

(CONVENTION. By one or more persons and/or a Company.)

Form 4

603682

COMMONWEALTH OF AUSTRALIA

Patents Act 1952-1969

CONVENTION APPLICATION FOR A PATENT

(1) Here insert (in full) Name or Names of Applicant or Applicants, followed by Address (es).

~~XX~~ (1) ATOCHEM

We La Defense 10
of 4 & 8 Cours Michelet - 92800 Puteaux, France

(2) Here insert Title of Invention.

hereby apply for the grant of a Patent for an invention entitled: (2)
~~POLYFLUORINATED COMPOUNDS~~ ESTERS OF POLYFLUORINATED AMINO CARBOXYLIC ACIDS,
THEIR PREPARATION AND THEIR
USE AS LUBRICANT ADDITIVES

(3) Here insert number(s) of basic application(s)

which is described in the accompanying complete specification. This application is a
Convention application and is based on the application numbered (3)
87 08663

(4) Here insert Name of basic Country or Countries, and basic date or dates

for a patent or similar protection made in (4) France
on 19th June 1987

DECLARATION ACCEPTED AND AMENDMENTS

ACCEPTED 24-8-90

~~My~~ Our address for service is Messrs. Edwd. Waters & Sons, Patent Attorneys,
50 Queen Street, Melbourne, Victoria, Australia.

DATED this 16th day of June 1988

(5) Signature (s) of Applicant (s) or Seal of Company and Signatures of Officers as required by its Rules of Application

(5)

ATOACHEM

by

Louis C. Gebhardt

Louis C. Gebhardt

Registered Patent Attorney



COMMONWEALTH OF AUSTRALIA

AM 0232

Patents Act 1952-1969

DECLARATION IN SUPPORT OF A CONVENTION APPLICATION FOR A PATENT OR PATENT OF ADDITION

(1) Here insert (in full) Name of Company.

In support of the Convention Application made by(1)..... ATOCHEM

(hereinafter referred to as the applicant) for a Patent

(2) Here insert title of Invention.

for an invention entitled:(2)..... POLYFLUORINATED COMPOUNDS, THEIR PREPARATION AND THEIR USE AS LUBRICANT ADDITIVES

(3) Here insert full Name and Address, of Company official authorized to make declaration.

I, (3) JEAN LEBOULENGER of La Defense 10 - 4 & 8, Cours Michelet, 92800 Puteaux, France

do solemnly and sincerely declare as follows:

1. I am authorised by the applicant for the patent to make this declaration on its behalf.

2. The basic application as defined by Section 141 of the Act was made in(4) France on the 19th day of June 1987, by ATOCHEM

(4) Here insert basic Country or Countries followed by date or dates and basic Applicant or Applicants.

or ~~XXXXX~~ ~~XXXXX~~ 19XXXXXX

(5) Here insert (in full) Name and Address of Actual Inventor or Inventors.

3. (5) LAURENT GERMANAUD, 79, Route Neuve, 69540 Irigny, France and MARC HERMANT, 10, ter, rue Lamartine, 95240 Corneilles-en-Parisis, France

is/are the actual inventors of the invention and the facts upon which the applicant is entitled to make the application are as follow:

The applicant is the assignee of the said actual inventors.

4. The basic application referred to in paragraph 2 of this Declaration was.....the first application made in a Convention country in respect of the invention the subject of the application.

DECLARED at Puteaux, France 9th day of May 19 88

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 (19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 603682

(54) Title
 ESTERS OF POLYFLUORINATED AMINO CARBOXYLIC ACIDS, THEIR PREPARATION
 AND THEIR USE AS LUBRICANT ADDITIVES

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(71) Applicant(s)
 ATOCHEM

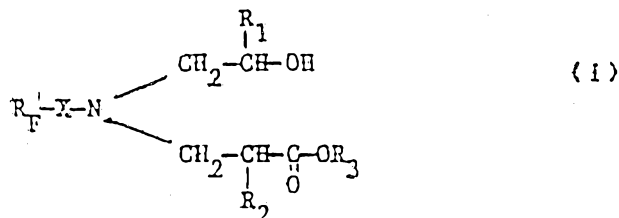
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 3122

(56) Prior Art Documents
 AU 18101/88

(57) Claim

1. Polyfluorinated compounds, characterized in that
 they correspond to the general formula:



in which:

R_F denotes a ~~perfluorinated~~ ^{perfluoroalkyl} radical,

X denotes a divalent linkage $-(\text{CH}_2\text{CF}_2)_a(\text{CH}_2)_b-$,
 $-\text{CF}=\text{CHCH}_2-$ or $-\text{CFHCH}_2\text{CH}_2-$, a being an integer rang-
 ing from 0 to 10, and b an integer which can
 range from 1 to 4 but is equal to 2 when a is
 other than 0,

