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(54) Title: FLUOROORGANIC COMPOUNDS AND ANTI-FOULING TREATMENTS

(57) Abstract: The production of fluoroorganic compounds in the form of amidoamines, quaternised compounds thereof, amides and ethers, guanidides, hydrazides, ureides, thioureides, perfluoropolyoxaalkylenesulfo- or perfluoropolyoxaalkylenecarboxylic acids and a biocidal antiseptic substance produced on the basis of this fluoroorganic compound and intended for coatings preventing from bio-fouling of various articles and constructions.

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"FLUOROORGANIC COMPOUNDS AND ANTI-FOULING TREATMENTS"

THE PRESENT INVENTION relates to the synthesis of fluoroorganic compounds and their use as biocidal antiseptic substances, an anti-fouling treatment for a surface, and a method of treating a surface. In particular the invention relates to a method of and a material for treating a surface which is to be used under water, such as, for example, the hull of a ship or boat.

More particularly, the invention relates, to a new method of producing derivatives of fluoroorganic compounds such as amidoamines, quaternised compounds thereof, amides, ethers, guanidides, hydrazides, ureides and thioureides, perfluoropolyoxaalkylenesulfo-or perfluoropolyoxaalkylenecarboxylic acid, as well as to their use as substances having biocidal antiseptic properties enabling their use as coatings or additives preventing bio-fouling of various articles and constructions in the process of their operation and storage.

The hull of a ship or boat, especially if used in a marine situation, may be subjected to fouling. Fouling is a gradual process in which various forms of marine life attach themselves to the hull of the boat. The marine life may take many forms and may be in the form of plants or may be in the form of live creatures, especially certain types of shell fish.

It has long been known that when the hull of a ship or boat is fouled with such marine life the power needed to drive the ship or boat through the water is increased, and the maximum speed of the ship or boat is reduced. Consequently it has been proposed to provide a treatment for a surface, such as a surface that forms the underwater part of the hull of a ship or boat, to provide that surface with anti-fouling properties.

Many treatments involve the use of a anti-fouling paint or similar material, and many anti-fouling paints that have been proposed before include an active ingredient which effectively poisons any life form that attempts to adhere itself to the hull. The poison, in some cases, is a tin based compound.

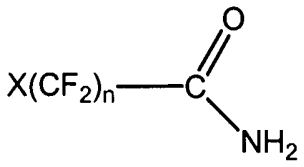
A difficulty with such prior proposed anti-fouling paint is that the poison may be released into the sea and may damage life forms other than life forms which are adhering themselves to the hull of the ship or boat. Thus paints of this type may damage the environment.

Thus there is a requirement for a treatment for a surface which is to be located under water, that provides the surface with an anti-fouling property, so that fouling of the surface is obviated, or at least minimised, but which does not harm the environment.

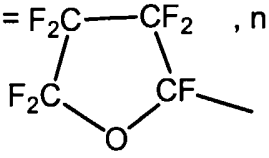
Many attempts have been made to isolate a material that can be used in the treatment of a surface to provide the surface with anti-fouling properties, with the material being non-toxic, or substantially non-toxic, so that the risk to marine life that is not specifically adhered to the surface is reduced to an absolute minimum.

It is widely known to use fluoroorganic compounds in different fields of industry where, for example, their surfactant properties are employed. ("Encyclopaedia of polymers", Moscow, 1972, vol.2, p.670).

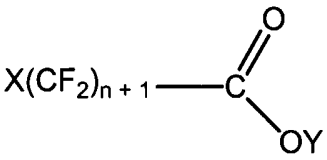
A method is known for producing amides of perfluorocarboxylic acids having the general formula:



where

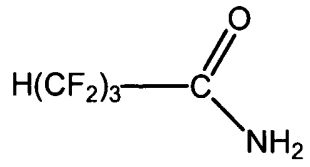
a) X = H, n = 3-5; b) X =  , n = 0 c) X = F, n = 5-7

according to which the mother compound of the general formula:



where Y is hydrogen or lower alkyl and the values of X, n are indicated above, is treated with sodium azide in proportion 1-1.5 - 2.25, respectively, in 10-25% oleum medium at a temperature of 70-100 °C with subsequent decomposition of the reaction mixture with ice.

This method allows the production of a number of amides of perfluorocarboxylic acids such as amides of ω-monohydroperfluorobutyric acid



amides of α-perflurofuranidinecarboxylic acid, and amides of perfluorocaprylic acid.

These compounds are generally used as parent substances in synthesis of various practically valuable fluoroorganic compounds - ligands forming volatile co-ordination compounds with metals, physiologically active preparations, lightfast dyes, monomers for thermally resistant polymers (SU 687064, 25.09.1979).

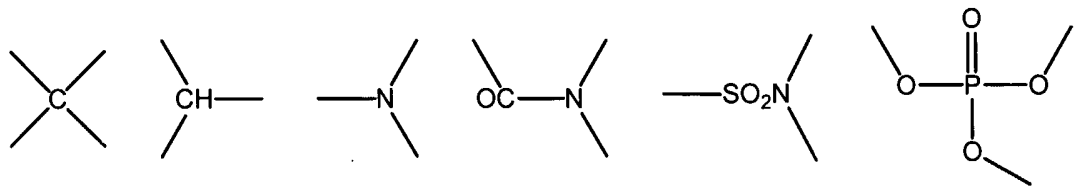
A method is known of producing fluoroorganic compounds corresponding to the general formula:

$$(R_F)_X - (A)_Y - (R_H)_Z,$$

wherein x means 1, 2 or 3;
y means 0 or 1;
z means 0, 1, 2 or 3.
On condition that y and z are not simultaneously 0, and when z=0, y=2 or 3,
R_F means fluorinated aliphatic or aromatic radical, saturated or unsaturated, having a linear, branched or cyclic chain, wherein this chain may contain functional groups and/or may be interrupted by bivalent atoms such as oxygen or sulphur; or by trivalent atoms such as nitrogen, and/or may be substituted with hydrogen atoms or halogen atoms with the proviso that the two atoms of the carbon skeleton do not have more than one of these substituents, other than fluorine.

R_H means aliphatic or aromatic, saturated or unsaturated, hydrocarbon radical having a linear, branched or cyclic chain, wherein this chain may contain functional groups and/or may be interrupted by one or more bivalent atoms such as oxygen or sulphur; or by one or more trivalent atoms such as nitrogen.

A means a bivalent, trivalent or quadrivalent radical such as



of the cyclic, aliphatic or aromatic structure or ethylene structure.

The term "contains functional groups" should be understood to equate to the substitution of the skeleton (by including at the ends or in side-chains) at least one organic functional group, such as alcohol, thiol, acid, carbonyl, sulfoxide, ester, amide, amine, phosphate, ethylene, acetylene and enamine or sulfonamide group.

By the expression "ethylene structure" is meant, for example:

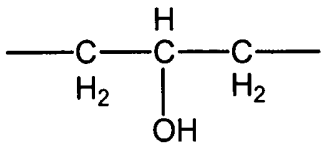
C=C , C=CH- or -CH=CH-

Preferably, R_H means a linear or branched alkyl radical with C_1-C_{22} or a mixture of linear and branched C_1-C_{22}-alkyl radicals; C_6-C_{10}-aryl radicals, or C_7-C_{15}-aralkyl radicals. Preferably, R_F means a perfluoroalkyl radical having 4-22 carbon atoms (RU 2130766, 27.05.1999).

Fluoroorganic compounds similar to the above fluorocarbons are known that are described in French patent application 91-15019, the general structure of which is defined by formula I

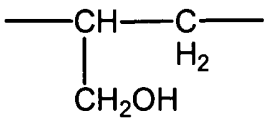
$$R_1 - (CH_2)_n - X - [C_3H_5(OH)] - (Y)_P - R_2 \quad (I)$$

wherein $C_3H_5(OH)$ group has the structure



(Ia)

or



(Ib)

R_1 is a perfluorinated C_4-C_{20}-alkyl radical or a mixture of perfluorated alkyl radicals C_4-C_{20}

R_2 is a linear or branched C_1-C_{22}-alkyl radical or a mixture of linear or branched C_1-C_{22}-alkyl or aryl, or aralkyl radical;

n means 0 - 4;

X means O, S-O or SO_2;

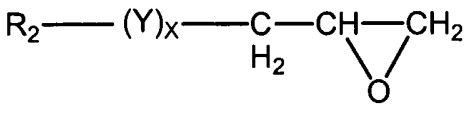
Y means O, S-O or SO_2;

with the proviso that when X= SO or SO_2, then Y is not SO or SO_2.

Compounds can be produced either by reaction of a fluorinated compound with acid hydrogen of formula IIa

$$R_1 - (CH_2)_n - X - H \quad (IIa)$$

with epoxide of formula IIb

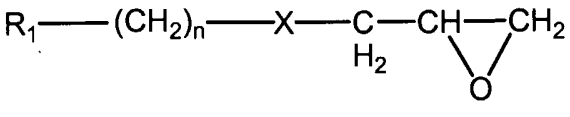


(IIb)

or by interacting a hydrocarbon compound with acid hydrogen of formula IV.

$$R_2 - (Y)_X - H \quad (IV)$$

with the fluorinated epoxide of formula V



(V)

wherein R_1, R_2, n and X have the above values;

X means oxygen or sulphur; Y means oxygen or sulphur;

in the presence of a base or acid compound acting as a reagent or catalyst; by means of possible oxidation of the mercaptan function to sulfoxide or sulfone using hydrogen peroxide and recuperation of the produced compound of formula I.

These compounds are described in PCT Application WO 93/11103 and in European Patent Application EP-A-166 696.

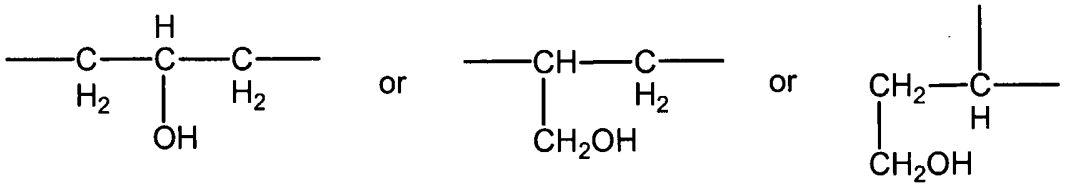
These compounds include, for example:

1-(2'-F-hexylethylthio)-3-(2''-ethylhexyloxy)-2-propanol;
1-(2'-F-octylethylthio)-3-(2''-ethylhexyloxy)-2-propanol;
1-(2'-F-octylethylthio)-3-butyloxy-2-propanol;
1-(2'-F-octylethylthio)-3-phenoxy-2-propanol;
1-(2'-F-hexylethylthio)-3-dodecyloxy-2-propanol;
1-(2'-F-fluoro-hexylethylthio)-2-decanol;
1-(2'-fluoro-hexylethylthio)-2-hexanol;
1-(2'-fluoro-octylethylthio)-2-hexanol;
1-(2'-fluoro-octylethylthio)-3-(2''-ethylhexyloxy)-2-propanol.

