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3,839,425

**PERFLUOROALKYLETHERAMIDOALKYL
BETAINES AND SULFOBETAINES**

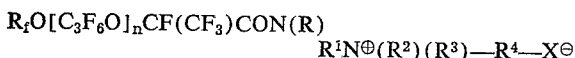
Philip Lee Bartlett, Wilmington, Del., assignor to E. I. du Pont de Nemours and Company, Wilmington, Del.
No Drawing. Filed Sept. 16, 1970, Ser. No. 72,803
Int. Cl. C07c 101/04

U.S. Cl. 260—501.12

1 Claim

ABSTRACT OF THE DISCLOSURE

Perfluoroalkyletheramidoalkyl betaines and sulfobetaines having the formula



wherein R_f is a perfluoroalkyl group of 1 to 6 carbon atoms, n is an integer of 0 to 8, R is hydrogen or an alkyl group of 1 to 6 carbon atoms, R^1 is an alkylene group of 1 to 12 carbon atoms, R^2 and R^3 are alkyl groups each containing 1 to 6 carbon atoms, R^4 is an alkylene group of 1 to 4 carbon atoms and X is selected from a group consisting of CO_2 and SO_3 are useful as surface active agents, foaming agents, foam stabilizers and aqueous film spreading agents. They are particularly useful in fire extinguishant foam formulations.

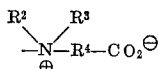
BACKGROUND OF THE INVENTION

Surface-active agents are generally characterized as anionic, cationic, or nonionic depending upon the physicochemical properties. Anionic surface-active agents contain anionogenic group, usually a carboxyl, sulfonic acid or sulfuric ester, which in basic solutions form anions. Cationic surface-active agents contain cationogenic group, usually an amine group, which in acidic solutions form cations. Nonionic surface-active agents on the other hand are incapable of forming ions and depend upon highly hydrophilic groupings such as those of ether or hydroxyl for their activity.

There exists, however, another group of surface-active agents which is characterized by having both the anionogenic and the cationogenic groups within the molecule. This type of compound as exemplified by aminoacids is amphoteric and ampholytic. In strongly basic solutions, ionization occurs mainly at the acidic group and the molecule is predominantly anionic and acidic. In strongly acidic solution ionization occurs mainly at the amine group as ammonium ion and the molecule is predominantly cationic and basic.

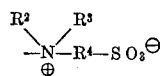
The betaines and the sulfobetaines of this invention constitute a distinct group of ampholytic surface-active agents in that the betaines and the sulfobetaines contain cationic quaternary ammonium group and anionic carboxylate or sulfonate group within the molecule and do not depend upon ionization to form these ions. They are basic and have a positive charge at the quaternary ammonium nitrogen but at the same time they are acidic and have a negative charge at the carboxylate or the sulfonate group.

Betaines are defined as inner quaternary ammonium salts wherein the positive charge on the quaternary ammonium nitrogen is balanced intramolecularly by an anionic carboxylate group, i.e. compounds having the groupings



within the molecule. Sulfobetaines are defined as betaine compounds wherein the anionic group within the molecule is a sulfonate group, i.e. the compounds having the groupings

2

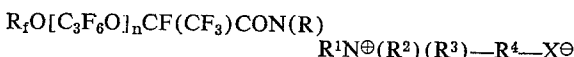


within the molecule.

The ampholytic surface-active agents in general have not achieved commercial importance of anionic, cationic, or non-ionic surface-active agents. Greater cost of manufacture of ampholytic surface-active agents undoubtedly is one of the reasons for the lack of commercial acceptance. Absence of some unusual properties that are not possessed by the usual anionic, cationic or nonionic surface-active agents may also account for the lack of commercial success.

