18101/88

(CONVENTION. By one or more persons and/or a Company.) Form 4

COMMONWEALTH OF AUSTRALIA 60220

Patents Act 1952-1969

CONVENTION APPLICATION FOR A PATENT

ACCEPTED AND AMENDMENTS

25-7-90

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

I/We (1) ATOCHEM

of La Defense 10, 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 AMINO ALCOHOLS AND THEIR ESTERS, PREPARATION OF THESE COMPOUNDS 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 08662

(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

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

DATED this 16th day of June 19 88

(5) Signature (s) of Applicant (s) or Seal of Company and Signatures of its Officers as prescribed by its Articles of Association.

(5) ATOCHEM

by Louis C. Gebhardt

Registered Patent Attorney

(CONVENTION. Company.) Form 8

COMMONWEALTH OF AUSTRALIA AM 0231

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 AMINO ALCOHOLS AND THEIR ESTERS, PREPARATION OF THESE COMPOUNDS 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

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

on the 19th day of June 1987, by ATOCHEM

on the XXXX day of XXXX 19XXXXXX, by

3.(5) PIERRE DURUAL, "Les Essarts No. 2", 481 Chemin de la Rossignole, 69390 Vernaison, MARC HERMANT, 10 ter, rue Lamartine, 95240 Cormeilles-En-Parisis and CHARLES LAVIRON, 27 A, Rue Soeur Bouvier, 69005 Lyon, France

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

is/are the actual inventor s 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

this 9th day of May 1988

(12) PATENT ABRIDGMENT (11) Document No. AU-B-18101/88
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 602220

(54) Title
POLYFLUORINATED AMINO ALCOHOLS AND THEIR ESTERS, PREPARATION OF THESE COMPOUNDS AND THEIR USE AS LUBRICANT ADDITIVES

International Patent Classification(s)
(51)[4] C07C 091/06 C07C 091/22 C07C 093/20 C10M 133/08
(51)[5] C07C 215/08 C07C 215/28 C07C 215/30

(21) Application No. : 18101/88 (22) Application Date : 17.06.88

(30) Priority Data

(31) Number	(32) Date	(33) Country
87 08662	19.06.87	FR FRANCE

(43) Publication Date : 22.12.88

(44) Publication Date of Accepted Application : 04.10.90

(71) Applicant(s)
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(74) Attorney or Agent
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(56) Prior Art Documents
AU 18102/88 C07C 101/18
AU 73644/87 C07C 91/22

(57) 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 or for hydraulic power transmitters by 0.02 to 0.2 % of organofluorine compounds according to the invention makes it possible to achieve a level of protection against wear

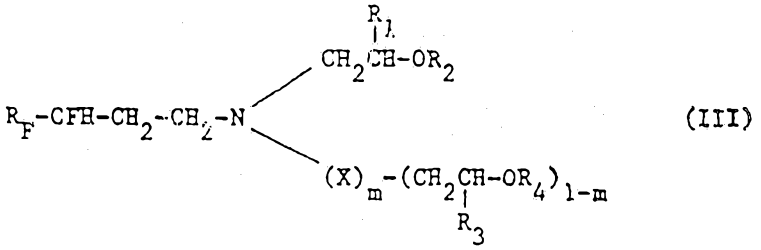
.../2

which is equal to or greater than that obtained with this traditional additive.

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

CLAIM

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



(III)

in which:

R_F denotes a linear or branched perfluoroalkyl radical containing from 1 to 19 carbon atoms,

R_1 and

R_3 which may be identical or different, each denote a hydrogen atom, an alkyl radical containing from 1 to 20 carbon atoms, a cycloalkyl radical containing 5 to 6 carbon atoms or an ~~optionally substituted~~ aryl radical,

R_2 and

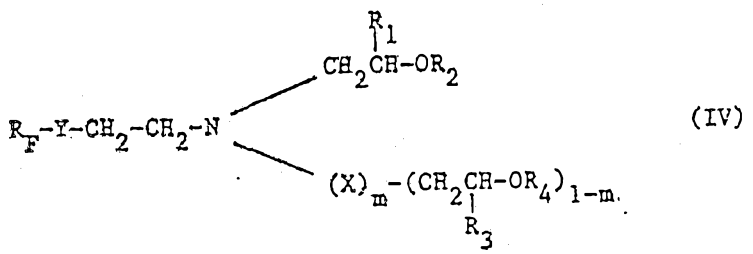
R_4 which may be identical or different, each denote a hydrogen atom or the acyl residue of an ali-

phatic, cycloaliphatic or aromatic carboxylic acid,

m equals zero or one,

X denotes a hydrogen atom or a 2-hydroxy-1-phenyl-ethyl group.