Fluoroorganic compounds of formula (1) are known

$R_F - (CH_2)_n - X - [C_3H_5(OH)] - Y - (CH_2)_m - R'_F$

wherein $C_3H_5(OH)$ signifies the structures:



R_F and R'_F are the same or different, mean perfluorinated, linear or branched, C_4-C_{20}-alkyl radical or a mixture of perfluorinated, linear or branched, C_4-C_{20}-alkyl radicals;

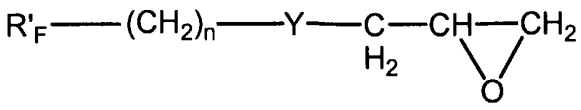
m and n are the same or different, mean 0, 1, 2, 3 or 4, and

X means oxygen and Y means sulphur; or X means sulphur and Y means oxygen.

The compounds of formula I can be produced by carrying out reaction of a fluorinated compound with acid hydrogen of the formula:

$$R_F - (CH_2)_n - X - H$$

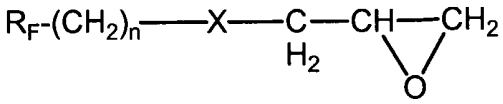
with the epoxide of the formula:



Or by carrying out interaction of a fluorinated compound with acid hydrogen of the formula:

$$R_F - (CH_2)_m - Y - H$$

with the fluorinated epoxide of the formula



in the presence of a base or acid compound acting as a reagent or catalyst (Patent FR 936605).

All these listed fluoroorganic compounds are used as emulsifiers in producing cosmetic compositions in the form of solid non-aqueous dispersions.

A method is known of producing fluoroorganic compounds - amides or ethers of perfluoropolyoxaalkylenesulfo acids or perfluoropolyoxaalkylenecarboxylic acids of the general formula:

$$R_F\ R'_F\ ZQ$$

wherein

$R_F = CF_3O^-$-, $C_2F_5O^-$-, $C_3F_7O^-$-, $C_8F_{17}O^-$-,

R'_F =

$$(-CFCF_2O^-)_nC_2F_4-$$
$$|$$
$$CF_3$$

$(-CF_2CF_2O^-)n\ C_qF_{2q}$-, where q=1, 2

$(-CF_2CF_2 - CF_2O^-)_n\ CF_2CF_2$-, where n=8-55

Z= -CO-, SO_2-;

$Q=N(C_mH_{2m}OH)_2$, where m=2,3,4,6,8,10.

$-N[(C_2H_4O)_4\ C_3H_6\ OH]_2$

$-HN-\ C_2H_4OR_H$, where $R_H=CH_3$-, C_2H_5-, C_3H_7-

$-HN-\ (C_2H_4O)_5\ H$,

$-OC_\eta H_{2\eta}N(C_\eta H_{2\eta}OH)_2$, where η=2, 4

$-OC_kH_{\ 2k+1}$, where k=6, 8, 10,

which are produced by condensing fluoroanhydrides of perfluoropolyoxaalkylenesulfo- or perfluoropolyoxaalkylenecarboxylic acids with primary, or secondary, or tertiary amines or alkanolamines, or higher fatty

alcohols in the presence of fluorides of alkaline or alkaline-earth elements, or aluminium fluoride, or metal carbonates or bicarbonates.

These fluorine-containing compounds amides or ethers of perfluoropolyoxaalkylenesulfo- or perfluoropolyoxaalkylenecarboxylic acids produced by the known method are used to make anti-wear additives for lubricants (RU 2061020).

The known method is not intended for producing such derivatives of fluoroorganic compounds as amidoamines, quaternised compounds thereof, guanidides, hydrazides, ureides and thioureides. Further, it does not allow the production of fluoroorganic compounds (different derivatives) having biocidal and antiseptic properties.

It is known to use for protecting from fouling, for example, concrete surfaces operated in an aqueous medium, dyes of complex composition, including a complex of toxic compounds: copper protoxide, zinc oxide, mercury and tin salts, etc.

The effect of preventing fouling is achieved due to metal ions which are toxic for hydrobionts entering laminar (near-wall) water layer due to ion diffusion from the dye film. Non-fouling of coatings depends on intensity of toxicant leaching from the lacquer/paint base and its concentration in the laminar water layer of the surfaces to be protected. Service life of such coatings is 3 years.

Enamel XB-5153 is known among coatings. Effect of its action is achieved due to copper ions toxic for hydrobionts entering the water laminar layer. Disadvantages of the known coating are an insignificant coating service life of 3 years and high material consumption.

In addition, making the coating is connected with significant expenditure of labour since it requires performing a large number of labour-extensive operations in order to clean the surface and deposit 6-8 layers of paint.

Further, performing the operations is only possible at a positive air temperature and with a completely dried surface. Lacquer/paint materials are explosive and fire-hazardous and toxic for humans, which causes harmful labour conditions during coating (L.Ya.Popilov "New materials for shipbuilding" Leningrad Sudostroyeniye, 1972, pp.323-352; A.M.Forst «Anti-fouling coatings having long service life», Leningrad, LDNTP, 1989, 20 p.).

It is known to use as reagents to control bio-fouling in technical water supply systems such compounds as styrylpyridone iodine-metals or styrylquinoline iodine-metals, or iodinemethylate-4-styrylpyridine, or iodinemethylate-4-n-dimethylaminostyrylpyridine, or iodinemethylate-4-styrylquinoline, or iodinemethylate-4-n-dimethylaminostyrylquinoline, which are introduced into water preferably in the amount of 0.02-0.2 g/l (SU 1638119, 30.03.1991).

These reagents are used generally for cleaning from biological fouling of constructions, pipelines and heat-exchangers of technical water supply systems by adding them to water, that is they do not form any coating on the surface of these articles, which restricts their field of application.

In particular, heterocyclic arsenic-fluoroorganic compounds are known, for example, 10-fluoro-5,10-dihydro-phenarsazine as a chemical reagent to control bio-fouling of water supply systems, which are also introduced into water in the amount of 1-30 mg/l.

This reagent is an effective biocide in respect to fouling organisms (blue-green, green algae, infusoria, rotifers), however, it is also introduced into water

(into the water supply system) and is not intended for coatings preventing bio-fouling, which also restricts its field of application (SU 686992, 25.09.1979).

Currently, various derivatives of polyhexamethyleneguanidine, in particular, polyhexamethyleneguanidine hydroxyethylidenbiphosphonate are widely used as reagents preventing bio-fouling (RU 2109847, RU 2100294).

This preparation is used in rather high concentrations - 10-20 mg/l, it has low toxicity, but also is basically used to protect water-circulation systems by introducing it also directly into water, which restricts its application as a biocide.

The technical object of the claimed invention is to produce different derivatives of fluoroorganic compounds having biocidal and antiseptic properties, which enables one to broaden their field of application.

The present inventors have also surprisingly discovered that a material initially contemplated as an additive to a lubricating oil or grease, forms an ideal material for use as an anti-fouling treatment.

According to one aspect of this invention there is provided an anti-fouling treatment for a surface, the treatment comprising at least one perfluoropolyoxalkylene-sulfo or perfluropolyoxlyalkylene-carboxylic acid having the general formula:

$$R_F R_F' ZQ,$$

where

R_F = CF_3O-, C_2F_5O-, C_3F_7O-, or $C_8F_{17}O$-,

R_F'=

$$-(CFCF_2O)_nCF-$$
$$\quad\;\; |\qquad\quad |$$
$$\quad CF_3 \qquad CF_3$$

$-(CF_2CF_2O)_nCF_2-$, or $-(CF_2CF_2CF_2O)_nCF_2CF_2-$,

where

$n = 8 - 55$;
$Z = CO-$, SO_2,
$Q = N(C_mH_{2m}OH)_2$, where $m = 2, 3, 4, 6, 8, 10$
$-N[C_2H_4O)_4C_3H_6OH]_2$,
$-NH-C_2H_4OR_n$, where $R_n = CH_3-$, C_2H_5-, or C_3H_7-,
$-NH(C_2H_4O)_5H$,
$-OC_LH_{2L}N(C_LH_{2L}OH)_2$, where $L = 1, 2, 4$ or
$C_kH_{2k+1}O-$, where $k = 6, 8, 10$.

According to another aspect of this invention there is provided an anti-fouling treatment for a surface, the treatment comprising a perfluoropolyoxaalkylene-sulfo or -carboxylic acid and/or a mixture with perfluoroxaalkylene-ketones with the general chemical formula

$R_fR_f'ZQ$ where

$R_f =$ 1) CF_3O;
2) C_2F_5O;
3) C_3F_7O; or
4) $C_8F_{17}O$

$R_f' =$ 1) $-(CF_2O)_n\,(CF_2O)_m\,(CFO)_k\,(CF_2)$, where the first (CF_2O) unit carries a branch $|$ CF_2 and the (CFO) unit carries a branch $|$ CF_3;
where
$n = 8 \ldots 50$
$m = 0 \ldots 10$
$k = 0 \ldots 1$

2) $-(CF_2O)_n\,(CF_2O)_m\,(CF_2)$, where
$n = 5 \ldots 200$
$m = O \ldots 30$

3) $-(CF_2CF_2CF_2O)n\ CF_2\ CF_2$, where
$n = 8 \ldots 50$

or

4) $-(CH_2CF_2CF_2O)n\ CH_2\ CF_2$, where n = 8 ... 40

Z = CO; or - SO_2
Q = OH; $-CF_3$; or - $CF(CF_3)_2$

Furthermore the present invention provides a new method of producing derivatives of fluoroorganic compounds according to which the compound of general formula I:

$$R_FR'_F\ QX\ (I),$$

where X=F or OCH_3
$R_F = C_nF_{2n+1}O-$, where n=1-8,
$R'_F = (ZCYCF_2O)_k\ (CF_2)_m-$, where k=5-200, m=1-2,
and Z = Y = F, or
Z = $-CF_3$, Y = F, or
Z = $-CF_2-$, $Y = F_2$,
Q = -CO- or $-SO_2-$
is mixed with the compound of formula II:

$$NH_2LNTR_H\ (II)$$

where T = H or R_H
L = $-(CH_2)_e-$, where e=1-5 at R_H = H, C_1-C_4-alkyl, $-CH_2C_6H_5$, $-C_6H_5$,
$-C_2H_4OH$, $-C_2H_4COOM$, $-CH_2COOM$, where M= Na, K, Ca,
L = $-(C_2H_4NH)_{1-3}$ at RH = H,

L = -C(=NH)- or –C(=O)- or –C(=S)- at R_H=H

or with the compound of formula (III):

$$NH_2NTR_H \quad (III),$$

where T= H or R_H, R_H=
H, $-CH_3$, Ph, $Ar(NO_2)_2$,

or with the iso-alcohols of formula IV:

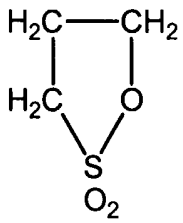
$$HOC_nH_{2n-1}(CH_3)_2 \quad (IV),$$

where n=1-6.