SUMMARY OF THE INVENTION

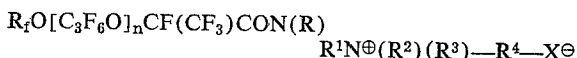
Perfluoroalkyletheramidoalkyl betaines and sulfobetaines having the formula



wherein R_f is a perfluoroalkyl group of 1 to 6 carbon atoms, n is an integer of 0 to 8, R is hydrogen or an alkyl group of 1 to 6 carbon atoms, R^1 is an alkylene group of 1 to 12 carbon atoms, R^2 and R^3 are alkyl groups each containing 1 to 6 carbon atoms, R^4 is an alkylene group of 1 to 4 carbon atoms and X is selected from the group consisting of CO_2 and SO_3 have unusual chemical properties which make them suitable not only as surface active agents and foaming agents but also as foam stabilizers and aqueous film spreading agents. The latter two properties make these compounds particularly useful in fire extinguishant foam formulations.

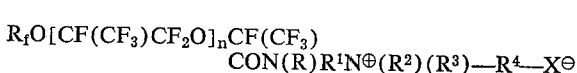
DESCRIPTION OF THE INVENTION

The compounds of the present invention are the betaines and the sulfobetaines of the formula



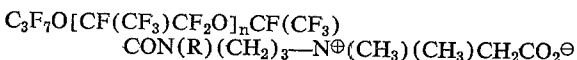
wherein R_f is a perfluoroalkyl group of 1 to 6 carbon atoms, n is an integer of 0 to 8, R is hydrogen or an alkyl group of 1 to 6 carbon atoms, R^1 is an alkylene group of 1 to 12 carbon atoms, R^2 and R^3 are alkyl groups each containing 1 to 6 carbon atoms, R^4 is an alkylene group of 1 to 4 carbon atoms and X is chosen from the group consisting of CO_2 and SO_3 .

The preferred compounds of the present invention have the formula

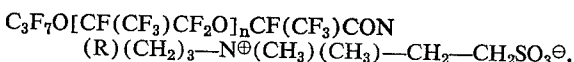


wherein R_f , n , R , R^1 , R^2 , R^3 , R^4 and X are as designated above.

The most preferred compounds are



and



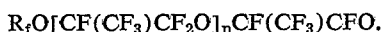
The starting materials for the preparation of the betaines and the sulfobetaines of this invention are the perfluoroalkylether acid fluorides of the formula



These acid fluorides are available either by the polymerization of hexafluoropropylene oxide or by the polymerization of a mixture of hexafluoropropylene and oxygen.

3

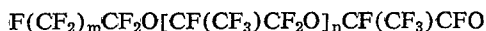
The polymerization of hexafluoropropylene oxide is taught by Moore et al. in U.S. 3,250,808 and the acid fluorides have the structure



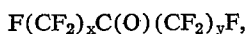
If hexafluoropropylene oxide alone is polymerized, the products are



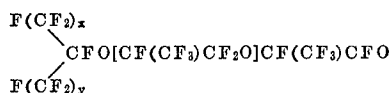
as described by Moore in Canadian Patent 725,740. If the polymerization of hexafluoropropylene oxide is carried out in the presence of carbonyl fluoride (COF₂) or a perfluoroacidfluoride of the formula F(CF₂)_mCFO, the products are of the formula.



where *m* is 0-5 as more fully described in French Patent 1,362,548. When the polymerization is carried out in the presence of a perfluoroketone of the formula

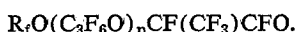


as described by Selman in U.S. Pat. 3,274,239, the product is the formula of

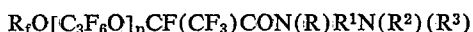


where *x* and *y* are 1-4 and the total of *x*+*y* is 2-5. Thus, R_f may be a branched or straight-chain perfluoroalkyl group of 1-6 carbon atoms.