5. Mixtures, characterized in that they contain one or more compounds according to one of Claims 1 to 3 and up to approximately 80 % of one or more compounds of formula:



(IV)

in which the symbols R_F, m, X, R_1, R_2, R_3 and R_4 have the same meanings as in Claim 1 and Y denotes a CF_2 or CH_2 radical.

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

COMMONWEALTH OF AUSTRALIA 602220 Form 10

PATENTS ACT 1952-69

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: PIERRE DURUAL, MARC HERMANT and CHARLES LAVIRON

Address for Service : EDWD. WATERS & SONS,
50 QUEEN STREET, MELBOURNE, AUSTRALIA, 3000.

Complete Specification for the invention entitled:

POLYFLUORINATED AMINO ALCOHOLS AND THEIR ESTERS, PREPARATION OF THESE COMPOUNDS 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

POLYFLUORINATED AMINO ALCOHOLS AND THEIR ESTERS, PREPARATION OF THESE COMPOUNDS 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 polyfluorinated compounds which are usable as anti-wear additives for lubricants.

The application of certain organofluorine derivatives as additives to lubricant compositions is known; for example, the application of salts of aliphatic amines and perhalogenated monocarboxylic acids has been described in US Patent 3,565,926, and similarly the application of the derivatives obtained by the reaction of an aromatic amine and a fluorinated organic compound chosen from fluorinated monocarboxylic acids has been disclosed in French Patent 2,026,493. However, these carboxylic derivatives have the disadvantage of losing their anti-wear efficacy in the presence of traditional additives such as dispersant-detergent additives, either as a result of physicochemical interactions which prevent their absorption at the surfaces to be lubricated, or due to chemical interactions, especially when the dispersant-detergent additives are neutral or overbased salts of alkaline earth metals.

According to French Patent 2,520,377, lubricant compositions possessing exceptional anti-wear properties and an exceptional friction-reducing power have been

obtained using, as an organofluorine additive, amines or amino alcohols containing a polyfluorinated chain, and more especially amino alcohols which can be represented by the formula:

$$C_nF_{2n+1}C_2H_4\text{-}\underset{\underset{R}{|}}{N}\text{-}C_2H_4OH \qquad (I)$$

where n is an integer between 2 and 20 and R is a hydrogen atom or a hydroxyethyl radical. As stated on page 4 of that patent, these amino alcohols, obtained by condensing a 2-(perfluoroalkyl)ethyl iodide with ethanolamine or diethanolamine, occur industrially in the form of mixtures containing a not insignificant proportion (most often from 30 to 50 % by weight) of unsaturated amino alcohols of formula:

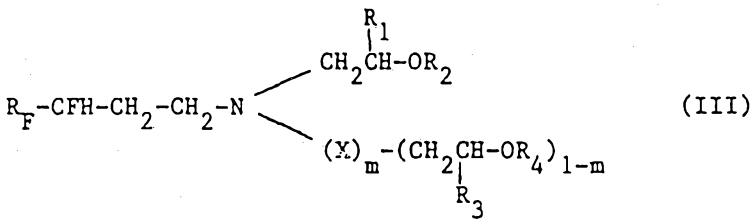
$$C_{n-1}F_{2n-1}CF{=}CHCH_2\text{-}\underset{\underset{R}{|}}{N}\text{-}C_2H_4OH \qquad (II)$$

which it is not economical to separate. These unsaturated amino alcohols are also obtained by reacting an olefin $C_nF_{2n+1}\text{-}CH{=}CH_2$ with an amino alcohol $R\text{-}NH\text{-}CH_2CH_2OH$ (US Patent 3,535,381).

It has now been found that the fluorinated products obtained by hydrogenation of the compounds of the formula (II) or of the industrial mixtures containing them show substantially improved anti-wear efficacy. It has also been found that the derivatives obtained by

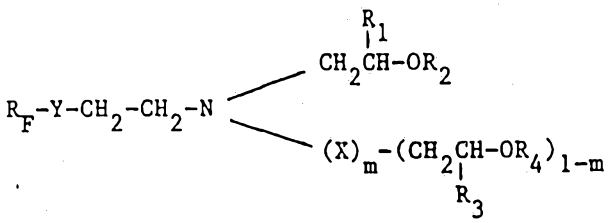
reaction of the hydrogenated products with an epoxide and/or esterification of these products also, for their part, show an excellent anti-wear efficacy.

