine, and the like.

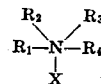
Tertiary amines with which the hydrocarbon derivatives described supra may be reacted are exceedingly great in number, and since they are well known no attempt will be made herein to describe them in detail. For purposes of illustration, however, reference may be made to amines such as trimethylamine, trialkylamines generally, cyclohexyl dimethylamines, dialkylcyclohexylamine generally, dicyclohexyl alkylamines, ethanol dialkylamines generally, tertiary amines containing one to three alkylol groups, triethanolamine, pyridine, alkyl piperidine, alkylol piperidine, etc. It is to be understood that these tertiary amines may contain additional non-hydrocarbon radicals. As such radicals are well known and have been referred to herein previously, they need not be further described.

Quaternary ammonium compounds formed by reacting the above described higher hydrocarbon derivatives with the described tertiary amines may be used as such, or may be converted into their inner salts or anhydrides, these latter compounds being of the betaine type. The examples hereof describe several methods of converting the quaternary ammonium compounds to derivatives of the betaine type. Such methods briefly comprise treating the quaternary ammonium compounds with an alkali. This treatment probably results in the removal of the anion from the nitrogen nucleus, and removal of acid hydrogen from the salt-forming group. The resulting compound has the nitrogen group bound through the oxygen of the salt-forming group to the higher hydrocarbon substituent. In its secondary embodiment it is contemplated that the salt-forming group or substituent containing an acid hydrogen may be present on a lower hydrocarbon radical.

The aforementioned quaternary ammonium compounds may likewise be formed by alkylation, aralkylation or similar treatment of an amino fatty acid. In place of the amino fatty

acid other amino compounds containing a salt-forming group might be substituted. Moreover, an unsaturated tertiary amine might be reacted in known manner to add on a salt-forming group, for example, by treating with cold concentrated sulfuric acid.

Quaternary ammonium compounds made in accordance with the instructions just referred to as preferred may for the most part be designated by the following general formula:



wherein X represents an anion, preferably chlorine or bromine; R₁ represents an aliphatic hydrocarbon radical containing at least six carbon atoms, preferably a straight chain aliphatic hydrocarbon radical containing from twelve to eighteen carbon atoms, and also containing a salt-forming group, preferably carboxylic or sulfonic acid; R₂, R₃, and R₄ represent hydrocarbon radicals, preferably aliphatic hydrocarbon radicals containing less than eight carbon atoms.

As previously mentioned, instead of substituting the salt-forming group upon the radical represented by R₁ in the above formula it may be substituted upon one of the radicals represented by R₂, R₃ and R₄. In the same manner, the following instructions with respect to inner salts or anhydrides may be varied by attaching the residue of the salt-forming group, represented by —Y—, to one of the radicals represented by R₂, R₃ and R₄.

Inner salts or anhydrides of the aforementioned quaternary ammonium compounds, in general, conform to the following illustrative formula:



wherein R₁ represents the residue of a higher hydrocarbon radical which contains at least six carbon atoms and is preferably an aliphatic hydrocarbon radical containing from twelve to eighteen carbon atoms; R₂, R₃ and R₄ represent hydrocarbon radicals, preferably aliphatic hydrocarbon radicals of less than eight carbon atoms; Y represents the residue of a salt-forming group, preferably CO or SO₂. In this formula R₁, R₂, R₃ and/or R₄ may be further substituted by non-hydrocarbon radicals. Each of the aforementioned substituents represented by R is connected to the nitrogen nucleus through a carbon atom. Where these compounds are to be used as substitutes for soap and soap-like products it is usually advisable to have the salt-forming group and the pentavalent nitrogen atom quite close together. In other words, they should preferably be separated by no more than about four carbon atoms.

It is contemplated that the compounds described herein may be made by various additional processes. For example, a refined petroleum fraction may be chlorinated and converted to a tertiary amine. This amine, which contains a long hydrocarbon radical, may then be converted to a quaternary ammonium compound by reaction with a chlorinated hydrocarbon containing an acid hydrogen, such as a halogen acid. The resulting compound may, if desired, be converted to an inner salt by treatment with an alkali. The position of the carboxyl, or other group containing an acid hydrogen, in the halogen acid

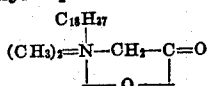
determines its position in the resulting product, whether alpha-, beta-, gamma-, etc.

