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3,555,089

PERFLUOROALKYL ETHER AMIDO QUATERNARY AMMONIUM SALTS

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No Drawing. Continuation-in-part of application Ser. No. 621,128, Mar. 7, 1967. This application Feb. 16, 1968, Ser. No. 705,923

Int. Cl. C07c 103/34

U.S. Cl. 260-561

5 Claims

ABSTRACT OF THE DISCLOSURE

Perfluoroalkyl ether amido quaternary ammonium salts of the formula



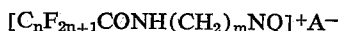
in which Q is selected from certain radicals containing a quaternary ammonium nitrogen atom and 4-25 carbon atoms are useful as surface active agents or antiwetting agents and are noncorrosive to steel.

CROSS-REFERENCE TO RELATED APPLICATION

This is a continuation-in-part of application Serial No. 621,128, filed Mar. 7, 1967, now abandoned.

BACKGROUND OF THE INVENTION

In U.S. Patent 2,764,602, Ahlbrecht discloses surface active quaternary salts of the structure



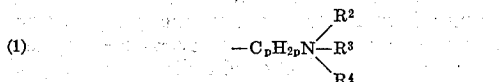
where n is 3-11, m is 2-6, N is a quaternary nitrogen atom, Q is an organic terminal structure which satisfies three of the covalences of the quaternary nitrogen atom and A is an anion.

DESCRIPTION OF THE INVENTION

Quite surprisingly, it has now been discovered that certain perfluoroalkyl ether amido quaternary ammonium salts are useful as surface active agents or antiwetting agents and have corrosion inhibiting properties toward steel. These salts have the formula



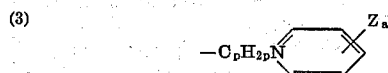
wherein R_1 is a perfluoroalkyl group of 1-6 carbon atoms, n is an integer from 0-8, R' is hydrogen or an alkyl of 1-6 carbon atoms, Q is a radical containing a quaternary ammonium nitrogen atom and 4-25 carbon atoms and is selected from the group consisting of



wherein p is an integer from 1-12, R^2 , R^3 and R^4 are alkyl groups of 1-18 carbon atoms, and R^2 , R^3 and R^4 contain a total of 3-20 carbon atoms,

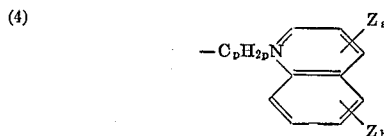


wherein Y is a divalent group of the formula $-(CH_2)_4-$, $-(CH_2)_5-$ or $-(CH_2)_2O(CH_2)_2-$, R^5 is an alkyl group of 1-16 carbon atoms, and R^5 and Y contain a total of 5-20 carbon atoms,

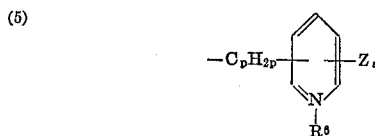


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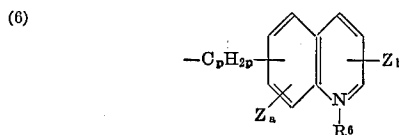
wherein Z is halogen or methyl and a is an integer from 0-3,



wherein b and $a+b$ are integers from 0-3,



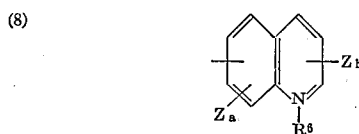
wherein R^6 is an alkyl of 1-4 carbon atoms,



wherein $a+b$ is an integer from 0-3,



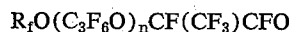
and



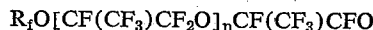
wherein $a+b$ is an integer from 0-3,

and A^- is any anion which forms an ammonium salt of the formula $NH_4^+A^-$ having a solubility in water of at least about 1%.

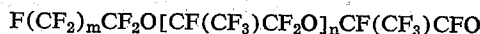
The starting materials for preparing the products of this invention are the perfluoroalkyl ether acid fluorides of the formula



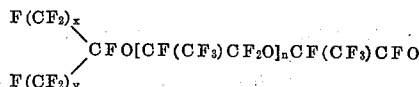
These acid fluorides are available from two sources, polymerization of hexafluoropropylene oxide and polymerization of mixtures of hexafluoropropylene and oxygen. The acid fluorides prepared by the polymerization of hexafluoropropylene oxide are taught by Moore et al. in U.S. Patent 3,250,808 and have the structure



If hexafluoropropylene oxide alone is polymerized, the products are $n-C_3F_7O[CF(CF_3)CF_2O]_nCF(CF_3)CFO$ as described more fully by Moore in Canadian Patent 725,740. If the polymerization is carried out in the presence of carbonyl fluoride (COF_2) or a perfluoroacid fluoride of the formula $F(CH_2)_mCFO$, as described more fully in French Patent 1,362,548, the product is of the formula

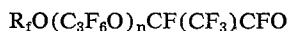


where m is 0-5. When the polymerization is carried out in the presence of a perfluoroketone of the formula $F(CF_2)_xC(O)(CF_2)_yF$, as described by Selman in U.S. Patent 3,274,239, the product is of the formula



where x and y are 1-4 and the total of $x+y$ is 2-5. Thus, R_1 may be a branched or straight chain perfluoroalkyl group of 1-6 carbon atoms.

