(12) PATENT
(19) AUSTRALIAN PATENT OFFICE

(11) Application No. AU 199660710 B2
(10) Patent No. 707666

(54) Title

Perhalogenated polyorganosiloxanes and the processes for their preparation

(51)[6] International Patent Classification(s)
C08G 077/04 C08G 077/22
C08G 077/14 C08G 077/24

(21) Application No: 199660710 (22) Application Date: 1996.07.25

(30) Priority Data

(31) Number	(32) Date	(33) Country
95 09269	1995.07.25	FR

(43) Publication Date : 1997.01.30
(43) Publication Journal Date : 1997.01.30
(44) Accepted Journal Date : 1999.07.15

(71) Applicant(s)
Rhone Poulenc Chimie

(72) Inventor(s)
Philippe Jost; Philippe Karrer; Gerard Mignani; Philippe Olier

(74) Agent/Attorney
BALDWIN SHELSTON WATERS,Level 21,60 Margaret Street,SYDNEY NSW 2000

AU9660710

(12) PATENT ABSTRACT (11) Document No. AU-A-60710/96
(19) AUSTRALIAN PATENT OFFICE

(54) Title
PERHALOGENATED POLYORGANOSILOXANES AND THE PROCESSES FOR THEIR PREPARATION

International Patent Classification(s)
(51)[6] **C08G 077/04** **C08G 077/14** **C08G 077/22** **C08G 077/24**

(21) Application No. : **60710/96** (22) Application Date : **25.07.96**

(30) Priority Data

(31) Number	(32) Date	(33) Country
95 09269	**25.07.95**	**FR FRANCE**

(43) Publication Date : **30.01.97**

(71) Applicant(s)
RHONE POULENC CHIMIE

(72) Inventor(s)
PHILIPPE JOST; PHILIPPE KARRER; GERARD MIGNANI; PHILIPPE OLIER

(74) Attorney or Agent
SHELSTON WATERS , Level 21, 60 Margaret Street, SYDNEY NSW 2000

(57)

The present invention relates to chemically stable, perfluorinated, linear or cyclic polyorganosiloxanes (POS) comprising perfluorinated grafts Gf of the formula

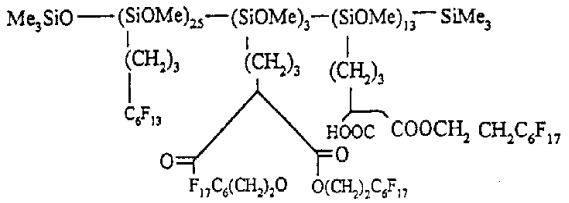
$$—C_mH_{2m}—Rf$$

in which $m \geq 2$ and Rf = perfluorinated radical:

$$—(CF_2)_{q=1\text{ to }10}F$$

with the proviso that if m = 2, then at least one other graft Gf of a different type is present.

The POS can have *e.g.* the following formula:



The invention further relates to a process for the preparation of these perfluorinated POS.

Applications: antifoams, agents for lowering surface tension, dirt repellents, antiadhesives, lubricants, oleophobic and/or hydrophobic agents, coatings *etc.*

ABSTRACT OF THE DISCLOSURE:

The present invention relates to chemically stable, perfluorinated, linear or cyclic polyorganosiloxanes (POS) comprising perfluorinated grafts Gf of the formula

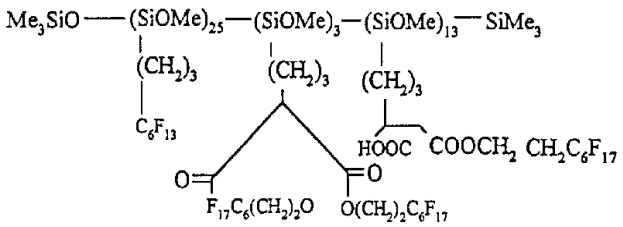


in which $m \geq 2$ and Rf = perfluorinated radical:



with the proviso that if $m = 2$, then at least one other graft Gf of a different type is present.

The POS can have *e.g.* the following formula:



The invention further relates to a process for the preparation of these perfluorinated POS.

Applications: antifoams, agents for lowering surface tension, dirt repellents, antiadhesives, lubricants, oleophobic and/or hydrophobic agents, coatings *etc.*

AUSTRALIA

PATENTS ACT 1990

COMPLETE SPECIFICATION

FOR A STANDARD PATENT

ORIGINAL

Name of Applicant/s: Rhone Poulenc Chimie

Actual Inventor/s: Philippe JOST, Philippe KARRER, Gerard MIGNANI and Philippe OLIER

Address of Service: SHELSTON WATERS
60 MARGARET STREET
SYDNEY NSW 2000

Invention Title: "PERHALOGENATED POLYORGANOSILOXANES AND THE PROCESSES FOR THEIR PREPARATION"

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

(File: 18950.00)

PERHALOGENATED POLYORGANOSILOXANES AND THE PROCESSES FOR THEIR PREPARATION

The invention relates to (per)halogenated polyorganosiloxanes (POS) derived from (per)halogenated olefins (*e.g.* α-olefins) by means of a hydrosilylation reaction, it also being possible to present said reaction as the addition of a hydrogenated silicon compound onto a halogenated reactant having one or more ethylenic or alkynylic units of unsaturation.

Without implying a limitation, fluorine is more particularly intended as the halogen.

The present invention thus relates to halogenated - preferably fluorinated - cyclic or non-cyclic (poly)organosiloxanes having at least one silicon atom substituted by at least one halogenated (*e.g.* fluorinated) radical **Rf**.

The present invention further relates to a process for the preparation of such compounds.

The role of halogens, particularly fluorine, and the carbon-fluorine bond in providing organic polymer systems with specific properties is well known in polymer chemistry.

It is known in particular that the effects of fluorination, and more precisely of the introduction of perfluorinated units into polymers, are:

- to lower the surface energies,
- to improve the thermal and chemical stability and
- to impart organophobicity and oleophobicity properties.

This type of functionalization by halogenation, and in particular by perfluorination, has been applied to silicone polymers, particularly of the cyclic or non-cyclic polyorganosiloxane type, since the 1970s.

Silicone oils grafted by fluorinated units are thus available which have applications in the textile field as stain or dirt repellents or which can be used as lubricants, as antiadhesives specific for certain adhesives (silicones of high adhesive strength), as fat repellents or else as antifoams. Fluorinated silicone fluids can also be formulated with different thickeners to form mastics or any other sealing and/or jointing materials.

In crosslinked form these fluorinated silicones can be shaped into a variety of engineering parts by molding or extrusion.

For further details on these fluorinated silicones, reference may be

made to the article by OGDEN R. PIERCE entitled "Fluorosilicones" - 1970 - John Wiley & Sons Inc., pages 1 to 15.

