

Description

The present invention relates to the field of lubricants and, more particularly, to the incorporation of fluorinated organic compounds into lubricants in order to improve the anti-wear properties of the latter.

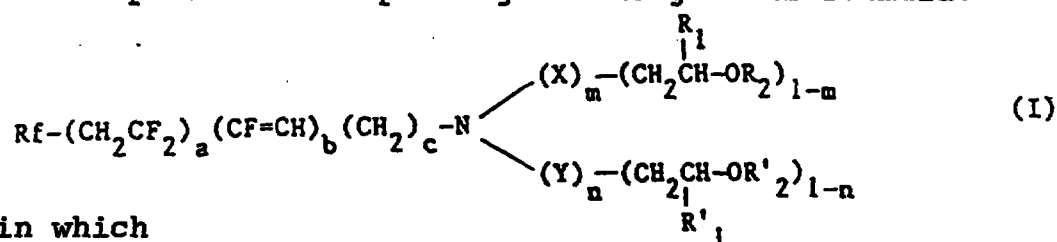
The use of certain organofluorinated derivatives as additives to lubricant compositions is known; for example, the use of salts of aliphatic amines and of perhalogenated monocarboxylic acids has been described in US Patent 3,565,926 and, similarly, the use of derivatives obtained by reacting an aromatic amine and a fluorinated organic compound, selected from fluorinated saturated monocarboxylic acids or the chlorides of fluorinated monocarboxylic acids, has been disclosed in French Patent 2,026,493. However, these carboxylic derivatives have the disadvantage of losing their anti-wear effectiveness in the presence of conventional additives such as dispersant-detergent additives, either due to physico-chemical interactions which impede their adsorption at the level of the surfaces to be lubricated or because of chemical interactions, in particular when the dispersant-detergent additives are neutral or super-basic salts of alkaline earth metals.

The use of amines or amino alcohols having a polyfluorinated chain, very briefly mentioned in French Patent 1,532,284 and the additions FR 93,239 and FR 2,102,753 thereto, have been the subject of French Patent 2,520,377.

Although these amines and amino alcohols, in association with dispersant-detergent additives, make it possible to obtain lubricant compositions which possess remarkable anti-wear properties and a remarkable capacity to reduce friction, their utilization is frequently limited because of their high volatility which entails a decrease in their effectiveness in the course of time.

It has now been found that this disadvantage can be overcome by using, as fluorinated anti-wear additives,

the compounds corresponding to the general formula:



in which

Rf denotes a perfluorinated radical, preferably a linear or branched perfluoroalkyl radical containing 2 to 20 carbon atoms and, more particularly, a linear perfluoroalkyl radical containing 6 to 16 carbon atoms,

a is an integer from 0 to 10, preferably 0 to 3,

b is equal to 0 or 1, but cannot be equal to 1 if simultaneously a is equal to 0 and c is equal to 1,

c is an integer from 1 to 4 if a is equal to zero, but is equal to 2 if a is other than 0,

m and n are each equal to 0 or 1,

X represents an optionally substituted aryl radical, preferably a phenyl radical which is unsubstituted or substituted by an alkyl or alkoxy group having 1 to 4 carbon atoms,

Y represents the 2-hydroxy-1-phenylethyl grouping,

R₁ and R'₁ which can be identical or different each represent a hydrogen atom, an alkyl radical containing 1 to 20 carbon atoms, a cycloalkyl radical having 5 or 6 carbon atoms or an optionally substituted aryl radical,

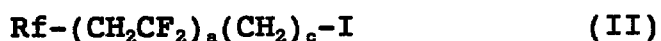
R₂ and R'₂ which can be identical or different each represent a hydrogen atom or the acyl radical of an aliphatic, cycloaliphatic or aromatic carboxylic acid,

at least one of the symbols R₁ and R₂ being other than hydrogen or a methyl radical if the total a + m + n is zero, and at least one of the symbols R'₁ and R'₂ is other than hydrogen if m is equal to 1.

According to the present invention, a single compound of the formula (I) or a mixture of these compounds can be used. Especially, it is particularly advantageous from the economic point of view to use a

mixture of compounds having different Rf radicals.

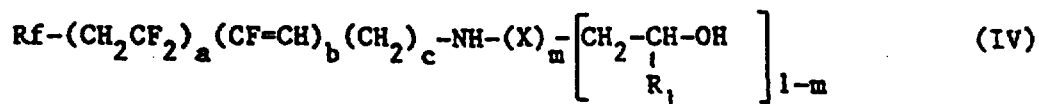
In a general way, the compounds of the formula (I) can be prepared by methods known per se (see, for example, French Patent 1,532,284 and the additions thereto No. 93,170, 93,239, 95,059 and 2,102,753, as well as French Patent 2,205,894) from iodinated derivatives of the formula:



by condensation with an arylamine X - NH₂ or an amino-alcohol of the formula:

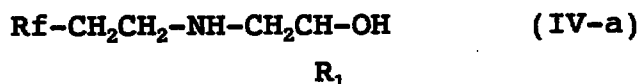


followed by the action of an epoxide on the resulting fluorinated amine of the formula:



and optionally esterification of the fluorinated amino-alcohol or diol thus obtained.

It should be pointed out that, when an iodide of the type Rf-CH₂CH₂I and an aminoalcohol (III) are used simultaneously, the condensation generally leads to a mixture of fluorinated amines of the formulae:



and



where R'f is a perfluorinated radical containing one carbon atom less than the radical Rf. However, it is possible, if desired, to separate these two amines by gas chromatography. The saturated amine (IV-a) can also be prepared selectively by using a large excess of amino-alcohol (III). Equally, the unsaturated amine (IV-b) is selectively accessible by condensing the aminoalcohol (III) with a fluorinated olefine Rf-CH=CH₂ according to US Patent 3,535,381.

The condensation reaction of the iodide (II) with

the arylamine $X-NH_2$ or the aminoalcohol (III) can be carried out in the absence of a solvent at a temperature which can go up to $160^\circ C$, but it can also be effected under reflux in an inert solvent which is advantageously selected from aliphatic C_4 - to C_6 -alcohols.

As non-limiting examples of epoxides, it is possible to mention more especially ethylene oxide, propylene oxide, 1,2-epoxybutane, 1,2-epoxyhexane, 1,2-epoxydodecane, 1,2-epoxyoctadecane and styrene oxide. The reaction of the epoxide with the fluorinated amine (IV) intermediates can be carried out in various ways depending on the nature of the epoxide employed. If a normally gaseous epoxide is used, the operation is preferably carried out by bubbling or in an autoclave, and, with a liquid epoxide, this can be carried out by simple heating of the mixture of the amine and epoxide.

The optional esterification of the fluorinated amino-alcohol or -diol to obtain the compounds of the formula (I), where R_2 and/or R'_2 represent an acyl radical, can be carried out between 0 and $100^\circ C$ by means of a carboxylic acid or a derivative of the formula:



where Z represents the OH grouping, a chlorine atom or an alkoxy group containing 1 to 5 carbon atoms and R_3 represents a linear or branched, saturated or unsaturated aliphatic radical containing 1 to 30 and preferably 4 to 22 carbon atoms, a cycloaliphatic radical or an aromatic radical.

If an acid ($Z = OH$) is used, the operation is carried out in the presence of a water acceptor such as sulphuric acid or a molecular sieve. The water formed can be eliminated by azeotropic distillation with the aid of an inert solvent, preferably an aromatic solvent such as, for example, benzene, toluene or xylene.