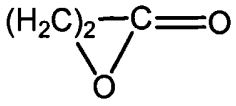
in the presence of acceptor HF released during the reaction process, in the case when X=F, at molar ratio of the reaction components compound of formula (I): compound of formula (II) or (III), or (IV): acceptor = 1: 1.1 : 0.001-0.0001 and temperature not higher than 60°C, with subsequent alkylation during heating in the presence of a solvent with the compound of general formula (V)

$$R'_H A \quad (V)$$

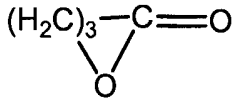
wherein
$R1_H$ = C_1-C_{10}-alkyl, $-CH_2CH_2OH$, $-CH_2COOM$, $-C_2H_4COOM$, $-CH_2C_6H_5$,
$-C_6H_5$ at M= Na, K, Ca;
A= F^-, Cl^-, Br^-, J^-;
or
propane sulfone



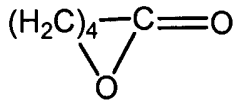
β-propiolactone



γ-butyrolactone



δ, γ-valerolactone



The claimed method according to the invention allows production of different derivatives of fluoroorganic compounds, such as amidoamines, quaternised compounds thereof, amides, ethers, guanidides, hydrazides, ureides and thioureides of perfloropolyoxaalkylenesulfo- or perfluoropolyoxaalkylenecarboxylic acids, which have biocidal antiseptic properties, which enables their use in producing coatings that prevent bio-fouling of different articles and constructions in the process of storing and operating them.

The above mentioned compounds prepared using the method of the present invention may be used in an anit-fouling treatment for a surface.

Preferably the treatment is in the form of a paint including at least one added solvent or thinner.

The invention also relates to a method of treating a surface, the method comprising painting or spraying on to the surface an anti-fouling treatment as described above.

Conveniently the surface is a surface which is to be exposed to water and which would be subject to fouling.

Preferably the surface is the hull of a ship or boat.

In order that the invention may be more readily understood, and so that further features thereof may be appreciated, the invention will now be described, by way of example.

The fluoroorganic derivative produced according to the method of the invention has biocidal antiseptic properties and is used as a biocidal substance for coatings that prevent bio-fouling of different articles and constructions. Thus, according to the invention the method of producing amidoamines, quaternised compounds thereof, amides and ethers, guanidines, hydrazides, ureides and thioureides consists in that the solution of fluoroanhydrides or the ester of perfluoropolyoxaalkylenesulfo- or perfluoropolyoxaalkylenecarboxylic acids of general formula I:

$$R_F R'_F QX \quad (I)$$

where X= F or OCH_3

$R_F = C_nF_{2n+1}O-$, where n= 1-8

$R'_F = (ZCYCF_2O)_k (CF_2)_m$, where k= 5-200, m= 1-2

and Z= Y= F, or

Z= $-CF_3$, Y= F, or

Z= $-CF_2$, Y= F_2

Q= -CO- or $-SO_2-$

is mixed with amines, di- and polyamines, guanidine, thio-or carbamide of general formula II:

$$NH_2LNTR_H, \text{ (II)},$$

where T= H or R_H

L= $-(CH_2)_e$, where e= 1-5, at R_H= H, C_1-C_4-alkyl, $-CH_2C_6H_5$, $-C_6H_5$, $-C_2H_4OH$, $-C_2H_4COOM$, $-CH_2COOM$

where M= Na, K, Ca;

L= $-(C_2H_4NH)_{1-3}$ at R_H= H

L = -C(=NH)- or –C(=O)- or –C(=S)- at R_H=H

or with the compounds of formula (III):

$$NH_2NTR_H \text{ (III)},$$

where

T= H or R_H

R_H = H, $-CH_3$, Ph, $Ar(NO_2)_2$

or with the iso-alcohols of formula (IV):

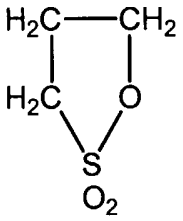
$$HOC_nH_{2n-1}(CH_3)_2 \text{ (IV)},$$

where n= 1-6.

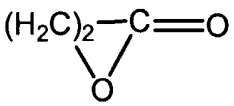
in the presence of acceptor HF released during the reaction process, in the case when X=F, at molar ratio of the reaction components of the compound of formula (I): compound of formula (II), or (III), or (IV):

acceptor = 1:1.1: 0.001-0.0001 and temperature not higher than 60° with subsequent alkylation during heating in the presence of a solvent with compound of general formula (V) R^1_H A, where R^1_H = C_1-C_{10} alkyl, -CH_2CH_2OH, -CH_2COOM,
-C_2H_4COOM, -$CH_2C_6H_5$, -C_6H_5
at M= Na, K, Ca
A= F^-, Cl^-, Br^-, J^-
or

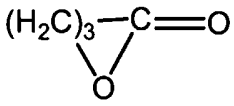
propane sulfone



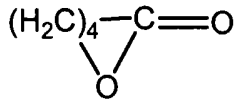
β-propiolactone



γ-butyrolactone



δ, γ-valerolactone



The temperature due to exothermic reaction of amino- and hydroxyl-containing components with fluoroanhydrides of perfluoro acids is maintained within the range of 40°C-60°C by the feed rate of one of the reaction components. Solvents in these reactions can be fluorine-containing substances having relatively low molecular weight and boiling point (trifluorotrichloroethane or coolant (khladon)-113, perfluoro- or polyfluoroalkanes with the number of atoms C_6-C_{10}, perfluorotriethyl-, tripropyl-, tributylamines, etc).

The reaction mixture, to make the reaction complete, is allowed to stand with stirring for 1-3 hours at temperatures of 60-130 °C followed by release of the target product. In order to provide a high degree of product purity, the method of fractional precipitation was often used. Thus, the reactions of fluoroanhydrides of perfluoropolyoxaalkylenesulfo- or perfluoropolyoxaalkylenecarboxylic acids with amine-containing substances run according to the following scheme:

$$R_FR'_FQF + NH_2LNT(R_H) \xrightarrow[\text{Solvent}]{N(C_2H_5)_3} \dashrightarrow R_FR'_FQNHL\text{-}NT(R_H) + (C_2H_5)_3N * (HF)_q$$

$$q = 1\text{-}100$$

and with iso-alcohols:

$$R_FR'_FQF + HO(CH2)_{1\text{-}3}\,CH(CH_3)_2 \xrightarrow[N(C_2H_5)_3]{\text{heat, solvent}}$$

$R_FR'_FQ\text{-}O(CH_2)_{1\text{-}3}\,CH(CH_3)_2 + (C_2H_5)_3\,N^*(HF)_q$

where q=1-100

All the above compounds contain various donor/acceptor groups, which allows them to be used as a material for producing monomolecular coatings of solid surfaces of metals, stones and polymer materials with the view of reducing their surface energy, imparting them with anti-adhesion, anti-friction and anti-corrosive properties with a low friction and wear co-efficient.

The above compounds were also produced through esters of perfluoropolyoxaalkylenecarboxylic acids. The latter were produced by etherification of perfluoropolyoxaalkylenecarboxylic acid with methyl or ethyl alcohol when boiling the acid and the corresponding alcohol in the presence of a water-depriving means. 98% H_2SO_4, H_3PO_4, P_2O_5, molten Na_2SO_4, $CaCl_2$, calcined ceolites, etc., were used as the water-depriving means. Ether yield reached 90%. Almost quantitative yield of esters of perfluoropolyoxaalkylenecarboxylic acids was attained using dimethyl- or diethylsulfates, here the reaction runs according to the scheme:

$$R_FCOOH + NaOH \longrightarrow R_FCOONa + H_2O$$

$$R_FCOONa + (CH_3)_2SO_4 \xrightarrow[20\text{-}60^\circ C,\ \text{solvent}]{} 2\ R_FC(=O)OCH_3 + Na_2SO_4$$

The molar ratio R_FCOOH, NaOH, $(CH_3)_2SO_4$ is strictly controlled as 1 : 1.05 : 1.

After filtration, the solvent is removed from the reaction mass and an ester of perfluoroacid is obtained as a residue.

This method appears the most preferable as the free perfluoroacids are produced by hydrolysis of fluoroanhydride and by binding fluoro-ion in complex $AlF_3*3HF*2H_2O$, which is insoluble in water and in organic solvents and, therefore, is easily separated by filtration. Hydrolysis occurs according to the scheme:

$$R_FCOF + 2AlF_3 + 4\ H_2O \xrightarrow{\text{solvent}} R_F\ COOH + AlF_3*3HF*3H_2O$$

A mixture of 2 moles AlF_3 and 4 moles H_2O is prepared, this mixture is added to 30% solution of R_FCOF in Khladon 113. Khladon 113 is a synonym or trade name for the solvent containing 1,1,2-trichlorotrifluoroethane having the CAS Registry index # 76-13-1. The mixture is stirred for 20 minutes, filtered, Khladon 113 solvent is distilled away from the filtrate. The residue is dried in vacuum, acid yield is 99.0-100%. The content of fluorion is ≤0.002%.

It has been experimentally established that with the content of F- ion > 0.05% in the acid and its derivatives, anti-friction, anti-corrosive, anti-wear, bactericidal, etc., effects are significaltly reduced.

Esters of perfluorooxaalkylenecarboxylic acids are mixed with amidoamines, polyamines, guanidine, hydrazines to form amide-derivatives of corresponding acids according to the scheme:

$$R_FR'_FQ\text{-}OCH_3 + NH_2LNTR_H \xrightarrow[\text{Solvent}]{\text{Heating}} R_FR'_FQ\ NHLNT(R_H) + CH_3OH$$

$NHLNTR_H$, where T= R_H or H.