The acid fluorides prepared by polymerization of mixture 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 and the polymeric acid fluorides obtained are best characterized by the formula

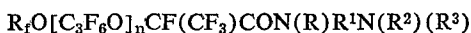


The above-described perfluoroalkylether acid fluorides are converted to perfluoroalkylether amidoalkylamines of the formula



by the reaction of the acid fluoride with a suitable diamine or by the reaction of an alkyl ester derived from the above perfluoroalkylether acid fluoride with the diamine. The formation of perfluoroalkyletheramide by the reaction of perfluoroalkylether acid fluoride with an amine is described by MacKenzie in U.S. Pat. 3,274,244. The reaction is preferably carried out in the presence of inert solvents such as diethylether, tetrahydrofuran, benzene, trichlorotrifluoroethane and the like. Hydrogen fluoride formed in the reaction may be removed by using the amine in excess of that required for the reaction or by using an acid scavenger such as pyridine or triethylamine.

The perfluoroalkylether amidoalkylamines of the formula



may also be prepared by first converting the perfluoroalkylether acid fluoride to the corresponding alkylperfluoroalkylether ester and preferably the methyl ester of the formula



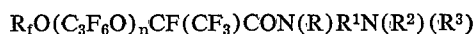
The esters are prepared by esterification of the corresponding acid fluoride using standard methods, for example, reaction of the acid fluoride with an alcohol such as methanol as taught by Diesslin et al. in U.S. Pat. 2,567,011. Preferably, the esterification is carried out by reacting the perfluoroalkylether acid fluoride with excess methanol at 10-20° C., optionally in an inert solvent, in the

4

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 alkylperfluoroalkylether esters are then reacted with diamines of the formula



to form the perfluoroalkylether amidoalkylamine of the formula



by well-known procedures such as those described in U.S. Pat. 2,764,603.

A large number of diamines of the formula



are known and useful examples include:

NH ₂ (CH ₂) ₂ N(CH ₃) ₂	NH ₂ (CH ₂) ₁₀ N(C ₂ H ₅) ₂
NH ₂ (CH ₂) ₂ N(C ₄ H ₉) ₂	C ₂ H ₅ NH(CH ₂) ₂ N(C ₂ H ₅) ₂
NH ₂ (CH ₂) ₃ N(CH ₃) ₂	NH ₂ (CH ₂) ₃ N(C ₃ H ₇) ₂
NH ₂ (CH ₂) ₂ N(C ₂ H ₅) ₂	NH ₂ (CH ₂) ₄ N(CH ₃) ₂
NH ₂ (CH ₂) ₂ N(C ₅ H ₁₁) ₂	NH ₂ (CH ₂) ₅ N(CH ₃) ₂
NH ₂ (CH ₂) ₃ N(C ₂ H ₅) ₂	NH ₂ (CH ₂) ₆ N(C ₃ H ₇) ₂
NH ₂ (CH ₂) ₂ N(C ₃ H ₇) ₂	NH ₂ (CH ₂) ₈ N(C ₄ H ₉) ₂
NH ₂ (CH ₂) ₂ N(C ₆ H ₁₃) ₂	NH ₂ (CH ₂) ₁₂ N(CH ₃) ₂
CH ₃ NH(CH ₂) ₂ N(CH ₃) ₂	C ₄ H ₉ NH(CH ₂) ₂ N(CH ₃) ₂
CH ₃ NH(CH ₂) ₂ N(C ₂ H ₅) ₂	NH ₂ (CH ₂) ₃ N(C ₄ H ₉) ₃
C ₂ H ₅ NH(CH ₂) ₂ N(CH ₃) ₂	NH ₂ (CH ₂) ₄ N(C ₂ H ₅) ₂
NH ₂ (CH ₂) ₃ N(C ₆ H ₁₃) ₂	NH ₂ (CH ₂) ₅ N(C ₂ H ₅) ₂
CH ₃ NH(CH ₂) ₄ N(CH ₃) ₂	NH ₂ (CH ₂) ₆ N(C ₄ H ₉) ₂
NH ₂ (CH ₂) ₆ N(C ₂ H ₅) ₂	NH ₂ (CH ₂) ₁₀ N(CH ₃) ₂
NH ₂ (CH ₂) ₈ N(CH ₃) ₂	NH ₂ (CH ₂) ₁₂ N(C ₂ H ₅) ₂

A special procedure is required to obtain a perfluoroalkylether amidoalkylamine wherein R¹ is —CH₂—. They are readily prepared by the reaction of the perfluoroalkyletheramide of the formula



with formaldehyde and hydrogen chloride to form N-chloromethylperfluoroalkyletheramide of the formula



which is then converted to the tertiary amine by the reaction with a secondary amine HN(R²)(R³).