If a carboxylic acid ester ($Z = \text{alkoxy}$) is used, the operation is carried out in the presence of a transesterification catalyst, for example sulphuric acid, p-toluenesulphonic acid or an aluminium alcoholate. An excess of the ester R_3COZ can be used as the reaction

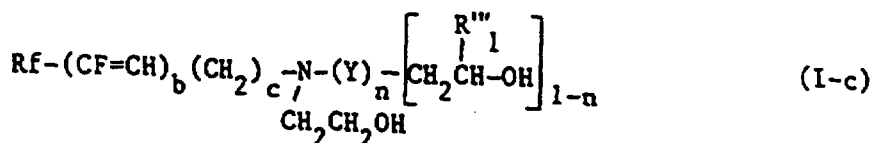
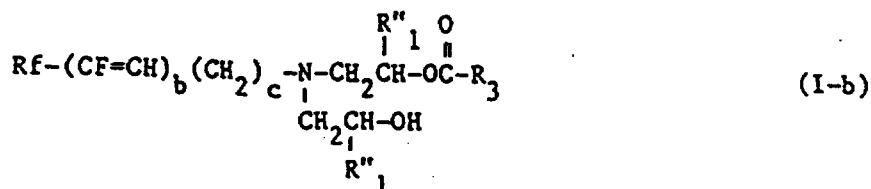
solvent.

If the esterification is carried out by means of an acid chloride ($Z = Cl$), the operation is carried out in the presence of a hydracid acceptor, such as tertiary amines containing 3 to 20 carbon atoms and selected preferably from trimethylamine, triethylamine, tripropylamine, tributylamine, tripentylamine and pyridine. This type of esterification is generally carried out in a solvent consisting of an aliphatic ether (ethyl ether, propyl ether, isopropyl ether, butyl ether, isobutyl ether or amyl ether, methyl tert.-butyl ether or methyl tert-amyl ether) or a halogenated aliphatic hydrocarbon such as, for example, methylene chloride and chloroform.

As examples of acid chlorides which can be used, it is possible to mention more particularly butyryl chloride, caproyl chloride, caprylyl chloride, isovaleryl chloride, lauroyl chloride, linoleyl chloride, heptanoyl chloride, oleyl chloride, palmitoyl chloride, pelargonyl chloride, phenylacetyl chloride, pivaloyl chloride, stearoyl chloride, undecenoyl chloride, benzoyl chloride, 2-methylbenzoyl chloride, 4-tert.-butyl-benzoyl chloride or cinnamoyl chloride.

Most of the iodinated derivatives of the formula (II) are known products, the preparation of which has been described, for example, by R.N. Haszeldine (J.C.S. 1949, 2856-2861 and J.C.S. 1953, 3761) and G.V.D. Tiers (J.A.C.S. 1953, 75 5978), and also in French Patent 2,211,430 and in Phosphorus and Sulfur 1984, 20, 197.

Among the compounds of the formula (I) according to the invention, those are very particularly preferred which correspond to the following formulae:



in which the sum of $b + c$ is equal to 2, R''_1 is a hydrogen atom or a methyl radical and R''_1 represents an alkyl radical containing an even number of carbon atoms from 2 to 16.

5 The quantity of additive(s) of the formula (I) to be added to a lubricating oil to obtain optimum effectiveness is at least 0.01 % relative to the weight of the oil and preferably is between 0.05 and 0.5 %. The additives according to the invention consist preferably
10 of industrial products in which the proportion of compounds of the formula (I) with $b = 0$ is at least equal to 10 % by weight.

 The lubricating oil can be a mineral oil, a synthetic hydrocarbon, a synthetic oil belonging to the
15 following different families: glycols, glycol ethers, glycol esters, polyoxyalkylene glycols and ethers and esters thereof, and esters of monocarboxylic or polycarboxylic acids and monoalcohols or polyalcohols, this enumeration not being limiting.

20 If the lubricant bases used are petroleum cuts intended for the manufacture of engine oils, such as "Neutral Solvent" bases, the fluoro-organic derivatives according to the invention are advantageously combined with conventional dispersant-detergent additives such as
25 calcium or barium alkylarylsulphonates and alkylphenates, or "ash-free" dispersants such as succinic derivatives. The dispersant-detergent additives promote the solubilization of the fluorinated additives in the oil without adversely affecting the anti-wear properties of the
30 latter and without losing their own capacity.

 The addition of fluorinated derivatives according to the invention to formulated oils already containing additives such as zinc alkyl dithiophosphates leads to a noticeable improvement in the anti-wear capacity and an
35 increase in the loading capacity of these oils without interfering with the properties provided by the other additives: dispersivity, detergency and anti-corrosive activity for example.

 The total or partial replacement of zinc

dithiophosphate used as anti-wear additive in formulations for internal combustion engine oils by 0.1 to 0.2 % of organo-fluorinated compounds according to the invention makes it possible to reach a protection level against wear which is equal to or superior to that obtained with this conventional additive.

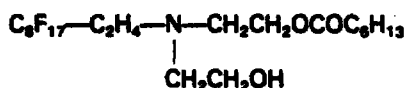
The fluorinated additives according to the invention can thus be used either as a replacement for zinc alkyl dithiophosphates in lubricating oils for petrol engines or diesel engines, or as a further addition in these oils.

The examples and tests which follow illustrate the invention without limiting it. The percentages are to be understood as being by weight, unless otherwise stated.

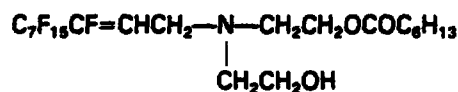
EXAMPLE 1

At ambient temperature and with constant stirring, 5.84 g of heptanoyl chloride are added dropwise to a solution of 21.4 g of a mixture of the fluorinated aminodiols $C_8F_{17}CH_2CH_2N(CH_2CH_2OH)_2$ and $C_7F_{15}CF=CHCH_2N(CH_2CH_2OH)_2$ (65 and 35 mol % respectively) and 4 g of triethylamine in 100 g of diisopropyl ether.

After the end of the addition of the heptanoyl chloride, the solution is heated for two hours at 60°C. After cooling, the triethylamine hydrochloride is filtered off and washed with ether, and the solvent is then eliminated by evaporation in vacuo. The residue characterized by infrared spectroscopy (alcohol band at $3,400\text{ cm}^{-1}$ and ester band at $1,730\text{ cm}^{-1}$) corresponds mainly to esters of the formulae:



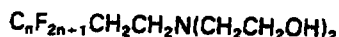
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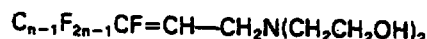
Yield : 94 %

EXAMPLE 2

The procedure of Example 1 is followed, but replacing the mixture of fluorinated aminodiols by the same molar proportion of an industrial mixture of fluorinated aminodiols of the formulae:

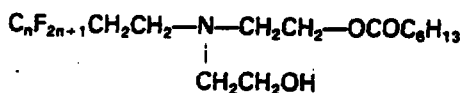


and

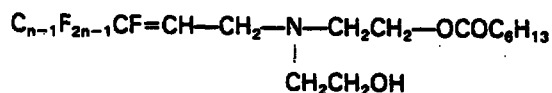


where n is equal to 6, 8, 10, 12 and 14 in respective percentages by weight of 56.2 %, 27.2 %, 12.3 %, 3.7 % and 0.6 %. This mixture, the mean molecular mass of which is 510, contains about 65 mol % of saturated aminodiols and 35 mol % of unsaturated aminodiols.

This gives a yield of 96 % of a mixture consisting principally of esters of the formulae:



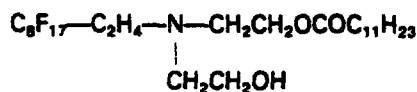
and



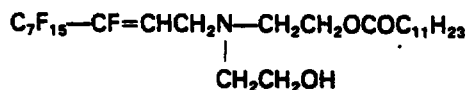
EXAMPLE 3

The procedure of Example 1 is followed, but replacing the heptanoyl chloride by 8.6 g of lauroyl chloride and replacing the diisopropyl ether by 150 g of methyl tert.-butyl ether.

This gives a yield of 95 % of a mixture principally consisting of esters of the formulae:



and

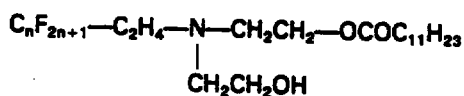


characterized by infrared spectroscopy (alcohol band: 3,400 cm⁻¹, ester band : 1,735 cm⁻¹).