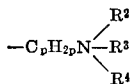
The acid fluorides prepared by polymerization of mixtures of hexafluoropropylene and oxygen are taught by Pasetti Sianesi and Corti in *Die Makromolekulare Chemie*, 86, pages 308-311 (1965); Sianesi and Fontanelli in *Die Makromolekulare Chemie*, 102, pages 115-124 (1967); and French Patent 1,434,537. The polymerization is carried out at temperatures of about -100°C . to 25°C . in the presence of ultraviolet radiation. Unlike the products obtained from the polymerization of hexafluoropropylene oxide, these polymers have backbones which are not in a regular head to tail arrangements; they contain both head to head and tail to tail as well as head to tail arrangements. These polymeric acid fluorides are thus best represented by the formula



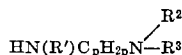
Generically, the polymers from hexafluoropropylene oxide and hexafluoropropylene-oxygen mixtures are best represented by this more general formula.

The perfluoroalkyl ether amido quaternary salts of this invention are prepared by first converting the perfluoroalkyl ether acid fluoride to a corresponding alkyl perfluoroalkyl ether ester, and preferably the methyl ester of the formula $R_1O(C_3F_6O)_nCF(CF_3)CO_2CH_3$, or to a corresponding perfluoroalkyl ether amide of the formula $R_1O(C_3F_6O)_nCF(CF_3)CONHR'$ in which R' is hydrogen or an alkyl of 1-6 carbon atoms. The esters are prepared by esterification of the corresponding acid fluoride using standard methods, for example reaction of the acid fluoride with an alkanol such as methanol as taught by Diesslin et al. in U.S. Patent 2,567,011. Preferably, the esterification is carried out by reacting the perfluoroalkyl ether acid fluoride with excess methanol at $10-20^\circ\text{C}$., optionally in an inert solvent, in the presence of sufficient pyridine to consume the hydrogen fluoride formed. In place of methanol one can also use ethanol, propanol, butanol or the like equally well. The amides are prepared by reaction of the corresponding acid fluoride with ammonia or an alkylamine of the formula $R'NH_2$ as also taught in the Diesslin et al. patent.

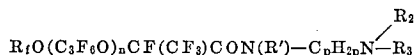
When Q is



wherein p is an integer from 2-12, R^2 , R^3 and R^4 are alkyl groups of 1-18 carbons, and R^2 , R^3 and R^4 contain a total of 3-20 carbons, the products are readily prepared by reaction of the alkyl perfluoroalkyl ether ester with a diamine of the formula

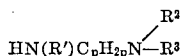


to form a dialkyl-N-tert.-aminoalkyl perfluoroalkyl ether amide of the formula

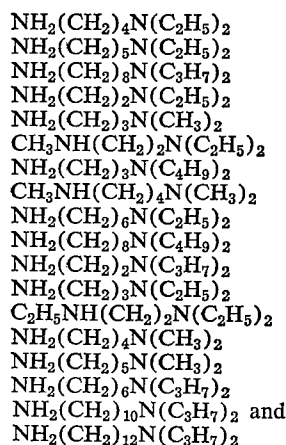
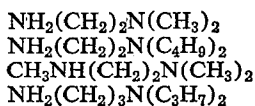


by well known techniques such as those described in U.S. Patent 2,764,603. The amide is then reacted with an alkyl halide, sulfate or arylsulfonate of the formula R^4A to form the quaternary salt as described in the above cited patent to Ahlbrecht.

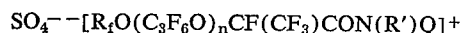
A large number of diamines of the type



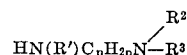
are known. Useful examples include:



Suitable compounds of the formula R^4A are those in which R^4 is an alkyl group of 1-18 carbon atoms and A is any anion which forms an ammonium salt of the formula $NH_4^+A^-$ having a solubility in water of at least about 1%. Useful examples of R^4A are the methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, hexyl, octyl, ethylhexyl, decyl, dodecyl, tetradecyl, hexadecyl and octadecyl chlorides, bromides and iodides. The normal alkyl halides, i.e., n-propyl, n-butyl, n-octyl or n-hexadecyl, are preferred. Also useful are the toluene, benzene and chlorobenzene sulfonate esters of methyl, ethyl, propyl, butyl and like alcohols, and methyl and ethyl sulfate. When methyl or ethyl sulfate (R_2SO_4) is used, the anion A^- in the product of the present invention will usually be a mixture of RSO_4^- and

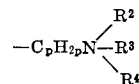


If the desired diamines of the formula

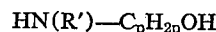


containing a tertiary amino group are not available, primary diamines of the formula $NH_2-C_pH_{2p}NH_2$ may be used. The N-aminoalkyl perfluoroalkyl ether amide product obtained by reacting the perfluoroalkyl ether ester with the primary diamine is then alkylated with at least three moles of alkyl halide, sulfate or sulfonate to form the quaternary salt. Alternatively, the aminoalkyl amide may be alkylated by other procedures such as reductive alkylation with formaldehyde and formic acid, followed by salt formation as before.

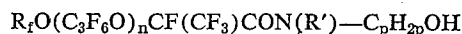
Another route to the products in which Q is



and p is 2-12 is to react the methyl perfluoroalkyl ether ester with an alkanolamine of the formula



to form an N-hydroxyalkyl perfluoroalkyl ether amide of the formula



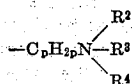
The hydroxyalkyl amide is then treated with a halogenating agent, for example hydrogen chloride, thionyl chloride or the like, to form the N-haloalkyl perfluoroalkyl ether amide which is treated with a tertiary amine of the formula



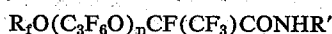
to form the quaternary salt. Suitable alkanolamines include ethanolamine, propanolamine, butanolamine, octanolamine and dodecanolamine.

