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2,764,602

QUATERNARY AMMONIUM ALKYL-PERFLUOROAMIDES

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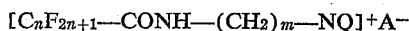
4 Claims. (Cl. 260—404.5)

This invention relates to my discovery of a new and useful class of reactive fluorocarbon compounds. These compounds have utility as cationic surface active agents, as surface treating and coating agents, as starting compounds for making derivatives, and for other purposes.

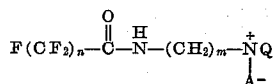
These novel compounds are perfluoralkyl quaternary nitrogen compounds having in the molecule an intermediate amidopolymethylene linkage and uniquely characterized by having a terminal carbonyl-bonded perfluoralkyl chain which provides a nonpolar saturated fluorocarbon "tail" that is both hydrophobic and oleophobic. This fluorocarbon "tail" is repellent not only to water but to oils and hydrocarbons and imparts unique surface active and surface treatment properties not possessed by corresponding compounds having a carbonylbonded hydrocarbon "tail."

The invention provides surface active agents which have extraordinary activity in reducing by a large amount the surface tension of oils and waxes even when present in very small concentrations, notwithstanding that they are water-soluble as well as oil-soluble and are also highly effective for reducing the surface tension of water and aqueous solutions. This combination of properties is highly unusual. The corresponding non-fluorinated compounds of conventional organic chemistry do not have significant surface tension reduction properties when dissolved in oils and waxes, although they may have a high degree of activity in water and aqueous solutions when the hydrocarbon chains are of sufficient length. So far as I am aware, there are no non-fluorinated surface active agents capable of markedly reducing the surface tension both of water and oils at low concentrations; nor is this a general characteristic of fluorinated surface active agents.

My perfluoralkyl-amidopolymethylene quaternary nitrogen compounds constitute a class of related compounds that can be represented by the generic formula:



and by the equivalent formula for normal compounds:



where n (the number of carbon atoms in the terminal straight chain or branched chain perfluoralkyl "tail") has an integer value of 3 to 11, and m (the number of carbon atoms in the intermediate polymethylene linkage) has an integer value of 2 to 6. "A" is an anion, such as a halogen anion (fluorine, chlorine, bromine or iodine) or a sulfate anion, or a hydroxyl anion, which is electrostatically bonded to the quaternary nitrogen atom. "NQ" is a terminal oleophilic organic cationogenic group united to the polymethylene linkage and contains a quaternary nitrogen atom (N) covalently bonded to hydrogenated carbon atoms and electrostatically bonded to the anion (A), "Q" representing an organic terminal structure which satisfies three of the covalencies of the

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quaternary nitrogen atom by means of carbon-nitrogen bonds and is linked through this nitrogen atom to the polymethylene linkage. It is this cationogenic group that causes the organic chain to be a cation having a positive charge at the quaternary nitrogen position.

As is clearly evident from the above structural formulas, the complete molecule consists of an anion (negatively charged) electrostatically united to a long-chain cation (positively charged owing to the positive charge of the quaternary nitrogen atom). When dissolved in water or other suitable ionizing solvent, the ionized molecules provide long-chain surface-active free cations which have a terminal nonpolar fluorocarbon "tail" that is both hydrophobic and oleophobic. The intermediate amido linkage to which the fluorocarbon "tail" is united enhances solubility of the molecule in water and other polar solvents. The polymethylene chain provides a stable linkage between the nitrogen atom of the amido group and the quaternary nitrogen atom and also serves to enhance solubility in oils and waxes. The terminal organic "Q" structure united to the quaternary nitrogen atom renders the cation or complete molecule oil-soluble at this end. The quaternary nitrogen atom imparts greatly increased solubility in water and other ionizing solvents. Thus the molecule is water-soluble and oil-soluble, and is oleophobic at one end and oleophilic at the other end. It is repellent to water, oils and hydrocarbons at the fluorocarbon end and yet is soluble therein at the quaternary nitrogen end.