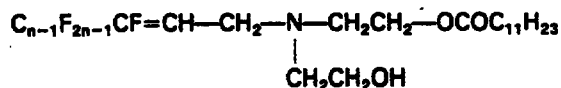
EXAMPLE 4

5 Example 3 is repeated, but replacing the C₈F₁₇- and C₇F₁₅-aminodiols by an equivalent molar proportion of the industrial mixture of fluorinated aminodiols, defined in Example 2.

This gives a yield of 98 % of a mixture principally consisting of esters of the formulae:



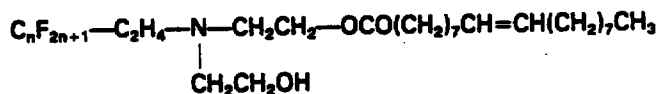
10 and



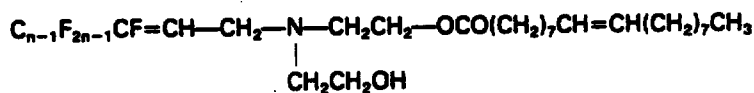
EXAMPLE 5

15 The procedure of Example 1 is followed, but replacing, respectively, the heptanoyl chloride and the C₈F₁₇- and C₇F₁₅-aminodiols by equivalent molar quantities of oleyl chloride and the same mixture of fluorinated aminodiols as in Example 2. The mixture is heated to 60°C for only one hour.

This also gives a yield of 94 % of a mixture principally composed of esters of the formulae:



20 and



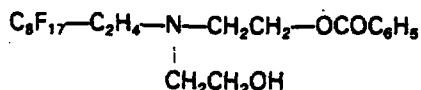
in the form of a dark liquid, characterized by infrared spectroscopy (alcohol band : 3,420 cm⁻¹; ester band : 1,740 cm⁻¹).

EXAMPLE 6

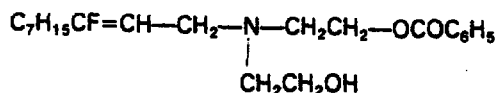
25 The procedure of Example 1 is followed, but

replacing the heptanoyl chloride by 5.52 g of benzoyl chloride and heating for 4 hours at 60-70°C.

This gives a yield of 95 % of a mixture principally consisting of esters of the formulae:



5 and



in the form of an orange viscous liquid, characterized by infrared spectroscopy (alcohol band: 3,440 cm⁻¹; ester band: 1,720 cm⁻¹).

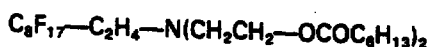
EXAMPLE 7

10 Example 6 is repeated, replacing the C₈F₁₇- and C₇F₁₅-aminodiols by the industrial mixture of fluorinated aminodiols, defined in Example 2. The product obtained is a viscous liquid, slightly turbid at ambient temperature. Yield 87 %.

15 EXAMPLE 8

12.2 g of heptanoyl chloride are added dropwise at ambient temperature and with continuous stirring to a solution of 22.5 g of the mixture of C₈F₁₇- and C₇F₁₅-fluoro-aminodiols defined in Example 1 and 8.3 g of triethylamine in 120 g of diisopropyl ether. The solution is then heated under reflux for 4 hours. After cooling, the triethylamine hydrochloride is filtered off and washed with ether, and the solvent is then eliminated by evaporation in vacuo.

25 This gives, in the form of a highly mobile yellow-orange liquid, a mixture of diesters of the formulae:



and



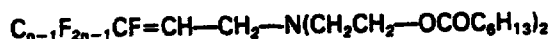
characterized by infrared spectroscopy (OH band at 3,400 cm^{-1} absent; ester band present at 1,730 cm^{-1}). Yield : 88 %.

EXAMPLE 9

5 The procedure of Example 8 is followed, but replacing the C_8F_{17} - and C_7F_{15} -aminodiols by 20.9 g of the industrial mixture of fluorinated aminodiols defined in Example 2. The yield of diesters of the formulae:



and



10 is 96 %.

EXAMPLE 10

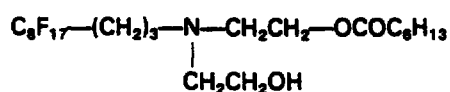
15 a) 0.2 l of ethanol, 23.65 g of 3-perfluorooctyl-propanonitrile and 1 g of Raney nickel suspended in 20 ml of ethanol are introduced into a 1 litre Hastelloy C autoclave fitted with a magnetically driven stirrer device. After closure of the autoclave, 19 g of ammonia and then 6 MPa of hydrogen are introduced and the autoclave is heated up to 90°C. Stirring is then started and maintained at 90°C until the fall in pressure ceases (about 1.5 hours).

20 The autoclave is then cooled, let down and purged with nitrogen. After filtering off the catalyst and evaporating the ethanol, this gives 21 g of 3-perfluorooctyl-propylamine in the form of a white powder melting at 70°C.

25 b) 71.6 g of this amine and 14.2 g of ethylene oxide are introduced into a 0.5 litre Hastelloy C autoclave fitted with a PTFE liner and a magnetically driven stirring device, and the mixture is then heated up to 30 75°C with stirring. The temperature then rises spontaneously up to 105°C. The autoclave is cooled to 85°C and maintained at this temperature for one hour. After let-down of the autoclave, the product is maintained

under 133 Pa at 120°C for one hour, and this gives 77 g of N-(3-perfluorooctylpropyl)-diethanolamine in the form of a grey solid which melts at 58-59°C.

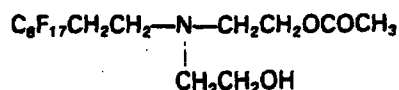
5 c) The procedure of Example 1 is followed, but replacing the C₈F₁₇- and C₇F₁₅-aminodiols by 22.2 g of N-(3-perfluorooctylpropyl)-diethanolamine. 24.7 g of a yellow-orange liquid are recovered, which solidifies at about 20°C. In infrared spectroscopy, an OH band at 3,400 cm⁻¹ and an ester band at 1,720 cm⁻¹ are observed,
10 corresponding to an ester of the formula:



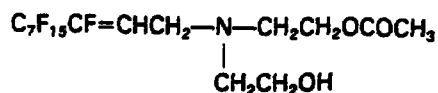
EXAMPLE 11

4.3 g of acetyl chloride are added dropwise with constant stirring to a solution of 30 g of the mixture of C₈F₁₇- and C₇F₁₅-aminodiols defined in Example 1 and 5.5 g
15 of triethylamine in 100 g of diisopropyl ether, and the mixture is then heated at 60°C for two hours.

After cooling, filtering off the triethylamine hydrochloride and evaporating the solvent in vacuo, this gives a 95 % yield of a mixture principally consisting of
20 esters of the formulae:



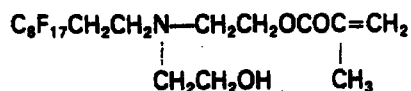
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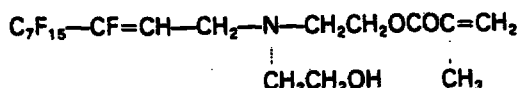
EXAMPLE 12

The procedure of Example 11 is followed, but replacing the acetyl chloride by methacryloyl chloride.

25 This gives a 96 % yield of a very mobile product principally consisting of esters of the formulae:



and



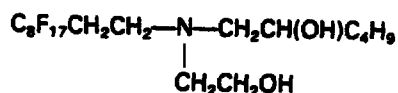
In infrared spectroscopy, an OH band at $3,380 \text{ cm}^{-1}$ and an ester band at $1,710 \text{ cm}^{-1}$ are observed.

EXAMPLE 13

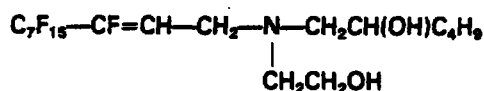
5 57.5 g of a mixture of the fluorinated amino-
alcohols $\text{C}_8\text{F}_{17}\text{CH}_2\text{CH}_2-\text{NH}-\text{CH}_2\text{CH}_2\text{OH}$ and
10 $\text{C}_7\text{F}_{15}\text{CF}=\text{CH}-\text{CH}_2-\text{NH}-\text{CH}_2\text{CH}_2\text{OH}$ (67 and 33 mol % respectively)
and then 10 g of 1,2-epoxyhexane are introduced into a
0.1 litre conical flask with a condenser on top, and
fitted with a magnetic rod stirrer and heated by an oil
bath.