The subject of the present invention is hence the polyfluorinated compounds of general formula:



(III)

and the mixtures thereof with one another and/or with up to approximately 80 % of polyfluorinated compounds of formula:



(IV)

in which formulae:

R_F denotes a linear or branched perfluoroalkyl radical containing from 1 to 19 carbon atoms, and preferably from 5 to 15,

R_1 and

R_3 which may be identical or different, each denote a hydrogen atom, an alkyl radical containing from 1 to 20 carbon atoms, a cycloalkyl radical containing 5 to 6 carbon atoms or an optionally substituted

aryl radical,

R_2 and

R_4 which may be identical or different, each denote a hydrogen atom or the acyl residue of an aliphatic, cycloaliphatic or aromatic carboxylic acid,

m equals zero or one,

X denotes a hydrogen atom or a 2-hydroxy-1-phenylethyl group, and

Y denotes a CF_2 or CH_2 radical.

The compounds and mixtures according to the invention may be prepared from amino alcohols of formula:

$$R_F-CF=CH-CH_2-NH-CH_2\underset{R_1}{\underset{|}{C}}H-OH \qquad (V)$$

or from mixtures of these amino alcohols with one another and/or with up to approximately 70 % of saturated amino alcohols of formula:

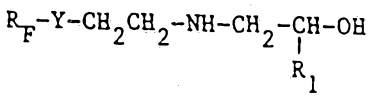
$$R_F-CF_2-CH_2-CH_2-NH-CH_2\underset{R_1}{\underset{|}{C}}H-OH \qquad (IV\text{-}a)$$

by hydrogenation followed, where appropriate, by reaction with an epoxide and/or esterification.

The hydrogenation which leads to the polyfluorinated compounds of formula:

$$R_F-CFH-CH_2-CH_2-NH-CH_2\underset{R_1}{\underset{|}{C}}H-OH \qquad (III\text{-}a)$$

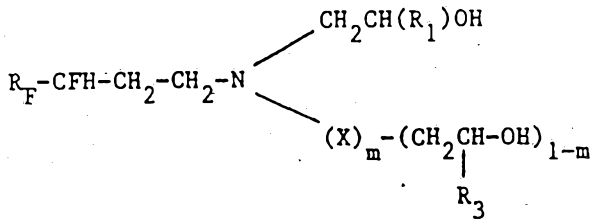
(formula III with m=1 and $X=R_2=H$) or to the mixtures of these compounds III-a with the amino alcohols of formula:



(IV-b)

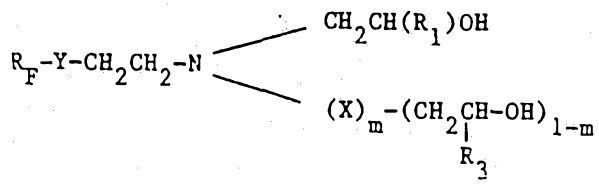
may be performed according to known methods of hydrogenation, using a catalyst chosen from group 8 metals and their oxides, preferably palladium on charcoal or Raney nickel. It is possible to work in the presence or absence of a solvent, under a hydrogen pressure ranging from atmospheric pressure to 200 bars (preferably between 5 and 100 bars) and at a temperature which can range from 25 to 250°C (preferably between 50 and 150°C). To facilitate the recovery of the catalyst, it is advantageous to work in a solvent, preferably an alcohol and more especially methanol or ethanol, whose boiling points facilitate their removal.

It is possible to obtain the fluorinated compounds of formula:



(III-b)

(formula III with m = 0 or 1 and X = 2-hydroxy-1-phenylethyl) and the mixtures thereof with the aminodiols of formula:



(IV-c)

by reacting an epoxide with the amino alcohols III-a or with the mixtures of amino alcohols III-a + IV-b.

As non-limiting examples of epoxides, ethylene oxide, propylene oxide, 1,2-epoxybutane, 1,2-epoxyhexane, 1,2-epoxydodecane, 1,2-epoxyoctadecane and styrene oxide may be mentioned more especially. The reaction with an epoxide may be carried out in different ways, according to the nature of the epoxide employed. If an epoxide that is normally gaseous is employed, it is preferable to work by bubbling or in an autoclave, whereas, with a liquid epoxide, it is possible to work by simply heating a mixture of the epoxide and the amino alcohol or alcohols.