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A special procedure is required to obtain the products in which Q is



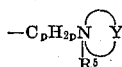
and p is 1. They are readily prepared by reaction of the perfluoroalkyl ether amide of the formula



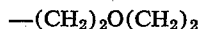
with formaldehyde and hydrogen chloride to give an N-chloromethyl perfluoroalkyl ether amide of the formula $R_fO(C_3F_6O)_nCF(CF_3)CON(R')-CH_2Cl$, which is then converted to the quaternary salt by reaction with a tertiary amine of the formula



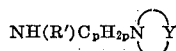
When Q is



wherein p is an integer from 1-12, Y is a divalent group of the formula $-(CH_2)_4-$, $-(CH_2)_5-$ or



R^5 is an alkyl group of 1-16 carbons, and R^5 and Y contain a total of 5-20 carbons, the products of this invention are prepared by the same general methods as described above. One procedure is by reaction of a diamine of the formula

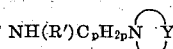


with the methyl perfluoroalkyl ether ester and the resulting product with an alkyl halide, sulfate or arylsulfonate of the formula R^5A where R^5 is an alkyl group of 1-16 carbon atoms to form the quaternary salt. They can also be prepared by reaction of the N-haloalkyl perfluoroalkyl ether amides described above, including the N-chloromethyl amides, with a cyclic tertiary amine of 5-20 carbons of the formula



to form the quaternary salt.

Useful examples of diamines of the formula

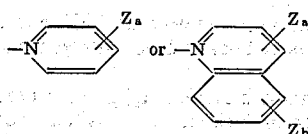


are N-(2'-aminoethyl)piperidine, N-(4'-aminobutyl)piperidine, N-(2'-aminoethyl)morpholine and N-(2'-aminoethyl)pyrrolidine. Suitable examples of R^5A include those mentioned in connection with R^4A except that R^5 should not exceed 16 carbon atoms. Useful examples of cyclic tertiary amines of the formula



are N-methyl-piperidine, N-methylpyrrolidine, N-butylpiperidine, N-methylmorpholine, N-octylpiperidine and N-tetradecylpiperidine.

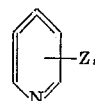
When Q is $-C_pH_{2p}Q'$ wherein p is an integer from 1-12 and Q' is



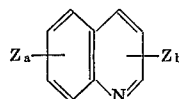
wherein Z is halogen or methyl, and a , b and $a+b$ are 75

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integers from 0-3, the products of this invention can be prepared by reaction of the N-haloalkyl perfluoroalkyl ether amides described above, including the N-chloromethylamides, with a pyridine of the formula



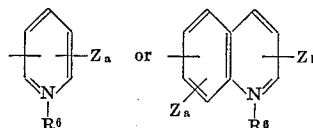
10 or a quinoline of the formula



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These pyridines and quinolines are well known. Some useful examples of pyridines are pyridine, picoline, lutidine, chloropyridines, bromopyridines, dichloropyridines, dibromopyridines, chloropicolines, bromopicolines, chlorolutidines, bromolutidines and the like. Useful examples of quinolines are quinoline, chloroquinolines, bromoquinolines, quinaldine, chloroquinaldines, bromoquinaldines and the like.

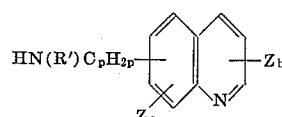
20 When Q is $-C_pH_{2p}Q'$ wherein p is an integer from 1-12 and Q' is



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wherein Z is halogen or methyl, a , b and $a+b$ are integers from 0-3, and R^6 is an alkyl of 1-4 carbon atoms, the products of this invention can be prepared by reaction of the methyl perfluoroalkyl ether esters described above with an aminoalkylpyridine of the formula

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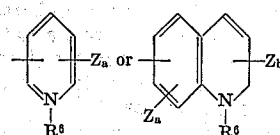
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45 The resulting perfluoroalkyl ether amide is then reacted with an alkyl halide, sulfate or sulfonate of the formula R^6A where R^6 is an alkyl group of 1-4 carbon atoms.

50 Suitable examples of aminoalkyl pyridines include 2-aminomethylpyridine, 2-(2'-aminoethyl)pyridine, 3-(2'-aminoethyl)pyridine, 3-aminomethylpyridine, 2,6-dichloro-3-aminomethylpyridine, 2-methyl-3-(2'-aminoethyl)pyridine, 3-(4'-aminobutyl)pyridine, 4-aminomethylpyridine and 4-(2'-aminoethyl)pyridine. Suitable aminoalkylquinolines include 2-, 3-, 4-, 5-, 6-, 7- and 8-aminomethylquinolines, 2-, 3-, 4-, 5-, 6-, 7- and 8-(2'-aminoethyl)quinolines, 2-, 3-, 4-, 5-, 6-, 7- and 8-(4'-aminobutyl)quinolines, and 2-, 3-, 4-, 5-, 6-, 7- and 8-(3'-methylaminopropyl)quinolines.

60 Suitable examples of alkyl halides include methyl, ethyl, propyl and butyl chlorides, bromides and iodides. Although the alkyl halides are preferred with these amides, methyl sulfate or methyl toluenesulfonate could be used with some success, if desired.