The produced amido acid derivatives, amidoamines, guanidides, ureides and hydrazides, are alkylated with the compounds of structural formula:

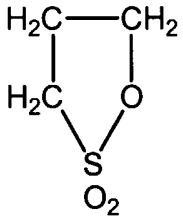
R'_HA, where R'_H = alkyls C_1-C_{10}, $-CH_2CH_2OH$, $-CH_2COOM$, $-C_2H_4COOM$, $-CH_2C_6H_5$, $-C_6H_5$

at M = Na, K, Ca

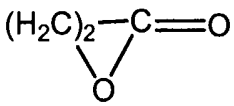
at A = F^-, Cl^-, Br^-, J^-;

or

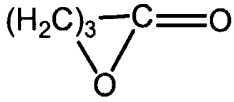
with propane sulfone



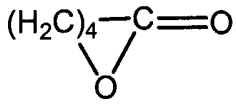
β-propiolactone



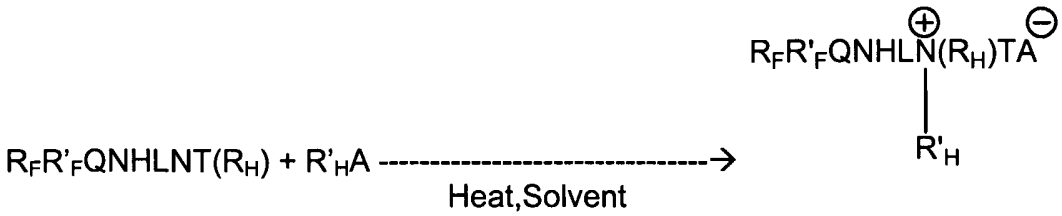
γ-butyrolactone



δ, γ-valerolactone



when heated in the solvent. The reaction runs according to the scheme:



T= H or R_H

wherein

R_F= C_nF_{2n+1} at n= 1-8

R'_F= $(Z\text{-}CY\text{-}CF_2O)_k(CF_2)_m$ at k= 5-200, m=1,2

and Z= Y= F or

Z= $-CF_2-$, $Y= F_2$,

Q= -CO-, $-SO_2-$

L= $-(CH_2)_e-$ at e= 1-5

R'_H = alkyls C_1-C_{10}, $-CH_2CH_2OH$, $-CH_2COOM$, $-C_2H_4COOM$, $-CH_2C_6H_5$, $-C_6H_5$

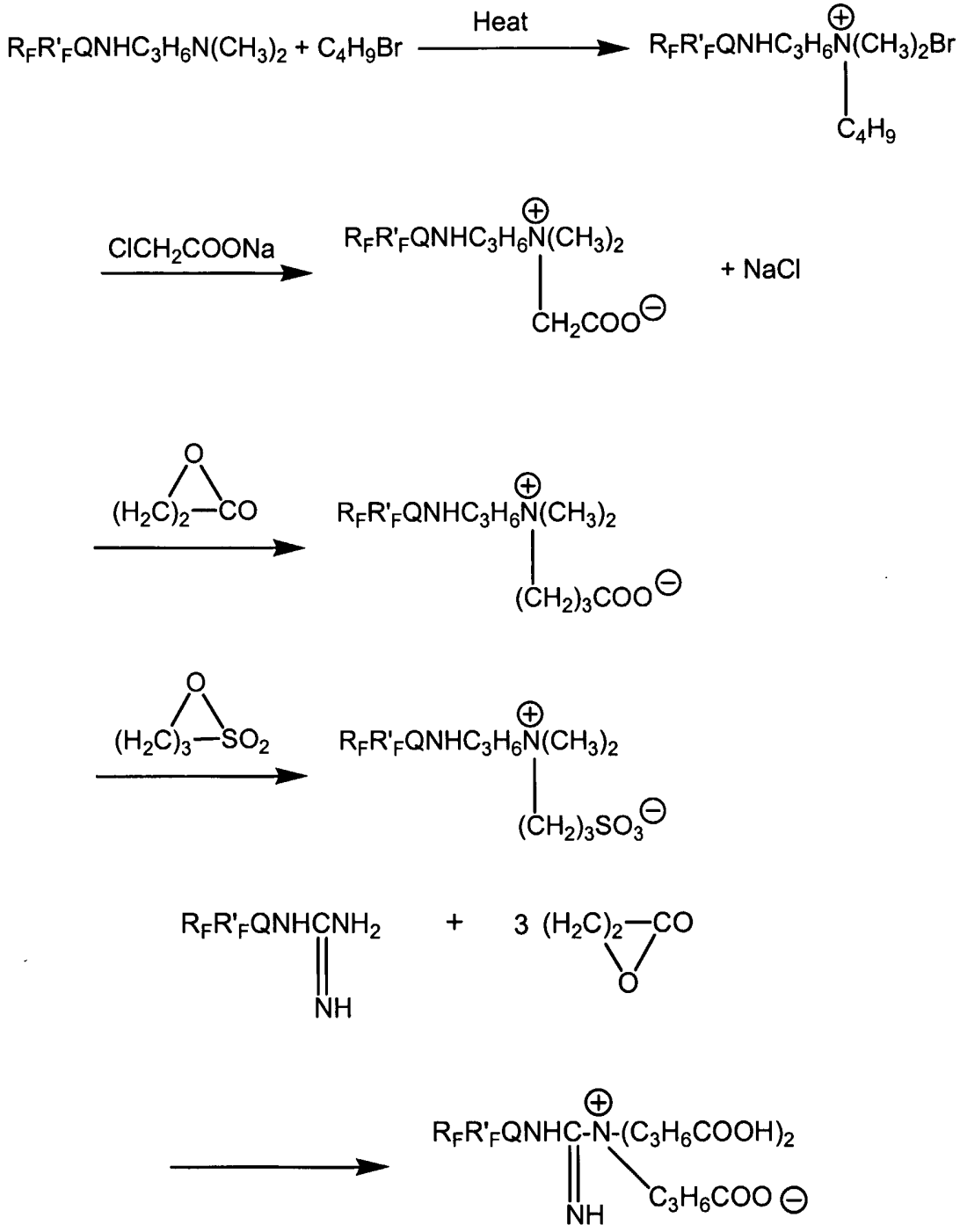
at M= Na, K, Ca

R'_H = alkyls C_1-C_{10}, $-CH_2CH_2OH$, $-CH_2C_6H_5$, $-C_6H_5$, $-CH_2COOM$, $-C_2H_4COOM$

and/or $-C_3H_6SO_3^-$, $-C_2H_4COO^-$, $-C_3H_6COO^-$, $-C_4H_8COO^-$, $-C_5H_{10}COO^-$.

at $A=F^-$, Cl^-, Br^-, J^-.

The reactions run according to the scheme:



Quaternised (quaternary) ammonium salts or betaines were produced with nearly quantitative yields. The solvent was distilled away from the reaction

mixture and the residue was dried in vacuum at 1-10 mm Hg for 1-3 hours during heating.

They have high antiseptic and biocidal properties, which enables their use as coatings from bio-fouling of hulls of sea and river vessels, hydro-constructions. Further, these coatings allow to reduction of aero-and hydraulic resistance due to high anti-adhesion properties of surfaces and imparting the latter with water- and oil-repellent properties. Some of biocidal properties are provided in the Table. Production of amides, amidoamines and ethers of perfluorooxaalkylene sulfo- or carboxylic acids is performed as follows. A reactor provided with a mixer, thermometer, jacket, reverse refrigerator and dosers of reaction components and solvents, was loaded with fluoroanhydride of perfluoropolyoxaalkylene sulfo- or carboxylic acid, solvent, acceptor HF (triethylamine) and during stirring from the doser amine-derivatives or alcohols were added in a suitable solvent (Khladon-113, perfluorine -diethyl- dipropyl-amines, fluoro-carbons, polyfluoro-carbons with C_6-C_{10} atoms) at such a rate as not to increase the temperature of the reaction mixture above 60°C. Or conversely, an amine derivative or alcohol in a solvent, with acceptor HF, was dosed with a solution of fluoroanhydride of perfluoropolyoxaalkylen sulfo- or carboxylic acid, the temperature of the reation mixture was kept <60°C. Further, the reaction mixture during stirring and at a temperature of 60-130 °C was allowed to stand for 0.5-2 hours, after which it was washed with 2-fold volume of water, the target product solution was separated, dried with ceolites, filtered and the target product was isolated by the method of fractional precipitation and cleaned on cationite and anionite sorbents. Whereupon the solvent was removed and the product was dried in vacuum at 1-10 mm Hg and 80°C during 0.5-3 hours. When using esters of perfluoropolyoxaalkylenecarboxylic acids in the same or similar reactor, an ester of perfluoro acid in a solvent was added to the amine derivatives and the reaction mixture was heated, allowed to stand during stirring for 0.5-2 hours at a temperature of 60-130°C, after which the target substance was isolated from

the reaction mixture by the method of fractional precipitation: 1 volume of the reaction mass was added with 0.2-0.4 volumes of the solvent, not dissolving the target substance but dissolving unreacted components and admixtures - acetone, heptane, sulphuric ether, etc.

The isolated target product was separated and dried in vacuum 1-10 mm Hg at a temperature of 60-80°C for 0.5-3 hours. The dried product is an amine derivative perfluoropolyoxaalkylene of carboxylic or sulfo-acid. A reactor similar to that described above was loaded with amide derivatives - amidoamine, or hydrazide, or ureide, or polyamidoamine, it was added with an alkylating agent (R'_HA) based on 5% of molar excess, and the mixture during stirring was heated and allowed to stand at a temperature of 90-130°C for 1-3 hours, after which the excess of the alkylating agent was removed in vacuum <10 mm Hg at a higher temperature that alkylation during 0.5-2 hours. At a temperature not lower 80°C, ammonium salts or betaines or sulfobetaines were discharged from the reactor. Examples illustrate the aforecited.

Example 1

Suspension 1.2 g (0.02 mole) of urea $NH_2C(NH_2)=O$

in 20 g of perfluorotripropylamine, at stirring and temperature of 15°C, was added to 40 g (0.015 mole) of fluoroanhydride of perfluoropolyoxapropylenecarboxylic acid

$[C_3F_7O(C\{CF_3\}FCF_2O)_{12}C\{CF_3\}FCOF]$

in 80 g of perflorotripropylamine and 0.2 g (0.0022 mole) triethylamine $[N(C_2H_5)_3]$. the mixture was boiled with a reverse refrigerator at 130°C and with stirring for 1.5 hours, after which it eas cooled (here the suspension was absent). The mixture was washed twice by 60 ml of distilled water and ureid of

perfluoropolyoxapropylenecarboxylic acid was put down from the reaction mass solution. To this end, 45 ml of ethyl alcohol was added to the reaction mass solution, the mixture was vigorously agitated for 20 minutes and allowed to stand for 1 hour. The lower layer, ureide, was separated and dried at 10 mm Hg at the temperature of 80°C for 3 hours.