(11) AU-B-18102/88
(10) 603682

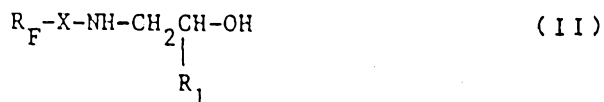
-2-

R₁ denotes a hydrogen atom or a linear or branched alkyl radical containing from 1 to 12 carbon atoms,

R₂ denotes a hydrogen atom or a methyl radical, and

R₃ denotes a linear or branched alkyl radical containing from 1 to 24 carbon atoms.

6. Process for preparing polyfluorinated compounds or mixtures of such compounds, characterized in that an amino alcohol of formula



or a mixture of such amino alcohols, is condensed with an acrylic ester of formula:



or a mixture of such esters, the symbols R_F, X, R₁, R₂ and R₃ having the same meanings as in Claim 1.

10. Lubricants, characterized in that they contain at least 0.01% by weight of a polyfluorinated compound or a mixture of polyfluorinated compounds according to any one of Claims 1 to 5.

603682

COMPLETE SPECIFICATION

(ORIGINAL)

Class

Int. Class

Application Number:
Lodged:

Complete Specification Lodged:
Accepted:
Published:

Priority :

This document contains the amendments made under Section 49 and is correct for printing.

Related Art :

Name of Applicant : ATOCHEM

Address of Applicant :

La Defense 10,
4 & 8, Cours Michelet, 92800 Puteaux, France

Actual Inventor:

LAURENT GERMANAUD and MARC HERMANT

Address for Service :

EDWD. WATERS & SONS,
50 QUEEN STREET, MELBOURNE, AUSTRALIA, 3000.

Complete Specification for the invention entitled:

ESTERS OF POLYFLUORINATED AMINO CARBOXYLIC ACIDS,
~~POLYFLUORINATED COMPOUNDS~~, THEIR PREPARATION AND THEIR
USE AS LUBRICANT ADDITIVES

The following statement is a full description of this invention, including the best method of performing it known to : US

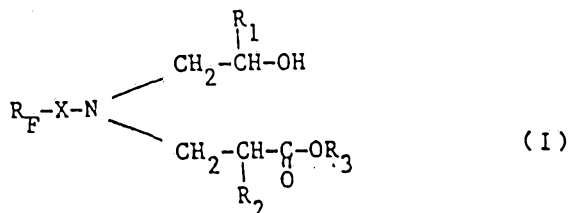


ESTERS OF POLYFLUORINATED AMINO CARBOXYLIC
~~POLYFLUORINATED COMPOUNDS~~ ^{ACIDS}, THEIR PREPARATION AND
THEIR USE AS LUBRICANT ADDITIVES

The present invention relates to the field of fluorinated products and that of lubricants. It relates more especially to new fluorinated compounds which are usable as anti-wear additives for lubricants.

It is already known to incorporate certain organo-fluorine derivatives in lubricants for the purpose of improving their anti-wear properties. Thus, for example, in French Patent 2,520,377, the incorporation of amines or amino alcohols having a polyfluorinated chain has been proposed; however, although these compounds enable lubricant compositions possessing exceptional anti-wear properties and an exceptional friction-reducing power to be obtained, their use is often limited as a result of their high volatility, which leads to a decrease in their efficacy with the passage of time.

It has now been found that this drawback can be substantially remedied by using, as fluorinated anti-wear additives, the compounds corresponding to the general formula:



in which:

R_F denotes a ~~perfluorinated~~ ^{perfluoroalkyl} radical, preferably a linear or branched perfluoroalkyl radical containing from 2 to 20 carbon atoms,

X denotes a linkage $-(CH_2CF_2)_a(CH_2)_b-$,



$-\text{CF}=\text{CHCH}_2$ or $-\text{CFHCH}_2\text{CH}_2-$,

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

b is an integer which can range from 1 to 4, but is equal to 2 when a is other than 0,

R_1 denotes a hydrogen atom or a linear or branched alkyl radical containing from 1 to 12 carbon atoms,

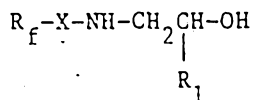
R_2 denotes a hydrogen atom or a methyl radical, and

R_3 denotes a linear or branched alkyl radical containing from 1 to 24 carbon atoms.