When Q is

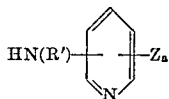


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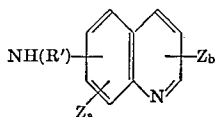
wherein Z is halogen or methyl, a , b and $a+b$ are integers from 0-3, and R^6 is an alkyl of 1-4 carbons, the products of this invention can be prepared by reaction of the methyl

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perfluoroalkyl ether ester described above with an aminopyridine of the formula



or an aminoquinoline of the formula



The resulting perfluoroalkyl ether amide is then reacted with the above defined alkyl halide sulfate or sulfonate of the formula R^bA .

Suitable aminopyridines include 2-aminopyridine, the 3, 4, 5 or 6-methyl-2-aminopyridine, the 3, 4, 5 or 6-chloro-2-aminopyridines, 3-aminopyridine, 2-chloro-6-methyl-3-aminopyridine, 4-aminopyridine, the dichloro-4-aminopyridines, and the like. Suitable aminoquinolines include 2, 3, 4, 5, 6, 7 or 8-aminoquinolines, the chloro-aminoquinolines, the methylaminoquinolines and the like.

All of the above procedures are generally well known in the art. A convenient inert solvent such as ethers, hydrocarbons, halogenated aromatic hydrocarbons or alcohols may be used at temperatures between 0°C . and the reflux temperature of the system. Alternatively, particularly when the product is a liquid, the methyl perfluoroalkyl ether ester may be heated alone with the amine, allowing the methyl alcohol formed to distill from the system. When a quaternary salt is being formed, the solvent is chosen conveniently to dissolve the reactants but not the solid product which is then readily recovered by filtration.

While specific schemes have been described for preparing the compounds of this invention, it is not intended that this invention be limited to any particular method of synthesis. Other methods may occur to those skilled in the art.

When n is 0-1, the products of the formula



of this invention are useful as surface active agents in aqueous systems, for example, as emulsifying agents, dispersants, wetting agents, and the like. These products are particularly useful as dispersing agents for aqueous emulsion polymerizations. Compounds in which n is 2 or greater are insufficiently soluble in water to be useful as surface active agents in aqueous systems.

All of the products of this invention, that is, those in which n is 0-8, are effective as anticorrosion agents for steel. The products wherein n is 0-1 are particularly useful as surface active agents in applications where they come in contact with steel such as in steel treating processes, for example in pickling baths. Those products wherein n is 2-8 are useful for other purposes. For example, they are useful as antiwetting agents in applications requiring mold release agents, release agents for glass, and flotation agents. The preferred products of this invention are those obtained from the polymerization of hexafluoropropylene oxide and hence of the formula



The following examples, illustrating the preparation and utility of the novel compounds of this invention, are given without any intention that the invention be limited thereto. All parts and percentages are by weight.

EXAMPLE 1

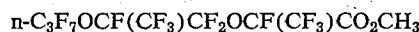
Perfluoroalkyl ether esters were prepared as follows:
(a) A solution of 450 parts of



prepared by the polymerization of hexafluoropropylene oxide and 100 parts of pyridine in 500 parts of anhydrous diethyl ether was cooled to $10-15^\circ\text{C}$. under anhydrous

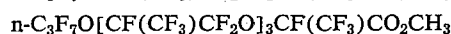
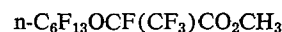
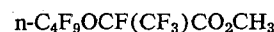
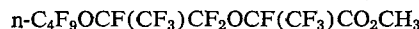
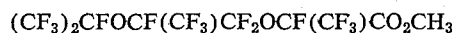
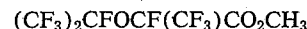
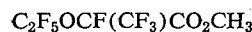
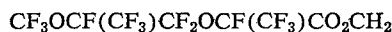
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conditions. Then 100 parts of anhydrous methanol was added over a period of one hour with agitation while maintaining the temperature of the reaction mass at $10-15^\circ\text{C}$. Agitation was continued for four hours at $10-15^\circ\text{C}$., then the pyridine hydrofluoride was collected by filtration and the filtrate was washed twice with 250 parts of water, twice with 250 parts of 5% aqueous sodium bicarbonate solution and finally five times with water until the final water was neutral. The ether solution was dried over anhydrous sodium sulfate and the ether was evaporated. The residue was distilled under reduced pressure, giving 430 parts (93.3% of theory) of

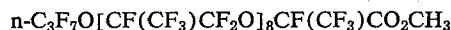


boiling point $43^\circ\text{C}/9\text{ mm. Hg}$.

(b) Using essentially the same procedure, the ester, $n-C_3F_7OCF(CF_3)CO_2CH_3$, boiling point $109-110^\circ\text{C}/760\text{ mm. Hg}$, was prepared in 75.1% yield from 200.0 parts of the acid fluoride and 50.0 parts of methanol. Likewise, the methyl esters,



and



can be prepared from the corresponding acid fluorides by the same procedure.

EXAMPLE 2

N-tert.-aminoperfluoroalkyl ether amides were prepared as follows:

(a) A solution of 100 parts of



in 250 parts of anhydrous diethyl ether was cooled to $10-15^\circ\text{C}$. under anhydrous conditions and a solution of 22.5 parts of 3-dimethylaminopropylamine in 50 parts of anhydrous diethyl ether was added over a one hour period with agitation. Agitation was continued for four hours at $10-15^\circ\text{C}$. The ether and excess amine were evaporated at reduced pressure ($50^\circ\text{C}/5\text{ mm. Hg}$) and the residue filtered, giving 112.4 parts (98.6% of theory) of

$n-C_3F_7OCF(CF_3)CF_2OCF(CF_3)CONH(CH_2)_3N(CH_3)_2$ as a light yellow liquid.