Another illustrative method of obtaining these compounds is to oxidize a refined petroleum fraction to the acid. This acid is then halogenated and converted to a quaternary ammonium salt by reaction with a tertiary amine. The resulting product may, if desired, be converted to an inner salt by treatment with sodium hydroxide. While petroleum from practically any source may be used herein it is ordinarily advisable to select an oil predominating in paraffin hydrocarbons. It is to be understood, however, that naphthenic and asphaltic base oils are also suitable for use herein.

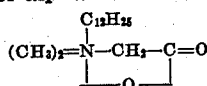
A representative few of the many "betaine-type" compounds which may be made in accordance with the instructions given supra are:

1. Alpha-betaines:

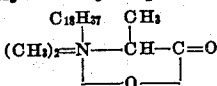
(a) N-stenyl-alpha-betaine



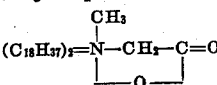
(b) N-lorol-alpha-betaine



(c) N-stenyl-methyl-alpha-betaine

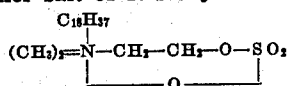


(d) N-distenyl-alpha-betaine

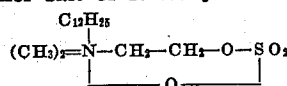


2. Beta-betaines:

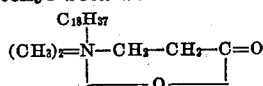
(a) N-stenyl-beta-betaine-sulfate Inner salt of N-stenyl-choline-sulfate



(b) N-lorol-beta-betaine-sulfate Inner salt of N-stenyl-choline-sulfate

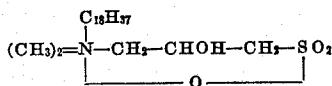


(c) N-stenyl-beta-betaine

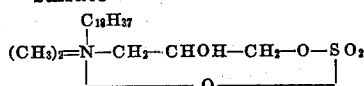


3. Gamma-betaines:

(a) N-stenyl-beta-hydroxy-gamma-betaine-sulfonate



(b) N-stenyl-beta-hydroxy-gamma-betaine-sulfate



In one of its secondary embodiments this invention is concerned with the production of non-condensed or uncondensable compounds having the following general formula:



wherein X represents a non-hydrocarbon radical such as hydroxyl, chlorine, bromine or iodine groups, R₁ represents a hydrocarbon radical of at least six carbon atoms, and R₂, R₃ and R₄ represent hydrocarbon radicals having one or more carbon atoms present therein. The radicals represented by R may be unsubstituted, or one or more of them may contain one or more non-hydrocarbon substituents in accordance with the preceding instructions. These radicals may be of open chain or cyclic character, and may be saturated or unsaturated. For example, R₂, R₃ and R₄ may each represent methyl or ethyl groups or higher alkyl groups, R₁ may represent a hexyl, octyl, decyl, lauryl or myristyl group, and X may represent a hydroxyl, chlorine, bromine or iodine group. Compounds of this type are of considerable value for use as wetting agents, particularly when R₁ represents the lower alkyl groups specified. If these compounds are to be used as detergents it is advisable to substitute groups such as stearyl, oleyl and higher members of the same series for R₁, the remainder of the molecule being the same as before. The substitution of non-hydrocarbon radicals upon one or more of the substituents designated by R is also contemplated, substituents such as hydroxyl, halogen, ether and ester groups being quite satisfactory.

Quaternary ammonium salts described herein, and their described derivatives are capable of use for innumerable purposes. One of their chief uses is for wetting, detergent, emulsifying and dispersing purposes. In this connection it may be stated that they are capable of use either in admixture with one another and/or in admixture with soap or soap-like products for utilization in all the processes where soap or soap-like products have heretofore been used or are capable of use. A relative few of these uses will now be given merely for purposes of illustration:

A. Treatment for the processing and improvement of natural or synthetic textile materials involving:

- 1 Cleansing vegetable and animal fibers when removing fatty or oily materials.
- 2 Carbonization.
- 3 As an addition to flax retting baths.
- 4 Fulling.
- 5 Sizing.
- 6 As an addition when sizing is removed from textile materials.
- 7 Impregnating.
- 8 Bleaching.
- 9 Mordanting.
- 10 As an addition to soap in an acid or hard water bath.
- 11 Mercerizing lye liquors.
- 12 Improvement of absorption capability of fibrous materials particularly when subjected to a treatment for finishing, softening, stiffening, coloring or special chemical treatment such as waterproofing or mildewproofing.
- 13 Delustering or lustering.
- 14 Degumming.
- 15 Kier boiling.
- 16 Scouring.
- 17 Stripping.
- 18 Felting.
- 19 Oiling or lubricating.
- 20 Weighting or loading.