Among the compounds of formula (I), more special preference is given to those in which R_F is a linear perfluoroalkyl radical containing from 6 to 16 carbon atoms, X is a linkage $-\text{CH}_2\text{CH}_2-$, $-\text{CF}=\text{CHCH}_2$ or $-\text{CFHCH}_2\text{CH}_2-$, R_1 and R_2 are hydrogen atoms and R_3 is an alkyl radical with 8 to 18 carbon atoms.

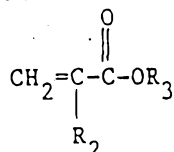
According to the present invention, it is possible to use a single compound of formula (I) or a mixture of these compounds. From the economic standpoint, it is, in particular, especially advantageous to use an industrial mixture of compounds having different groups R_F , X and/or R_3 .

Generally speaking, the compounds of formula (I) may be obtained by condensing an amino alcohol of formula:



(II)

5 with an acrylic ester of formula:



(III)

in which formulae the symbols R_f , X , R_1 , R_2 and R_3 have the same meanings as above.

10 The addition of non-fluorinated amines to α,β -unsaturated esters or amides has been known for a long time (see, for example, J. Chem. Soc., 1970, p. 343 and 469 and J. Amer. Chem. Soc., 1949, 2533). These known methods may be applied to the condensation of the amino

15 alcohols of formula (II) with the esters of formula (III). This condensation can, in particular, be performed at a temperature of between 20 and 120°C, and preferably between 20 and 80°C. It can be carried out in the absence of solvent, but is preferably conducted

20 in a solvent for the ester and the amino alcohol used. This solvent is preferably a low molecular mass (C₁-C₄) alcohol, but may also be chosen from ethers, nitriles and mixtures thereof (especially an ether/acetonitrile mixture). The condensation takes place satisfactorily in

25 the absence of catalyst, but the reaction may be accelerated by adding an acid catalyst such as acetic acid or sulphuric acid.

The fluorinated amino alcohol (II) and the ester (III) are generally used in substantially equimolar quantities. However, in the case of esters (III) having a low boiling point (for example methyl acrylate), it will be advantageous to use an excess of ester as solvent for the reaction. This excess, which can range up to 5 moles per mole of amino alcohol is, after the reaction, removed by distillation at atmospheric pressure or under vacuum.

The compounds of formula (I) in which R₃ is a long-chain (C₅-C₂₄) alkyl radical may also be prepared from a compound of formula (I) where R₃ is a lower (C₁-C₄) alkyl radical, by transesterification of the latter using a long-chain alcohol.

According to a particular embodiment of the invention, the condensation of the amino alcohol (II) with the ester (III) may be conducted with a deficit of ester (III), it being possible for this deficit to range up to one half of the theoretical quantity. A mixture comprising, in addition to the compound (I), up to 50% of the starting amino alcohol is then obtained. Such mixtures are also usable as anti-wear additives for lubricants, and hence form part of the present invention. The same applies to the more complex mixtures obtained from an industrial mixture of amino alcohols (II) and/or from an industrial mixture of esters (III).

As examples of esters of formula (III), methyl, n-butyl, 2-ethylhexyl, n-dodecyl, n-tetradecyl, n-hexa-

decyl and n-octadecyl acrylates or methacrylates may be mentioned more especially, the acrylates being preferred.

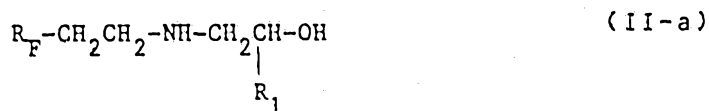
With the exception of those in which X denotes a -CFHCH₂CH₂- linkage, the amino alcohols (II) are known products (see, for example, French Patent 1,532,284 and its additions 93,170, 95,059 and 2,102,753, as well as US Patent 3,535,381), which may be obtained by condensing an iodo derivative of formula:



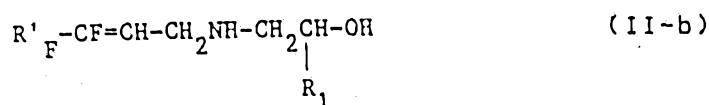
with an amino alcohol of formula



R_F, a, b and R₁ having the same meanings as above. It is appropriate to point out that, when an iodide of the type R_F-CH₂CH₂I is employed, the condensation generally leads to a mixture of fluorinated amino alcohols of formulae:



and



where R'_F is a perfluorinated radical containing one carbon atom fewer than the radical R_F. It is, however, possible, if so desired, to separate these two amino alcohols

by gas chromatography. It is also possible to prepare the saturated amino alcohol (II-a) selectively by using a large excess of amino alcohol (V). Similarly, the unsaturated amino alcohol (II-b) may be obtained selectively
5 by condensing the amino alcohol (V) with a fluorinated olefin $R_F-CH=CH_2$ according to US Patent 3,535,381 cited above.