Yield was 38.1 g (91%). Congelation temperature was -18°C, F=0.002 wt.%.

IR-spectrum (CaF_2), v, cm^{-1}: 1735 (-C=O). 1620 (-C=O)
I I
NH- NH_2

Spectrum NMR F^{19} in CCl_3F, δ, m.d. : 81.5 $-CF_3-$, 130 $-CF_2-$, 82.4 $-CF_2O-$, 141.0 -OCF-, 131.0 -OCF-C=O
I I
N-

Example 2

50 g (0.027 mole) of methihydazide of perfluoropolyoxaethylenecarboxylic acid was added to 3.96 g (0.055 mole) propiolactone and 60 g dihydroperfluorononane, the mixture was heated to 100°C and allowed to stand with stirring for 2 hours. After cooling, 20 ml heptane was added to the reaction mass, the mixture was mixed for 20 minutes and allowed to stand for 40-60 minutes. The lower layer was separated and dried in vacuum at 1 mm Hg and temperature of 60° for 3 hours. Yield was 43.2 g (80%).

IR-spectrum (CaF_2), v, cm^{-1} : 1950 and 2550 (-$\overset{+}{N}$-), 1740 (-C=O)
I I
OH

Found %: C23.10, F 59.20, N 1.38, H 0.40

$C_{39}F_{63}O_{17}N_2H_4[C_8F_{17}O(CF_2CF_2O)_{11}CF_2CONHN\text{-}C_2H_4COOH]$
$C_2H_4COO\text{-}$

Calculated%: C 23.70, F 60.6, O 13.80, N 1.40, H 0.45
Molecular weight of the product was 1970.

Example 3

2000 g (0.972 mole) of perfluoropolyoxapropylenecarboxylic acid $(CF_3O(CFCF_2O)_{11}C_2F_4COOH$ in 2500 g of Khladon-113 at 20°C and with
CF_3
stirring was added to solution of 40 g NaOH in 60 ml H_2O. The temperature of mixture was 35°C, pH = 8.

126 g (1 mole) of dimethylsulfate $(CH_3)_2SO_4$ was dropped to the salts during 30 minutes. The temperature of the reaction mixture was raised to 45°C. 2g more of NaOH were added to 5 ml H2O and the mixture was heated to 60°C and allowed to stand during stirring for 1 hour. 900 ml of hexane were added to the reaction mass, the mixture was mixed for 20 minutes and allowed to settle. The exfoliated heavy residue of methyl ether of perfluoropolyoxapropylenecarboxylic acid was separated and dried in vacuum at 10 mm Hg at 80°C for 2 hours.

Yield was 1990 g (98.9%)
1150 and 1760 (-C=O)
OR_H

Example 4

52 g (0.015 mole) of methyl ether of perfluoropolyoxapropylenecarboxylic acid

$$CF_3O(\underset{\displaystyle CF_3}{\underset{|}{C}}FCF_2O)_{19}\,\underset{\displaystyle CF_3}{\underset{|}{C}}FCOOCH_3$$

at 20°C and stirring is added to 1.74 g dimethylpropanediamine in 40 g of perfluorotriethylamine at a rate such that the temperature of the reaction mass does nor exceed 60°C. The reaction mixture is allowed to stand at this temperature for 0.5 hour. After that, the reaction mixture, with stirring and heating to 95-100°C, is allowed to stand for 1 hour followed by cooling at the room temperature. The mixture is washed with two portions by 100 ml water, cleaned on cationite and anionite columns, dried with molten Na_2SO_4, filtered, the solvent is distilled away and the residue is dried in vacuum at 1 mm Hg and temperature 60°C for 1 hour. Yield of acid amidoamine is 50.9 g (96%). Congelation temperature is –30°C. F^- content is 0.0009 wt.%. IR-spectrum (CaF_2), v, cm^{-1} : 1730 (-CO-N=), 1350 ($-N(CH_3)_2$). Spectrum NMR F^{19} in CCl3F, δ, m.d. : 56.0 CF_3O-, 81.3 $-CF_3$, 81.2 $-CF_2$, 141 –OCF-, 131.5 –OCF-CO-.

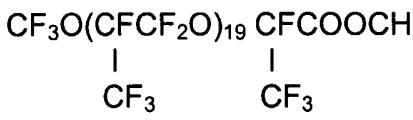
Found: C23.2; F 64.3; H 04.; N 0.75.

$$C_{66}F_{121}H_{13}N_2O_{21}(CF_3O(\underset{\displaystyle CF_3}{\underset{|}{C}}FCF_2O)_{19}CF\underset{\displaystyle CF_3}{\underset{|}{C}}ONHC_3H_6\underset{\displaystyle CH_3}{\underset{|}{N}}\text{-}CH_3)$$

Calculated: C 22.80; F 66.20; H 0.37; N 0.80. Molecular weight of the product is 3460.

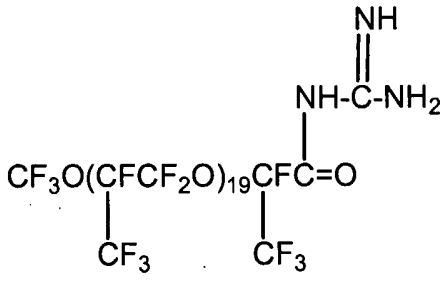
Example 5

1.18 g (0.02 mole) of guanidine in 30 ml of absolute ethanol was added to 33 g (0.0095 mole) of a solution of methyl ether of perfluoropolyoxapropylenecarboxylic acid



in 50 g Khladon-113 for 0.5 hour.

The reaction temperature rises from 20 to 45°C. The reaction mixture is boiled at the temperature of 55°C and stirred for 1 hour, after which the reaction mass is thrice washed with distilled water by 60 ml and cleaned on cationite and anionite columns. The target product solution in Khladon-113 is dried with molten Na_2SO_4, filtered and Khladon is distilled away at the atmospheric pressure and then in vacuum at 10 mm Hg, temperature 60°C, for 2.5 hours. Guanidide of perfluoropolyoxapropylenecarboxylic acid is produced.



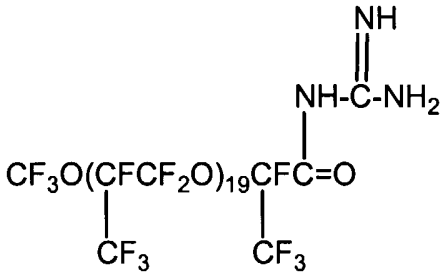
Yield is 28.2 g (84.8%), congelation temperature is –31°C.

IR-spectrum (CaF_2), v, cm^{-1} ; 1715 (-CO-N=), 1690 (-C-), 1650 (C-NH_2)
NH

Spectrum NMR F^{19} in CCL3F, δ, m.d. : 132.5 –OCF-CO-
I

Found %: C20, F 59.1; N 1.2; H 0.15

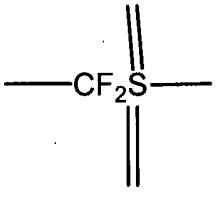
$C_{62}F_{121}O_{21}H_4N_3$



Calculated: C 19.8; F 61.2; N 1.1; H 0.1.
Molecular weight of the product is 3740.

Example 6

At 20°C a solution 45 g (0.016 mole) of perfluoropolyoxaethylenesulfofluoride $CF_3O(CF_2CF_2O)_{22}CF_2CF_2SO_2F$ in 150 g perfluorotriethylamine was added to 2.6 g (0.025 mole) of diethanolamine and 0.2 g triethylamine. The mixture was boiled with a reverse refrigerator with stirring at 70°C for 1.5 hours, after which it was cooled and twice washed with distilled water by 200 ml. The solution was dried with molten Na_2SO_4 and filtered. 46.5 ml acetone (mark KhCh) were added to the filtrate, stirred for 20 minutes, after which the mixture was allowed to settle for 40 min. The mixture peeled, the lower layer, the target product was diethanolamide of perfluoropolyoxaethylensulfonic acid. It was dried in vacuum at 5 mm Hg and the temperature of 80°C for 2 hours. Yield was 30.5 g (65.7%). F^- content was 0.0009 wt.%. IR-spectrum (CaF_2), v, cm^{-1} : 1410 (-SO_2N=), 3320 (-OH). Spectrum NMR F^{19} in CCl_3F, 5, m.d. : 87.9 –CF_3, 89.0 –CF_2O-, 91.0 –OCF_2-,



118.1

Found, %: C 21.8, H 0.35, F 59.6, S 1.1, N 0.43.

Calculated, %: C 21.0, H 0.34, F 62.1, S 1.1, N 0.48.
Molecular weight of the product was 2890.

Example 7

3.1 g (0.03 mole) diethylenetriamine in 30 g Khladon-113 at the temperature of 18°C and with vigorous stirring were added for 20 min to 32 g (0.015 mole) of ethyl alcohol of perfluoropolyoxapropylenecarboxylic acid $C_2F5O(CF_2CF_2CF_2O)_{11}CF_2CF_2COOC_2H_5$ in 50 g Khladon-113. The reaction mixture temperature did not exceed 55°C. The mixture was boiled with stirring for 1 hour, after which it was cooled and washed twice by 100 ml of distilled water. The reaction mixture was dried with molten Na_2SO_4 and cleaned with ion-exchange resin (cationite and anionite) and filtered.

Khladon-113 was distilled from the filtrate and the residue was dried in vacuum at 1 mm Hg and the temperature of 60°C for1 hour. Yield of diethyleneaminoamine of perfluoropolyoxapropylenecarboxylic acid was 26.8 g (81.5%), F^- content was 0.0002 wt.%. IR-spectrum (CaF_2), v, cm^{-1} : 1705 (-C(NH)=O)
1680 ($-CH_2-NH_2$), 1530 and 3400 ($-CH_2NHCH_2-$)

Spectrum NMR F^{19} in CCl3F, δ, m.d. : 85.5 CF_3-, 89.5 $-CF_2O-$, 83.0 $-OCF_2$, 130.7 $-CF_2$, 81.9 $-CF_2O$, 82.3 $-OCF_2-$, 118.9 $-CF_2C=O$
|
NH-

Found, %: 23.60, F 62.10, N 1.77, H 0.47

$C_{42}F_{75}O_{13}N_3H_{12}$

$C_2F_5O(CF_2CF_2CF_2O)_{11}CF_2CF_2C=O$

$NHC_2H_4NHC_2H_4NH_2$

Calculated %: C 23.0, F 65.0, N 1.9, H 0.5. Molecular weight of the product was 2190.