B. Dyeing processes:

- 1 Dyeing in neutral, acid or alkaline baths.
- 2 Reserving cotton in acid baths.
- 3 Dyeing with developed dyes.
- 5 4 Dyeing of animal fibers with vat dyes.
- 5 Dyeing cellulose acetate fibers with insoluble dyes.
- 6 Dyeing and printing with aniline black.
- 7 Dyeing of leather.
- 10 8 In printing pastes to assist in the dispersion of the dye or dye component and in the penetration into the natural or synthetic fiber.

C. Dyes and coloring material:

- 15 1 For making pastes of dyes or dye components.
- 2 For the production of pigments of azo, basic, acid, vat, and sulfur dyes in a finely divided condition.
- 20 3 For the production of finely divided inorganic pigments.

D. Miscellaneous uses:

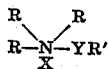
- 1 For converting liquid or solid substances normally insoluble in water, such as hydrocarbons, higher alcohols, other oxygen containing compounds, fats, oils, waxes, resins, pitches and pitchy substances into clear solutions or stable emulsions or dispersions.
- 25 2 As cleansing agents particularly in hard water and where a fatty or oily film resists the ordinary cleansing media.
- 30 3 In tanning.
- 4 In softening and treating baths for hides and skins, particularly the fat liquor treatment.
- 35 5 In flotation processes including minerals and oils such as the recovery of fixed oil from the oil sands.

E. General:

- 1 The reagents may be used in pure or standardized form.
- 2 May be used in conjunction with the known processing or treating agents.
- 45 As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that the invention is not limited to the specific embodiments thereof except as defined in the appended claims.

We claim:

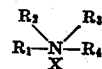
1. Quaternary ammonium compounds wherein at least one of the substituent groups attached to the pentavalent nitrogen atom is an aliphatic hydrocarbon group containing at least six carbon atoms and wherein one of the substituent groups attached to said nitrogen atom contains a neutralized acidic salt-forming group which is separated from said nitrogen atom by not more than four carbon atoms.
2. The compounds defined in claim 1 wherein the said aliphatic hydrocarbon group contains from twelve to eighteen carbon atoms and the acidic salt-forming group is a carboxyl group.
3. Compounds of the group consisting of the metal salts and inner anhydrides of quaternary ammonium compounds having the general formula;



wherein X represents an anion, Y represents a carbon chain containing not more than four

carbon atoms and an acidic salt-forming group, R' represents hydrogen or an aliphatic group, the three R's represent aliphatic groups, and at least one of the groups denoted as R or R' contains at least eight carbon atoms.

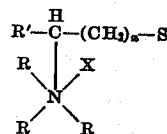
4. Compounds of the group consisting of the metal salts and inner anhydrides of quaternary ammonium compounds having the general formula;



wherein X represents an anion, R₁ represents an aliphatic hydrocarbon radical containing from twelve to eighteen carbon atoms, R₂, R₃, and R₄ each represent aliphatic hydrocarbon radicals containing less than eight carbon atoms, and at least one of the radicals denoted as R₁, R₂, R₃, or R₄ has attached thereto an acidic salt-forming group which is separated from the pentavalent nitrogen atom by not more than four carbon atoms.

5. Compounds as defined in claim 4 wherein the acidic salt-forming group is selected from the class consisting of carboxyl groups and sulfonic acid groups.

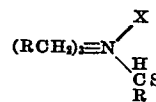
6. Compounds of the group consisting of the metal salts and inner anhydrides of quaternary ammonium compounds having the general formula:



wherein R' represents hydrogen or alkyl, X represents an anion, n stands for 0, 1, 2, or 3; S represents an acidic salt-forming group, and the three R's each denote alkyl radicals, one of the alkyl radicals denoted as R or R' containing eight or more carbon atoms.

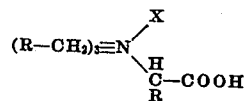
7. Compounds as defined in claim 6 wherein S represents a member of the class consisting of carboxyl groups and sulfonic acid groups.

8. Compounds of the group consisting of the metal salts and inner anhydrides of quaternary ammonium compounds having the general formula:



wherein one of the R's represents a long chain alkyl group of eight or more carbon atoms and all of the other R's represent hydrogen, X represents an anion, and S denotes an acidic salt-forming group.

9. Compounds of the group consisting of the metal salts and inner anhydrides of quaternary ammonium compounds having the general formula:



wherein one of the R's represents a long chain alkyl group of eight or more carbon atoms and all of the other R's represent hydrogen, and X represents a halogen atom.

