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2,764,603

ALKYLAMINOALKYL-PERFLUOROAMIDES

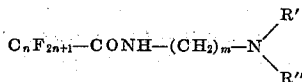
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No Drawing. Application April 21, 1954, Serial No. 424,789

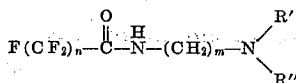
1 Claim. (Cl. 260—404.5)

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

These novel compounds are perfluoroalkyl dialkylamine compounds uniquely characterized as to structure by having in the molecule a terminal carbonyl-bonded perfluoroalkyl chain which provides a nonpolar saturated fluorocarbon "tail" that is both hydrophobic and oleophobic. These compounds may be termed perfluoroalkylamidopolymethylene-dialkylamine compounds and are represented by the generic formula:



and by the equivalent formula for compounds containing a normal perfluoroalkyl chain:



where n (the number of carbon atoms in the terminal straight-chain or branched-chain perfluoroalkyl "tail") has an integer value of 3 to 11, m (the number of carbon atoms in the intermediate polymethylene linkage) has an integer value of 2 to 6, and R' and R'' are alkyl groups each containing 1 to 6 carbon atoms.

As is evident from the above structural formulas, the complete molecule has a perfluoroalkyl "tail" at one end and a tertiary amine group at the other end; the tertiary nitrogen atom being joined to the fluorocarbon "tail" by an interposed amidopolymethylene linkage.

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 carbonyl-bonded hydrocarbon "tail." The polymethylene chain provides a stable linkage between the terminal tertiary nitrogen atom and the nitrogen atom of the amido group, and also serves to enhance solubility in oils and waxes. The terminal dialkyl amino group renders the molecule oil-soluble at this end. Thus the molecule is sufficiently oil-soluble, and is oleophobic at one end and oleophilic at the other end. It is repellent to water, oils and waxes at the fluorocarbon end and yet is soluble in oils and waxes at the tertiary amine end. These compounds are relatively insoluble in water (even the lowest members of the series having a solubility in water of less than about 1% by weight at room temperature).

This makes possible water-insoluble molecules that can be dissolved in oils and waxes and yet will concentrate at the surface to form an oriented surface layer having the fluorocarbon "tails" pointing outwardly and the opposite ends of the molecules pointed inwardly and dissolved in the oil or wax mass. A surface film results that is out-

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wardly nonpolar and is both water and oil repellent, and which greatly reduces the surface tension.

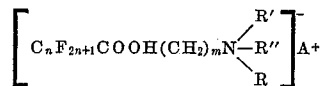
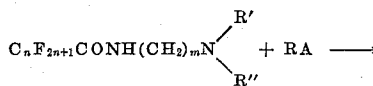
The solubility of the present compounds in oils and waxes decreases with increase in length of the fluorocarbon "tail," and water-insolubility is enhanced. In contrast, the corresponding compounds of conventional organic chemistry having a carbonyl-bonded hydrocarbon "tail" decrease as to water solubility but increase as to oil solubility with increase in length of this chain. Increase in length of the alkyl groups that are bonded to the terminal nitrogen atom, and increase in length of the intermediate polymethylene chain, serve to further decrease solubility in water but increase solubility in oils and waxes. Thus the properties of the compounds can be varied to best serve a desired particular use.

It is of critical importance 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 this 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 of dehydrofluorination, and provides opportunity for chemical attack.

These fluorocarbon-type tertiary amine compounds provide surface active agents that are highly effective as additives for oils and waxes. A remarkable degree of surface tension reduction can be achieved at concentrations of 0.1% by weight and less in animal, vegetable and mineral oils and waxes, 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. The corresponding non-fluorinated compounds of conventional organic chemistry do not have any significant surface tension reduction effect in oils and waxes.

These compounds 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 opposite ends of the molecules dissolved in the oil phase).

The present compounds also have particularly noteworthy value in serving as starting compounds for making the corresponding quaternary ammonium compounds, which can be readily prepared by using a hydrocarbon halide or sulfate quaternizing agent:

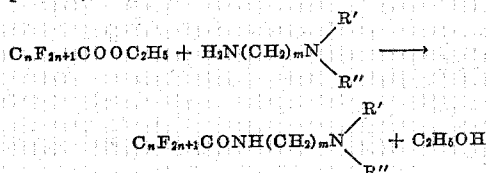


where RA is the quaternizing agent (e. g., methyl iodide or dimethyl sulfate), R is the hydrocarbon group thereof (e. g., an alkyl or benzyl group) that is covalently bonded to the quaternary nitrogen atom, and A is the anion of the quaternizing agent that is electrostatically bonded to the quaternary nitrogen atom. These fluorocarbon quaternary ammonium compounds are unusually effective surface active agents both in water and aqueous solutions and in oils and waxes. Quaternization renders the compounds much more soluble in water and surface

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active in aqueous systems, but does not destroy utility as surface active agents in oils and waxes. These quaternary derivatives are described in more detail and are claimed in my companion application filed of even date herewith, S. N. 424,788.