The fluorinated amino alcohols (II) in which X denotes a $-CFHCH_2CH_2-$ linkage may be obtained by hydrogenation of the fluorinated amino alcohols (II-b).
10

This hydrogenation can be carried out, for example, in an alcohol (preferably in methanol or ethanol) in the presence of a catalyst such as Raney nickel or palladium on charcoal, at a temperature which can range from 25 to
15 $250^{\circ}C$ (preferably between 50 and $150^{\circ}C$), and under a hydrogen pressure which can reach 200 bars but is preferably between 5 and 100 bars.

This hydrogenation reaction may also be applied to a mixture of fluorinated amino alcohols (II-a) and
20 (II-b) to obtain a mixture of saturated fluorinated amino alcohols.

The quantity of compound(s) of formula (I) to be incorporated in a lubricating oil in order to obtain optimal anti-wear efficacy is at least 0.01% with respect
25 to the weight of the oil, and is preferably between 0.05 and 0.5%.

The lubricating oil can be a mineral oil, a

synthetic hydrocarbon or a synthetic oil belonging to the following different families: glycols, glycol ethers, glycol esters, polyoxyalkylene glycols, their ethers and their esters, and esters of monocarboxylic or polycarboxylic acids and monohydric or polyhydric alcohols, this list not being limiting.

When petroleum cuts intended for the manufacture of engine oils, such as "Neutral Solvent" bases, are used as lubricant bases, the organofluorine derivatives of the invention are advantageously combined with traditional dispersant-detergent additives such as calcium or barium alkylphenates and alkylarylsulphonates, or "ashless" dispersants such as succinic derivatives. The dispersant-detergent additives promote the solubilization of the fluorinated additives in the oil without impairing the anti-wear properties of the latter additives and without losing their own power.

The addition of fluorinated derivatives according to the invention to formulated oils already containing additives such as zinc alkyldithiophosphates brings about a substantial improvement in the anti-wear power and an increase in the load-carrying ability of these oils without interfering with the properties conferred by the other additives: dispersivity, detergency, anti-corrosion power, for example.

The replacement of all or part of the zinc dithiophosphate used as an anti-wear additive in oil formulations

for internal-combustion engines by 0.1 to 0.2 % of organo-
fluorine compounds according to the invention makes it
possible to achieve a level of protection against wear
which is equal to or greater than that obtained with this
5 traditional additive.

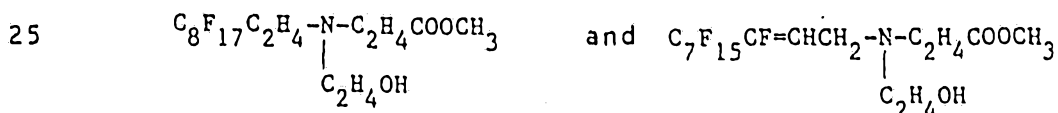
The fluorinated additives according to the in-
vention may hence be used either as a replacement for
zinc alkyldithiophosphates in lubricating oils for petrol
or diesel engines or as an extra additive in these oils.

10 The examples and tests which follow illustrate
the invention without limiting it. The percentages are
understood to be by weight, except where otherwise stated.

EXAMPLE 1

4 g of methyl acrylate are added with constant
15 stirring to a solution of 20 g of a mixture of fluorinated
amino alcohols $C_8F_{17}-CH_2CH_2-NH-CH_2CH_2OH$ and $C_7F_{15}CF=$
 $CHCH_2-NH-CH_2CH_2OH$ (65 and 35 mol%, respectively) in 10 g
of ethanol in a 100-ml round-bottomed flask surmounted by
a condenser. The mixture is then brought to reflux for
20 10 hours, after which the ethanol and excess methyl acry-
late are removed by evaporation under vacuum.

The residue (22 g), characterized by infrared
spectroscopy (ester band: $1,730\text{ cm}^{-1}$), corresponds to the
esters of formulae:



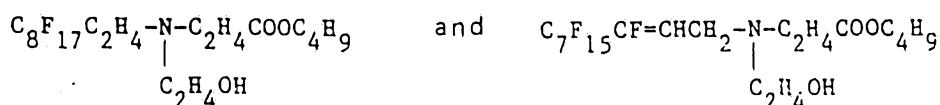
and takes the form of an orange liquid which is slight'

turbid at room temperature but fully homogeneous at 60°C.