15 The mixture is heated with stirring for 6 hours
at $105-110^\circ\text{C}$, and 4 g of the same mixture of fluorinated
aminoalcohols are then added again and heating is con-
tinued for 3 hours at 110°C .

This gives 69.5 g of an orange-coloured mixture
of the compounds of the formulae:



and

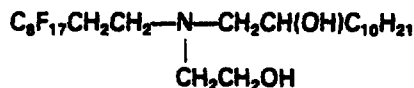


in the form of a viscous liquid at 40°C .

20 EXAMPLE 14

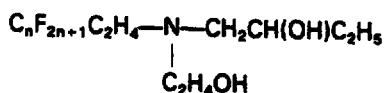
24.8 g of the same mixture of fluorinated amino-
alcohols and 9.2 g of 1,2-epoxydodecane are introduced
into the same apparatus as in Example 13, and the mixture
is then heated with stirring for 3.75 hours at 125°C .

25 This gives 33 g of an orange liquid viscous at
 40°C , consisting of a mixture of the aminodiols of the
formulae:

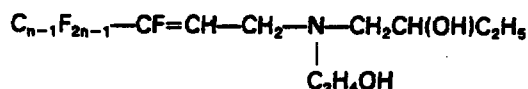


21.6 g of 1,2-epoxybutane and 146.8 g of a mixture of fluorinated aminoalcohols $C_nF_{2n+1}-C_2H_4-NH-C_2H_4OH$ (67 mol %) and $C_{n-1}F_{2n-1}-CF=CH-CH_2-NH-C_2H_4OH$ (33 mol %), in which the weight distribution of the linear C_nF_{2n+1} chains is as follows:

After cooling, evacuation of the autoclave and topping at 80°C under 133 Pa, this gives 154 g of an orange liquid showing a slight deposit at ambient temperature, but entirely clear at 30°C. This product is a mixture of the aminodiols of the formulae:



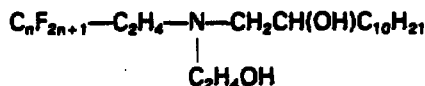
and



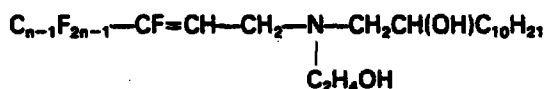
EXAMPLE 17

476 g of the same mixture of fluorinated aminoalcohols as in Example 16 and 184 g of 1,2-epoxydodecane are introduced into a 1 litre conical flask with a condenser on top, fitted with a magnetic rod stirrer and heated by an oil bath, and the mixture is then heated for 3 hours at 120-125°C.

This gives 651 g of a mixture of the aminodiols of the formulae:



and

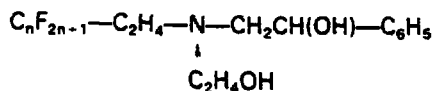


in the form of an orange viscous liquid showing a slight deposit at ambient temperature but entirely clear at 40°C.

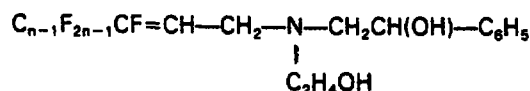
EXAMPLE 18

570 g of the same mixture of fluorinated aminoalcohols as in Example 16 and 144.3 g of styrene oxide are charged to the same apparatus as in Example 17, and the mixture is then heated up to 113°C with stirring. The temperature then rises spontaneously up to 134°C. The mixture is cooled to 113-115°C and maintained for one hour at this temperature.

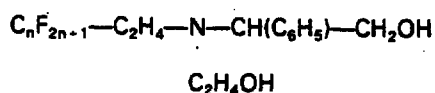
This gives 702 g of a yellow-orange liquid which is very viscous at ambient temperature but mobile at 40°C. The NMR analysis shows that this product consists of a 78 % molar proportion of aminodiols of the formulae:



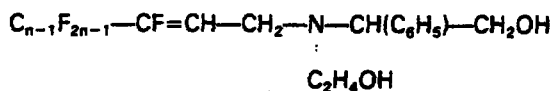
5 and



and a 22 % molar proportion of aminodiols of the formulae:



and



EXAMPLE 19

10 a) 6 g of a mixture consisting of 4.5 g of ethanolamine and 1.5 g of cuprous chloride is introduced into a 1 litre stainless steel autoclave, and the autoclave is then evacuated and cooled with liquid nitrogen, and 246 g of perfluoroethyl iodide and 64 g of vinylidene fluoride are introduced therein. The mixture is then heated with stirring for 21 hours at 145°C, and a further 64 g of vinylidene fluoride are then introduced and heating is continued for 21 hours at 145°C.

15 After cooling and purging of the autoclave, 146 g of a product are recovered, of which the GC analysis of the principal components is as follows:

	$\text{C}_2\text{F}_5\text{I}$ unconverted	:	29.3 %
	$\text{C}_2\text{F}_5(\text{CH}_2\text{CF}_2)_n\text{I}$ where		
	$n = 1$	:	23.5 %
	$n = 2$	:	19.9 %
	$n = 3$	:	10.2 %
	$n = 4$	:	4.12 %
	$n = 5$	:	1.3 %
	$n = 6$	:	0.4 %
	$n = 7$	:	0.1 %

This product is distilled in vacuo and the fraction boiling at 59°C under 4,666 Pa is recovered. This gives 28.6 g of the compound $C_2F_5-(CH_2CF_2)_2I$.

5 b) 4 g of a mixture consisting of 3 g of ethanol-amine and 1 g of cuprous chloride and then 374 g of $C_2F_5(CH_2CF_2)_2I$ are charged to the same autoclave as above. Ethylene is then injected for 7 hours in such a way that a pressure of 2.6 MPa is maintained at 145°C.

10 After let-down and purging of the autoclave, the product is distilled and the fraction boiling at 70-75°C under 133 Pa is recovered. It weighs 276 g and consists of the compound $C_2F_2-(CH_2CF_2)_2-CH_2CH_2I$, a white solid melting at 54°C.

15 c) 100 g of this compound and 100 g of tert-amyl alcohol are charged to a 0.25 litre reactor. The mixture is heated to 100°C with stirring, and 61 g of ethanol-amine are then introduced in 30 minutes, while maintaining this temperature. The mixture is then heated to reflux and maintained there for 7 hours.

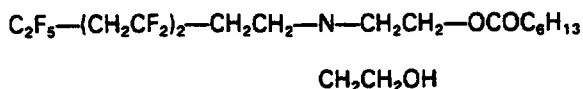
20 After cooling, the mixture is allowed to separate and the upper phase is recovered and washed by decantation at ambient temperature first with 0.1 litre of 10 % sodium hydroxide solution and then three times with 0.1 litre of water and subsequently topped at 31°C under 25 6,000 Pa. The residue weighs 60.8 g and consists of the aminoalcohol $C_2F_5(CH_2CF_2)_2C_2H_4NHC_2H_4OH$.

30 d) 64 g of this aminoalcohol are introduced into the same apparatus as in Example 13 and heated up to 65°C with stirring. At this temperature and always with stirring, a mixture of ethylene oxide (4.4 l/hour) and nitrogen (0.5 l/hour) is injected by bubbling at atmospheric pressure for 4.5 hours. This gives 72 g of the crude aminodiol $C_2F_5(CH_2CF_2)_2-C_2H_4-N(C_2H_4OH)_2$ which is in the form of a red paste.

35 EXAMPLE 20

4.7 g of heptanoyl chloride are added dropwise at ambient temperature and with constant stirring to a solution of 12 g of the aminodiol from the preceding example and 3.2 g of triethylamine in 100 ml of acetone.