The betaines and the sulfobetaines of the present invention are then prepared by reacting the above described perfluoroalkyletheramidoalkylamines with salts of haloalkylcarboxylic acid or haloalkyl sulfonic acid. The formation of quaternary ammonium salts by the reaction of a tertiary amine with haloalkyl compounds are well-known and is described for example by Ahlbrecht in U.S. Pat. 2,764,602. Haloalkylcarboxylic acids and haloalkylsulfonic acids from which salts, for example the alkali metal salts, are readily obtained, are well-known and useful examples include bromoacetic acid, chloroacetic acid, 2-bromopropionic acid, 3-bromopropionic acid, 2-chloropropionic acid, 3-chloropropionic acid, 3-chlorobutyric acid, 4-chlorobutyric acid, 5-chlorovaleric acid, chloromethylsulfonic acid, 2-bromoethane sulfonic acid, 2-chloroethane sulfonic acid, 1-chloroethane sulfonic acid and 3-chloropropane sulfonic acid.

The betaines and the sulfobetaines of the present invention are particularly effective surface active agents in water, and in neutral, strongly acidic and strongly basic aqueous solutions. In contrast to the usual cationic and anionic surface active agents whose activities are markedly altered by the acidic or basic nature of the solutions, the compounds of the present invention are equally effective in neutral, strongly acidic and strongly basic aqueous solutions. It is clear from the structural feature of the compounds of this invention that the ionic character of the molecule is maintained in neutral, acidic and basic aqueous solutions.

5

The compounds of this invention are particularly useful in the formation of aqueous foams and in stabilizing such foams after they are formed. The ability to form foams and to stabilize such foams are valuable, for example in fire extinguishant foam formulations. The insensitivity of the compounds to the action of acid, alkali or salt make these compounds particularly valuable since the loss of foams upon contact with acid, alkali or salt solutions is eliminated.

The compounds of this invention are useful in spreading aqueous film over the surface of hydrocarbon surfaces. As is known, when a drop of water is very carefully placed on the surface of a hydrocarbon liquid, the water drop remains as a drop on the surface until subsequent agitation causes it to sink. If a drop of water containing a compound of this invention is placed on the surface of

6

low solid, obtained in 97.4% yield. Elemental analysis showed the following: Percent fluorine calculated 50.6; percent fluorine found 50.7; percent nitrogen calculated 4.4; percent nitrogen found 4.3

Examples 2-10

Using the procedure of Example 1 and equimolar amounts of the starting materials listed in Table I the perfluoroalkyletheramidoalkyl betaines listed in Table I were prepared. In Table I, A, B, C and D have the meaning as follows:

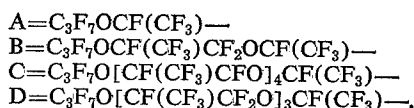


TABLE I

Example	Reactants	Betaine	Percent fluorine		Percent nitrogen		Yield, percent
			Calc'd	Found	Calc'd	Found	
2	A—CON(H)(CH ₂) ₃ N(CH ₃) ₂ and ClCH ₂ CO ₂ Na.	A—CON(H)(CH ₂) ₃ N [⊕] (CH ₃) ₂ CH ₂ CO ₂ [⊖] -----	42.3	42.2	5.7	5.8	90.6
3	B—CON(C ₂ H ₅)(CH ₂) ₂ N(CH ₃) ₂ and ClCH ₂ CO ₂ Na.	B—CON(C ₂ H ₅)(CH ₂) ₂ N [⊕] (CH ₃) ₂ CH ₂ CO ₂ [⊖] ---	49.5	49.4	4.3	4.3	92.4
4	B—CON(H)(CH ₂) ₂ N(C ₂ H ₅) ₂ and ClCH ₂ CO ₂ Na.	B—CON(H)(CH ₂) ₂ N [⊕] (C ₂ H ₅) ₂ CH ₂ CO ₂ [⊖] -----	48.5	48.2	4.2	4.1	93.2
5	B—CON(H)(CH ₂) ₃ N(CH ₃) ₂ and Cl(CH ₂) ₂ CO ₂ Na.	B—CON(H)(CH ₂) ₃ N [⊕] (CH ₃) ₂ (CH ₂) ₂ CO ₂ [⊖] ---	49.5	49.3	4.3	4.2	97.3
6	B—CON(H)(CH ₂) ₃ N(C ₂ H ₅) ₂ and Cl(CH ₂) ₂ CO ₂ Na.	B—CON(H)(CH ₂) ₃ N [⊕] (C ₂ H ₅) ₂ (CH ₂) ₂ CO ₂ [⊖] ---	46.8	46.6	4.1	4.0	94.3
7	B—CON(H)(CH ₂) ₃ N(C ₄ H ₉) ₂ and ClCH ₂ CO ₂ Na.	B—CON(H)(CH ₂) ₃ N [⊕] (C ₄ H ₉) ₂ CH ₂ CO ₂ [⊖] -----	44.7	44.5	3.9	3.9	97.3
8	B—CON(H)(CH ₂) ₃ N(C ₄ H ₉) ₂ and Cl(CH ₂) ₂ CO ₂ Na.	B—CON(H)(CH ₂) ₃ N [⊕] (C ₄ H ₉) ₂ (CH ₂) ₂ CO ₂ [⊖] ---	43.9	43.8	3.8	3.7	94.2
9	C—CON(H)(CH ₂) ₃ N(CH ₃) ₂ and ClCH ₂ CO ₂ Na.	C—CON(H)(CH ₂) ₃ N [⊕] (CH ₃) ₂ CH ₂ CO ₂ [⊖] -----	58.5	58.3	2.5	2.3	92.7
10	D—CON(H)(CH ₂) ₃ N(CH ₃) ₂ and ClCH ₂ CO ₂ Na.	D—CON(H)(CH ₂) ₃ N [⊕] (CH ₃) ₂ CH ₂ CO ₂ [⊖] -----	60.8	60.4	1.5	1.4	96.3

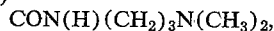
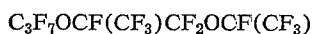
a hydrocarbon liquid, the water drop immediately spreads and covers the hydrocarbon surface with an aqueous film. The ability to form aqueous film in hydrocarbon surface is not a general property of surface active agents. It is not known at present, which structural portion of the compounds of the present invention is responsible for the aqueous film spreading ability but it is believed that the perfluoroalkylether chain of the molecule is involved in this unique characteristic.

The aqueous film spreading property is extremely valuable, particularly in aqueous foam fire extinguishant compositions wherein rapidly covering of burning hydrocarbon surfaces is desirable. After such a fire has been extinguished, it is desirable to maintain foam covering to prevent reignition.

EXAMPLES

Example 1

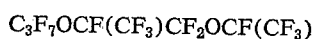
N-dimethylaminopropylamide of perfluoroalkylether acid,



50 g. (0.086 m.) and the sodium salt of chloroacetic acid, ClCH₂CO₂Na, 10.1 g. (0.086 m.) and 20 ml. of isopropanol were placed in a 500 ml. reaction flask equipped with a reflux condenser, a thermometer and an agitator. The reaction mixture was heated at reflux (83° C.) with agitation for 16 hours. The reaction mixture was then cooled to room temperature and the precipitated sodium chloride was removed by filtration. The filtrate was transferred to a distillation assembly wherein isopropanol was removed by distillation at reduced pressure. The isopropanol was considered to be completely removed when the contents of the distillation flask reached 50° C. at 5 mm. Hg pressure. The residue in the flask weighing 53.7 g. was the product, which was a very tacky, slightly yel-