This makes possible molecules that can be dissolved both in water and in oils and waxes and yet will concentrate at the surface to form an oriented surface layer having the fluorocarbon "tails" pointing outwardly. A surface film results that is outwardly nonpolar and is both water and oil repellent, and which greatly reduces the surface tension.

This structure also provides cations that can plate out from solutions to form tightly adsorbed polar surface films on hydrophilic or electronegative type surfaces, such as glass, lithic materials, metals, paper, textiles, etc., with the fluorocarbon "tails" oriented outwards to provide a nonpolar fluorocarbon outer surface.

These fluorocarbon quaternary nitrogen compounds provide surface active agents that are highly effective in water and in neutral, acidic and basic aqueous solutions, serving to greatly reduce the surface tension even when present in minute concentrations. The fluorocarbon "tail" provides a hydrophobic chain that can be even more effective in aqueous solutions than is a much longer hydrocarbon chain such as is employed in corresponding compounds of conventional organic chemistry. Thus a fluorocarbon "tail" containing 7 carbon atoms (a perfluorocapryl chain) is even more effective for this purpose than is a hydrocarbon "tail" containing 17 carbon atoms (a stearyl chain).

The present compounds provide surface active agents which have amazing utility as additives for oils and waxes and greatly reduce the surface tension even when present in minute proportion. A high degree of surface tension reduction can be achieved at concentrations of 0.1% by weight or less in animal, vegetable and mineral oils and waxes (the latter being in a dissolved or molten state), including petroleum solvents, gasoline, kerosene, fuel oils, lubricating oils, and paraffin waxes, thereby, for instance, improving such properties as surface protection, flow, spreading, penetration, and atomization or sprayability.

These compounds also have utility as emulsifying agents for fluorocarbons and oils (the agent collecting at the interfaces with the fluorocarbon "tails" dissolved in the fluorocarbon phase and the other portions of the molecules dissolved in the oil phase). They can be used as emulsifying agents for fluorocarbon-water systems.

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Other factors remaining the same, the solubility of the present compounds both in water and in oils decreases with increase in length of the fluorocarbon "tail." In contrast, the corresponding compounds having a carbonyl-bonded hydrocarbon "tail" decreases as to water solubility but increase as to oil solubility with increase in length of this chain.

The properties of the compounds can be varied to best serve a desired particular use by varying the length of the fluorocarbon "tail," the length of the intermediate polymethylene chain, and the nature of the nitrogen-bonded "Q" structure. However, it is critical that the molecule have a fluorocarbon "tail" containing at least three carbon atoms and the preferred number is 5 to 11.

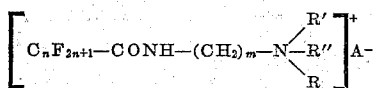
It is also of critical importance that the fluorocarbon chain be free from hydrogen atoms. In particular, the presence of even one hydrogen atom on the last or next to last carbon atom of the "tail" will markedly alter the surface active and solubility properties, reducing surface activity and the hydrophobic and oleophobic characteristics of surface coatings. Hydrogen is electropositive whereas fluorine is strongly electronegative, hence the presence of hydrogen and fluorine in the terminal portion of the "tail" renders it polar instead of nonpolar; and also renders the "tail" less stable to heating owing to the opportunity for dehydrofluorination and provides opportunity for chemical attack.

In general, the halide salts and sulfate salts are most convenient and useful to employ as surface active agents; and they can be readily prepared by processes illustrated in the subsequent examples. In dry form the simpler halide salts are solid crystalline ionic substances. They are stable and are soluble to sparingly soluble in water and in oils (the solubility decreasing with increase in number of fluorinated carbon atoms).

The corresponding hydroxides can be obtained by reacting the halide salts with an aqueous suspension of silver oxide to form a solution of the hydroxide, i. e., the free quaternary base, which can be filtered to remove the silver halide reaction product and any unreacted silver oxide. This solution can be distilled under high vacuum to obtain the free base, but ordinarily the aqueous hydroxide solution would be utilized when employed as an additive for aqueous solutions.