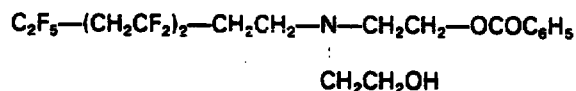
After complete addition of the heptanoyl chloride, the mixture is heated under reflux for two hours and then cooled, the triethylamine hydrochloride is filtered off and the solvent is evaporated by distillation in vacuo. The residue is then redissolved in ethyl ether, and the solution is then filtered to eliminate the last traces of triethylamine hydrochloride. After evaporation of the ether, this gives principally the ester of the formula:



characterized by infrared spectroscopy (OH band at $3,360\text{ cm}^{-1}$, ester band at $1,735\text{ cm}^{-1}$). Yield: 98 %.

EXAMPLE 21

The procedure of Example 20 is followed, but replacing the heptanoyl chloride by 4.45 g of benzoyl chloride. This gives principally the ester of the formula:



characterized by infrared spectroscopy (band at $3,330\text{ cm}^{-1}$; ester band at $1,710\text{ cm}^{-1}$).

EXAMPLE 22

48.2 g of 3-perfluorooctylpropylamine and 18.5 g of 1,2-epoxydodecane are introduced into the same apparatus as in Example 13, and the mixture is heated with stirring at $80-90^\circ\text{C}$ for 3 hours. A further 18 g of 1,2-epoxydodecane are then added and the mixture is heated at 100°C for 6 hours, and a further 3.8 g of 3-perfluorooctylpropylamine are then added and heating is continued for 5 hours at 110°C .

This gives 87 g of the aminodiol



in the form of a light beige solid melting at 40°C .

ANTI-WEAR TESTS

The anti-wear capacity of the lubricant compositions containing, as the base oil, the mineral oil 200 Neutral Solvent and, as an additive, a compound according to the invention with a fluorinated chain was determined by means of the 4-ball EP machine from SHELL, the description of which is given in the "Annual Book of ASTM Standards", Part 24 (1979), pages 680 to 688.

The test consists of causing a ball of 12 mm diameter to rotate at a speed of rotation of 1500 rpm on three other balls which are held immobile and are covered by the lubricant to be investigated. A load of 40 or 70 daN is applied by a lever system which pushes the three fixed balls against the upper ball placed in a chuck.

The anti-wear effectiveness of a lubricant is determined by the mean value of the diameters of the wear indentations on the three fixed balls after running for one hour.

The results obtained with different fluorinated additives according to the invention, identified under the form Fx where x corresponds to the number of the example describing the preparation of the fluorinated additive, are assembled in Table I which follows. The proportion by weight of the fluorinated additive incorporated in the base oil is indicated in the second column.

TABLE I

5	Fluorinated additive	Proportion in % by weight	Indentation diameter in mm for an applied load of	
			40 daN	70 daN
	None (control)		1.44	2.37
10	F 1	0.1	0.60	0.56
	F 2	"	0.67	1.1
	F 3	"	0.42	0.50
	F 4	"	0.65	0.78
	F 5	"	0.68	1.08
15	F 6	"	0.39	0.61
	F 7	"	0.66	0.77
	F 8	"	0.77	-
	F 9	"	0.80	-
	F 10	"	0.72	1.1
20	F 11	"	0.57	0.79
	F 12	"	0.37	0.77
	F 13	0.1	0.69	0.94
	F 14	"	0.67	0.76
	F 15	"	0.65	0.77
25	F 17	"	0.70	1.10
	F 18	"	0.68	0.90
	F 19	"	0.84	1.05
	F 20	"	0.59	0.78
30	F 21	"	0.63	0.78

The same method was used for determining the anti-wear effectiveness of lubricant compositions obtained by adding to the mineral oil 200 N the principal conventional additives of a category SAE 15W40 oil for petrol engines, with the exception of the zinc dithiophosphate which is replaced by a compound according to the invention having a fluorinated chain. The principal conventional additives for a SAE 15W40 type oil are a detergent (overbased sulphonate), a dispersant

(succinimide) and an antioxidant (aromatic amine). The results of these tests are assembled in Table II which follows:

TABLE II

5	Fluorinated additive	Proportion in % by weight	Indentation diameter in mm for an applied load of		
			40 daN	60 daN	70 daN
10	None (control)		0.60	1.80	2.10
	F 1	0.1	0.37	-	0.82
	"	0.3	0.37	-	0.86
	F 2	0.2	0.37	-	0.70
15	F 3	"	0.37	-	0.86
	F 4	"	0.38	-	0.68
	F 5	"	0.38	-	0.63
	F 6	"	0.45	-	0.86
	F 7	"	0.36	-	0.68
20	F 8	"	0.41	-	-
	F 9	"	0.44	-	-
	F 10	"	0.40	-	0.75
	F 11	"	0.36	-	0.66
	F 12	"	0.36	-	0.69
25	F 13	0.23	0.56	-	0.89
	F 14	0.3	-	0.59	0.75
	F 15	0.15	-	0.57	-
	F 15	0.2	-	-	0.82
	"	0.3	-	0.59	0.75
30	F 17	0.2	-	0.45	1.84
	"	0.27	-	0.45	1.28
	F 18	0.2	0.37	-	0.75
	F 21	"	0.54	-	0.77
35	F 22	"	0.46	-	-

The same method was also used for examining the anti-wear properties of lubricant compositions which combine the zinc dithiophosphates and the fluorinated

derivatives according to the invention, in such a way that the contents of zinc, phosphorus and sulphur are lower than those in conventional oils. The results obtained are assembled in Table III which follows, where the anti-wear additive A is a zinc dialkyl dithiophosphate and the antioxidant additive B is a zinc alkylaryl dithiophosphate.

TABLE III

Lubricant composition	Zinc content (ppm)	Indentation diameter for a load of:	
		40 daN	70 daN
<u>Controls</u> : 200N oil + 1 % of A	1060	0.41	0.90
200N oil + 0.5 % of A	530	0.42	0.90
200N oil + 0.5% of A + 0.1% of F ₃	"	0.40	0.60
" + " + " F ₄	"	0.39	0.64
" + " + " F ₁₈	"	0.42	0.60
" + " + 0.2% of F ₁₈	"	0.40	0.50
<u>Control</u> = 200N oil + 1 % of B	330	0.77	1.97
200N oil + 1 % of B + 0.1% of F ₃	"	0.37	0.54
" + " + " F ₄	"	0.35	0.55

These results show that the combination of the fluorinated derivatives according to the invention with zinc dithiophosphates makes it possible to obtain compositions of low zinc content, which have remarkable anti-wear properties.

The anti-wear properties of the fluorinated compounds according to the invention were also tested by means of the FALEX machine described in "Annual Book of ASTM Standards" Part 24 (1978), pages 594 to 601, using an SAE 15W40 type oil, in which the zinc dithiophosphate has been replaced by a fluorinated compound according to the invention. After subjection to a load of 250 kg for 3 hours, either rupture of the tool or its weight loss (wear) is recorded. The results obtained are assembled in Table IV which follows.

TABLE IV

Fluorinated additive	Proportion (% by weight)	Weight loss in mg
None (control)		Fracture
F 1	0.22	106
F 13	0.23	100
F 15	0.31	66
F 18	0.20	30

TESTS ON THE ENGINE TEST BENCH

An SAE 15W40 category oil for petrol engines, containing a fluorinated compound according to the invention, was tested on an engine test bench in comparison with a commercial oil of the same category, containing a zinc dialkyl dithiophosphate (anti-wear additive normally used in engine oils).

The control oil (H_1) is a commercial oil which contains, in addition to zinc dialkyl dithiophosphate, the other conventional additives entering the composition of this type of lubricant (detergent, dispersant, anti-oxidant, viscosity improver, pour point depressant).

The oil (H_2) according to the invention differs from the control oil (H_1) only by the replacement of the zinc dialkyl dithiophosphate by 0.3 % of compound F_1 in the oil (H_2).

The tests were carried out under the following conditions:

- RENAULT 20TS engine, type 829/7, having a cubic capacity of 2,000 cm³, a nominal rating of 81 kW and a nominal engine speed of 5,600 rpm.