The products according to the invention in which R_2 and/or R_4 denote an acyl residue may be prepared by esterification of the aminodiols III-b (or mixtures of III-b + IV-c), by means of a carboxylic acid or of a derivative of formula:

$$R - CO - Z \qquad \text{(VI)}$$

where Z denotes an OH group, a chlorine atom or an alkoxy group containing from 1 to 5 carbon atoms, and R denotes a saturated or unsaturated, linear or branched aliphatic radical containing from 1 to 30, and preferably from 4 to 22, carbon atoms, a cycloaliphatic radical or an aromatic

radical. This reaction may be carried out at between 0 and 100°C.

When an acid (Z=OH) is employed, the reaction is performed in the presence of a water-trapping agent such as sulphuric acid or a molecular sieve. The water formed can be removed by azeotropic distillation using an inert solvent, preferably an aromatic solvent such as, for example, benzene, toluene or xylene.

If a carboxylic acid ester (Z=alkoxy) is used, the reaction is performed in the presence of a trans-esterification catalyst, for example sulphuric acid, p-toluenesulphonic acid or an aluminium alcoholate. It is possible to use the ester R COZ in excess as a reaction solvent.

When the esterification is performed using an acid chloride (Z=Cl), the reaction is performed in the presence of a hydracid-trapping agent, such as tertiary amines containing 3 to 20 carbon atoms and preferably chosen 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, propyl, iso-propyl, butyl, isobutyl or amyl ether, methyl tert-butyl ether, methyl tert-amyl ether) or a halogenated aliphatic hydrocarbon such as, for example, methylene chloride and chloroform.

As examples of acid chlorides which are usable,

butyryl, caproyl, caprylyl, isovaleryl, lauroyl, linoleyl, heptanoyl, oleyl, palmitoyl, pelargonyl, phenylacetyl, pivaloyl, stearoyl, undecenoyl, benzoyl, 2-methylbenzoyl, 4-tert-butylbenzoyl and cinnamoyl chlorides may be mentioned more especially.

Among the polyfluorinated products according to the invention, most special preference is given to those in which:

- m equals 1 and R_1 and R_2 are hydrogen atoms;
- m equals 0, R_1, R_2 and R_4 are hydrogen atoms and R_3 is an ethyl radical; or
- m equals 0, R_1, R_2 and R_3 are hydrogen atoms and R_4 is a benzoyl radical.

The quantity of perfluorinated product according to the invention to be added to a lubricating oil in order to obtain an anti-wear efficacy is at least 0.01 % based on the weight of the oil, and is preferably between 0.02 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 or for hydraulic power transmitters by 0.02 to 0.2 % of organofluorine 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 traditional additive.

The fluorinated additives according to the invention may hence be used either as a replacement for zinc alkyldithiophosphates in lubricating oils for petrol

or for hydraulic power transmitters
or diesel engines, or as an extra additive in these oils.

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

EXAMPLE 1

a/ A 4-litre reactor equipped with a stirrer, a condenser and a thermometer is charged with 1,410 g of 95 % pure (perfluorooctyl)ethylene $C_8F_{17}-CH=CH_2$, 0.96 litre of n-pentanol, 252 g of sodium bicarbonate and 732 g of monoethanolamine, and the mixture is then heated to reflux (117 to 121°C) for 7 hours.

The chestnut-coloured mixture is then cooled to 35-40°C, and thereafter washed 5 times with 1.5 litres of water at 35-40°C. The organic phase thereby obtained (2,155 g) is then topped in a film evaporator at 85°C, under 667 Pa, at the rate of 0.42 l/h, in order to remove the residual water, a part of the n-pentanol and the unreacted (perfluorooctyl)ethylene. 1,306 g of a mixture containing 78.5 % of fluorinated product and 21.5 % of n-pentanol are thereby obtained.

This mixture is then topped at 50°C on a distillation column under 1,333 Pa, and the tail product (1,242 g) is distilled in a film evaporator at 167°C under 67 to 133 Pa, at the rate of 0.15 l/h. 1,180 g of a yellow oil are thereby collected as the top product, whose molar composition, determined by NMR, is as follows:

$C_7F_{15}-CF=CH-CH_2-NH-CH_2CH_2OH$: 88.5 %

$C_8F_{17}-CH_2CH_2-NH-CH_2CH_2OH$: 11.5 %

b/ A 2-litre stainless steel autoclave equipped with a magnetically driven stirring system is charged with 1,000 g of the oil obtained above, 0.6 litre of 99 % pure ethanol and 16 g of an approximately 60 % strength suspension of Raney nickel in 99 % pure ethanol, and 3 purges are then performed with nitrogen under 20 bars and then 3 purges with hydrogen under 20 bars. The mixture is then hydrogenated for 12 hours at 70-75°C, stirring at 1,500 r.p.m. and maintaining the hydrogen pressure at between 8 and 11 bars.