It is a feature of my compounds that a wide variety of oleophilic cationogenic groups ("NQ") can be employed, cyclic as well as non-cyclic. This portion of the molecule is the same as in the corresponding quaternary compounds of conventional organic chemistry, the distinctive fluorocarbon "tail" being at the other end of the molecule, and a wide variety will be evident to those skilled in the art of quaternary surface active agents.

Thus the quaternary nitrogen atom can be bonded to three hydrocarbon side groups, forming quaternary nitrogen compounds of the type:

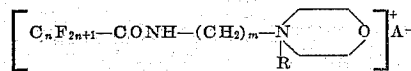
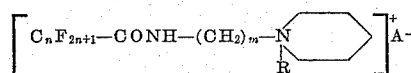


where R', R'' and R are hydrocarbon groups, such as alkyl, cyclohexyl, alkaryl and aryl groups. Preferred compounds of this type are those in which R' and R'' are alkyl groups each containing one to six carbon atoms (i. e., methyl, ethyl, propyl, butyl, amyl or hexyl groups), and R is a stable oleophilic hydrocarbon group, such as an alkyl, cycloalkyl, alkaryl, aryl or aralkyl group, containing 1 to 17 carbon atoms.

Another type of compound is one where the quaternary nitrogen atom is included as a member of a saturated heterocyclic ring and is bonded to two carbon atoms thereof (such as a piperidine ring or a morpholine ring), and the nitrogen atom is also bonded to a side group, 75

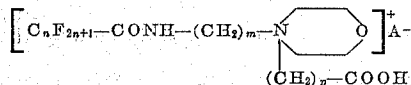
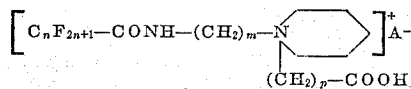
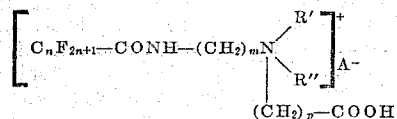
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for instance an alkyl group, as illustrated by compounds of the following types:



The above compounds can be readily prepared from the corresponding amine starting compounds which contain a trivalent nitrogen atom, by quaternizing with a compound of the "RA" type which provides the nitrogen-bonded "R" group and "A" anion of the product, as by using a halide or a sulfate quaternizing agent.

A further type of compound is represented by the above formulas when the "R" group is a normal alkylenecarboxyl group, i. e., an N-bonded normal alkyl chain in which the terminal methyl group has been replaced by an anionogenic carboxyl group; the terminal carboxyl group thus being united to the quaternary nitrogen through a methylene or polymethylene linkage containing one to six carbon atoms. These compounds can be made by quaternizing with a halogenated monocarboxylic acid, such as chloroacetic acid. The corresponding specific formulas of these compounds are:



where p has an integer value of 1 to 4.

This type of molecule is cationic but it is also anionic owing to the presence of the carboxyl group which is able to readily release hydrogen ions in strongly basic aqueous solutions, and to a lesser extent in other aqueous solutions, thereby providing a carboxyl anion owing to the negative charge on the hydroxylic oxygen atom. This type of compound is amphoteric and ampholytic. It is basic and has a positive charge at the quaternary nitrogen position, and it is acidic and has a negative charge at the carboxyl position. In strongly acidic solutions, ionization occurs mainly at the quaternary nitrogen position and the molecule is predominately cationic and basic. In strongly basic solutions, ionization occurs mainly at the carboxyl position and the molecule is predominately anionic and acidic. In the weakly acidic to weakly basic range, the ionized molecule shifts from being predominately cationic and basic to being predominately anionic and acidic, but always has both characteristics in appreciable degree since the ionization sites are separated in the molecule. The carboxyl group is hydrophilic and increases the water-solubility of the molecule, but it does not prevent the "NQ" structure from being oleophilic as a whole.