A first known strategy for the industrial synthesis of silicones containing perfluorinated units consists essentially in "hydrosilylating" a dihalogenohydrogenoorganosilane, such as $MeHSiCl_2$ (Me = methyl), with an unsaturated compound carrying a perfluorinated unit and having the general formula CH_2=CH-**Rf** (**Rf** = perfluorinated unit). The addition of the silane onto this olefin yields a perfluorinated dihalogenoorganosilane, which can be hydrolyzed to produce a functionalized silicone; this can be a cyclic tetramer, for example. It is possible to subject the latter to a redistribution reaction to give a perfluorinated linear polyorganosiloxane (POS). The hydrosilylation reactions which are involved in this kind of synthesis, and which use various combinations of silicone hybrids and perfluorinated olefins, are known to be catalyzed by selected metal compounds, particularly certain group VIII metals such as platinum. Pt/Sn complexes have thus been employed as hydrosilylation catalysts - *cf.* patent **US no. 4 089 882** (SHINETSU). This synthetic strategy appears to be relatively complex and hence expensive.

With a view to industrial simplification, a second synthetic strategy has been proposed which is based on the direct hydrosilylation of a silicone containing an SiH unit with an α-fluorinated olefin, *e.g.* of the type CH_2=CH-**Rf**, this perfluorinated unit **Rf** being attached directly to the olefinic CH by a carbon atom carrying at least one fluorine atom. Here again a variety of group VIII metal catalysts, in particular those based on platinum, are used in this hydrosilylation reaction. It has been found, however, that these catalysts do not afford very high yields. In particular, the conventional industrial hydrosilylation catalysts based on platinum (for example of the KARSTEDT type) are not very efficient. Moreover, it has been observed that substantial amounts of by-product are generated, obviously to the detriment of the perfluorination of the silicones. In these known perfluorinated POS, the radical **Rf** is joined directly to the Si of the silicone chain. In other words, the linkage in this case corresponds to $-CH_2-CH_2-(CH_2)_m-$ where m = 0.

It is these linkages which are used in patent **US no. 5 233 071**. They originate from the hydrosilylation of α-olefins. However, to overcome the deficiencies of the hydrosilylation catalysts used in the prior art, the process described in said patent involves cobalt-based organometallic complexes

[$(Co_2CO_8$, $Co_2CO_6)(PR_3)_3$, where R = alkyl, aryl]. Such a technical proposal has appeared unsatisfactory because the reaction times obtained are of the order of a few days and it is essential to use a substantial amount of catalyst (1-2%), which is particularly unfavorable in terms of the economics of the process.

One appreciable disadvantage of these cobalt-based complexes is that they catalyze reactions other than hydrosilylation. In particular, they are capable of taking part in polymerization processes involving the rupture of epoxy rings. This lack of specificity is particularly troublesome. Moreover, these are not industrial catalysts.

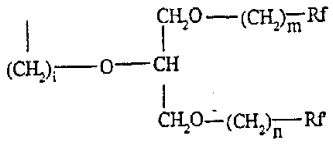
Patent **US no. 5 348 769** discloses linear or cyclic polyorganosiloxanes comprising siloxy units **D** substituted by a first perfluorinated functional unit of the formula -R^3**ZRf**, and other siloxy units **D** carrying a second functional unit of the ether-hydroxyl or alkyl-hydroxyl type. The linkage or bridge joining Si to **Rf** in the first perfluorinated functional unit consists especially of -$(CH_2)_xZ$, where x = 2, 3 or 4 and Z = NHCO, $NHSO_2$, O_2C, O_3S, OCH_2CH_3, $NHCH_2CH_2$ or $CH_2CHOHCH_2$. The catalyst used is preferably chloroplatinic acid. This is not one of the simplest techniques as it requires the prior preparation of the perfluoroalkylated olefinic reactant. This considerably lengthens the synthesis times and hence increases the cost of the process.

Apart from these linkages whose precursors are perfluoroalkylated α-olefins of the formula CH_2=CH-**Rf**, the technical literature of the prior art also describes bridges whose olefinic precursors are of the type CH_2=CH-Ⓛ-**Rf**, the chemical bond between Ⓛ and **Rf** being an ester bond. The latter results from the reaction of a carboxyl group with a perhalogenated alcohol, preferably perfluorinated alcohol, and said carboxyl group is generally the hydrolysis product of an acid anhydride.

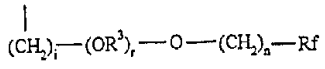
Thus PCT patent application **WO 94/12561** discloses POS grafted by fluorinated units only in the α and ω positions at the ends of the silicone chains. These POS α,ω-perfluorinated on alkyl ester groups do not exhibit optimum properties in respect of surface tension lowering or oleophobicity and hydrophobicity.

European patent application **no. 0 640 644** describes perfluorinated (**Rf**) silicone derivatives which can be used in cosmetic formulations. These perfluorinated silicone derivatives are characterized by siloxy units D carrying

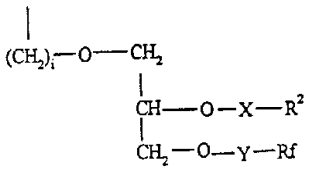
three different types of perfluorinated grafts, namely:



(1)



(2)



(3)

where R^2, R^3 = alkyl, *e.g.* CH_3;

$2 \leq i \leq 16$, *e.g.* $i = 3$; $1 \leq m,n \leq 6$; $0 \leq r \leq 50$;

the number of siloxy units D grafted in this way is between 1 and 200; and

X, Y = single bond, -CO- or C_1-C_6-alkylene.

A common feature of these perfluorinated grafts **(1)** to **(3)** is the presence of ether bonds within the linkage joining the perfluorinated radical **Rf** to the silicon. Each of these ether bonds represents a possible point of rupture by chemical attack, under certain conditions.

This is a major disadvantage of these known perfluorinated POS because the labile character of the perfluorinated groups is clearly unacceptable in certain applications.

This review of the prior art shows that there are no chemically stable, halogenated - preferably (per)fluorinated - POS in which the fluorinated, pendent, lateral grafts result from the hydrosilylation of perfluorinated olefins with SiH units and have alkyl and/or alkyl ester linkages but not ether linkages.

Furthermore, the prior art contains even fewer disclosures of such POS which can be obtained in a simple, economic and hence perfectly industrial

manner.

It is an object of the present invention to overcome or ameliorate at least some of the disadvantages of the prior art, or to provide a useful alternative.

Under these circumstances, one of the preferred objects of the present invention is to overcome this deficiency of such halogenated - preferably (per)fluorinated - POS and preferably to provide novel perfluorinated POS possessing bifid grafts each having one or two parallel perfluorinated chains, said POS thus having a crystalline character which makes them particularly suitable for application as dirt repellents.