Example 11

N-dimethylaminopropylamide of perfluoroalkylether acid,



50 g. (0.086 m.) sodium salt of 2-bromoethanesulfonic acid, Br—CH₂CH₂—SONa, 18.2 g. (0.086 m.), 300 ml. isopropanol and 300 ml. water were placed in a 1-liter reaction flask equipped with a reflux condenser, a thermometer and an agitator. The reaction mixture was heated at reflux (83° C.) with agitation for 16 hours. The reaction mixture was transferred to a distillation assembly wherein isopropanol and water were removed by distillation at reduced pressures. The residue in the distillation flask was extracted with 300 ml. of isopropanol. The isopropanol extract was then placed in a distillation assembly wherein isopropanol was removed by distillation at reduced pressures. The isopropanol was considered to be completely removed when the contents of the distillation flask reached 50° C. at 5 mm. Hg pressure. The residue in the flask weighing 53.1 g. was the desired product, which was a sticky yellow semi-solid, obtained in 91% yield. The elementary analysis showed the following: Percent fluorine, calculated 46.9, found 46.8; percent nitrogen, calculated 4.1, found 4.0 and percent sulfur, calculated 4.7, found 4.5.

Examples 12 and 13

Using the procedure of Example 11 and equimolar amounts of the starting materials listed in Table II the perfluoroalkyletheramidoalkylsulfobetaines listed in Table II were prepared. In Table II

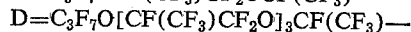
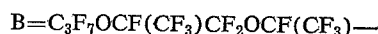


TABLE II

Example	Reactants	Sulfobetaine	Percent fluorine		Percent nitrogen		Yield, percent
			Calc'd	Found	Calc'd	Found	
12.....	B—COH(CH ₃)(CH ₂) ₂ N(CH ₃) ₂ and Cl(CH ₂) ₂ SO ₃ Na.	B—CON(CH ₃)(CH ₂) ₂ N [⊕] (CH ₃) ₂ (CH ₂) ₂ SO ₃ [⊖]	45.2	45.4	3.9	3.9	94.2
13.....	D—CON(H)(CH ₂) ₂ N(CH ₃) ₂ and Br(CH ₂) ₂ SO ₃ Na.	D—CON(H)(CH ₂) ₂ N [⊕] (CH ₃) ₂ (CH ₂) ₂ SO ₃ [⊖]	59.3	59.1	1.5	1.3	94.2

Examples 14-19

The utility of the compounds of the present invention as surface active agents is clearly demonstrated by the data summarized in Table III below which shows measurements of surface tension of dilute aqueous solutions of these compounds at 25° C. using a DuNouy tensiometer. It is to be noted that even at a concentration as low as 0.001% outstanding reduction in the surface tension is evident. It is also to be noted that even in the presence of 5% hydrochloric acid or 5% sodium hydroxide the

10 ample. As discussed above, the spreading of an aqueous film on the surface of a hydrocarbon is of particular importance to aqueous fire extinguishant foam formulations. The aqueous film spreading test was carried out by carefully placing 10 drops of the aqueous solution of the compounds on the surface of cyclohexane contained in a 125 mm. diameter evaporating dish and recording the time (in seconds) for the cyclohexane surface to be covered by the aqueous film. Example 24 is comparative using the prior art compound of Examples 19 and 21.

TABLE IV

Example	Compound	Concentration (g./100 ml.)	Aq. film spreading time (sec.)
22.....	C ₃ F ₇ O[CF(CF ₃)CON(H)(CH ₂) ₂ N [⊕] (CH ₃) ₂ CH ₂ CO ₂ [⊖]	0.1 1.0	(¹) 4
23.....	C ₃ F ₇ O[CF(CF ₃)CF ₂ O[CF(CF ₃)CON(H)(CH ₂) ₂ N [⊕] (CH ₃) ₂ CH ₂ CO ₂ [⊖]	0.1 1.0	45 2
24.....	C ₇ F ₁₅ CON(H)(CH ₂) ₂ N [⊕] (CH ₃) ₂ (CH ₂) ₂ CO ₂ [⊖]	1.0	(¹)

¹ Does not spread.

same reduction of surface tension is evident. Example 19 is comparative using the closest known prior art compound. In Table III R₁=CF₃—CF₂—CF₂—.