Example 8

50 g (0.027 mole) ethyl alcohol of perfluoropolyoxaethylenecarboxylic acid $C_8F_{17}O(CF_2CF_2O)_{11}CF_2COOC_2H_5$ in 100 g Khladon-113 were dropped with 1.12 g methylhydrazine in 5 ml of ethyl alcohol. The mixture was boiled with stirring for 1 hour, after which the reaction mixture was twice washed with by 50 ml of distilled water, dried with molten Na_2SO_4 and filtered. Methylhydrazoamide of perflouropolyoxaethylenecarboxylic acid was isolated from the filtrate by the putting down method, to which end 50 ml heptane was added to the Khladon solution, the mixture was stirred and allowed to settle for 60 min. The lower peeled-off layer of amide was separated, the solvent was distilled away and the residue was dried in vacuum at 1 mm Hg at 70°C for 2 hours. Yield of methylhydrazide perfluoropolyoxaethylenecarboxylic acid was 42.1 g (84.2%), congelation temperature was –37°C, F^- content was <0.0001 wt.%, IR-spectrum (CaF^2), v, cm^{-1} ; 1715 $\begin{matrix}(\text{-C=O})\\ \text{NH-}\end{matrix}$, 1350 and 3700 (-NHR).

Spectrum NMR F^{19} in CCl3F, δ, m.d. : 81.0 $-CF_3$, 126.9 $-CF_2$-, 122.8 $-CF_2$, 123.8 $-CF_2$-, 122.3 $-CF_2$-, 124.5 $-CF_2$-, 130.0 $-CF_2$-, 82.1 $-CF_2O$, 91.0 – OCF_2-, 80.6 $-CF_2$-C=O

Found %: C 21.0, H 0.24, F 64.10, N 1.53

$C_{33}F_{63}O_{13}N_2H_5$

$C_8F_{17}O(CF_2CF_2O)_{11}CF_2C(=O)NHNHCH_3$

Calculated %: C 21.60, H 0.27, F 65.26, N 1.52

Molecular weight of the product was 1825.

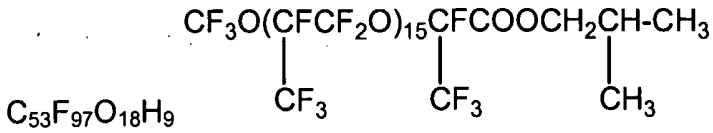
Hydrazide-, phenylhydrazide-, dinitrophenylhydrazides of perfluoropolyoxaethylenecarboxylic acid were obtained and characterised similar to Example 8 with yields from 55.0 to 91.0%.

Example 9

40 g (0.0147 mole) fluoroanhydride of perfluoropolyoxapropylenecarboxylic acid $CF_3O(CFCF_2O)_{15}CFCOF$ (CF_3 / CF_3)

in 60 g Khladon-113 were mixed at 20°C with 5.5 g (0.07 mole) of isobutyl alcohol, 0.1 g triethylamine and 60 g Khladon-113. The mixture was boiled with stirring and heating to 50 °C for 1.5 hours, cooled and ester of perfluoro acid was put down from the Khladon solution by adding to it 15 ml sulphuric ether. The ester of perfluoropolyoxapropylenecarboxylic acid was separated and dissolved in 60g of fresh Khladon-113 and the ether was again put down 15 ml sulphuric acid. From the peeled-off ester, the solvent (Khladon-113) was removed and the residue was dried in vacuum (1mm Hg) at the temperature of 60°C for 2.5 hours. Ether yield was 28.5 g (69.8%), F'' content was 0.0002 wt.%. IR-spectrum (CaF_2), v, cm^{-1} : 1785 (-C=O)O—.

Found %: C 22.4, F 65.6, H 0.30.



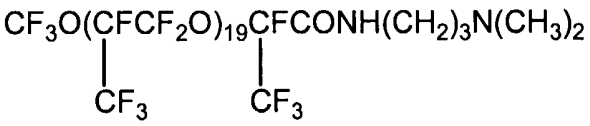
$C_{53}F_{97}O_{18}H_9$

Calculated %: C 22.9, F 66.4, O 10.4, H 0.32.

Molecular weight of the product is 2770.

Example 10

30 g (0.0086 mole) of N,N-dimethylpropameamise perfluoropolyoxapropylenecarboxylic acid (obtained in experiment 2)



were mixed with stirring at 20°C with 2.4 g (0.0175 mole) bromobutane and 50 g perfluorotriethylamine. The mixture was boiled (t_{boil} = 70°C) with stirring for 3 hours and the solvent was distilled away. The residue at 70°C was vacuumed for 2 hours at the pressure of 1 mm Hg.

Yield was 31.17 g (99.7%).

IR-spectrum (CaF_2), ν, cm^{-1} : 1720 (-C=O), 1680 and 1960 (-N-)av.

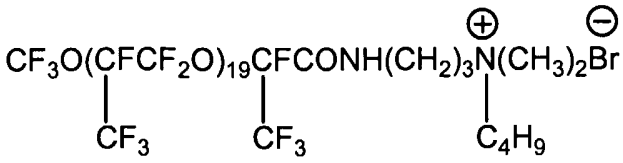
I

N=

Found %: C 23.00, F 62.30, H 0.62, N 0.80, Br 2.15

(potentiometric argentometry)

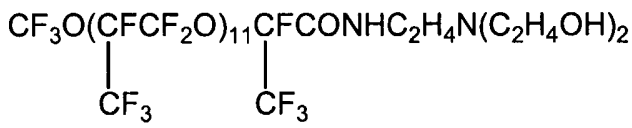
$C_{70}F_{12}H_{22}O_{21}N_2Br$



Calculated %: C 23.30, F 63.70, H 0.60, N 0.77, O 9.30, Br 2.20.
Molecular weight was 3600.

Example 11

55 g (0.025 mole) of N,N-diethylolathaneamide of perfluoropolyoxapropylenecarboxylic acid



were mixed with 3 g (0.0257 mole) of sodium salt of monochloroacetic acid $ClCH_2COONa$, 50 g absolute alcohol and 100 g perfluorotriethylamine. The mixture was boiled with stirring at 70°C for 1 hour, then perfluorotriethylamine was distilled away for 1 hour and the reaction mass was stirred and heated for 2 more hours at 78°C. Alcohol was distilled away and the residue was dried for 1 hour at 1 mm Hg. After cooling, the reaction mass was dissolved in 100 g Khladon-113, filtered away from NaCl, Khladon was removed and the residue vacuumed for 0.5 hour at 10 mm Hg and the temperature of 50°C.

Yield of N,N-diethylol N-acetylethaneamide of perfluoropolyoxapropylenecarboxylic acid was 55.1 g (97.5%).

IR-spectrum (CaF_2), v, cm^{-1} : 1710 (-C=O), 3400 (-OH)wid.
|
N=

1440 and 1580 $(-N^{+}-)$ with CH_2COO^- on the N

Found %: C 23.80, F 60.70, N 1.22, H 0.69.

$C_{45}F_{73}O_{17}H_{17}N_2$

$CF_3O(CF(CF_3)CF_2O)_{11}CF(CF_3)CONHC_2H_4\overset{\oplus}{N}(CH_2COO^{\ominus})(C_2H_4OH)_2$

Calculated %: C 24.00, F 61.80, N 1.25, H 0.75, O 12.10.
Molecular weight of the product was 2250.

<u>Example 12</u>

A slow ammonia current (~ 30 cm^3/min) was passed through a mixture 40 g (0.0189 mole) of methyl ether of perfluoropolyoxapropylenecarboxylic acid $C_2F_5O(CF_2CF_2CF_2O)_{11}CF_2CF_2COOCH_3$ in 50 g Khladon-113 at the temperature of 0oC and with stirring for 1 hour (0.08 mole). Temperature was raised to 20°C. Khladon-113 was distilled away from the reaction mixture and the residue was vacuumed for 30 min at 20 mm Hg on a water jet pump. 39.6 g (99.7%) amide of perfluoropolyoxapropylenecarboxylic acid was produced.

IR-spectrum of amide (CaF_2), v, cm^{-1} : 1700 (-C=O) with NH_2 on the C

3450 ($-CO-NH_2$)av.

60 g perfluorotriethylamine were added to 39.6 g amide of perfluoropolyoxapropylenecarboxylic acid. The reaction mixture was cooled to

5°C and dry HCl was passed through the solution at the rate of –20 cm^3/min with continuous cooling and stirring for 1 hour. Then temperature was raised to 50°C and dry HCl was passed through the reaction mixture at a rate of -8-10 cm^3/min for 3 hours. The reaction mixture, after cooling, was thrice washed with portions by 60 ml of 5% sodium bicarbonate solution (Na HCO_3) and perluorotriethylamine was distilled away from the residue. Yield was 29.0 g (71.6%).

IR-spectrum (CaF_2), v, cm^{-1}: 1710 (-C=O), 3200 (-C=O)
| |
N= NH-

Molecular weight of the product:

$C_2F_5O(CF_2CF_2CF_2O)_{11}CF_2CF_2C(=O)NHCH_2Cl$

according to experiment – 2145;
calculated – 2153.

Example 13

A mixture 29 g (0.013 mole) of chloromethyleneamide of perfluoropolyoxapropylenecarboxylic acid and 4.0 g (0.039 mole) triethylamine ($N(C_2H_5)_3$) and 50 g perfluorotripropyleamine with stirring were heated to 130°C for 1 hour and allowed to stand for 1 hour at this temperature and with stirring. In cooling, the reaction mixture laminated. The lower layer was the quaternised target product and the upper layer was the solvent. The solvent was separated and the residue was washed twice with 30 ml of sulphuric ether. The washed product was chloride of ammonium salt of N,N,N-triethylmethyleneamide perfluoropolyoxaprppylenecarboxylic acid

$C_2F_5O(CF_2CF_2CF_2O)_{11}CF_2CF_2CONHCH_2N^+(C_2H_5)_3Cl^-$

Yield was 25 g (81.6%)

Solubility in water was complete.