EXAMPLE 2

A solution containing 20 g of the same mixture of fluorinated amino alcohols as in Example 1, 5.55 g of n-butyl acrylate and 10 g of n-butanol is brought to 100°C for 10 hours. The reaction mixture is then filtered, after which the solvent and excess butyl acrylate are evaporated off under vacuum.

The product obtained (23 g) corresponds to the esters of the formulae:



and takes the form of an orange liquid which is turbid at room temperature.

EXAMPLE 3

Example 2 is repeated, but with 0.1 g of acetic acid added and the reaction mixture heated for only 6 hours.

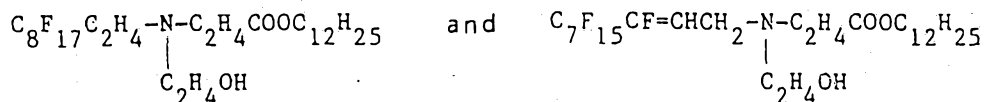
The same product is obtained in a 91% yield.

EXAMPLE 4

11.4 g of lauryl acrylate are added with constant stirring to a solution of 23.72 g of the same mixture of fluorinated amino alcohols as in Example 1 in 10 g of n-butanol in the same apparatus as in Example 1. The mixture is then brought to 100°C for 10 hours, after which the n-butanol is removed by evaporation under vacuum, the residue taken up with dichloromethane, the solution

filtered and the dichloromethane evaporated off.

The mixture of esters of formulae:



5 thereby obtained takes the form of a clear orange liquid (32.7 g; yield: 93%).

EXAMPLE 5

20 g of methyl acrylate and 20 g of an industrial mixture of fluorinated amino alcohols of formulae:

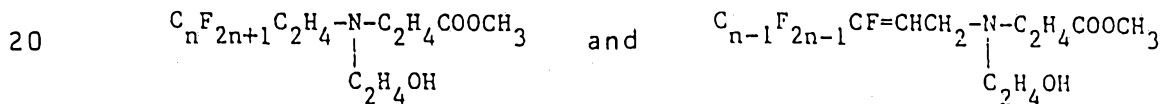


where n equals 6, 8, 10, 12 and 14 in respective percentages by weight of 56.2%, 27.2%, 12.3%, 3.7% and 0.6%,

are heated to 80°C with stirring for 8 hours. The said industrial mixture, whose average molecular mass is 466,

15 contains approximately 65 mol% of saturated amino alcohols and 35 mol% of unsaturated amino alcohols.

After evaporation of the excess methyl acrylate, a mixture of the esters of formulae:



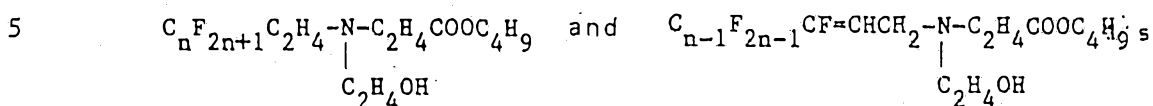
is obtained in a 91.3% yield in the form of a clear yellow liquid, which is characterized by IR spectroscopy (ester band: 1,730 cm⁻¹).

25 EXAMPLE 6

The procedure is as in Example 2, but with the C₈F₁₇ and C₇F₁₅ amino alcohols replaced by 20 g of the

industrial mixture of fluorinated amino alcohols defined in Example 5, and 6 g of butyl acrylate being used.

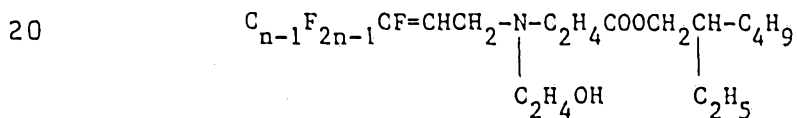
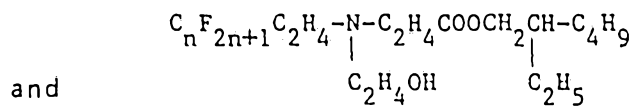
24.05 g of a clear liquid are thereby obtained, corresponding to the esters of formulae:



EXAMPLE 7

7.9 g of 2-ethylhexyl acrylate are added with constant stirring to a solution of 20 g of the industrial mixture of fluorinated amino alcohols defined in Example 5 in 10 g of n-butanol in a 100-ml Erlenmeyer equipped with a condenser, and the mixture is then heated to 80°C for 8 hours.

After removal of the n-butanol by evaporation under vacuum, a clear yellow liquid consisting of the esters of formulae:

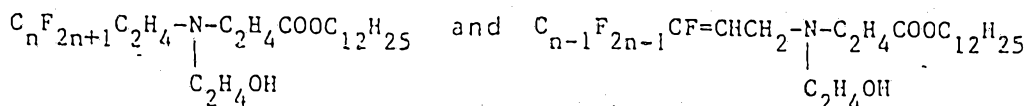


is obtained in a 95% yield.