A feature of the present compounds is that they can be readily prepared, by reaction of the alkyl esters of perfluoroalkyl monocarboxylic acids (conveniently the ethyl esters) with dialkylaminopolymethyleneamine compounds, as shown by the following equation:

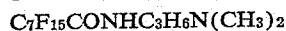


The perfluoro ester starting compounds are disclosed in the U. S. patent of Diesslin, Kauck and Simons, No. 2,567,011 (Sept. 4, 1951).

Example

This example illustrates the preparation of the present compounds by a procedure of general utility, making it unnecessary to individually describe similar experiments by which other compounds have been made.

A 1000 ml. 1-necked flask was charged with 426 grams (0.965 mole) of ethyl perfluorocaprylate, $C_7F_{15}COOC_2H_5$, and 200 ml. of absolute diethyl ether as solvent. The flask was cooled in an ice bath and 98.2 grams (0.965 mole) of dimethylaminopropyleneamine, $H_2NC_3H_6N(CH_3)_2$, was added slowly enough to maintain a temperature below 35° C. in the cooled reaction flask. The flask was then removed from the ice bath and allowed to warm to room temperature. It was placed under a 5 plate column for vacuum distillation. As the pressure was reduced, the ether distilled off, leaving the amine reaction product, which was distilled off at about 20 mm. pressure at the boiling range of 154–158° C. A total of 440 grams (0.882 mole) was obtained (yield of 91.5%). The product was identified as relatively pure:



Analysis showed 5.68% nitrogen (5.61% calc.). The boiling point was 155° C. at 18 mm. pressure. The refractive index at 25° C. was 1.3559. The product was a colorless viscous liquid having a characteristic amine odor. This compound may be designated as N,N-dimethyl-N'-perfluorocaprylamidopropyleneamine.

The surface activity of this compound was demonstrated by measurements showing the reduction in surface tension of mineral oils and waxes caused by the presence of minute proportions of the compound.

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The surface tension value for a refined mineral oil at 25° C. was reduced from 31 dynes/cm. to 18 dynes/cm. at a concentration of 0.1% by weight. The value for a refined paraffin wax, in a fluid melted state at 100° C., was reduced from 24 dynes/cm. to 18 dynes/cm. at a concentration of 0.1%; and that of a microcrystalline paraffin wax, also measured at 100° C., was reduced from 27.5 dynes/cm. to 24 dynes/cm. at a concentration of 0.1%.

This compound in minute proportion materially inhibits the evaporation of volatile hydrocarbons, such as gasoline, owing to formation of a surface barrier film.

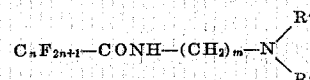
The following table lists other illustrative compounds that have been similarly prepared and gives the measured vacuum boiling points (at the indicated pressures in millimeters) and refractive indices (at the indicated temperatures in degrees centigrade). These compounds are all high-boiling liquids at room temperature except for the last one, which is solid.

Compounds	B. P. (° C.)	R. I.
$C_3F_7CONHC_2H_4N(C_2H_5)_2$	113 (16 mm.)	1.3797 (20°)
$C_5F_{11}CONHC_2H_4N(C_2H_5)_2$	145 (17 mm.)	1.3762 (20°)
$C_7F_{15}CONHC_2H_4N(C_2H_5)_2$	162 (30 mm.)	1.3597 (25°)
$C_7F_{15}CONHC_3H_6N(C_2H_5)_2$	162 (30 mm.)	1.3656 (25°)
$C_7F_{15}CONHC_3H_6N(CH_3)_2$	162 (15 mm.)	1.3540 (20°)
$C_{11}F_{23}CONHC_3H_6N(CH_3)_2$	159 (3 mm.)	-----

The surface activity of the third compound in the above list is illustrated by experiments on surface tension reduction wherein the value for linseed oil at 25° C. was reduced from 32 to 19 dynes/cm. at 0.1% concentration; that for mineral oil at 25° C. from 31 to 19 dynes/cm. at 0.1% concentration; that for kerosene at 25° C. from 26 to 22 dynes/cm. at 0.1% concentration.

I claim:

The new and useful perfluoroalkylamidopolymethylenedialkylamine compounds represented by the formula:



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

References Cited in the file of this patent

UNITED STATES PATENTS

2,567,011	Diesslin et al.	Sept. 4, 1951
2,589,674	Cook et al.	Mar. 18, 1952
2,593,737	Diesslin et al.	Apr. 22, 1952
2,691,043	Husted	Oct. 5, 1954