After the autoclave has been cooled and purged, the catalyst is filtered off and the ethanol removed by distillation. 1,025 g of a pale yellow waxy solid is thereby obtained, the GC analysis of which yields the following molar composition:

$C_7F_{15}-CFH-CH_2CH_2-NH-CH_2CH_2OH$: 64.1 %

$C_7F_{15}-CH_2CH_2CH_2-NH-CH_2CH_2OH$: 24.9 %

$C_8F_{17}-CH_2CH_2-NH-CH_2CH_2OH$: 11 %

By purification on a silica column, the main product:

$C_7F_{15}-CFH-CH_2CH_2-NH-CH_2CH_2OH$

is isolated, which product has the following characteristics:

Melting point: 54-55°C

Boiling point: 260°C under 10^5 Pa

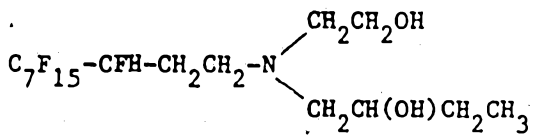
$^{13}CNMR$ ($CDCl_3$, TMS): δ (ppm)

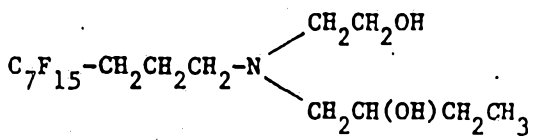
- $\underline{C}FH-$: 86.9
- $\underline{C}H_2OH$: 60.7
- $\underline{C}H_2CH_2OH$: 51.0
- $\underline{C}H_2-NH-$: 44.0
- $CFH-\underline{C}H_2-$: 27.6

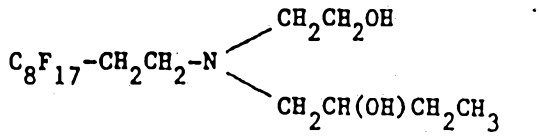
EXAMPLE 2

25.35g of the waxy solid obtained in Example 1-b and 4.45 g of 1,2-epoxybutane are placed in a 0.1-litre Erlenmeyer surmounted by a condenser and stirred with a bar magnet, and the mixture is then heated with stirring for 18 hours to 65°C.

The excess epoxide is then allowed to evaporate off at 65°C at atmospheric pressure, after which the final traces are removed under vacuum. 28 g of a brown liquid are thereby obtained, consisting of the following diols:


: 64.1 mol %


: 24.9 mol %


: 11 mol %

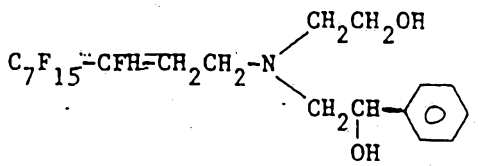
The $^{13}CNMR$ ($CDCl_3$) characteristics of the main diol are as follows:

	δ (ppm)
- $\underline{C}H(OH)-$	: 69.6
- $\underline{C}H_2CH(OH)-$	: 60.4
- $\underline{C}H_2OH$	: 59.3
- $\underline{C}H_2CH_2OH$	: 56.1
- $\underline{C}H_2-N<$	: 46.2
- $CFH-\underline{C}H_2-$	: 28.2
- $\underline{C}H_2-CH_3$	: 27.5
- $\underline{C}H_3$	: 9.6

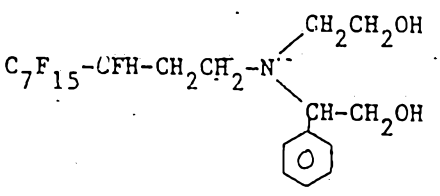
EXAMPLE 3

150 g of the waxy solid obtained in Example 1-b and 36.6 g of epoxystyrene are placed in a 0.25-litre reactor equipped with a stirrer, a thermometer and a condenser, and the mixture is then heated for 6 hours to 110°C.