EXAMPLE 8

The procedure is as in Example 4, but with the C₈F₁₇ and C₇F₁₅ amino alcohols replaced with 20 g of the industrial mixture of fluorinated amino alcohols defined in Example 5.

A mixture consisting of the esters of formulae:

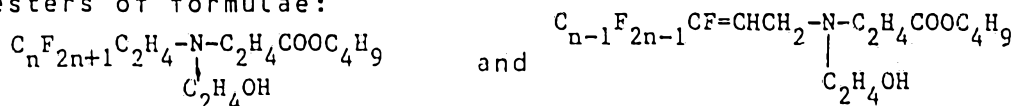


is obtained in a 92% yield.

5 EXAMPLE 9

To a flask containing 6.18 g of the industrial mixture of fluorinated amino alcohols defined in Example 5, a deficit of n-butyl acrylate (1.09 g, equivalent to approximately 0.65 molar equivalent) and 9 g of methanol are added. The mixture is then left with stirring and at room temperature for 96 hours.

After evaporation of the methanol, a product is obtained which is turbid at room temperature but becomes homogeneous at about 60°C. This product consists, in the proportion of approximately 60 mol%, of a mixture of esters of formulae:



and, in the proportion of approximately 40 mol%, of a mixture of unreacted fluorinated amino alcohols.

20 EXAMPLE 10

Example 9 is repeated, but with 1.42 g of n-butyl acrylate (0.847 molar equivalent) being used. A similar product is obtained in a 90% yield.

EXAMPLE 11

25 a/ A 4-litre stainless steel autoclave equipped with a magnetically driven stirring system is charged with 2,000 g of a mixture of fluorinated amino alcohols

$C_8F_{17}-CH_2CH_2-NH-CH_2CH_2OH$ and $C_7F_{15}-CF=CH-CH_2-NH-CH_2CH_2OH$
(67 mol% and 33 mol%, respectively), followed by 1.2
litre of 99% pure ethanol and 32 g of an approximately
60% strength suspension of Raney nickel in 99% strength
5 ethanol.

The autoclave is then purged three times with
nitrogen under 30 bars, and thereafter three times with
hydrogen under 30 bars. The mixture is then hydrogenated
for 6 hours 45 minutes at 70°C, while stirring at
10 2,000 rpm and maintaining the pressure at 20 bars. After
the autoclave has been cooled, the pressure released and
the autoclave purged, the catalyst is filtered off and
the ethanol then evaporated off.

1,940 g of a pale yellow solid product, melting
15 point 51°C, are thereby obtained, the GC analysis of
which gives the following results:

$C_8F_{17}-CH_2CH_2-NH-CH_2CH_2OH$ 65.6%

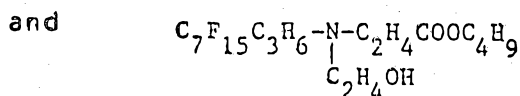
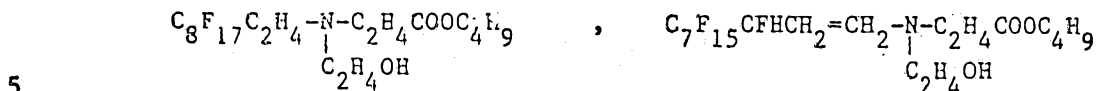
$C_7F_{15}-CFH-CH_2CH_2-NH-CH_2CH_2OH$.. 25.4%

$C_7F_{15}-CH_2CH_2CH_2-NH-CH_2CH_2OH$. 8.9%

20 b/ 1.87 g of n-butyl acrylate are added with constant
stirring to a solution of 6.27 g of the mixture of satura-
ted fluorinated amino alcohols obtained above in 10 g of
n-butanol in a 100-ml Erlenmeyer surmounted by a condenser.
The mixture is then brought to 100°C for 10 hours, after
25 which n-butanol and the excess butyl acrylate are removed
by evaporation, the yellow residue dissolved in dichloro-
methane, the solution filtered and the dichloromethane

evaporated off.

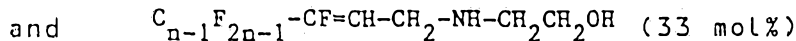
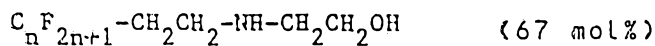
The mixture of esters of formulae:



10 thereby obtained in a 96% yield takes the form of a yellow liquid, which is characterized by IR spectroscopy (ester band at $1,725 \text{ cm}^{-1}$).