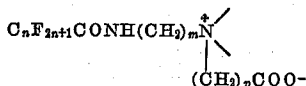
The carboxyl hydrogen atom can be substituted by a metal atom, to form salts (e. g., the sodium and potassium salts), and the carboxylate group in such compounds is also hydrophilic and anionic. Hydrolysis in acidic solutions yields the corresponding acid.

The carboxyl hydrogen atom can be substituted by an alkyl group to form esters (e. g., the methyl and ethyl esters). The esters can be made directly by quaternizing with a halogenated monocarboxylic ester (such as methyl chloroacetate). Hydrolysis yields the corresponding acid.

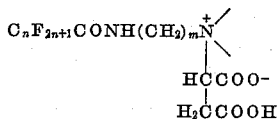
These carboxylic acid, salt, and ester compounds in ap-

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appropriate aqueous solutions all yield ionized molecular structures which can be represented by the generic formula:

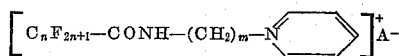


Instead of quaternizing with halogenated monocarboxylic acids, use can be made of halogenated dicarboxylic acids to obtain quaternary nitrogen compounds having two carboxyl groups in the "R" chain bonded to the quaternary nitrogen atom. Thus compounds formed by quaternizing with monochlorosuccinic acid will provide ionized molecular structures having the formula:



Corresponding salts and esters can also be prepared.

The quaternary nitrogen atom can be present in a pyridine ring, which satisfies the three available valencies, thus providing quaternary pyridinium compounds:



This type of compound can be readily made by reacting pyridine with a perfluoroalkyl-amidopolymethylene halide.

The following table lists illustrative quaternary compounds that have been prepared and shows the remarkable reductions in surface tension produced when a minute amount is dissolved in water, in oils and in a wax; the first row giving the surface tension values thereof in the absence of the additive. The formulas are given in a simplified or abbreviated form but can be readily related to the kind of structural formulas used elsewhere. All values were measured at 25° C. except in the case of the wax, which was a micro-crystalline type paraffin wax and the surface tension values were measured at 100° C. with the wax thus being in a melted fluid state.

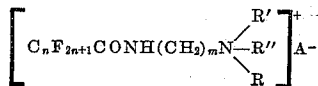
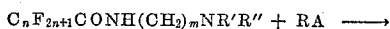
SURFACE TENSIONS (DYNES/CM.) WITH AND WITHOUT ADDITIVES

	Water	Min- eral Oil	Lin- seed Oil	Melted Wax
Value without additive.....	72	31	32	27
Amount of additive (percent by wt.).....	0.05	0.1	0.1	0.1
Additive compounds:				
$\text{C}_6\text{F}_{11}\text{CONHC}_2\text{H}_4\text{N}(\text{C}_2\text{H}_5)_2(\text{CH}_3)\text{I}$				18
$\text{C}_7\text{F}_{15}\text{CONHC}_2\text{H}_4\text{N}(\text{C}_2\text{H}_5)_2(\text{CH}_3)\text{I}$	17	18	18	15
$\text{C}_7\text{F}_{15}\text{CONHC}_2\text{H}_4\text{N}(\text{CH}_3)_3\text{I}$	15			16
$\text{C}_7\text{F}_{15}\text{CONHC}_2\text{H}_4\text{N}(\text{C}_2\text{H}_5)_2(\text{CH}_3)\text{I}$	15	19		15
$\text{C}_7\text{F}_{15}\text{CONHC}_2\text{H}_4\text{N}(\text{CH}_3)_2(\text{C}_{10}\text{H}_{21})\text{Br}$	15	19		
$\text{C}_6\text{F}_{10}\text{CONHC}_2\text{H}_4\text{N}(\text{CH}_3)_3\text{I}$	15			
$\text{C}_{11}\text{F}_{23}\text{CONHC}_2\text{H}_4\text{N}(\text{CH}_3)_3\text{I}$	22			
$\text{C}_7\text{F}_{16}\text{CONHC}_2\text{H}_4\text{N}(\text{CH}_3)_2(\text{CH}_2\text{C}_6\text{H}_5)\text{Cl}$	25	22		
$\text{C}_7\text{F}_{16}\text{CONHC}_2\text{H}_4\text{N} \text{---} \text{C}_6\text{H}_4 \text{---} \text{Cl}$	15	18	18	17
$\text{C}_7\text{F}_{16}\text{CONHC}_2\text{H}_4\text{N}(\text{C}_2\text{H}_5)_2(\text{CH}_3)\text{CH}_2\text{SO}_4$	15	21		
$\text{C}_7\text{F}_{16}\text{CONHC}_2\text{H}_4\text{N}(\text{C}_2\text{H}_5)_2(\text{CH}_2\text{COOH})\text{Cl}$	16	25		