171 g of a chestnut-coloured oil are thereby obtained, the main constituents of which have the following $^{13}CNMR$ ($CDCl_3$) characteristics:



δ (ppm)



δ (ppm)

C_6 ring:	142.1 - 127.4 - 127.2 and 125	C_6 ring	: 142 - 127.4 - 127.2 and 125
$-\underline{C}H(OH)-$	: 70.1	$-\underline{C}H-\phi$	: 65.9

$-\underline{C}H_2-CH(OH)-$	: 62.4	$>CH-\underline{C}H_2OH$	: 60.9
$-\underline{C}H_2OH$	: 58.6	$-CH_2-\underline{C}H_2OH$	: 58.3
$-\underline{C}H_2CH_2OH$	: 55.7	$-\underline{C}H_2CH_2OH$	: 55.7
$-\underline{C}H_2-N<$	: 45.4	$-\underline{C}H_2-N<$	: 43.2
$-CFH-\underline{C}H_2-$	: 27.8	$-CFH-\underline{C}H_2-$	: 29.3

EXAMPLE 4

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 $C_8F_{17}-CH_2CH_2-NH-CH_2CH_2OH$ (67 mol %) and $C_7F_{15}-CF=CH-CH_2-NH-CH_2CH_2OH$ (33 mol %), followed by 1.2 litres of 99 % pure ethanol and 32 g of an approximately 60 % strength suspension of Raney nickel in 99 % pure ethanol. The autoclave is then purged 3 times with nitrogen under 30 bars, and thereafter 3 times with hydrogen under 30 bars.

The mixture is then hydrogenated for 6 hours 45 minutes at 70°C, stirring at 2,000 r.p.m. 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 evaporated off.

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

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

b/ Working under the same conditions as above, but at 150°C, the hydrogenation took only one hour and similar results were obtained.

c/ Working in a 0.2-litre autoclave and on 115 g of the same mixture of fluorinated amino alcohols, without a solvent, in the presence of 0.5 g of catalyst containing 5 % of palladium on charcoal, the hydrogenation was carried out in 4 hours under 5 bars at 50°C, and identical results were obtained.

d/ If, in the same autoclave, the reaction is performed on the same quantities of amino alcohols and of palladium catalyst, but in the presence of 75 g of ethanol as solvent, the hydrogenation is carried out in one hour under 50 bars, the temperature varying from 55 to 65°C. The results are still identical. This is also the case when ethanol is replaced by methanol.

EXAMPLE 5

Working as in Example 4-a, 2,000 g of an industrial mixture of fluorinated amino alcohols of formulae:

$C_nF_{2n+1}-CH_2CH_2-NH-CH_2CH_2OH$ (67 mol %)

$C_{n-1}F_{2n-1}-CF=CH-CH_2-NH-CH_2CH_2OH$ (33 mol %)

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

n	%
6	55.7
8	27.2

10	10.15
12	3.9
14	2.9

are hydrogenated for 9 hours at 80°C.

After the catalyst has been filtered off and the ethanol evaporated off, 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:

$C_nF_{2n+1}-CH_2CH_2-NH-CH_2CH_2OH$	: 69.3 %
$C_{n-1}F_{2n-1}-CFH-CH_2CH_2-NH-CH_2CH_2OH$	: 18.6 %
$C_{n-1}F_{2n-1}-CH_2CH_2CH_2-NH-CH_2CH_2OH$	: 9.8 %

EXAMPLE 6

A 2-litre reactor equipped with stirrer, a thermometer and a condenser is charged with 1,200 g of the product obtained in Example 5 and 309 g of styrene oxide, the mixture is then heated with stirring to 118°C, and the heating thereafter stopped. The temperature then rises by itself to 125°C in the course of 5 minutes. The mixture is cooled to 108°C in the course of 15 minutes, heating is then resumed and the mixture is maintained at 118-120°C for a further 2 and a quarter hours.

4.8 g of styrene oxide are then added and the mixture is heated to 110-115°C for a further 3 hours. 1,508 g of an orange-yellow viscous product are thereby obtained, the GC analysis of which shows that it contains only 0.05 % of free styrene oxide.

EXAMPLE 7

a/ 1,250 g of the product obtained in Example 5 are placed in a 2-litre reactor equipped with a gas inlet with a dipping tube preceded by a bubble counter, a stirring system, a thermometer and a gas outlet with a bubble counter, and the mixture is then heated with stirring to 58°C and the gas line is flushed with nitrogen.

Ethylene oxide is then introduced at such a rate that only slight bubbling is observed in the outlet bubble counter. 189 g of ethylene oxide are thereby introduced in the course of 11 and a quarter hours, the temperature being maintained at 60°C.