EXAMPLE 12

15 a/ Working as in Example 11-a, 2,000 g of an industrial mixture of fluorinated amino alcohols of formulae:



in which the distribution by weight of the fluorinated chains is as follows:

20	<u>n</u>	<u>%</u>
	6	55.7
	8	27.2
	10	10.15
	12	3.9
25	<u>≥14</u>	2.9

is hydrogenated for 9 hours at 80°C .

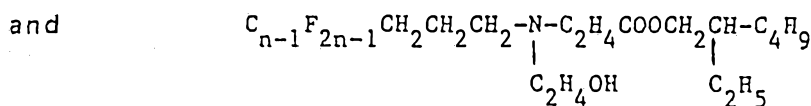
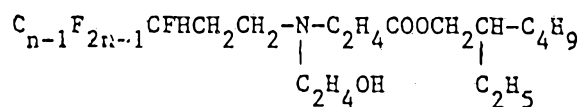
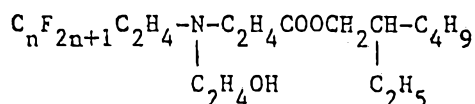
1,990 g of a semi-liquid, semi-solid pale yellow

product (completely liquid at 45°C) are obtained, the GC analysis of which gives the following results:

	$C_n F_{2n+1} -CH_2CH_2 -NH-CH_2CH_2OH$	69.3 %
	$C_n F_{2n-1} -CFH-CH_2CH_2 -NH-CH_2CH_2OH$	18.6 %
5	$C_n F_{2n-1} -CH_2CH_2CH_2 -NH-CH_2CH_2OH$	9.8 %

b/ 2.05 g of 2-ethylhexyl acrylate are added to 5.5 g of this mixture of saturated fluorinated amino alcohols, and the mixture is then brought to 100°C for 8 hours.

A clear orange liquid consisting of the esters of formulae:



is thereby obtained in a 93% yield.

EXAMPLE 13

Example 12-b is repeated, but with 2-ethylhexyl acrylate replaced by 3.3 g of lauryl acrylate, and 6.87 g of the mixture of saturated fluorinated amino alcohols obtained in Example 12-a being used.

The mixture of lauryl esters thereby obtained

(yield: 92%) takes the form of a clear yellow liquid.

EXAMPLE 14:

1.56 g (0.85 molar equivalent) of n-butyl acrylate are added to 6.73 g of the mixture of saturated fluorinated amino alcohols obtained in Example 12-a in 12 g of a mixture (3:1) of ether and acetonitrile in a 250-ml Erlenmeyer surmounted by a condenser. The mixture is then left with stirring at room temperature for 96 hours, after which the solvents are removed by distillation under vacuum.

7.5 g of a clear yellow liquid are thereby recovered, consisting, in the proportion of approximately 20 mol%, of the starting saturated fluorinated amino alcohols, and, in the proportion of approximately 80 mol%, of the butyl esters of these amino alcohols.

ANTI-WEAR TESTS

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

The test consists in rotating a ball 12 mm in diameter with a speed of rotation of 1,500 rpm on three other balls held immobile and covered with test lubricant. A load of 40 or 70 daN is applied by a lever

system, which pushes the three fixed balls towards the upper ball placed in a chuck.

The anti-wear efficacy of a lubricant is determined by the mean value of the diameters of the wear marks on the three fixed balls after one hour's operation.

Table I below collates the results obtained with different fluorinated additives according to the invention, which are identified in the form of F_x where x corresponds to the number of the Example describing the preparation of the fluorinated additive which, in all cases, was tested at the proportion by weight of 0.1%.

T A B L E I

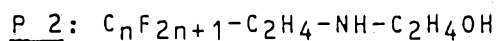
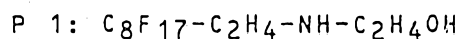
5	Fluorinated additive	Diameter of wear mark in mm for an applied load of	
		40 daN	70 daN
	None (control)	1.44	2.37
10	F 1	0.72	0.78
	F 2	0.65	0.79
	F 3	0.66	0.72
	F 4	0.62	0.73
	F 5	0.64	0.81
15	F 6	0.41	0.72
	F 7	0.45	0.68
	F 9	0.51	0.63
	F 10	0.41	0.69
20	F 14	0.39	0.55

THERMAL STABILITY TESTS

In order to test their behaviour under conditions similar to those existing in an engine, the fluorinated compounds according to the invention were subjected to a gravimetric thermal analysis under air. This test consists in subjecting a sample of product to a temperature rise (2°C/min) under a current of air at 10 l/h, and recording the percentage weight losses at 200, 250 and

300°C.