The preparation of the 3d, 9th, 10th and last compounds listed above are specifically described in the following Examples 1, 2, 3 and 4, respectively.

Example 1

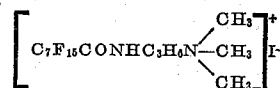
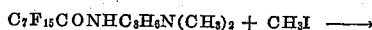
This example illustrates the preparation of quaternary ammonium halide salts by reaction of a perfluoroalkyl-amidopolymethylene-dialkylamine with a hydrocarbon halide:



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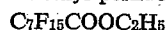
These tertiary amine starting compounds are described in more detail and are claimed in my companion application filed of even date herewith, S. N. 424,789.

The following illustrative experiment relates to the specific reaction:



In this example, N,N-dimethyl-N'-perfluorocaprylamido-propyleneamine is reacted with methyl iodide to make trimethyl (gamma-perfluorocaprylamido)propylene ammonium iodide, which has a fluorocarbon "tail" containing seven carbon atoms.

A 1000 ml. 1-necked flask was charged with 426 grams (0.965 mole) of ethyl perfluorocaprylate,



and 200 ml. of absolute diethyl ether. The flask was cooled in an ice bath and 98.2 grams (0.965 mole) of dimethylaminopropyleneamine, $\text{H}_2\text{NC}_3\text{H}_6\text{N}(\text{CH}_3)_2$, was added slowly enough to maintain a temperature below 35° C. in the flask. The flask was removed from the ice bath, allowed to warm to room temperature, and was then placed under a 5 plate column for vacuum distillation. As the reduced pressure was slowly applied, the ether distilled off to leave the above-mentioned perfluorocapryl amine product which was distilled off at about 20 mm. vacuum at the boiling range (154–158° C.). A total of 440 grams (0.882 mole) was obtained. The refractive index was 1.3559. The 440 grams of this product was mixed with 1000 ml. of absolute diethyl ether and 213 grams of methyl iodide (1.5 moles) in an unstoppered 3000 ml. Erlenmeyer flask, and left standing overnight. The quaternary ammonium iodide salt product was dried by pouring the reaction mixture into a large evaporating dish which was placed in a hood draft to evaporate off the ether. The dried salt was a free-flowing white powder, which dissolves easily in water, and which has a melting point of 148–150° C.

It was identified as the desired compound mentioned above. Analysis showed 4.33% N (calc. 4.37%) and 19.9% I (calc. 19.8%).

Data indicating the powerful surface activity of this compound have been given in the preceding table. Its water-solubility and strong surface tension reduction activity in water are in diametric contrast to the tertiary amine starting compound. Further illustration of surface activity is provided by the following demonstration experiments:

(A) A clean glass slide was coated with a thin film of water. A speck of the quaternary salt was dropped on the film and it caused an immediate separation of the film and a dry area was formed on the glass. The glass

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in this area had become plated with the cations and the resultant exposed fluorocarbon-like surface was repellent to water; drops of water when applied rolling off.

(B) Five drops of water were placed on the concave surface of a clean watch glass and formed a water area of 1.13 sq. cm. A speck of the quaternary salt was added to the water, causing the water to spread out to an area of 3.45 sq. cm., owing to the reduction in surface tension.