- Running in : 10 hours
- Duration of the test (after running in) : 100 hours without draining
- Power : full load
- Periodic check of the oil and water

temperatures (inlet and outlet)

After the test, the engine pieces were analysed and assessed according to European Standard MO2A78. The results are grouped in the table which follows:

5

TABLE V

	Maximum reading	Oil H ₁	Oil H ₂
10 <u>Rings</u> : free	20	20	20
<u>Pistons</u> :			
. skirt	10	8.4	8.9
. land (1+2)	10	2.5	5.4
15 . carbon grooves (1+2+3)	30	24.7	25.3
. varnish grooves (1+2+3)	20	6.2	11.1
. bottom	10	2.1	5.8
20 <u>TOTAL</u>	100	63.9	76.5

HEAT STABILITY TESTS

In order to estimate their behaviour in conditions close to those existing in an engine, the fluorinated compounds according to the invention were subjected to a thermogravimetric analysis in air. This test consists of subjecting a product sample to a temperature rise (2°C/minute) under an air rate of 10 l/hour and recording the percentage weight losses at 200, 250 and 300°C.

The results obtained are assembled in the table which follows. For comparison, the behaviour of the following fluorinated compounds described in the prior art (French patent 2,520,377) is indicated at the start of the table.

P 1 : C₈F₁₇-C₂H₄-NH-C₂H₄OH

P 2 : C₈F₁₇-C₂H₄-N(C₂H₄OH)₂

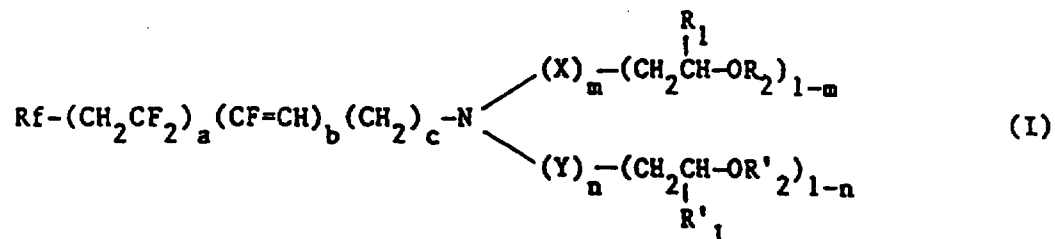
P 3 : $C_nF_{2n+1}-C_2H_4-N(C_2H_4OH)_2$
(n defined as in Example 2 above)

TABLE VI

5	Fluorinated compound	Weight loss (%) at		
		200°C	250°C	300°C
10	P 1	80	94.6	97
	P 2	27.5	92.6	96.4
	P 3	43.8	96.5	99.9
15	F 1	7.5	31.5	80
	F 2	7.5	30	80.6
	F 3	5	16.6	48
	F 4	4.4	15.6	43
	F 5	4.8	13.8	28.7
	F 6	2.4	18.1	61.2
	F 7	6.8	28.7	80.3
	F 8	6.2	37.5	97.5
20	F 9	8.1	37.5	85
	F 12	14.8	57	87
	F 13	5	17.5	58
	F 14	5	17.5	58
25	F 15	3	16	41
	F 17	4	20	62.5
	F 18	5	25	64.4
	F 21	9.4	43.8	86.3
	F 22	2.5	6.5	25

Claims

1. Lubricants, characterized in that they contain at least one polyfluorinated compound of the general formula:



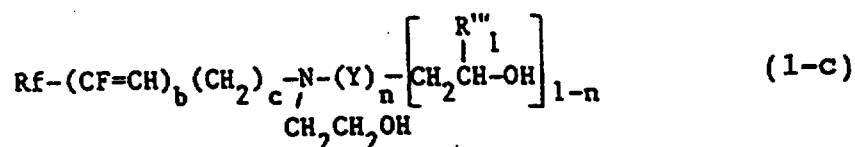
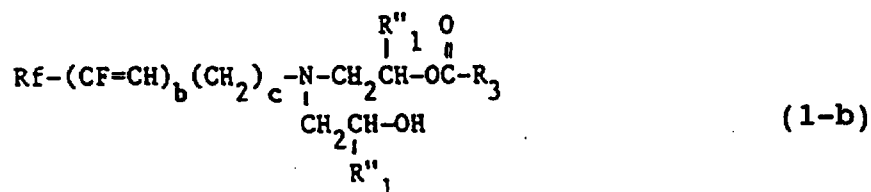
in which:

- Rf denotes a perfluorinated radical,
 - a is an integer from 0 to 10,
 - b is equal to 0 or 1, but cannot be equal to 1 if simultaneously a is equal to 0 and c is equal to 1,
 - c is an integer from 1 to 4 if a is equal to zero, but is equal to 2 if a is other than 0,
 - m and n are each equal to 0 or 1,
 - X represents an optionally substituted aryl radical,
 - Y represents the 2-hydroxy-1-phenylethyl grouping,
 - R₁ and R'₁ which can be identical or different each represent a hydrogen atom, an alkyl radical containing 1 to 20 carbon atoms, a cycloalkyl radical containing 5 or 6 carbon atoms or an optionally substituted aryl radical,
 - R₂ and R'₂ which can be identical or different each represent a hydrogen atom or the acyl radical of an aliphatic, cycloaliphatic or aromatic carboxylic acid, at least one of the symbols R₁ and R₂ being other than hydrogen or a methyl radical if the total a + m + n is zero, and at least one of the symbols R'₁ and R'₂ is other than hydrogen if m is equal to 1.
2. Lubricants according to Claim 1, in which Rf is a linear or branched perfluoroalkyl radical containing 2 to 20 carbon atoms.
3. Lubricants according to Claim 1 or 2, containing a mixture of polyfluorinated compounds, the Rf radicals of which are different.
4. Lubricants according to one of Claims 1 to 3, in which a is zero and c is equal to 1 or 2.
5. Lubricants according to one of Claims 1 to 4, in



which m is equal to 1 and X is a phenyl radical which is unsubstituted or substituted by an alkyl or alkoxy group having 1 to 4 carbon atoms.

6. Lubricants according to one of Claims 1 to 5, in which the polyfluorinated compound(s) is or are selected from those of the formulae:

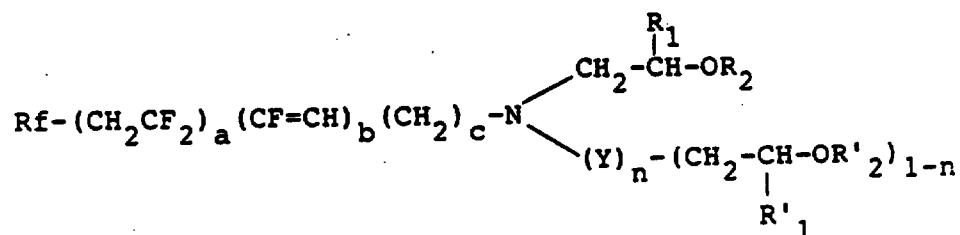


in which the sum of b + c is equal to 2, R''₁ is a hydrogen atom or a methyl radical, R'''₁ represents an alkyl radical containing an even number of carbon atoms from 2 to 16 and R₃ represents an aliphatic, cycloaliphatic or aromatic radical.

7. Lubricants according to one of Claims 1 to 6, in which the content of polyfluorinated compound(s) is at least 0.01% by weight and is preferably between 0.05 and 0.5%.

8. Lubricants according to one of Claims 1 to 7, in which the polyfluorinated compound(s) is or are associated with conventional additives.

9. Polyfluorinated compounds of the formula:

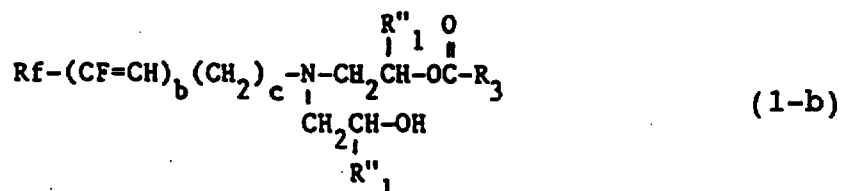


in which the symbols Rf, a, b, c, n, R₁, R₂, R'₁, R'₂ and Y are as defined in Claim 1.