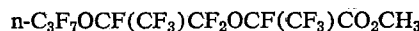
Analysis.—Calc'd for $C_{14}H_{13}F_{17}N_2O_3$ (percent): F, 55.4; N, 4.83. Found (percent): F, 55.3; N, 5.05.

(b) Using the same procedure, the amide,

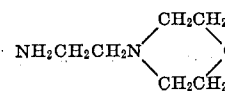
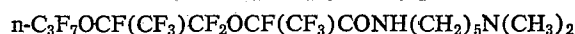


was prepared.

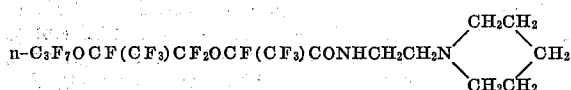
Using the same procedure



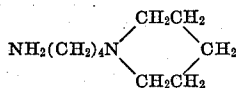
can be reacted with $NH_2(CH_2)_5N(CH_3)_2$ to form



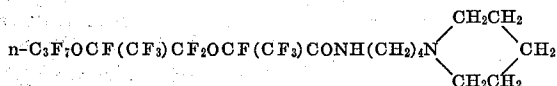
to form



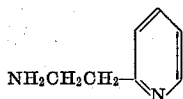
with



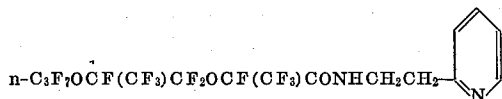
to form



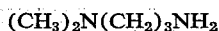
or with



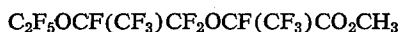
to form



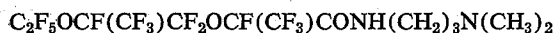
$\text{CF}_3\text{OCF}(\text{CF}_3)\text{CO}_2\text{CH}_3$ can be reacted with



to form $\text{CF}_3\text{OCF}(\text{CF}_3)\text{CONH}(\text{CH}_2)_3\text{N}(\text{CH}_3)_2$;



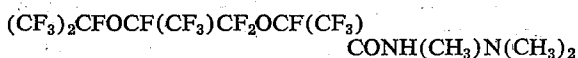
can be reacted with $\text{NH}_2(\text{CH}_2)_3\text{N}(\text{CH}_3)_2$ to form



and



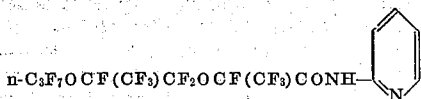
can be reacted with $\text{NH}_2(\text{CH}_2)_2\text{N}(\text{CH}_3)_2$ to form



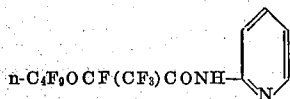
(c) Using the same procedure, 51.0 parts of



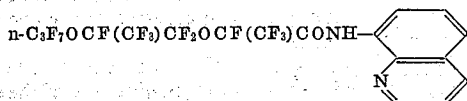
in 250 parts of diethyl ether were reacted with 18.8 parts of 2-aminopyridine to give 57.0 parts (99.8% of theory) of



In the same manner, $n\text{-C}_4\text{F}_9\text{OCF}(\text{CF}_3)\text{CO}_2\text{CH}_3$ can be reacted with 2-aminopyridine to give



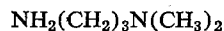
(d) Using essentially the same procedure, 51.0 parts of $n\text{-C}_3\text{F}_7\text{OCF}(\text{CF}_3)\text{CF}_2\text{OCF}(\text{CF}_3)\text{CO}_2\text{CH}_3$ was reacted with 28.8 parts of 8-aminoquinoline to give 79.2 parts (99.2% of theory) of



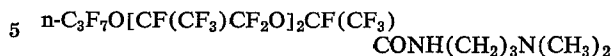
(e) Using the procedure of part (a),



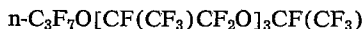
was reacted with



to give

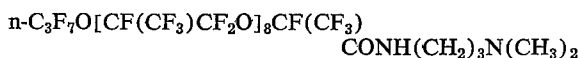


(f) Using the procedure of part (a)



10 was reacted with $\text{NH}_2(\text{CH}_2)_3\text{N}(\text{CH}_3)_2$

to give

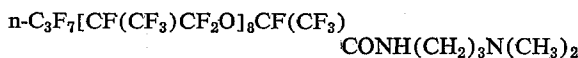


15 (g) Using the procedure of part (a)



was reacted with $\text{NH}_2(\text{CH}_2)_3\text{N}(\text{CH}_3)_2$

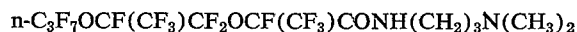
20 to give



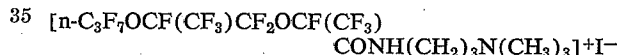
EXAMPLE 3

25 Perfluoroalkyl ether amino quaternary ammonium salts were prepared as follows:

(a) A solution of 100 parts of

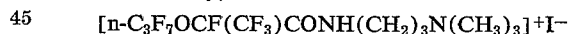


30 25.7 parts of methyl iodide and 200 parts of anhydrous methanol was heated under reflux for one hour. The solvent and excess methyl iodide were evaporated under reduced pressure (50° C./5 mm. Hg), to give 123.2 parts (99.1% of theory) of

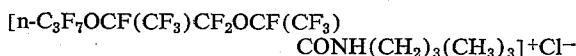


Analysis.—Calc'd for $\text{C}_{15}\text{H}_{16}\text{F}_{17}\text{N}_2\text{O}_3\text{I}$ (percent): F, 44.7; N, 3.88; I, 17.6. Found (percent): F, 44.5; N, 4.05; I, 17.4.