Another preferred object of the invention is to provide a process for the preparation of halogenated - preferably (per)fluorinated - POS, this process being of the type in which at least one halogenated (e.g. fluorinated) olefin is reacted with a POS containing at least one SiH unit, in the presence of an effective amount of catalyst, according to a hydrosilylation mechanism, it being desirable for said process to use available or easily preparable starting materials and also to be based on a methodology which is simple to put into effect, does not require sophisticated equipment and makes it possible to achieve high performance characteristics in terms of the yield and purity of the final perfluorinated POS.

Another preferred object of the invention is to offer a perhalogenation (perfluorination) process of the above-mentioned type which is characterized by excellent hydrosilylation kinetics and by a high degree of conversion of the SiH units to **SiRoRf** units, where **Ro** = divalent bridge and **Rf** = perfluorinated unit.

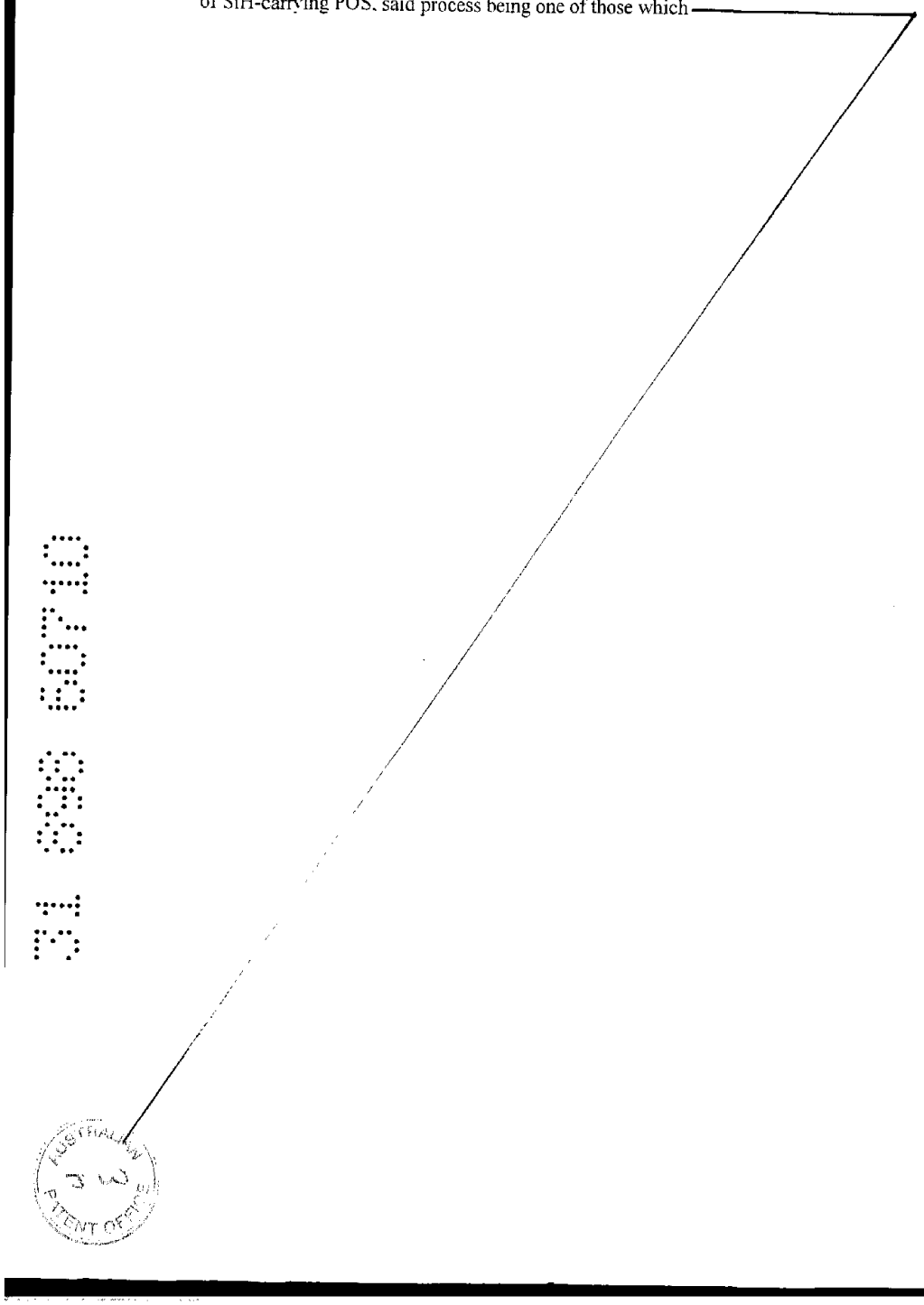
Another preferred object of the present invention is to provide a process for the perhalogenation - preferably (per)fluorination - of SiH-carrying POS which allows the use of traditional hydrosilylation catalysts that are simple to manipulate and inexpensive, for example of the platinic type (KARSTEDT), without sacrificing the desirable requirements of optimum efficiency, yield, purity of the final products and specificity.

Another preferred object of the invention is that the above-mentioned process makes it possible simply and economically to obtain perfluorinated POS (e.g. silicone oils) which are monofunctional.

These and other preferred objects are preferably achieved by the present invention, which relates principally to novel perhalogenated - preferably perfluorinated - POS and

AUSTRALIAN PATENT OFFICE 13

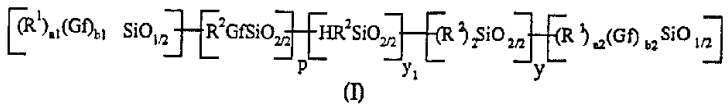
to a novel perhalogenation - preferably perfluorination - process by the hydrosilylation of SiH-carrying POS, said process being one of those which



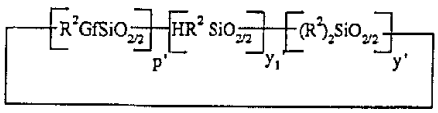
AUSTRALIAN PATENT OFFICE

make it possible to obtain the above-mentioned novel POS.