Table II below collates the results obtained. By way of comparison, the behaviour of the following fluorinated compounds, recommended in the prior art (French Patent 2,520,377), is shown at the beginning of the table:



(n defined as in Example 5 above)

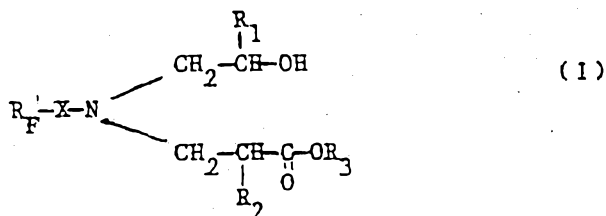
T A B L E I I

Fluorinated additive	Loss in weight (%) at:		
	200°C	250°C	300°C
P 1	80	94.6	97
P 2	78.7	96.5	98.2
F 3	16.3	85.5	96.9
F 4	7.7	33.1	83.7
F 5	25	87.5	95
F 6	15	71.2	94.6
F 7	16.2	70	91.8
F 8	5.6	24.3	81.8
F 11	21.2	71.9	94.4
F 12	12.1	48.1	93.1
F 13	5.8	23.1	75.6

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

~~CLAIMS~~

1. Polyfluorinated compounds, characterized in that they correspond to the general formula:



in which:

R_F denotes a ~~perfluorinated~~ ^{perfluoroalkyl} radical,

X denotes a divalent linkage $-(\text{CH}_2\text{CF}_2)_a(\text{CH}_2)_b-$, $-\text{CF}=\text{CHCH}_2-$ or $-\text{CFHCH}_2\text{CH}_2-$, a being an integer ranging from 0 to 10, and b an integer which can range from 1 to 4 but is equal to 2 when a is other than 0,

R_1 denotes a hydrogen atom or a linear or branched alkyl radical containing from 1 to 12 carbon atoms,

R_2 denotes a hydrogen atom or a methyl radical, and

R_3 denotes a linear or branched alkyl radical containing from 1 to 24 carbon atoms.

2. Compounds according to Claim 1, in which R_F is a linear or branched perfluoroalkyl radical containing from 2 to 20 carbon atoms and R_2 is a hydrogen atom.

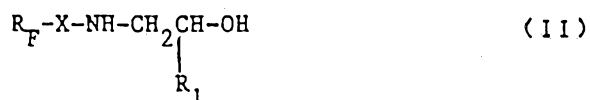
3. Compounds according to Claim 1, in which R_F is a linear perfluoroalkyl radical containing from 6 to 16 carbon atoms, X is a linkage $-\text{CH}_2\text{CH}_2-$, $-\text{CF}=\text{CHCH}_2-$ or $-\text{CFHCH}_2\text{CH}_2-$, R_1 and R_2 are hydrogen atoms and R_3 is an



alkyl radical containing from 8 to 18 carbon atoms.

4. Mixtures of compounds according to one of Claims 1 to 3, in which the groups R_F , X and/or R_3 are different.

5. Mixtures, characterized in that they contain one or more compounds according to one of Claims 1 to 3 and up to 50% of one or more amino alcohols of the formula:



in which the symbols R_F , X and R_1 have the same meanings as in Claim 1.

6. Process for preparing polyfluorinated compounds or mixtures of such compounds, characterized in that an amino alcohol of formula



or a mixture of such amino alcohols, is condensed with an acrylic ester of formula:



or a mixture of such esters, the symbols R_F , X, R_1 , R_2 and R_3 having the same meanings as in Claim 1.

7. Process according to Claim 6, in which the condensation is performed at a temperature of between 20 and 100°C, and preferably between 20 and 80°C, in a lower (C₁-C₄) alcohol.

8. Process for preparing compounds according to

Claim 1 in which R_3 is a long-chain (C_5-C_{24}) alkyl radical, characterized in that a compound according to Claim 1 in which R_3 is a lower (C_1-C_4) alkyl radical is transesterified using a long-chain alcohol.

9. Use of the polyfluorinated compounds and the mixtures according to one of Claims 1 to 5 as anti-wear additives for lubricants.

10. Lubricants, characterized in that they contain at least 0.01% by weight of a polyfluorinated compound or a mixture of polyfluorinated compounds according to any one of Claims 1 to 5.

11. Lubricants according to Claim 10, in which the content of polyfluorinated compound(s) is between 0.05 and 0.5% by weight.

12. Lubricants according to Claim 10 or 11, in which the polyfluorinated compound or compounds are combined with traditional additives.

DATED this 26th day of July, 1990.

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