(C) A 1% (by weight) solution of the quaternary salt in water was prepared. When a drop was placed on a sheet of writing paper, complete penetration occurred in a few seconds. The same result was obtained using a piece of nylon cloth and a piece of cardboard, penetration in these cases being almost instantaneous. Drops of pure water when applied to these materials did not penetrate. Thus the quaternary salt served as a highly effective wetting agent.

This compound in minute proportion (e. g., 30 p. p. m.) greatly inhibits the evaporation of volatile hydrocarbons, such as gasoline, owing to formation of a surface barrier film.

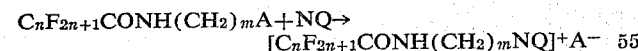
In the above example, the methyl iodide reacts readily in a mild exothermic reaction and no heating is required. The use of methyl iodide as a quaternizing agent is convenient in laboratory work because it readily reacts and it is a liquid at room temperature, whereas the other methyl halides (methyl bromide, methyl chloride and methyl fluoride) are gases at room temperature and must be reacted in a pressure vessel. The higher halides which are liquid at room temperature can be conveniently employed, although heating is generally required because they react more sluggishly.

Thus the same perfluorocapryl amine that was employed in the above example was quaternized with benzyl chloride and with n-decyl bromide. In both cases the reaction mixture was heated for 2 hours at 100° C., and the solid salt product was washed with ether to remove unreacted material, and dissolved in water. Data on the quaternary product compounds are included in the foregoing table.

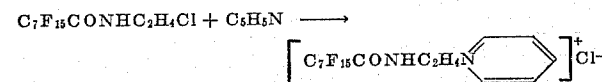
Similarly, amine starting compounds in which the nitrogen atom of the terminal amine group is a member of a heterocyclic ring (e. g., a piperidine ring or a morpholine ring) which satisfies two valence bonds, can be quaternized with a hydrocarbon halide.

Example 2

This example illustrates another process of making quaternary nitrogen halide salts, by reaction of a perfluoroalkyl-amidopolymethylene halide with a tertiary amine or other "NQ" compound that supplies the terminal quaternary nitrogen group:



This process is especially well suited to the preparation of quaternary pyridinium compounds and will be illustrated by the reaction:



In this example, beta-perfluorocaprylamidoethylene chloride is reacted with pyridine to yield beta-perfluorocaprylamidoethylene pyridinium chloride.

A 250 ml. Erlenmeyer flask cooled in an ice bath was charged with 100 ml. of absolute diethyl ether and 44.2 grams (0.1 mole) of ethyl perfluorocaprylate,



Then 6.1 grams (0.1 mole) of ethanolamine,



was slowly added and the mixture was left standing for one hour. The mixture was poured into a flat evaporat-

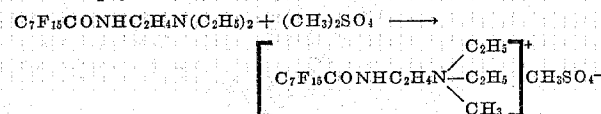
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ing dish and the ether and alcohol allowed to evaporate. The product, obtained in a quantitative yield of 45 grams, was a white crystalline solid having a melting point of 80–82° C., and was identified as the amido alcohol derivative, $\text{C}_7\text{F}_{15}\text{CONHC}_2\text{H}_4\text{OH}$. A 50 ml. 1-necked flask topped by a reflux condenser was charged with 22.5 grams (0.05 mole) of this amido alcohol and 6 grams (0.5 mole) of thionyl chloride, SOCl_2 . The mixture was refluxed for 30 minutes and poured into cold water. The white solid separating was filtered out, washed with cold water, and air-dried overnight. The yield was quantitative. This product was identified as the desired beta-perfluorocaprylamidoethylene chloride. It was converted to the desired quaternary salt by overnight refluxing with pyridine, using equal parts by weight mixed with 10 parts water. The product was a homogeneous solution of the quaternary pyridinium chloride salt, and the latter could be obtained in free form by evaporating the water.