The present invention therefore relates firstly to (per)halogenated - preferably (per)fluorinated - polyorganosiloxanes (POS) comprising species of the following general formulae (I) and (II):



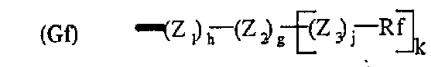
(I)



(II)

in which:

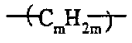
- a1 + b1 = 3, a2 + b2 = 3; a, a2 = 2 or 3; b1, b2 = 0 or 1;
  $1 \leq p \leq 200$, preferably $1 \leq p \leq 90$;
  $0 \leq y_1 \leq 10$, preferably $0 \leq y_1 \leq 5$;
  $0 \leq y \leq 100$, preferably $0 \leq y \leq 50$;
  where $5 \leq p + y_1 + y \leq 200$, preferably $10 \leq p + y_1 + y \leq 100$, and $[p/(p + y + y_1 + 2)].100 \geq 3$, preferably ≥ 5;
- $1 \leq p' \leq 9$, preferably $1 \leq p' \leq 4.5$;
- $0 \leq y'_1 \leq 1$, preferably $0 \leq y'_1 \leq 0.25$;
- $0 \leq y' \leq 5$, preferably $0 \leq y' \leq 0.5$;
- each radical R^1, R^2 on the one hand is identical to or different from like radicals of the same exponent and the other radical of different exponent, and on the other hand is a linear or branched C_1-C_{12}-(cyclo)alkyl - preferably C_1-C_6-(cyclo)alkyl - group or a hydrocarbon group, advantageously an aryl, an aralkyl or an alkylaryl, these groups optionally being substituted; and
- **Gf**:
  - is an optionally halogenated - preferably (per)fluorinated - functional monovalent radical of identical or different type in the p or p' siloxy units D and/or the two siloxy units M in which it is present,
  - and has the following average formula:

(Gf) 

- where h = 0, 1; g = 0, 1; j = 0, 1 and k = 1 or 2;

Legend: The free valences shown in bold ━ throughout the present disclosure are those attached directly or indirectly to the silicon of the POS and located closest to said silicon.

- **with the proviso** that at least one radical Gf in which k ≠ 0 is present in said POS (I) or (II);
- Z_1 being a divalent radical of the formula



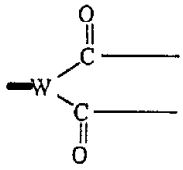
where m ≥ 2,

with the proviso that if m = 2, then at least some of the radicals Gf are radicals in which g ≠ 0,

and it optionally being possible for at least one of the hydrogens substituting the carbons of Z_1 to be replaced by a linear or branched C_1-C_6-lower alkyl, preferably by a methyl;

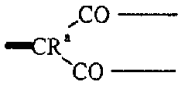
- Z_2 being a mono-, di- or tri-valent radical of one of the following formulae:

.α.



- one or both of the free valences of the carbonyl(s) being joined to $-Z_3Rf$ and, in the case where only one of said free valences is joined to $-Z_3Rf$, the other then being joined to a hydroxyl;

.β.

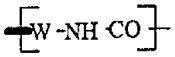


- at least one of the free valences of the carbonyls being joined to $-Z_3$-Rf and, in the case where only one of these free valences is joined to $-Z_3$-Rf, the other then being joined to a linear or branched C_1-C_6-alkoxy; and
- R^4 = H, aryl or linear or branched C_1-C_6-lower alkyl, preferably CH_3;

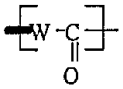
.γ.



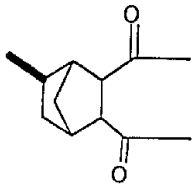
.δ.



.ε.

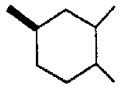


.η.



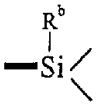
- h = 0 in **Gf**;
- one or both of the free valences of the carbonyl(s) being joined to $-Z_3$-Rf and, in the case where only one of said free valences is joined to $-Z_3$Rf, the other then being joined to a hydroxyl or to a linear or branched C_1-C_6-alkoxy;

.θ.



- one or both of the two free valences other than the valence ▬ being joined to $-Z_3$-Rf and, in the case where only one of these two valences is joined to $-Z_3$-Rf, the other then being joined to OH or to a linear or branched C_1-C_6-alkoxy; or

.λ.



- one or both of the two free valences other than the valence ▬ being joined to $-Z_3$-Rf and, in the case where only one of these two valences is joined to $-Z_3$-Rf, the other then being joined to OH or to a linear or branched C_1-C_6-alkoxy;
- R^b = H or linear or branched C_1-C_6-lower alkyl, methyl being preferred;

→ W being a cyclic or non-cyclic hydrocarbon radical, in particular an aliphatic and/or alkenyl and/or alkynyl and/or aromatic radical, and W also being devoid of an ether link -O-;

△ Z_3 is a divalent radical of the formula

$$\blacksquare\text{U-}C_nH_{2n}\text{-}$$

• where $n \geq 1$ and U = O, S, NH or $NHSO_2$, preferably O; and

△ and Rf being a perhalogenated - preferably perfluorinated - radical and particularly preferably a linear or branched perfluoroalkyl radical having one of the following formulae:

$$\blacksquare C_qF_{2q}\text{-}CF_3 \qquad \text{where } q \geq 0;$$

$$\blacksquare C_qF_{2q}\text{-}H \qquad \text{where } q \geq 1;$$

— $NR^{rf}SO_2\ Cq\ F_2q - CF_3$ where $q \geq 0$ and R^{rf} = H, aryl or linear or branched C_1-C_6-lower alkyl (preferably CH_3); and

— $NR^{rf}SO_2\ Cq\ F_2q - H$ where $q \geq 1$ and R^{rf} is as defined above.

Unless the context clearly requires otherwise, throughout the description and the claims, the words 'comprise', 'comprising', and the like are to be construed in an inclusive as opposed to an exclusive or exhaustive sense; that is to say, in the sense of "including, but not limited to".

It is to the credit of the Applicant to have produced these novel (per)halogenated - preferably (per)fluorinated - POS by the careful selection of different species of grafts perfluorinated by Rf, including the following species in particular:

- that with an alkylene linkage $-(C_mH_{2m})-$ where $m > 2$;
- that with an alkylene linkage $-(C_mH_{2m})-$ where $m = 2$, which is necessarily associated with at least one other species of linkage in a given POS;
- that with an alkylene linkage $-(C_mH_{2m})-$ ($m > 2$) extended by a divalent or trivalent hydrocarbon radical W devoid of an ether -O-, and having one or more free carboxyl ends or bonding with perfluorinated radicals Rf, with the proviso that if all the carboxyl ends are free on a given graft, then the POS comprises at least one other perfluorinated graft;
- that with an alkylene linkage $-(C_mH_{2m})-$ ($m > 0$) extended by W, which itself forms part of is joined to a cyclic unit comprising at least one divalent radical -O-, this unit containing for example:

  an acid anhydride

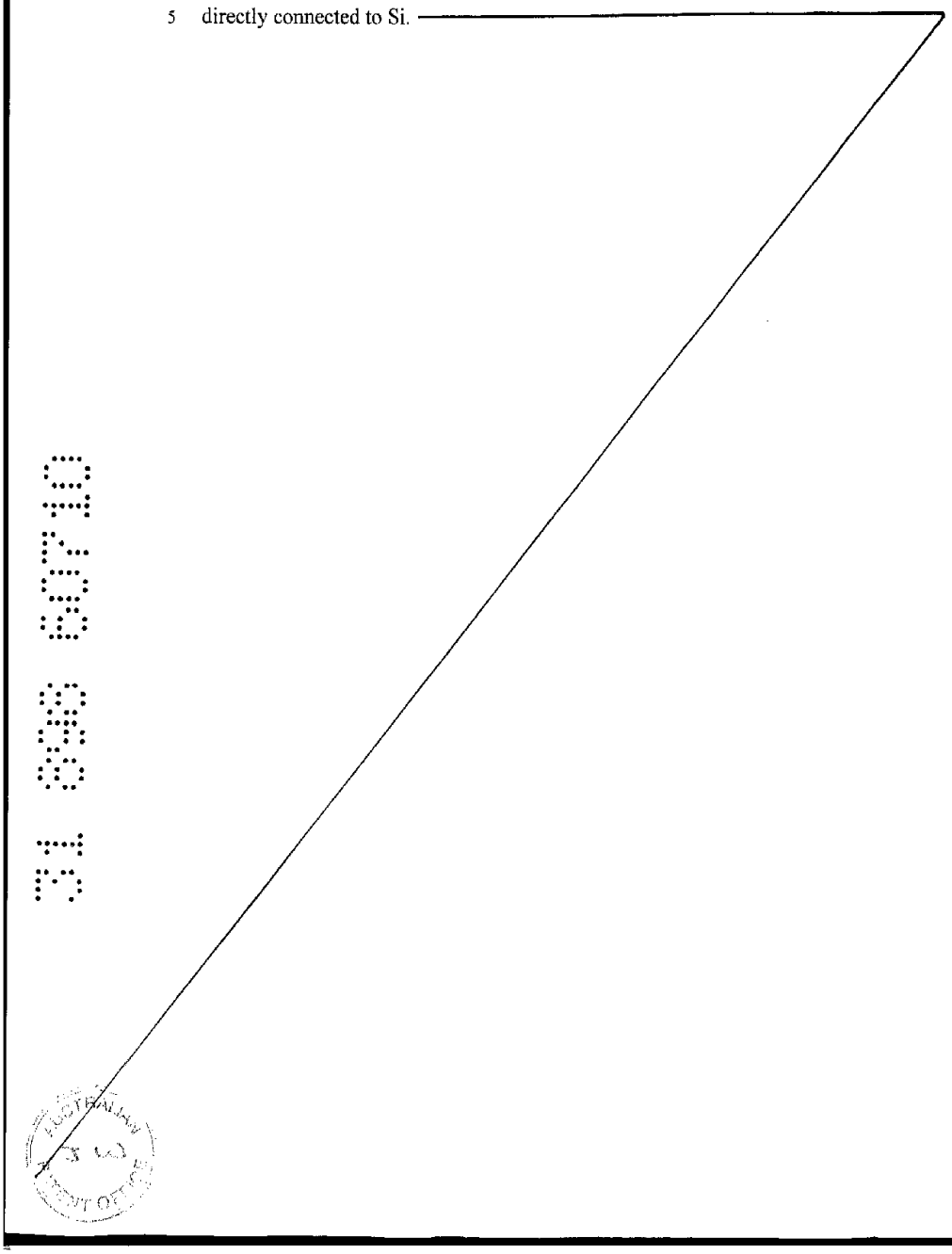
  and/or an epoxide

  and/or a cyclic ether;

- that with an alkylene linkage $-(C_mH_{2m})-$ ($m > 2$) extended by Wω- hydroxylated and/or alkoxylated by a radical whose free end is Rf;
- that with an alkylene linkage $-(C_mH_{2m})-$ ($m > 0$) extended by a divalent or trivalent radical belonging to the general family of the radicals W and joined to or forming part of a cyclic unit whose free valence(s), other than that joined to Si, bonds (bond) with any radical(s) Z_3Rf and/or with alkyl, alkoxy or hydroxyl substituents;

PATENT OFFICE

- that with an alkylene linkage $-(C_mH_{2m})-$ ($m > 0$) extended by a trivalent silyl radical in which the free valences, other than that joined to Si, bond with any radical(s) Z_3Rf and/or with alkyl, alkoxy or hydroxyl substituents; and
- that with a linkage not containing a divalent alkylene radical but having a radical W directly connected to Si.



AUSTRALIAN PATENT OFFICE

These novel POS monofunctionalized by perfluorinated radicals Rf satisfy the condition that at least one radical **Gf** in which $k \neq 0$ is present in the POS **(I)** or **(II)**.

All the grafts perfluorinated by Rf have the advantage of being chemically stable.

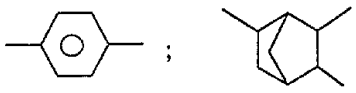
Another major advantage of the grafts **Gf** according to the invention is that they can be obtained with the aid of industrial catalysts, for example those based on platinum, such as the KARSTEDT catalyst. Apart from the fact that they are used in small amounts, these catalysts are intrinsically economic, thereby contributing to a reduction in the cost of the novel perhalogenated (perfluorinated) silicon compounds according to the invention.

This cost is all the lower because the structure of the graft according to the invention affords rapid hydrosilylation kinetics, high yields and high degrees of conversion of the SiH units to SiGf units.

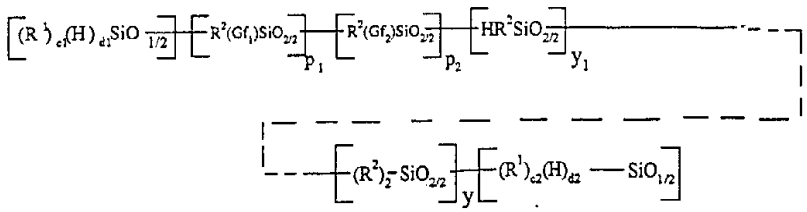
Preferably the monovalent radical Rf corresponds to $-C_pF_{2p}-CF_3$, where p is between 3 and 20, preferably between 5 and 12 and particularly preferably between 7 and 10. In practice it is also possible to use *e.g.* mixtures of Rf in which p = 7, 8 and 9.