IR-spectrum (CaF_2), v, cm^{-1} : 1710 (-C=O)
+ |
N=

1650 and 1990 ($-N^+=$ av.)

2500 and 3600 (-N= wk.)

Spectrum NMR F^{19} in CC_3F, δ, m.d. : 88.6 $-CF_3$, 89.5 $-CF_2O$, 83.0 $-OCF_2-$, 130.6 $-CF_2$, 82.5 $-OCF_2-$, 80.8 $-CF_2-C=O$
|
N=

Found %: C 23.5, F 61.8, O 9.20, N 1.20, H 0.75, Cl 1.60.

$C_{45}F_{75}H_{18}O_{13}N_2Cl$

$C_2F_5O(CF_2CF_2CF_2O)_{11}CF_2CF_2C=O$
|
$NHCH_2\overset{\oplus}{N}(C_2H_5)_3\overset{\ominus}{Cl}$

Calculated %: C 23.90, F 63.20, O 9.20, N 1.24, H 0.80, Cl 1.57.

Molecular weight of the product:

according to experiment 2242;

calculated 2254.5.

Example 14

40 g (0.0117 mole) methyl ether of perfluoropolyoxapropylenecarboxylic acid

$$CF_3O(\underset{\displaystyle CF_3}{\underset{|}{C}}FCF_2O)_{19}\underset{\displaystyle CF_3}{\underset{/}{C}}FCON(C_2H_4OH)_2$$

1.9 g (0.018 mole) diethanolamine $NH(C_2H_4OH)_2$ and 60 g Khladon-113 were mixed at 20°C, boiled with stirring for 4 hours, after which Khladon was distilled away.

"Raw" amide was washed twice with 50 ml of sulphuric ether and every time separated. The residue was dried in vacuum at 10 mm Hg for 1 hour. Yield was 38.2 g (93.5%), congelation temperature was –40°C.

IR-spectrum (CaF_2), v, cm^{-2} : 1730 (-$\underset{\displaystyle N=}{\underset{|}{C}}$=O),

3360 (-OH)

Spectrum NMR F^{19} in CCl_3F, 5 m.d. : 56.0 CF_3O, 81.2 –CF_3, 82.0 –OCF_2-, 141.0 OCF-, 130.2 -$\underset{\displaystyle N(C_2H_4OH)_2}{\underset{|}{C}}FCO$

Found %: C 22.0, F 65.3, H 0.32, N 0.38.

$C_{65}F_{121}O_{23}NH_{10}$

$$CF_3O(\underset{\displaystyle CF_3}{\underset{|}{C}}FCF_2O)_{19}\underset{\displaystyle CF_3}{\underset{/}{C}}FCON(C_2H_4OH)_2$$

Calculated %: C 22.4, F 66.2, H 0.29, N 0.40.

Molecular weight:

according to experiment 3480,
calculated 3471.

The presence on one square metre of the vessel hull of 10-11 barnacles begins to tell on the fuel consumption and leads to over-consumption of fuel that is needed to maintain the speed taken by the vessel, and as their colony grows, it becomes excessively large. It is known that the speed and fuel consumption depend on the vessel head resistance and friction resistance of the hull against water medium. Head resistance, fundamentally, is a constant value, whereas friction resistance against water is 60-80% for vessels with the speed of up to 15 knots and 25-40% for high-speed vessels and depends on roughness of the vessel [1]. Increase in roughness of the vessel hull is primarily associated with fouling by barnacles and other aqueous microorganisms. The size of a barnacle is 2 to15 mm, while increase in roughness by 10 μm results in friction increase by 1% and raises fuel consumption by 0.1%.

As discussed above, protection from bio-fouling is currently carried out by introducing into lacquer/paint coatings biocydes, components that, being soluble in water, are capable of exerting a biocidal, i.e. toxic effect on aqueous microorganisms in the near-surface layer of water. In order for this effect to be efficient and prolonged, biocides should be introduced in the coatings in excessively large amounts. Basic biocides include copper protoxide, zinc oxide and, up to date, tin-organic compounds. However, tin-organic biocides have prove to be extremely environmentally "dirty", they are capable of accumulating in bed deposits of port basins [2]. At the present, environmentalists are also concerned over copper-containing biocides due to their active absorption of oxygen from water, which results in oppression and death of marine invertebrates [3]. In connection with the foregoing, the object of the invention and the results of laboratory investigations (Table), bench tests have been conducted in the Black, South China Seas, in English

Channel and Atlantic Ocean. During 7 months, painted material samples were tested: construction steel, aluminium, composite material (coal-plastic) treated twice with 0.05% solutions of compounds sample 15 and 16 mixture (60 and 30%, respectively, see Table, on underwater benches in the Black Sea (Sochi). It was established that in all cases bio-fouling was absent, only separate units of barnacles were visible on the polymer sample, which were easily washed off with a jet of sea water under a slight pressure (0.5 atm).

In the Atlantic Ocean and the South China Sea, similar samples, only unpainted, were tested. The samples were immersed under the surface of the Atlantic Ocean (d = 1.022 g/cm^3) and of the South China Sea to the depth of 50 cm so that the samples were also exposed to sunlight. In 6 months, and for the South China Sea in 7 months, the absence of bio-fouling was found for steel and aluminium samples, in addition, corrosion markings were absent in sea water. Polymer samples were fully fouled by microorganisms but they were easily removed under the action of water jet of low pressure (up to 0.5 atm). Before testing, the samples were cleaned from contaminations, corrosion products, etc., and 2% solution of bromide-N-butyl-N,N,-

Table

Zones of suppressing growth of microorganism test-structures by derivatives of perfluoropolyoxaalkylenecarboxylic acid (M_M = 2800)

$CF_3O(CFCF_2O)_n$-C_2F_4C=O at n=15

CF_3 R_H

N n.n.	R_H	Asp. niger	P.granulat.	C. Utilis	Succh. Cerev.
1	$-OCH_2CH(CH_3)_2$	23 ± 1	6± 1	7± 1	8± 1
2	$-O(CH_2)_4CH_3$	10± 1	11± 1	9± 1	7± 1
3	$-O(CH_2)_5CH_3$	8± 1	12± 1	9± 1	7± 1
4	$-OCH_2CH(CH_3)_2$	21± 1	13± 1	7± 1	9± 1
5	$-NHNH_2$	-	15± 1	15± 1	8± 1
6	$-NHNHCH_3$	20± 1	26± 1	-	8± 1
7	-NHNHPh	30± 1	30± 1	21± 1	13± 1
8	$-NHNHAr(NO_2)_2$	16± 1	25± 1	19± 1	10± 1
9	$-NHC_3H_6N(CH_3)_2Br$ C_4H_9	56± 1	59± 1	53± 1	57± 1
10	$-NHC_3H_6N(CH_3)_2Cl$ C_4H_9	50± 1	52± 1	49± 1	47± 1
11	$-NH-C(=NH)-NH_2$	35± 1	30± 1	18± 1	12± 1
12	$-NH-C(=NH)-N^+(CH_3)_2C_3H_7\ Br^-$	53± 1	58± 1	54± 1	50± 1
13	$NH-N^+(CH_3)_2C_4H_9\ Br^-$	60± 1	59± 1	50± 1	47± 1
14	$-NH-N(C_2H_4COOH)(CH_3)(C_2H_4COO^-)$	57± 1	53± 1	50± 1	56± 1
15	$-NHC_3H_6N(CH_3)_2$	32± 1	30± 1	38± 1	39± 1
16	-OH	17± 1	25± 1	22± 1	20.3± 1
17	$-CO-CF(CF_3)_2$	19± 1	23± 1	29± 1	26.4± 1

dimethylpropaneamideperfluoropolyoxapropylenecarboxylic acid (Example 9) in a mixture consisting of 40% ethylcellozolv and 60% ethylacetate (or isopropyl alcohol) was applied with a brush on their clean and dry surface.

Further, reduction in surface energy of the solid surface of the vessel hull allows to significantly decrease hydrodynamic resistance when the vessel moves in water medium. It was empirically established (when sea water was drained from a reservoir through a conduct) that hydrodynamic resistance in the case of solid treated surfaces contacting with current water is lower by 13-17% than in the case when these surfaces are usual and not treated. Here the surface acquires anti-friction and anti-corrosion properties. Such reduction in hydrodynamic resistance will allow the vessel to keep the speed it takes with less fuel expenditure and with the same power consumption, to achieve higher speeds.

EP 0,693,514 A1 discloses a group of amides and ethers, and indicates that the amides or ethers may be used for producing anti-friction, anti-scuff and anti-wear additives to lubricating oils and greases.

It has now, surprisingly, been found that the same compounds may be used either or alone, or, with solvents and/or thinners, in the form of a "paint", as a treatment for use in treating a surface which is to be located under water, such as part of the hull of a ship or boat, and the compounds will, when applied to the surface, provide the surface with good anti-fouling properties.

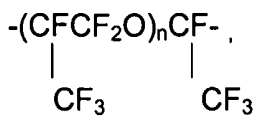
The compounds of interest are perfluropolyoxaalkylene-sulfo- or perfluoropolyoxaalkylene-carboxylic acids which have the following general formula:

$$R_F\ R_F'ZQ,$$

where

$R_F = CF_3O-$, C_2F_5O-, C_3F_7O-, or $C_8F_{17}O-$,

R_F' =



$-(CF_2CF_2O)_nCF_2-$, or $-(CF_2CF_2CF_2O)_nCF_2CF_2-$,

where

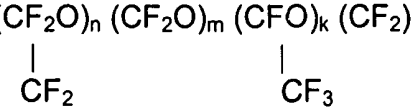
n = 8 - 55;
Z = CO-, SO_2,
Q = $N(C_mH_{2m}OH)_2$, where m = 2, 3, 4, 6, 8, 10
$-N[C_2H_4O)_4C_3H_6OH]_2$,
$-NH-C_2H_4OR_n$, where R_n = CH_3-, C_2H_5-, or C_3H_7-,
$-NH(C_2H_4O)_5H$,
$-OC_LH_{2L}N(C_LH_{2L}OH)_2$, where L = 1, 2, 4 or
$C_kH_{2k+1}O$-, where k = 6, 8, 10.

The compounds are found to be colourless or faintly yellow liquids having a viscosity of 600-3,500 cSt, a density of 1620-1810kg/m^3, and a congelation point of plus 36 to minus 65°C.