10. Compounds of the group consisting of the metal salts and inner anhydrides of quaternary

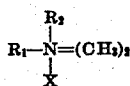
ammonium compounds having the general formula:



wherein R_1 represents an aliphatic hydrocarbon radical containing from twelve to eighteen carbon atoms which has attached thereto an acidic salt-forming group which is separated from the pentavalent nitrogen atom by no more than four carbon atoms, R_2 , R_3 , and R_4 each represent aliphatic hydrocarbon radicals, and X represents an anion.

11. Compounds as defined in claim 10 wherein the acidic salt-forming group is selected from the class consisting of carboxyl groups and sulfonic acid groups.

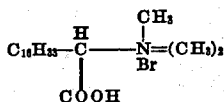
12. Compounds of the group consisting of the metal salts and inner anhydrides of quaternary ammonium compounds having the general formula:



wherein R_1 represents an aliphatic hydrocarbon radical containing from twelve to eighteen carbon atoms which has attached thereto an acidic salt-forming group which is separated from the pentavalent nitrogen atom by no more than four carbon atoms, R_2 represents an aliphatic hydrocarbon radical containing less than eight carbon atoms, and X represents a halogen atom.

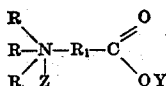
13. Compounds as defined in claim 12 wherein the acidic salt-forming group is selected from the class consisting of carboxyl groups and sulfonic acid groups.

14. Compounds of the group consisting of the metal salts and inner anhydride of a quaternary ammonium compound having the general formula:



15. The process of preparing high molecular betaines which comprises alkylating at the nitrogen atom an organic amine containing at least one straight aliphatic chain with at least 6 carbon atoms, the components taking part in the reaction being chosen so that the final product contains at least one carboxyl group.

16. The new products of the general formula:



wherein one R stands for a straight chain aliphatic radical with at least 6 carbon atoms and the other R 's stand for a member of the group consisting of the aliphatic, aralkyl and aromatic radicals, R_1 stands for a hydrocarbon radical, Z stands for a substituent of the group consisting of OH , Cl , OSO_3H , OSO_3CH_3 , Y stands for an alkali metal atom, the group



being separated from the nitrogen atom by not more than four carbon atoms.

17. Quaternary ammonium compounds wherein at least one of the groups attached to the pentavalent nitrogen atom is an aliphatic group containing at least six carbon atoms and wherein one of the substituent groups attached to said nitrogen atom contains a neutralized acidic salt-forming group, selected from the group consisting of carboxyl and sulfonic acid groups, which is separated from said nitrogen atom by not more than four carbon atoms.

18. Quaternary ammonium compounds wherein at least one of the groups attached to the pentavalent nitrogen atom is a straight chain aliphatic group containing at least six carbon atoms and wherein one of the substituent groups attached to said nitrogen atom contains a neutralized acidic salt-forming group which is separated from said nitrogen atom by not more than four carbon atoms.

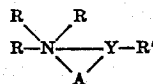
19. Quaternary ammonium compounds wherein at least one of the groups attached to the pentavalent nitrogen atom is an aliphatic group containing from twelve to eighteen carbon atoms and wherein one of the substituent groups attached to said nitrogen atom contains a neutralized acidic salt-forming group, selected from the group consisting of carboxyl and sulfonic acid groups, which is separated from said nitrogen atom by not more than four carbon atoms.

20. Quaternary ammonium compounds wherein one of the groups attached to the pentavalent nitrogen atom is a straight chain aliphatic group containing from twelve to eighteen carbon atoms, wherein three of the groups attached to said nitrogen atom are aliphatic groups containing less than eight carbon atoms and wherein one of the groups attached to said nitrogen atom contains a neutralized acidic salt-forming group which is separated from said nitrogen atom by not more than four carbon atoms.

21. Quaternary ammonium compounds wherein one of the groups attached to the pentavalent nitrogen atom is a straight chain aliphatic group containing from twelve to eighteen carbon atoms, wherein three of the groups attached to said nitrogen atom are aliphatic groups containing less than eight carbon atoms and wherein one of the groups attached to said nitrogen atom contains a neutralized acidic salt-forming group, selected from the group consisting of carboxyl and sulfonic acid groups, which is separated from said nitrogen atom by not more than four carbon atoms.

22. Quaternary ammonium compounds wherein one of the groups attached to the pentavalent nitrogen atom is an unsubstituted straight chain aliphatic group containing from twelve to eighteen carbon atoms, wherein three of the groups attached to said nitrogen atom are unsubstituted aliphatic groups containing less than eight carbon atoms and wherein one of the groups attached to said nitrogen atom contains a neutralized carboxyl group which is separated from said nitrogen atom by not more than four carbon atoms.