According to one advantageous provision of the invention, the perfluorinated polyorganosiloxanes **(I)** and **(II)** to which it relates comprise one or more grafts **Gf** in which:

h = 0 or 1 and g = 1, Z_2 being of the type comprising a group W corresponding to a substituted or unsubstituted, saturated, unsaturated or aromatic monocyclic or polycyclic radical preferably selected from the following rings:

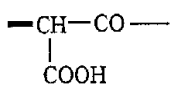


According to one preferred modality of the invention, the POS are linear and have the following formula **(I.1)**:

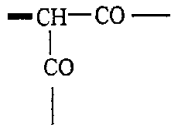


(I.1)

where
- R^1, R^2 = methyl, propyl or butyl;
- c1 + d1 = 3 and preferably c1 = 2, d1 = 1
  c2 + d2 = 3 and preferably c2 = 2, d2 = 1;
- p_1, $p_2 \geq 0$; $p_1 + p_2 \geq 1$;
- $0 \leq y_1 \leq 100$, preferably $0 \leq y_1 \leq 50$, with the proviso that if $y_1 = 0$, then d1 and/or d2 = 1;
- $0 \leq y \leq 500$, preferably $0 \leq y \leq 500$;
- $\mathbf{Gf_1} = \mathbf{Gf}$, where h = k = 1 and g = j = 0;
- $\mathbf{Gf_2} = \mathbf{Gf}$, where h = g = 1, k = 1 or 2 and Z_2 =

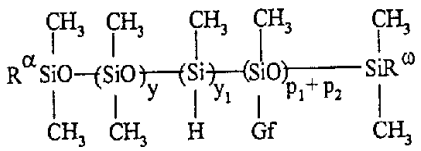


or



Even more preferably, the POS (I) according to the invention are perfluorinated linear polymers of the following formula (I.1.1):

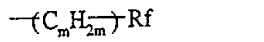
(I.1.1.)



where y, y_1, p_1, p_2 and **Gf** = $\mathbf{Gf_1}$ or $\mathbf{Gf_2}$ are as defined above and R^{α} and R^{ω}, which are identical or different, are H or C_1-C_6-alkyl.

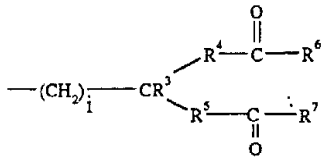
Advantageously **Gf** is selected from the following list of groups:

- .a.



where $m \geq 2$, h = 1, g = 0, j = 0 and k = 1;
if m = 2, then g = 1, where W = $-(CH_2)_{i\geq 1}-$, and/or provision is made for at least one other group **Gf** which is different from $\mathbf{Gf_1}$, m preferably being between 2 and 10;

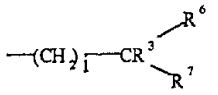
- .b.



where:

- h = 1, g = 1, j = 0 or 1, k = 1 and i = 2 to 10;
- R^3 = H or C_1-C_6-alkyl;
- R^4 and R^5 are mutually identical or different and correspond to $-(CH_2)-_{u\geq 0}$; and
- R^6 and R^7 are mutually identical or different and are OH or Z_3-Rf, where Z_3 = -O-(CH_2)-$_s$, s being between 0 and 10, at least one of the radicals R^6 and R^7 corresponding to Z_3Rf;

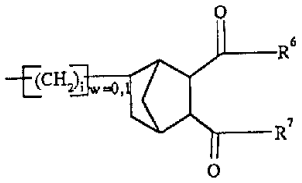
- .c.



where:

- h = 1, m ≥ 0, g = 1, j = 0 or 1, k = 1 and i = 2 to 10; and
- R^3, R^6 and R^7 are as defined above;

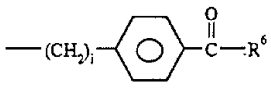
- .d.



where:

- h = 0 or 1, m ≥ 0, g = 1, i = 2 to 10, j = 1 and k = 1; and
- R^6 and R^7 are as defined above;

- .e.



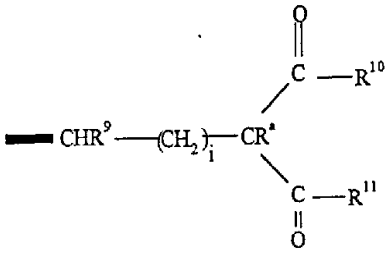
where:

- h = 1, m ≥ 0, g = 1, i = 2 to 10, j = 0 or 1 and k = 1; and
- R^6 is as defined above; and

- .f. mixtures thereof.

According to the invention, a subgroup of particular grafts **Gf** called "bifid grafts" are considered which are very especially preferred for the remarkable characteristics which they are capable of imparting to the POS onto which they are grafted. The invention therefore further relates to POS of the type defined above which comprise at least one species **(I)** and/or **(II)** substituted by at least one perhalogenated - preferably perfluorinated - radical **Gf** selected from the following subgroup of radicals:

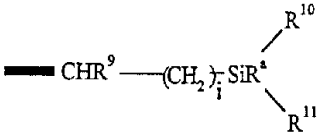
→ (i)



where:

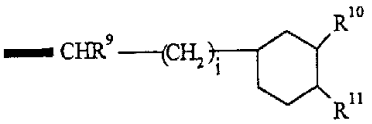
- △ R^a and R^9 independently are H or linear or branched C_1-C_6-lower alkyl, preferably CH_3;
- △ R^{10} and R^{11} independently are OH, linear or branched C_1-C_6-alkoxy or Z_3-Rf, at least one of the radicals R^{10} and R^{11} being $-Z_3Rf$; and
- △ i = 0 to 10, preferably 0 to 3 and particularly preferably 1;

→ (ii)



where R^9, R^a, R^{10}, R^{11} and i are as defined above;

→ (iii)



where R^9, R^{10}, R^{11} and i are as defined above, it optionally being possible for the hexyl ring to be substituted; and

→ mixtures of the above-mentioned radicals.

At this stage of the disclosure it is appropriate to dwell for a

moment on the particularly interesting species of POS compounds according to the invention which is represented by the perhalogenated - perfluorinated - POS carrying bifid grafts **Gf** as defined above. More precisely, the bifid **Gf** of interest here are those in which the two lobes each consist of a perhalogenated - perfluorinated - radical Z_3Rf. These bisperfluorinated bifid grafts **Gf** are crystalline and, in particular, impart a degree of crystallinity to the POS which they substitute. This optimizes the water-repelling properties of the latter, which thus make very suitable active products in dirt-repelling compositions, *inter alia*.

These bifluorinated bifid grafts **Gf** can be associated especially with monoperfluorinated and/or non-perfluorinated bifid **Gf**.

The POS of this species comprise at least one species **(I)** and/or **(II)** substituted by:

- at least one perhalogenated - preferably perfluorinated - radical **Gf** of formula **(i)**, **(ii)** or **(iii)** as defined above,
  the radicals R^{10} and R^{11} in the formula in question corresponding to Z_3Rf and preferably to:

$$\text{—O—}C_nH_{2n}\text{—}C_qF_{2q}\text{—}CF_3 \quad (q \geq 0)$$

or

$$\text{—O—}C_nH_{2n}\text{—}C_qF_{2q}\text{—}H \quad (q \geq 1)$$

- and optionally at least one radical **Gf (i)**, **(ii)** or **(iii)** in which one of the radicals R^{10} or R^{11} is Z_3Rf and the other radical R^{10} or R^{11} is different from Z_3Rf and advantageously corresponds to OH or linear or branched C_1-C_6-alkoxy.