After the reactor has been cooled, 1,402 g of a mixture of fluorinated diols are collected in the form of a yellow oil with pale yellow solid (completely liquid at 45-50°C). GC analysis shows that this product contains no monohydric alcohols.

b/ A 10-litre round-bottomed flask equipped with a condenser, a dropping funnel, a thermometer and a stirrer, and cooled in an ice bath, is charged with 940 g of the mixture of diols obtained above, 197 g of triethylamine and 4.5 litres of diisopropyl ether.

With stirring established at 200 r.p.m., a solution of 260 g of benzoyl chloride in 360 ml of diisopropyl ether is added in the course of 40 minutes while the temperature is maintained at 18-22°C. When the addition is complete, the dropping funnel is rinsed with 140 ml

of diisopropyl ether and the ice bath is removed. The mixture is then left with stirring for one hour at room temperature, after which it is heated to 60°C for 4 hours.

The mixture is then cooled to approximately 30°C, after which the solid (triethylamine hydrochloride) is filtered off and the diisopropyl ether evaporated off. 1,089 g of a dark yellow oil are thereby obtained, consisting chiefly of the monobenzoates of the initial fluorinated diols.

ANTI-WEAR TESTS

I- The anti-wear power of lubricant compositions, containing the mineral oil 200 Neutral Solvent as base oil and a fluorinated product 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 r.p.m. 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.

The following tableI collates the results obtained

with different fluorinated additives according to the invention, identified in the form Hx, where x corresponds to the number of the example describing the preparation of the fluorinated additive. A second column shows the proportion by weight of fluorinated additive incorporated in the base oil.

By way of comparison, the results obtained with the following non-hydrogenated homologues are also shown:

I 1 : oil of Example 1-a

I 2 : product obtained by reacting 3 g of 2-epoxybutane with 15 g of the oil of Example 1-a, under the same working conditions as in Example 2

I 3 : ditto, but replacing epoxybutane by 3.6 g of epoxystyrene and heating for 5 hours to 110°C

I 4 : mixture of fluorinated amino alcohols used as the starting material in Example 4-a

I 5 : industrial mixture of fluorinated amino alcohols, used as the starting material in Example 5

I 6 : product obtained by the action of styrene oxide (144.3 g) on the mixture I5 (570 g) under the same conditions as in Example 6

I 7 : product obtained by the action of 5.52 g of benzoyl chloride on 20.4 g of the mixture of diols obtained as in Example 7-a, but starting with the product I5.

Table I

Fluorinated additive	Proportion % by weight	Diameter of mark in mm for an applied load of	
		40 daN	70 daN
None (control)		1.44	2.37
I 1	0.05	0.85	0.90
H 1-b	0.05	0.48	0.59
I 2	0.1	0.76	1
H 2	0.1	0.59	0.76
I 3	0.1	0.71	0.96
H 3	0.1	0.55	0.78
I 4	0.1	0.74	0.98
H 4-a	0.1	0.51	0.75
I 5	0.05	0.75	0.81
H 5	0.05	0.55	0.66
I 6	0.1	0.68	0.9
H 6	0.1	0.40	0.52
I 7	0.1	0.66	0.8
H 7-b	0.1	0.44	0.55

Inspection of these results shows that the products H1 to H7 according to the invention exhibit a distinctly improved anti-wear efficacy compared with their homologues I1 to I7, which have not undergone hydrogenation.

II - The fluorinated additive H6 according to the invention has been tested comparatively to three anti-wear additives of the zinc dithiophosphate type currently used in hydraulic oils, namely :

DTPZ A : zinc dithiophosphate derived from a C_6 secundary alcohol

DTPZ B : zinc dithiophosphate derived from a C_8 primary alcohol

DTPZ C : zinc dithiophosphate derived from a mixture of primary and secundary alcohols.

These additives were dissolved at various concentrations in a paraffinic oil 200N, then each solution was submitted to the wear test using the EP 4 ball machine under a load of 40 daN for 1 and 2 hours, the temperature being maintained at 120°C during the test.

The following table II collates the results obtained. Their inspection shows that the wear diameter for the additive H6 according to the invention is always less than those corresponding to the zinc dithiophosphates, although the latter were used at concentrations ten times higher.