I claim:

1. A composition of matter having the chemical formula

TABLE III

Example	Compound	Medium	Compound concentration (g./100 ml.)				
			Surface tension (dynes/cm.) at 25° C.				
			0	0.001	0.01	0.1	1.0
14.....	R ₁ O[CF(CF ₃)CF ₂ O[CF(CF ₃)CON(H)(CH ₂) ₂ N [⊕] (CH ₃) ₂ CH ₂ CO ₂ [⊖]	Water	71.9	15.3	14.7	14.4	-----
15.....	R ₁ O[CF(CF ₃)CF ₂ O[CF(CF ₃)CON(H)(CH ₂) ₂ N [⊕] (C ₆ H ₅) ₂ (CH ₂) ₂ CO ₂ [⊖]	do	-----	15.4	14.9	14.8	-----
16.....	R ₁ O[CF(CF ₃)CF ₂ O[CF(CF ₃)CON(H)(CH ₂) ₂ N [⊕] (CH ₃) ₂ CH ₂ CO ₂ [⊖]	do	-----	20.1	-----	-----	-----
17.....	R ₁ O[CF(CF ₃)CF ₂ O[CF(CF ₃)CON(H)(CH ₂) ₂ N [⊕] (CH ₃) ₂ CH ₂ CO ₂ [⊖]	do	-----	18.7	14.8	14.3	-----
		5% HCl	72.0	17.2	14.3	14.1	-----
		5% NaOH	75.4	17.4	14.5	14.4	-----
18.....	R ₁ O[CF(CF ₃)CF ₂ O[CF(CF ₃)CONH(CH ₂) ₂ N [⊕] (CH ₃) ₂ (CH ₂) ₂ SO ₃ [⊖]	Water	71.9	20.1	17.0	16.2	15.5
		5% HCl	72.0	22.1	18.4	17.5	16.2
		5% NaOH	75.4	20.4	17.2	16.4	15.7
19.....	C ₇ F ₁₅ CON(H)(CH ₂) ₂ N [⊕] (CH ₃) ₂ (CH ₂) ₂ CO ₂ [⊖]	Water	71.9	43.2	28.0	20.0	14.4
		5% HCl	72.0	45.7	31.0	23.4	15.1
		5% NaOH	75.4	43.0	27.9	20.0	14.6

Example 20

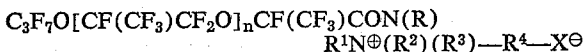
The utility of the compounds of the present invention as foaming agents and as foam stabilizers is illustrated in this example. The test was conducted by placing 50 ml. of a 1% aqueous solution of the compound in a 1000 ml. Erlenmeyer flask, stoppering the flask and then shaking the flask vigorously for 10 seconds. The volume of the foam produced, the nature of the foam, and the stability of the foam were observed. Tests with a 1% solution of the compound of Example 1 gave a foam volume of 400 ml. which was thick and uniform and was stable for hours.

Example 21

Using the procedure of Example 20 and the prior art compound of Example 19 a 1% aqueous solution of the compound gave a foam volume of 800 ml. but the foam was non-uniform with very large bubbles and was unstable.

Examples 22-24

The utility of the compounds of the present invention as aqueous film spreading agents is illustrated in this ex-



wherein

- n* is an integer of 0 to 8,
R is hydrogen or alkyl of 1 to 6 carbon atoms,
*R*¹ is alkylene of 1 to 12 carbon atoms,
*R*² is alkyl of 1 to 6 carbon atoms,
*R*³ is alkyl of 1 to 6 carbon atoms,
*R*⁴ is alkylene of 1 to 4 carbon atoms, and
X is CO₂ or SO₃.

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U.S. Cl. X.R.

26—501.13, 561 HL; 252—3, 8.05, 307, 311, Dig. 7