During the synthesis, those skilled in the art are perfectly capable of controlling the degrees of substitution of the POS of this species by bisperfluorinated and/or monoperfluorinated and/or non-perfluorinated bifid **Gf**. It is the intended applications of the grafted POS which determine how these degrees of substitution should be regulated.

Within this species the bifid **Gf** with an alkylmalonyl linkage **(i)** are chosen more especially in practice.

All these grafts **Gf** impart novelty and great technical value to the

POS to which they are attached.

On the basis of the details given above in respect of the POS according to the invention and their grafts **Gf**, it can be deduced that the POS to which the invention relates very specifically, but without implying a limitation, are *e.g.* poly(dimethyl,methylperfluoroalkyl)siloxanes or poly(methylalkyl, methylperfluoroalkyl)siloxanes where the first alkyl group is propyl, butyl, pentyl, hexyl *etc.*

The linear perfluorinated POS compounds of average formula **(I.1)** and **(I.1.1)** naturally have corresponding cyclic compounds of average formula **(II.1)** and **(II.1.1)**; in this case, however, the sum of $p' + y'_1 + y'$ is less than or equal to 10, preferably 5.

It should be noted that all the POS (I) and (II), in particular **(I.1)**, **(I.1.1)**, (II.1) and (II.1.1) according to the invention, contain at least one graft **Gf** carrying at least a first perfluorinated radical Rf, and optionally one or more **Gf** carrying other radicals Rf which are identical to or different from one another and the first radical Rf mentioned above.

It is possible to envisage multiple combinations of grafts **Gf** on the POS of the invention: **Gf** with Z_2 α to λ and in particular Gf_a to Gf_e, Gf(i), Gf(ii) and Gf(iii), these last three grafts being particularly preferred.

According to an optional but nevertheless advantageous provision of the invention, the POS contain, per molecule, at least one siloxy unit

$$T = \left[R^8 SiO_{3/2} \right]$$

where R^8 is defined in the same way as R^1, R^2 and **Gf**, as given above, and optionally siloxy units $Q = [SiO_{4/2}]$.

As far as the functional characteristics of the products according to the invention are concerned, it is necessary to emphasize the fact that the monofunctional or polyfunctional fluorinated polyorganosiloxanes described above have notable properties of surface tension lowering and oleophobicity and/or hydrophobicity, *inter alia*. These properties can be adjusted by controlling the proportions of grafted or non-grafted units **D** present in the fluorinated POS. This corresponds to the molar proportions p, y, y_1 and p', y',

y'_1 given by formulae **(I)** and **(II)** defined above.

It should be noted that m values of 2 or 3 in Z_1 guarantee that the fluorinated POS in question will have a good heat stability. This property can be advantageous especially in the context of application as a lubricant.

The fluorinated POS according to the invention can take the form of oils of greater or lesser viscosity, but can also take the form of resins Q and/or resins resulting from the crosslinking of linear or cyclic POS chains *via* crosslinking functional groups which can be present in said POS.

The invention further relates to a process for the preparation of cyclic or linear halogenated - preferably (per)fluorinated - POS, which consists essentially in reacting:

- A → at least one polyalkylhydrogenosiloxane - preferably polymethylhydrogenosiloxane - oil
- B → with at least one (per)halogenated - preferably (per)fluorinated - olefin which is a precursor of Gf_1 as defined above and has the formula Gf_{1p}:

$$Z_{1p}Rf$$

in which:

- ◁ Z_{1p} = olefinic precursor of Z_1,
- ◁ Rf is as defined above and
- ◁ m > 2 in Z_1,

- C → in the presence of an effective amount of a metal hydrosilylation catalyst preferably based on platinum.

This is a first method - the most direct method - of implanting perfluorinated grafts **Gf** on a POS chain by hydrosilylation. The grafts obtained are alkylene-perfluoroalkyls.

The olefinic, preferably vinylic, precursors are readily available or easy to obtain.

Throughout the description of the process, the precursor radicals of the radicals present in the final POS are identified by the subscript "p" following the subscript(s) already indicated.

To obtain a novel mixture of POS in the case where m = 2 in Z_{1p}, it will again be necessary to react the oil A with at least one other olefinic precursor Z_{1p} where m > 2, and/or with other precursors of different Gf, as explained below.

Thus, in a second mode of carrying out the process according to the

invention, the oil A is reacted:

- B' → with at least one (per)halogenated - preferably (per)fluorinated - olefin which is a precursor of Gf_1, as defined above, and has the formula Gf_{1p}:

$$Z_{1p}Rf$$

in which:

- ◁ Z_{1p} = olefinic precursor of Z_1,
- ◁ Rf is as defined above and
- ◁ m = 2 in Z_1,

- D → with at least one olefin of the formula

$$Z_{1p}Z_{2p}$$

in which Z_{1p} = olefinic precursor of Z_1 and Z_{2p} = precursor of Z_2,

- B → and/or with reactant B as defined above,
- C → in the presence of an effective amount of a metal hydrosilylation catalyst preferably based on cobalt and/or platinum,

the reaction product A + B' + D and/or B optionally being brought into contact with a reactant E:

- E → of the type $Z_{3p}Rf$, where Z_{3p} = precursor of Z_3 and Rf is as defined above, to form one or more radicals Gf_2.

In this second mode, at least one of reactants B and D must be used in order to ensure that the products obtained are novel. In practice this second mode of carrying out the invention is performed in several steps, the hydrosilylation of B' being carried out separately from that of the other olefins B or D. For example, the hydrosilylation of B' is catalyzed by a cobalt-based product whereas the other hydrosilylations are catalyzed by platinum.

In a third mode of carrying out the invention, the oil A is reacted:

- D' → with at least one olefin of the formula

$$Z_{1p}Z_{2p}$$

in which:

Z_{1p} = olefinic precursor of Z_1 and

Z_{2p} = olefinic precursor of Z_2,

- C → in the presence of an effective amount of a metal hydrosilylation catalyst preferably based on platinum,

the reaction product A + D' optionally being brought into contact with a reactant

- E' → of the type $Z_{3p}Rf$, where Z_{3p} = precursor of Z_3 and Rf is as defined above, to form one or more radicals $\mathbf{Gf_2}$.

In the second and third modes of carrying out the invention, the grafts **Gf** are constructed by growing roots of these grafts, these roots being fixed to the POS chains. In a manner of speaking, the constituent elements Z_1, Z_2, Z_3 and Rf are butted together.

By contrast, in the fourth mode of carrying out the invention, a global precursor of **Gf**, *i.e.* $\mathbf{Gf_p}$, is prefabricated and then fixed to the POS.