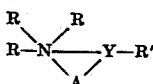
23. Compounds which in the form of their inner anhydrides have the following general formula:



wherein Y represents an aliphatic group containing not more than four carbon atoms, R' represents hydrogen or an aliphatic group, the three

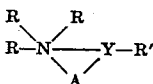
R's represent aliphatic groups, A represents the residue of a condensed acidic salt-forming group, and at least one of the groups denoted as R or R' contains at least eight carbon atoms.

24. Compounds which in the form of their inner anhydrides have the following general formula:



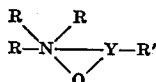
wherein Y represents an aliphatic group containing not more than four carbon atoms, R' represents hydrogen or an aliphatic group, the three R's represent unsubstituted aliphatic groups, A represents the residue of a condensed acidic salt-forming group selected from the group consisting of carboxyl and sulfonic acid groups, one of the groups denoted as R or R' contains at least eight carbon atoms, and the remainder of said groups contain less than eight carbon atoms.

25. Compounds which in the form of their inner anhydrides have the following general formula:



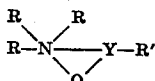
wherein Y represents an aliphatic group containing not more than four carbon atoms, R' represents hydrogen or an unsubstituted aliphatic group, the three R's represent unsubstituted aliphatic groups, A represents the residue of a condensed acidic salt-forming group selected from the group consisting of carboxyl and sulfonic acid groups, one of the groups denoted as R or R' contains at least eight carbon atoms, and the remainder of said groups contain less than eight carbon atoms.

26. Compounds which in the form of their inner anhydrides have the following general formula:



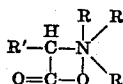
wherein Y represents an aliphatic group containing not more than four carbon atoms and a condensed carboxyl group, R' represents hydrogen or an aliphatic group, the three R's represent aliphatic groups, and at least one of the groups denoted as R or R' contains at least eight carbon atoms.

27. Compounds which in the form of their inner anhydrides have the following general formula:



wherein Y represents an aliphatic group containing not more than four carbon atoms and a condensed carboxyl group, R' represents hydrogen or an aliphatic group, the three R's represent aliphatic groups, one of the groups denoted as R or R' contains from eight to eighteen carbon atoms and the remainder of said groups contain less than eight carbon atoms.

28. Compounds which in the form of their inner anhydrides have the following general formula:



wherein R' represents an aliphatic group con-

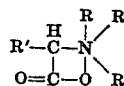
taining from ten to sixteen carbon atoms and the three R's represent aliphatic groups containing less than eight carbon atoms.

29. The compounds referred to in claim 28 wherein the radical denoted as



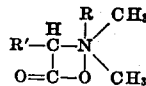
is obtained from naturally occurring oils, fats and waxes.

30. Compounds which in the form of their inner anhydrides have the following general formula:



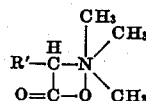
wherein R' represents an unsubstituted aliphatic group containing from ten to sixteen carbon atoms and the three R's represent unsubstituted aliphatic groups containing less than eight carbon atoms.

31. Compounds which in the form of their inner anhydrides have the following general formula:



wherein R' represents an aliphatic group containing from ten to sixteen carbon atoms and R represents an aliphatic group containing less than eight carbon atoms.

32. Compounds which in the form of their inner anhydrides have the following general formula:



wherein R' represents an aliphatic group containing from ten to sixteen carbon atoms.

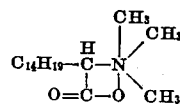
33. The compounds referred to in claim 32 wherein the radical denoted by



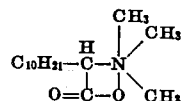
is obtained from naturally occurring vegetable oils.

34. The compounds referred to in claim 32 wherein the radical denoted by R'— is unsubstituted.

35. A compound which in the form of its inner anhydride has the following formula:



36. A compound which in the form of its inner anhydride has the following formula:



37. The process of preparing high molecular betains which comprises alkylating an organic amine at the nitrogen atom, the components taking part in the reaction being chosen so that the

final product contains a straight aliphatic chain with at least six carbon atoms and said product also contains an acidic salt-forming group.

5 38. The process of preparing high molecular betaines, which comprises alkylating an organic amine at the nitrogen atom, the components tak-

ing part in the reaction being chosen so that the final product contains a straight aliphatic chain with at least six carbon atoms and said product also contains a carboxyl group.

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FRANK WILLARD JOHNSON.