TABLE II

ADDITIVE	CONCENTRATION (% by weight)	DIAMETER OF MARK IN MM	
		1 hour	2 hours
NONE (control)		1.39	1.55
DTPZ A	0.2	0.87	1.27
	0.5	0.61	0.65
	1	0.59	0.66
DTPZ B	0.2	1	1.12
	0.5	0.92	1.01
	1	0.60	0.66
DTPZ C	0.2	0.72	0.74
	0.5	0.59	0.66
	1	0.66	0.79
H6	0.02	0.44	0.51
	0.05	0.46	0.50
	0.1	0.44	0.53

III - The fluorinated additive H6 according to the invention has been superadded to a commercial hydraulic oil ISO VG 46 at various concentrations. The anti-wear power was tested on the EP 4 ball machine under a load of 40 daN at 120°C for 1 and 2 hours.

Results are collated in the following table III.

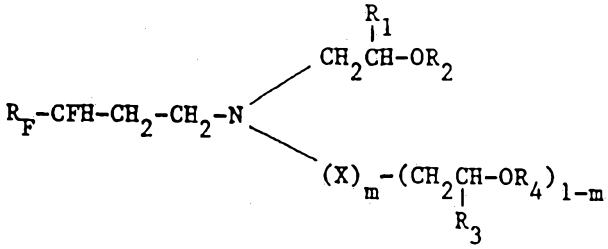
TABLE III

CONCENTRATION OF FLUORINATED ADDITIVE H6 (% by weight)	DIAMETER OF MARK IN MM	
	1 hour	2 hours
0 (control)	0.62	0.72
0.02	0.57	0.63
0.05	0.46	0.49
0.1	0.46	0.49

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

~~CLAIMS~~xx

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



(III)

in which:

R_F denotes a linear or branched perfluoroalkyl radical containing from 1 to 19 carbon atoms,

R_1 and

R_3 which may be identical or different, each denote a hydrogen atom, an alkyl radical containing from 1 to 20 carbon atoms, a cycloalkyl radical containing 5 to 6 carbon atoms or an ~~optionally substituted~~ aryl radical,

R_2 and

R_4 which may be identical or different, each denote a hydrogen atom or the acyl residue of an aliphatic, cycloaliphatic or aromatic carboxylic acid,

m equals zero or one,

X denotes a hydrogen atom or a 2-hydroxy-1-phenyl-ethyl group.

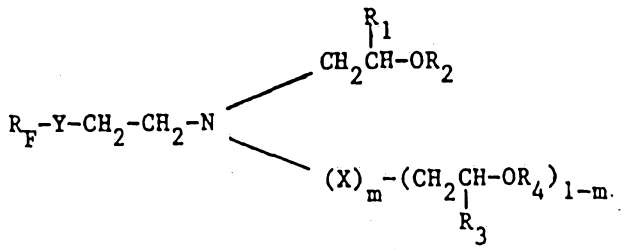
2. Compounds according to Claim 1, in which R_F is a linear perfluoroalkyl radical containing from 5 to 15 carbon atoms.

3. Compounds according to Claim 1 or 2, in which:

- m equals 1 and R_1 and R_2 are hydrogen atoms;
- m equals 0, R_1, R_2 and R_4 are hydrogen atoms and R_3 is an ethyl radical; or
- m equals 0, R_1, R_2 and R_3 are hydrogen atoms and R_4 is a benzoyl radical.

4. Mixtures of compounds according to any one of Claims 1 to 3, in which the groups R_F are different.

5. Mixtures, characterized in that they contain one or more compounds according to one of Claims 1 to 3 and up to approximately 80 % of one or more compounds of formula:



(IV)

in which the symbols R_F, m, X, R_1, R_2, R_3 and R_4 have the same meanings as in Claim 1 and Y denotes a CF_2 or CH_2 radical.

6. Process for preparing the fluorinated products according to any one of Claims 1 to 5, characterized in that an amino alcohol of formula:

$$R_F-CF=CH-CH_2-NH-CH_2\underset{\underset{1}{R}}{CH}-OH \qquad (V)$$

or a mixture of these amino alcohols with one another and/or with up to approximately 70% of saturated amino alcohols of formula:

$$R_F-CF_2-CH_2-CH_2-NH-CH_2\underset{\underset{1}{R}}{CH}-OH \qquad (IV\text{-}a)$$

is subjected to a hydrogenation and, where appropriate, the product obtained is subjected to a reaction with an epoxide and/or to an esterification.

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

8. 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.

9. Lubricants according to Claim 8, in which the content of polyfluorinated compound(s) is between 0.02 and 0.5% by weight.

10. Lubricants according to Claim 8 or 9, in which the polyfluorinated compound or compounds are combined with traditional additives.

DATED THIS 5TH DAY OF JULY 1990

ATOCHEM

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