(b) Repeating the above procedure using 15.0 parts of $n\text{-C}_3\text{F}_7\text{OCF}(\text{CF}_3)\text{CONH}(\text{CH}_2)_3\text{N}(\text{CH}_3)_2$, 6.0 parts of methyl iodide and 50.0 parts of methanol gave 20.1 parts (99.6% of theory) of



(c) Repeating procedure (a) except that the methyl iodide was replaced with 66.7 parts of methyl chloride and the reaction was carried out under autogeneous pressure gave 106.9 parts (98.5% of theory) of



(d) Repeating procedure (a) except that the methyl iodide was replaced with 60.7 parts of hexadecyl iodide, gave 146.0 parts (99.4% of theory) of



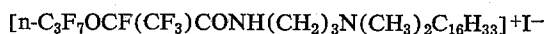
(e) Repeating procedure (a) except that the methyl iodide was replaced with 32.0 parts of methyl p-toluenesulfonate gave 132.0 parts (100% of theory) of



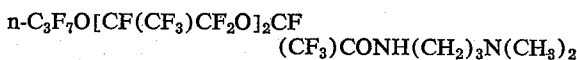
(f) Using procedure (a) 10.0 parts of



8.5 parts of hexadecyl iodide and 25.0 parts of methanol gave 18.2 parts (98.4% of theory) of

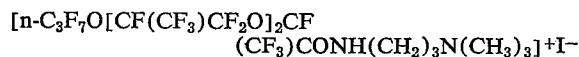


(g) Using the procedure of part (a),



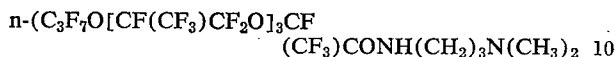
11

was reacted with methyl iodide to give

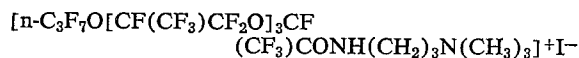


Analysis.—Calc'd for $C_{18}H_{16}F_{23}O_4N_2I$ (percent): F, 49.2; N, 3.2; I, 14.3. Found (percent): F, 48.9; N, 3.1; I, 14.1.

(h) Using the procedure of part (a),

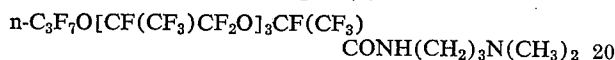


was reacted with methyl iodide to give

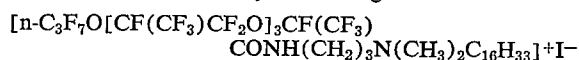


Analysis.—Calc'd for $C_{21}H_{16}F_{29}N_2I$ (percent): F, 52.3; N, 2.; I, 12.0. Found (percent): F, 52.1; N, 2.6; I, 12.7.

(i) Using the procedure of part (a)

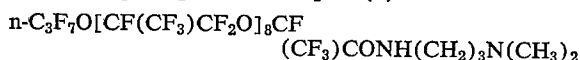


was reacted with hexadecyl iodide to give

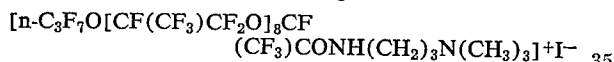


Analysis.—Calc'd for $C_{36}H_{50}F_{29}O_5N_2$ (percent): F, 59.7; N, 1.5; I, 6.7. Found (percent): F, 59.5; N, 1.4; I, 6.5.

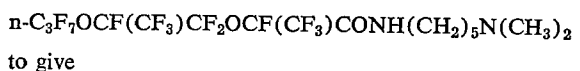
(j) Using the procedure of part (a)



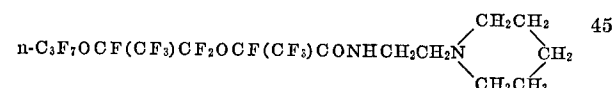
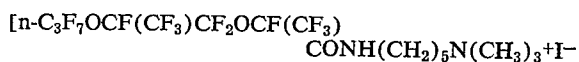
was reacted with methyl iodide to give



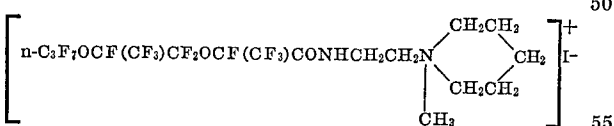
Using the same procedure methyl iodide can be reacted with



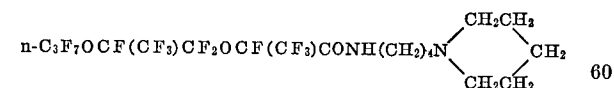
to give



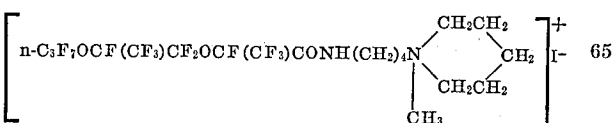
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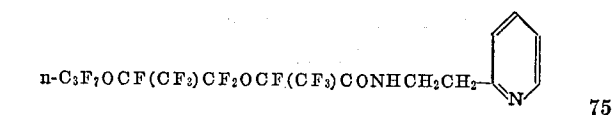
with



to form

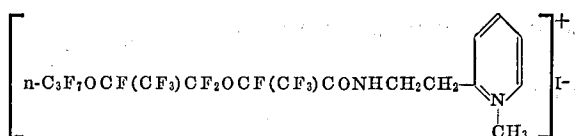


or with

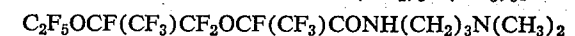
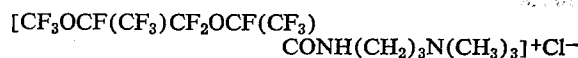