Other compounds of interest are perfluoropolyoxaalkylene-sulfo or -carboxylic acid and/or a mixture with perfluoroxaalkylene-ketones with the general chemical formula

$R_fR_f'ZQ$ where

R_f = 1) CF_3O;
2) C_2F_5O;
3) C_3F_7O; or
4) $C_8F_{17}O$

R_f' = 1)  , where

n = 8 ... 50

m = 0 ... 10
k = 0 ... 1

2) $-(CF_2O)_n (CF_2O)_m (CF_2)$, where
n = 5 ... 200
m = O ... 30

3) $-(CF_2CF_2CF_2O)n\ CF_2\ CF_2$, where
n = 8 ... 50

or

4) $-(CH_2CF_2CF_2O)n\ CH_2\ CF_2$, where
n = 8 ... 40

Z = CO; or - SO_2
Q = OH; $-CF_3$; or - $CF(CF_3)_2$

A single compound, or a mixture of compounds, within this general formula may be applied as an anti-fouling treatment directly to a surface, such as a surface that is to be located under water and which would thus at least potentially be subject to fouling, for example part of the hull of a ship or boat. The compound or compounds will generally be applied using a painting technique or using a spraying technique.

It is envisaged that the selected compound or compounds may be applied directly, without the presence of any solvent or thinner, but if desired the compound may be formulated into a paint with the paint incorporating at least one solvent or thinner or a plurality of solvents or thinners.

Example 15

A diethanolamide of perfluoropolyoxapropylene-carboxylic acid was made in accordance with Example 1 of EP 0, 693,514 B1. The resultant viscous liquid was applied as a treatment to one side of a steel plate. The steel plate was immersed in sea water for a period of six weeks. At the end of six weeks the

treated side of the plate was found to have no sign of fouling. The other, untreated, side of the plate showed substantial signs of fouling commencing.

Example 16

A diethanolamide of perfluoropolyoxaethylene-carboxylic acid was made in accordance with Example 4 of EP 0,693,514 B1. The resultant viscous liquid was applied to one side of a steel plate. The steel plate was immersed in sea water for a period of six weeks. At the end of six weeks the treated side of the plate coated with the amide was found to have no sign of fouling. The other, untreated, side of the plate showed substantial signs of fouling commencing.

Example 17

A diethanolamide of perfluoro-n-polyoxapropylenesulfo acid was made in accordance with Example 5 of EP 0,693,514 B1. The resultant viscous liquid was applied as a treatment to one side of a steel plate. The steel plate was immersed in sea water for a period of six weeks. At the end of six weeks the treated side of the plate was found to have no sign of fouling. The other, untreated, side of the plate showed substantial signs of fouling commencing.

Example 18

An octylester of perfluropolyoxaethylene-carboxylic acid was made in accordance with Example 18 of EP 0,693,514 B1. The resultant viscous liquid was applied as a treatment to one side of a steel plate. The steel plate was immersed in sea water for a period of six weeks. At the end of six weeks the treated side of the plate was found to have no sign of fouling. The other, untreated, side of the plate showed substantial signs of fouling commencing.

Example 19

A decyl ester of perfluoro-n-polyoxaethylene-carboxylic acid was made in accordance with Example 19 of EP 0,693,514 B1. The resultant viscous liquid was applied as a treatment to one side of a steel plate. The steel plate was immersed in sea water for a period of six weeks. At the end of six weeks the treated side of the plate was found to have no sign of fouling. The other, untreated, side of the plate showed substantial signs of fouling commencing.

It is envisaged that surfaces treated with a treatment as herein described will resist fouling for a substantial period of time. If the hull of a ship or boat is treated, it is believed that the ship or boat will not foul, or will not foul to a substantial extent. The absence of fouling will effectively minimise the energy required to drive the ship or boat through the water, and also optimise the speed of the ship or boat.

References.

[1] Luchina M.A., Norokha Yu.M. Protection from mollusk fouling of hydro-electro power plants and heat power stations having Dreissen metal construction. In coll.: "Corrosion and cavitation erosion protection of hydro-electro power plants constructions and equipment", Leningrad, VNIIG, 1974.

[2] Wong P.T.S., Chang Y.K., Kramar O., Bengert J.A., Structure-Toxicity Relationship of Tin Compounds on Algae. Canad. J. Fish. Agnat. Sci., 1982, v.39, No.3. pp.483-488.

[3] Yatsimirskiy K.B., Introduction to biological chemistry., Kiev, Naukova dumka, 1976, 144 p.

When used in this specification and claims, the terms "comprises" and "comprising" and variations thereof mean that the specified features, steps or integers are included. The terms are not to be interpreted to exclude the presence of other features, steps or components.

The features disclosed in the foregoing description, or the following claims, or the accompanying drawings, expressed in their specific forms or in terms of a means for performing the disclosed function, or a method or process for attaining the disclosed result, as appropriate, may, separately, or in any combination of such features, be utilised for realising the invention in diverse forms thereof.

CLAIMS:

1. A method of producing a fluoroorganic compound, the method comprising the steps of:

mixing a compound of formula I:

$$R_FR'_FQX \qquad (I)$$

where X=F or OCH_3

$R_F=C_nF_{2n+1}O^-$, where n=1-8

$R'_F= (ZCYCF_2O)_k(CF_2)_{m-}$,

where k=5-200, m=1-2

and Z=Y=F or Z= $-CF_3$, Y=F,

or Z= $-CF_2-$, Y= F_2

Q= -CO- or $-SO_2-$

with a compound of formula (II):

$$NH_2LNTR_H \qquad (II)$$

where T=H or R_H

L= $-(CH_2)_{e-}$, where e= 1-5 when R_H= H, C_1-C_4- alkyl, $-CH_2C_6H_5$, $-C_6H_5$, $-C_2H_4OH$, $-C_2H_4COOM$, $-CH_2COOM$

where M= Na, K, Ca;

L= $-(C_2H_4NH)_{1-3}$ when R_H=H

L= -C- or -C- or -C- when R_H= H
NH O S

or with a compound of formula (III):

NH_2NTR_H (III)

where T=H or R_H,

R_H= H, $-CH_3$, Ph, Ar $(NO_2)_2$

or with iso-alcohols of formula (IV):

$HOC_nH_{2n-1}(CH_3)_2$ (IV),

where n=1-6

in the presence of acceptor HF released in the process of the reaction, in the case when X=F, at molar ratio of the reaction components compound of formula (1): compound of formula (II), or (III), or (IV):
acceptor = 1: 1.1: 0.001-0.0001 and the temperature not higher than 60°C,
with subsequent alkylation during heating in the presence of a solvent with compound of general formula (V):

R^1_H A (V)

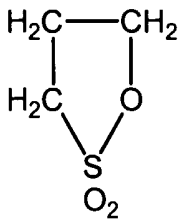
where

$R^1_{H=}$ C_1-C_{10} – alkyl, $-CH_2CH_2OH$, $-CH_2COOM$, $-C_2H_4COOM$, $-CH_2C_6H_5$, $-C_6H_5$, when M=Na, K, Ca;

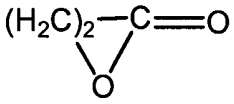
A = F^-, Cl^-, Br^-, J^-;

or

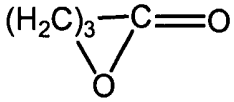
with propanesulfone



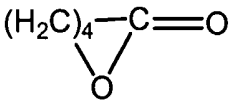
β-propiolactone



γ-butyrolactone



δ, γ-valerolactone



2. The method of producing a fluoroorganic compound according to claim 1, wherein the compounds is selected from amidoimines, quaternised compounds thereof, amides and ethers, guanidides, hydrazides, ureides, or thioureides.

3. An anti-fouling treatment for a surface, the treatment comprising a fluoroorganic compound produced by the method according to claim 1.

4. An anti-fouling treatment for a surface, the treatment comprising a fluoroorganic compound selected from amidoamines, quaternised compounds

thereof, amides, ethers, guanidides, hydrazides, ureides and thioureides, perfluoropolyoxaalkylenesulfo-or perfluoropolyoxaalkylenecarboxylic acid.

5. An anti-fouling treatment for a surface, the treatment comprising at least one perfluoropolyoxalkylene-sulfo or perfluropolyoxlyalkylene-carboxylic acid having the general formula:

$$R_FR_F'ZQ,$$

where

$R_F = CF_3O-$, C_2F_5O-, C_3F_7O-, or $C_8F_{17}O-$,
R_F' =

$$-(CFCF_2O)_nCF-,$$
$$\quad\;\; |\qquad\quad |$$
$$\quad CF_3 \qquad CF_3$$

$-(CF_2CF_2O)_nCF_2-$, or $-(CF_2CF_2CF_2O)_nCF_2CF_2-$,

where

n = 8 - 55;
Z = CO-, SO_2,
Q = $N(C_mH_{2m}OH)_2$, where m = 2, 3, 4, 6, 8, 10
$-N[C_2H_4O)_4C_3H_6OH]_2$,
$-NH-C_2H_4OR_n$, where $R_n = CH_3-$, C_2H_5-, or C_3H_7-,
$-NH(C_2H_4O)_5H$,
$-OC_LH_{2L}N(C_LH_{2L}OH)_2$, where L = 1, 2, 4 or
$C_kH_{2k+1}O-$, where k = 6, 8, 10.

6. An anti-fouling treatment for a surface, the treatment comprising a perfluoropolyoxaalkylene-sulfo or -carboxylic acid and/or a mixture with perfluoroxaalkylene-ketones with the general chemical formula

$R_fR_f'ZQ$ where

R_f = 1) CF_3O;

2) C_2F_5O;
3) C_3F_7O; or
4) $C_8F_{17}O$

R_f' = 1) $-(CF_2O)_n(CF_2O)_m(CFO)_k(CF_2)$ with CF_2 and CF_3 branches, where
n = 8 ... 50
m = 0 ... 10
k = 0 ... 1

2) $-(CF_2O)_n(CF_2O)_m(CF_2)$, where
n = 5 ... 200
m = O ... 30

3) $-(CF_2CF_2CF_2O)n\ CF_2\ CF_2$, where
n = 8 ... 50

or

4) $-(CH_2CF_2CF_2O)n\ CH_2\ CF_2$, where
n = 8 ... 40

Z = CO; or - SO_2
Q = OH; $-CF_3$; or - $CF(CF_3)_2$

7. A treatment according to any one of Claims 3 to 6 wherein the treatment is in the form of a paint including at least one added solvent or thinner.

8. A method of treating a surface, the method comprising painting or spraying on to the surface an anti-fouling treatment according to any one of Claims 3 to 7.

9. A method according to Claim 8 wherein the surface is a surface which is to be exposed to water and which would be subject to fouling.

10. A method according to Claim 9 wherein the surface is the hull of a ship or boat.

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