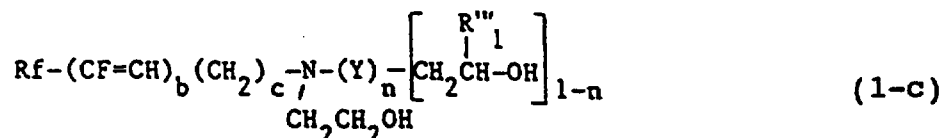
10. Compounds according to Claim 9, in which Rf is a linear or branched perfluoroalkyl radical containing 2 to 20 carbon atoms.

11. Compounds according to Claim 9 or 10, characterized in that they correspond to the formula:



in which the sum of b + c is equal to 2, R''₁ is a hydrogen atom or a methyl radical and R₃ is an aliphatic, cycloaliphatic or aromatic radical.

12. Compounds according to Claim 9 or 10, characterized in that they correspond to the formula:



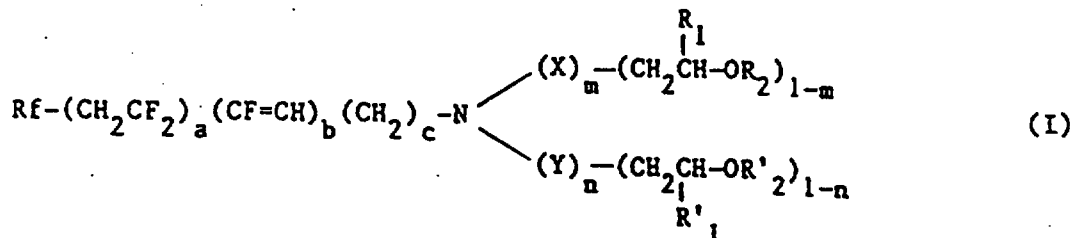
in which the sum of b + c is equal to 2 and R'''₁ represents an alkyl radical containing an even number of carbon atoms from 2 to 16.



As printed

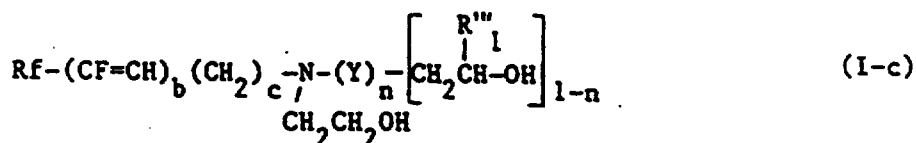
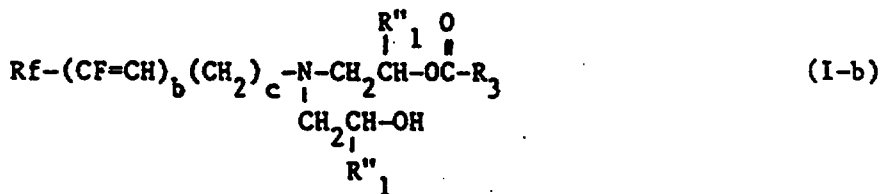
Patentansprüche

1. Schmiermittel, dadurch gekennzeichnet, daß sie wenigstens eine polyfluorierte Verbindung der allgemeinen Formel:



enthalten,
in der

- Rf einen perfluorierten Rest darstellt,
- a eine ganze Zahl von 0 bis 10 ist,
- b gleich 0 oder 1 ist, jedoch nur gleich 1 sein kann, wenn gleichzeitig a gleich 0 und c gleich 1 ist,
- c eine ganze Zahl von 1 bis 4 ist, wenn a gleich 0 ist, jedoch gleich 2 ist, wenn a von 0 verschieden ist,
- m und n jeweils gleich 0 oder 1 sind,
- X einen gegebenenfalls substituierten Arylrest darstellt,
- Y den Rest 2-Hydroxy-1-phenylethyl darstellt,
- R₁ und R'₁ gleich oder verschieden sind und jeweils ein Wasserstoffatom, einen Alkylrest mit 1 bis 20 Kohlenstoffatomen, einen Cycloalkylrest mit 5 oder 6 Kohlenstoffatomen oder einen gegebenenfalls substituierten Arylrest darstellen,
- R₂ und R'₂ identisch oder verschieden sind und jeweils ein Wasserstoffatom oder den Acylrest einer aliphatischen, cycloaliphatischen oder aromatischen Carbonsäure darstellt, wobei wenigstens eines der Symbole R₁ und R₂ von Wasserstoff oder dem Methylrest verschieden ist, wenn die Summe a+m+n gleich Null ist, und wenigstens eines der Symbole R'₁ und R'₂ von Wasserstoff verschieden ist, wenn m gleich 1 ist.
- 2. Schmiermittel gemäß Anspruch 1, bei denen Rf ein linearer oder verzweigter Perfluoralkylrest ist, der 2 bis 20 Kohlenstoffatome aufweist.
- 3. Schmiermittel nach Anspruch 1 oder 2, die ein Gemisch polyfluorierter Verbindungen enthalten, in denen die Reste Rf verschieden sind.
- 4. Schmiermittel nach einem der Ansprüche 1 bis 3, in denen a Null ist und c gleich 1 oder 2 ist.
- 5. Schmiermittel nach einem der Ansprüche 1 bis 4, in denen m gleich 1 ist und X ein nicht substituiertes oder mit einer Alkyl- oder Alkoxygruppe mit 1 bis 4 Kohlenstoffatomen substituierter Phenylrest ist.
- 6. Schmiermittel gemäß einem der Ansprüche 1 bis 5, bei denen die polyfluorierte(n) Verbindungen(en) ausgewählt wird (werden) aus denjenigen der Formeln:

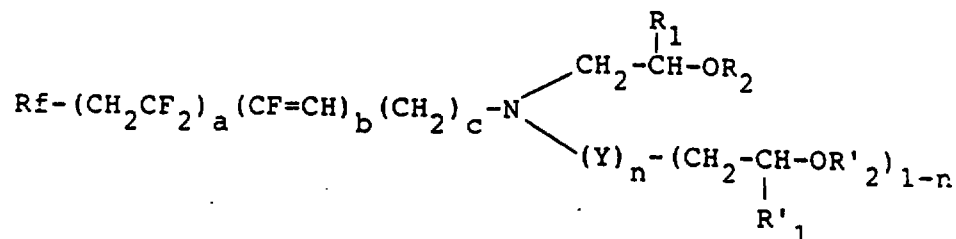


in denen die Summe $b+c$ gleich 2 ist, R''_1 ein Wasserstoffatom oder ein Methylrest ist, R'''_1 einen Alkylrest darstellt, der eine gerade Zahl an Kohlenstoffatomen zwischen 2 und 16 enthält und R_3 einen aliphatischen Rest, cycloaliphatischen Rest oder aromatischen Rest darstellt.

7. Schmiermittel gemäß einem der Ansprüche 1 bis 6, in denen der Gehalt an polyfluorierten Verbindungen wenigstens 0,01 Gew.% und vorzugsweise zwischen 0,05 und 0,5% beträgt.

8. Schmiermittel gemäß einem der Ansprüche 1 bis 7, in denen die polyfluorierte(n) Verbindung(en) mit klassischen Additiven kombiniert ist (sind).

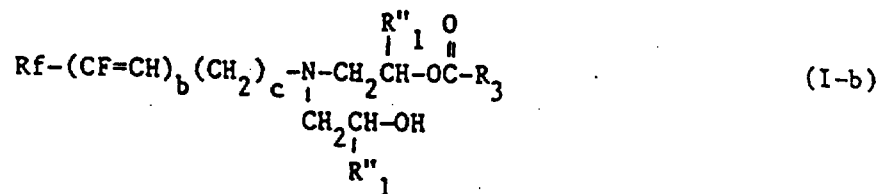
9. Polyfluorierte Verbindungen der Formel:



in der die Reste R_f , a , b , c , n , R_1 , R_2 , R'_1 , R'_2 und Y der Definition von Anspruch 1 entsprechen.