12

to form



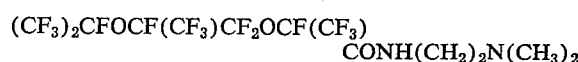
can be reacted with CH_3Cl to form



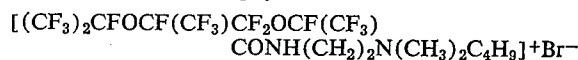
can be reacted with C_2H_5Br to form



and



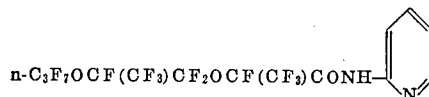
can be reacted with $n-C_4H_9Br$ to form



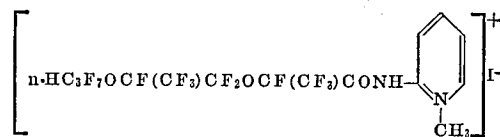
EXAMPLE 4

Perfluoroalkyl ether amido quaternary ammonium salts were prepared as follows:

(a) A solution of 10.0 parts of

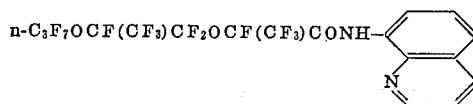


3.8 parts of methyl iodide and 50.0 parts of anhydrous methanol was heated under reflux for two hours. The solvent and excess methyl iodide were evaporated under reduced pressure (50° C./5 mm. Hg) to give 11.5 parts (94.3% of theory) of

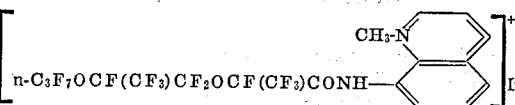


Analysis.—Calc'd for $C_{15}H_8F_7N_2O_3I$ (percent): F, 46.2; N, 3.70; I, 18.1. Found (percent): F, 46.1; N, 3.71; I, 18.3.

(b) In the same manner, 10.0 parts of

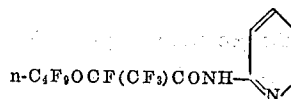


3.5 parts of methyl iodide and 50 parts of anhydrous methanol were reacted to give 12.0 parts (98.4% of theory) of



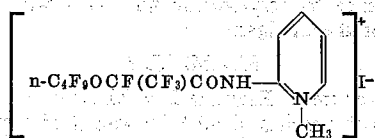
Analysis.—Calc'd for $C_{18}H_9F_{17}N_2O_3I$ (percent): F, 42.3; N, 3.63; I, 16.6. Found (percent): F, 42.2; N, 3.61; I, 16.4.

In the same manner,



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can be reacted with methyl iodine to form



EXAMPLE 5

Utility as surface active agents was determined as follows:

Surface activities of aqueous solutions of products prepared above were measured using a Du Nooy Tensiometer in the usual manner. The results are shown in the following table. Water containing no additive had a surface tension of 72 dynes per centimeter at 25° C.

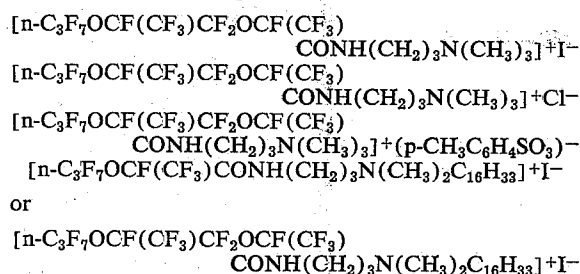
TABLE

Surface active agent	Surface tension, dynes/cm. at 25° C.					
	Concentration, percent					
	0.005	0.01	0.05	0.1	0.5	1.0
$[n-C_3F_7OCF(CF_3)CONH(CH_2)_3N(CH_3)_3]^+ I^-$	56.3	53.0	43.6	39.2	27.0	20.2
$[n-C_3F_7OCF(CF_3)CF_2OCF(CF_3)CONH(CH_2)_3N(CH_3)_3]^+ I^-$	22.1	17.9	16.9	14.7	14.4	14.3
$[n-C_3F_7OCF(CF_3)CF_2OCF(CF_3)CONH(CH_2)_3N(CH_3)_3]^+ Cl^-$	22.9	18.1	17.1	14.8	14.3	14.2
$[n-C_3F_7OCF(CF_3)CF_2OCF(CF_3)CONH(CH_2)_3N(CH_3)_3]^+ [p-CH_3-C_6H_4SO_3]^-$	23.1	19.1	18.4	15.1	14.5	14.3
$[n-C_3F_7OCF(CF_3)CF_2OCF(CH_3)CONH-\text{pyrrolidine}]^+ I^-$	-----	-----	-----	49.5	35.0	26.0
$[n-C_3F_7OCF(CF_3)CF_2OCF(CF_3)CO-NH-\text{quinoline}]^+ I^-$	-----	-----	-----	51.0	36.2	28.5

EXAMPLE 6

Utility of water-soluble salt products as anti-corrosion agents was determined as follows:

Five Type 1020 mild steel test coupons were each contacted for 5-6 weeks with a different 10% hydrochloric acid solution containing about 0.01% of



In all five cases, there was no indication of corrosion. The latter two compounds were effective in spite of the fact that they did not completely dissolve.

For comparison, a Type 1020 mild steel test coupon was contacted for the same period of time with 10% hydrochloric acid containing 0.01% of



which is not within the scope of the present invention but is illustrated in Example 1 of the Ahlbrecht patent described above. Severe corrosion occurred.