The extreme surface activity of this quaternary pyridinium salt is indicated by the fact that it reduces the surface tension of water at 25° C. from 72 to 18 dynes/cm. at a concentration of only 0.005% by weight (50 mg. per liter), and to 15 dynes/cm. at a concentration of 0.01%. It reduces the surface tension of kerosene at 25° C. from 26 to 21 dynes/cm. at a concentration of 0.1%. Other data are given in the foregoing table. This compound has been found to be highly effective as an ore flotation agent.

Example 3

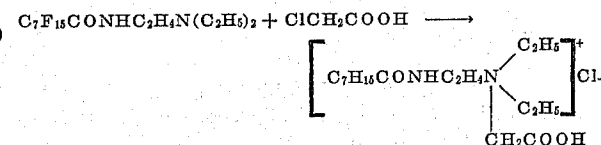
This example illustrates the use of sulfates as quaternizing agents in place of using halide agents that have been illustrated in Example 1. Specifically, N,N-diethyl-N'-perfluorocaprylamidoethyleamine is reacted with dimethyl sulfate to make methyldiethyl(gamma-perfluorocaprylamido)ethylene ammonium methylsulfate:



A 100 ml. Erlenmeyer flask was charged with 5.12 grams (0.01 mole) of the above-mentioned amine and then with 1.26 grams (0.10 mole) of dimethyl sulfate. A very exothermic reaction resulted and the mixture solidified. The solid product was dissolved in water and exhibited strong surface active properties. Data are given in the foregoing table.

Example 4

This example illustrates the making of the previously discussed ampholytic compounds which have an anionogenic carboxyl group covalently bonded to the quaternary nitrogen atom through a hydrocarbon linkage. Specifically, a perfluoroalkylamidopolymethylene tertiary amine is quaternized with chloroacetic acid in this example:



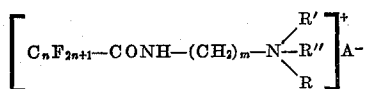
A 250 ml. Erlenmeyer flask was charged with 15.5 grams (0.03 mole) of the N,N-diethyl-N'-perfluorocaprylamidoethyleamine and then with 2.8 grams (0.03 mole) of chloroacetic acid, and the mixture was heated to 125–150° C. Upon cooling, the viscous liquid product solidified at about 55–60° C., forming a light-brown water-soluble solid having strong surface active properties. Data are given in the foregoing table.

I claim:

1. The new and useful perfluoroalkyl - amidopoly-

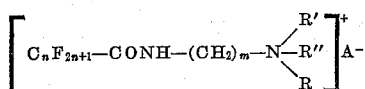
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methylene quaternary ammonium compounds represented by the formula:



where n has an integer value of 3 to 11, m has an integer value of 2 to 6, A is an anion, R' and R'' are alkyl groups each containing 1 to 6 carbon atoms, and R is a stable oleophilic hydrocarbon group containing 1 to 17 carbon atoms.

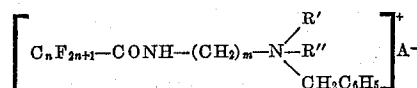
2. The new and useful perfluoroalkyl-amidopoly-methylene quaternary ammonium compounds represented by the formula:



where n has an integer value of 3 to 11, m has an integer value of 2 to 6, A is an anion, R' and R'' are alkyl groups each containing 1 to 6 carbon atoms, and R is an alkyl group containing 1 to 17 carbon atoms.

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3. The new and useful perfluoroalkyl - amidopoly-methylene quaternary ammonium compounds represented by the formula:



where n has an integer value of 3 to 11, m has an integer value of 2 to 6, A is an anion, R' and R'' are alkyl groups each containing 1 to 6 carbon atoms, and the $\text{CH}_2\text{C}_6\text{H}_5$ group is a benzyl group.

4. Trimethyl(gamma - perfluorocaprylamido)propylene ammonium iodide, having the formula:



References Cited in the file of this patent

UNITED STATES PATENTS

2,567,011	Diesslin et al.	Sept. 4, 1951
2,568,500	Husted et al.	Sept. 18, 1951
2,593,737	Diesslin et al.	Apr. 22, 1952