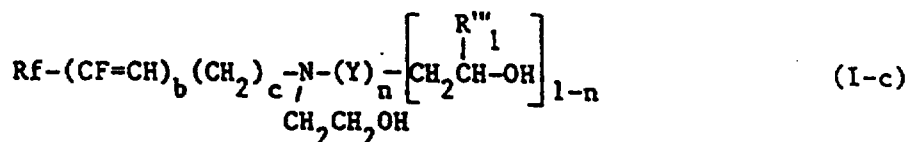
10. Verbindungen gemäß Anspruch 9, in denen R_f ein linearer oder verzweigter Perfluoralkylrest mit 2 bis 20 Kohlenstoffatomen ist.

11. Verbindungen gemäß Anspruch 9 oder 10, dadurch gekennzeichnet, daß sie der Formel:



entsprechenden, in der die Summe $b+c$ gleich 2 ist, R''_1 ein Wasserstoffatom oder ein Methylrest ist und R_3 ein aliphatischer, cycloaliphatischer oder aromatischer Rest ist.

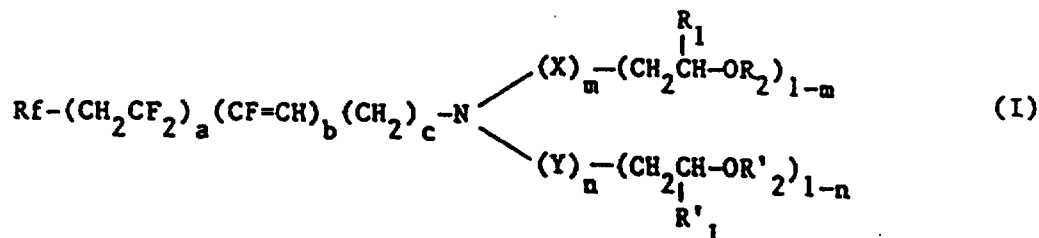
12. Verbindungen gemäß Anspruch 9 oder 10, dadurch gekennzeichnet, daß sie der Formel:



entsprechen, in der die Summe $b+c$ gleich 2 ist und R'''_1 einen Alkylrest mit einer geraden Anzahl von Kohlenstoffatomen zwischen 2 und 16 darstellt.

Claims

1. Lubricants, characterized in that they contain at least one polyfluorinated compound of the general formula:



in which:

R_f denotes a polyfluorinated radical,

a is an integer of from 0 to 10,

b is equal to 0 or 1, but cannot be equal to 1 if simultaneously a is equal to 0 and c is equal to 1,

c is an integer from 1 to 4 if a is equal to zero, but is equal to 2 if a is other than 0,

m and n are each equal to 0 or 1,



X represents an optionally substituted aryl radical,

Y represents the 2-hydroxy-1-phenylethyl grouping,

R₁ and R'₁ which can be identical or different each represent a hydrogen atom, an alkyl radical containing 1 to 20 carbon atoms, a cycloalkyl radical containing 5 or 6 carbon atoms or an optionally substituted aryl radical,

R₂ and R'₂ which can be identical or different each represent a hydrogen atom or the acyl radical of aliphatic, cycloaliphatic or aromatic carboxylic acid, at least one of the symbols R₁ and R₂ being other than hydrogen or a methyl radical if the total a+m+n is zero, and at least one of the symbols R'₁ and R'₂ is other than hydrogen if m is equal to 1.

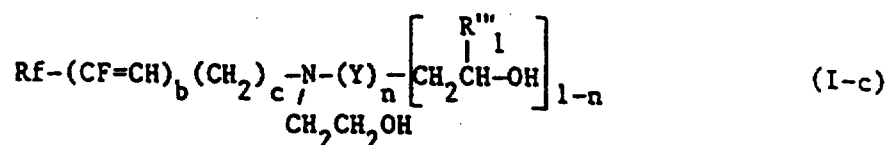
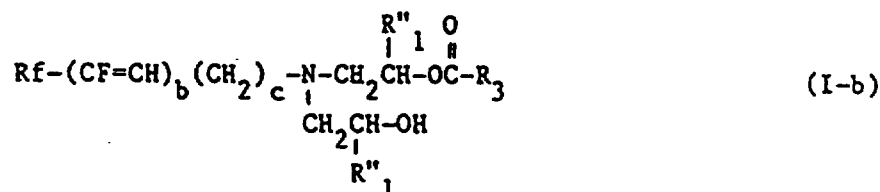
2. Lubricants according to Claim 1, in which R_f is a linear or branched perfluoroalkyl radical containing 2 to 20 carbon atoms.

3. Lubricants according to Claim 1 or 2, containing a mixture of polyfluorinated compounds, the R_f radicals of which are different.

4. Lubricants according to one of Claims 1 to 3, in which a is zero and c is equal to 1 or 2.

5. Lubricants according to one of Claims 1 to 4, in which m is equal to 1 and X is a phenyl radical which is unsubstituted or substituted by an alkyl or alkoxy group having 1 to 4 carbon atoms.

6. Lubricants according to one of Claims 1 to 5, in which the polyfluorinated compound(s) is or are selected from those of formulae:

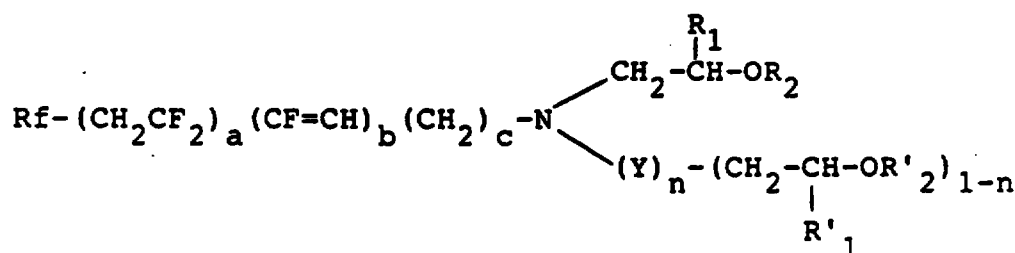


in which the sum of b+c is equal to 2, R''₁ is a hydrogen atom or a methyl radical, R'''₁ represents an alkyl radical containing an even number of carbon atoms from 2 to 16 and R₃ represents an aliphatic, cycloaliphatic or aromatic radical.

7. Lubricants according to one of Claims 1 to 6, in which the content of polyfluorinated compound(s) is at least 0.01% by weight and is preferably between 0.05 and 0.5%.

8. Lubricants according to one of Claims 1 to 7, in which the polyfluorinated compound(s) is or are associated with conventional additives.

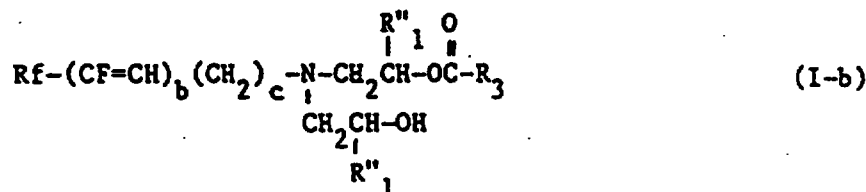
9. Polyfluorinated compounds of the formula:



in which the symbols R_f, a, b, c, n, R₁, R₂, R'₁, R'₂ and Y are as defined in Claim 1.

10. Compounds according to Claim 9, in which R_f is a linear or branched perfluoroalkyl radical containing 2 to 20 carbon atoms.

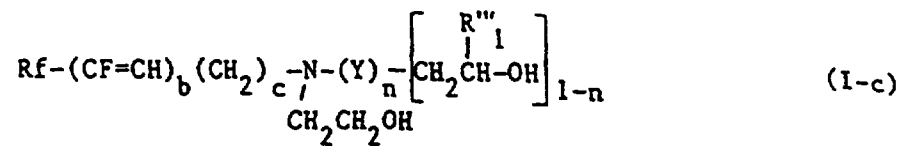
11. Compounds according to Claim 9 or 10, characterized in that they correspond to the formula:



in which the sum of b+c is equal to 2, R''₁ is a hydrogen atom or a methyl radical and R₃ is an aliphatic, cycloaliphatic or aromatic radical.



12. Compounds according to Claim 9 or 10, characterized in that they correspond to the formula:



in which the sum of b+c is equal to 2 and R''', represents an alkyl radical containing an even number of carbon atoms from 2 to 16.