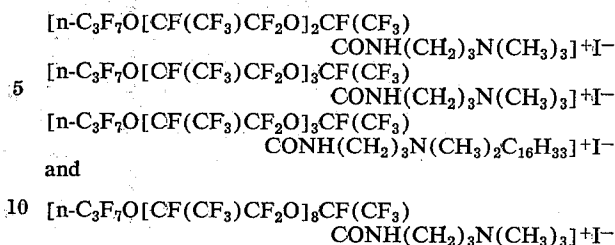
EXAMPLE 7

Utility of water-insoluble salt products as anti-corrosion agents was determined as follows:

Four Type 1020 mild steel test coupons were each treated with a different 1.0% solution of one of the follow-

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ing products in trichlorotrifluoroethane for five minutes and then air dried. The products used were:



The coupons were then immersed to one-half their length in 10% aqueous hydrochloric acid and allowed to stand for five days at ambient temperature. None of the four

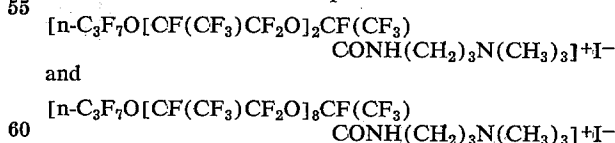
coupons had any evidence of corrosion on their surfaces which remained bright.

For comparison, another Type 1020 mild steel test coupon which had not been surface treated was immersed in 10% hydrochloric acid and allowed to stand for 5 days at ambient temperature. The coupon turned black and was badly corroded.

EXAMPLE 8

Utility as release agents for metal surfaces was determined as follows:

Two Type 1020 mild steel test coupons were each treated with a different 1.0% solution of one of the following products in trichlorotrifluoroethane for five minutes and then air dried. The products used were:



To test the antiwetting or release properties of the treated surfaces, each treated coupon was bonded to an untreated coupon with a typical epoxy resin metal bonding agent ("Epon" 828 cured with diethylene triamine). In each case the bond could be broken by hand.

For comparison, two untreated Type 1020 mild steel test coupons were bonded together with the same bonding agent. The bond was very strong and could not be broken by hand.

EXAMPLE 9

Utility as release agents for glass surfaces was determined as follows:

Two glass slides were each treated with a different one of the two 1.0% trichlorotrifluoroethane solutions de-

scribed in Example 8 for 5 minutes and air dried. The treated slides were then coated with poly(methyl 2-cyanoacrylate) which is known to be a good adhesive for glass. After setting, the adhesion of the resin coating to the glass was tested. In both cases, the coatings were easily removed with a knife.

For comparison, a similar coating was placed on an untreated glass slide. The film was strongly bonded to the glass as evidenced by the fact that it was not easily removed with a knife.

EXAMPLE 10

Usefulness as flotation agents was determined as follows:

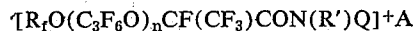
One drop of one of the 1.0% trichlorotrifluoroethane solutions of Example 8 was added to each of three beakers, each containing 100 ml. of water. One drop of the other of the 1.0% trichlorotrifluoroethane solutions of Example 8 was also added to three different beakers, each containing 100 ml. of water. For each solution, to one beaker was added powdered Cr_2O_3 , to the second was added powdered Cu_2O , and to the third was added powdered Fe_2O_3 . For comparison, similar samples of powdered Cr_2O_3 , Cu_2O and Fe_2O_3 were also to beakers containing 100 ml. of water, but no added solution. In all cases when the trichlorotrifluoroethane solution was added, the powdered oxide floated. In those cases where the trichlorotrifluoroethane solution was not added, the oxide sank.

In each of the preceding examples, one may substitute the corresponding compounds containing the group $\text{R}_1\text{O}(\text{C}_3\text{F}_6\text{O})_n\text{CF}(\text{CF}_3)-$ derived from the polymerization of mixtures of hexafluoropropylene and oxygen with essentially equivalent results.

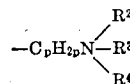
Although the invention has been described and exemplified by way of specific embodiments, it is intended that it not be limited thereto. As will be apparent to those skilled in the art, numerous modifications and variations of these embodiments may be made without departing from the spirit of the invention or the scope of the following claims.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A perfluoroalkyl ether amido quaternary ammonium salt of the formula



wherein R_1 is perfluoroalkyl of 1-6 carbon atoms; n is an integer of from 0-8; R' is hydrogen or alkyl of 1-6 carbon atoms; Q is a radical of 4-25 carbon atoms and is represented by the formula



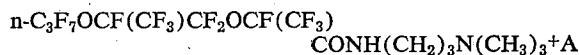
wherein p is an integer of from 1-12, R^2 , R^3 and R^4 are alkyl groups of 1-18 carbon atoms and the combined number of carbon atoms in the R^2 , R^3 and R^4 groups is between 3 and 20; and A is an anion selected from halide, sulfonate, SO_4^- , $\text{H}_3\text{C}-\text{SO}_4^-$ or $\text{H}_3\text{CCH}_2-\text{SO}_4^-$.

2. A salt of claim 1 in which the formula of the salt is



wherein R_1 , n , R' , Q and A are as defined in claim 1.

3. A salt of claim 1 in which the formula is



in which A is defined as in claim 1.

4. The salt of claim 3 in which A is chloride.

5. The salt of claim 3 in which A is iodide.

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260-247.2, 286, 294, 295; 117-6; 148-22; 252-60