In other words, this consists essentially in reacting:

- A → at least one polyalkylhydrogenosiloxane - preferably polymethylhydrogenosiloxane - oil
- F → with at least one halogenated - preferably (per)fluorinated - olefin which is a precursor of **Gf** and has the formula $\mathbf{(Gf_p)}$:

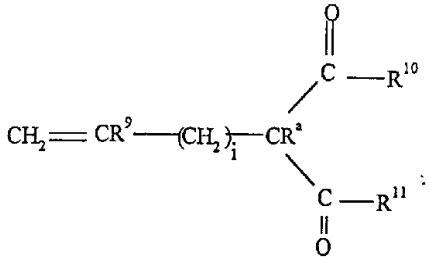
$$(Z_{1p})_h-(Z_2)_g-\left[(Z_3)_j-Rf\right]_k$$

in which:

- Z_{1p} is the olefinic precursor of the radical Z_1, as defined above, and
- Z_2, Z_3, Rf, h, g, j and k are also as defined above,
- with the provisos that:
  - * if h = 0, then g = 1 and Z_2 becomes an olefinic precursor Z_{2p},
  - * if k = h = 1 and m = 2, then g = 1 and $Z_2 = Z_{2p}$,
- C → in the presence of an effective amount of a metal hydrosilylation catalyst preferably based on platinum.

The precursor Gf_p of Gf preferably has one of the following formulae:

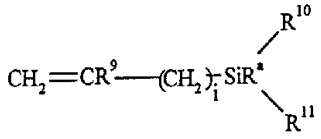
(i_p)



where:

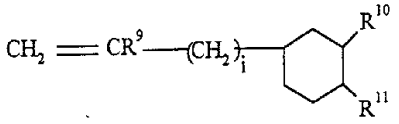
- △ R^8 and R^9 independently are H or linear or branched C_1-C_6-lower alkyl, preferably CH_3;
- △ R^{10} and R^{11} independently are OH, linear or branched C_1-C_6-alkoxy or Z_3-Rf, at least one of the radicals R^{10} and R^{11} being Z_3Rf; and
- △ i = 0 to 10, preferably 0 to 3 and particularly preferably 1;

(ii_p)



where R^9, R^8, R^{10}, R^{11} and i are as defined above; and

(iii_p)



where R^9, R^{10}, R^{11} and i are as defined above, it optionally being possible for the hexyl ring to be substituted.

These olefinic precursors **Gf_p** of the grafts **Gf** have one or two perfluorinated groups R^{10}, R^{11} (R^{10} and/or R^{11} = Z_3Rf) and are obtained by reacting:

→ at least one compound with a mobile hydrogen, consisting of the hydrogenated radical Z_3Rf, *i.e.* H-Z_3Rf, as defined above, preferably an alcohol or a thiol,

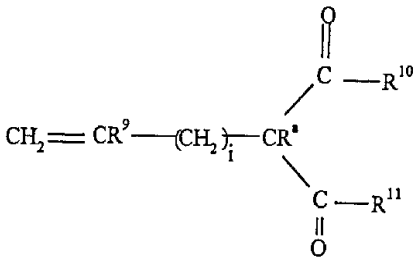
→ with starting materials formed by compounds of formula (i_p), (ii_p) or (iii_p), as defined above, in which at least one of the radicals R^{10} and R^{11} is a linear or branched C_1-C_6-alkoxy,

according to a transesterification mechanism.

It should be noted that the olefinic precursors **Gf_p** **(i_p)**, **(ii_p)** and **(iii_p)** referred to above constitute novel reaction intermediates (novel synthons).

It follows that the present invention further relates to a reaction intermediate (synthon) capable of being used especially in the process described above and having at least one of the following formulae:

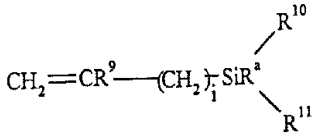
(i_p)



where R^a and R^9 independently are H or linear or branched C_1-C_6-lower alkyl, preferably CH_3; and

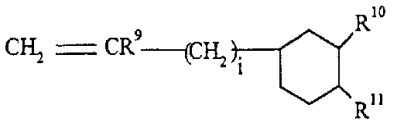
at least one of the radicals R^{10} and R^{11} corresponds to a linear or branched C_1-C_6-alkoxy, methoxy, ethoxy and propoxy being preferred;

(ii_p)



where R^9, R^a, R^{10}, R^{11} and i are as defined above; and

(iii_p)



where R^9, R^{10}, R^{11} and i are as defined above, it optionally being possible for the hexyl ring to be substituted.

One of the major advantages resulting from the use of unsaturated and perfluorinated precursor compounds $\mathbf{Gf}_p$ of this type lies in the possibility of using an industrial catalyst selected from compounds based on Ni, Pd or Pt, preferably based on Pt. This can be a KARSTEDT catalyst, for example, which is advantageously employed in small amounts, *e.g.* of the order of 10 to 50 ppm, relative to the POS compound in question, before hydrosilylation (Si-H oil).

The methodology determined by the process according to the invention is particularly simple. The hydrosilylation kinetics are rapid. The yield and the degree of conversion of the SiH are particularly high. The process is efficient and economic.

According to a preferred modality of the invention, the POS with ≡SiH units is gradually brought into contact with one or more perhalogenated or non-perhalogenated olefins $\mathbf{Gf}_p$, the catalyst being contained in one or both of these two constituents POS and $\mathbf{Gf}_p$ of the reaction medium. This applies in particular to the perfluorinated olefinic alkylene and the perfluorinated olefinic alkylene-acid anhydride.

The hydrosilylation conditions selected for the process according to the invention are conventional and can therefore be determined easily by those skilled in the art.

In practice the hydrosilylation takes place in as many stages as there are different olefinic reactants.

The reaction medium is stirred and heated to a temperature between 50 and 150°C. The reaction takes place at atmospheric pressure and generally over a period of several hours. The degree of conversion of the SiH units is greater than 99% by number.

In the case where **Gf** of the anhydride type are involved, it is possible to envisage hydrolyzing at least some of these anhydride groups so as to generate free carboxyl ends, and then esterifying at least some of said carboxyl ends with reactants of the type Z_{3p}-Rf, Z_{3p} being a hydrogenated precursor of Z_3, as defined above, and Rf also being as defined above.

As regards the other functional groups of the prelinkage type Rf which have been described above and which can be carried by the silicons of the POS according to the invention, they can be grafted before, during or after the grafting of the alkylene radicals perfluorinated by Rf.

The following may be mentioned as examples of the POS which can be used as starting materials for the process according to the invention:

* linear POS such as polymethylhydrogenosiloxanes, especially those of the type:
  - $Me_3SiO(SiMeHO)_eSiMe_3$,
    where e = 10 to 100, preferably 50;
  - or $Me_3SiO(SiMeHO)_{e1}(SiMe_2O)_{e2}SiMe_3$,
    where e1 = 10 to 100 and e2 = 0 to 50; and
* cyclic POS such as the tetramethyltetracyclosiloxane D'4.

The following may be mentioned as examples of POS which are capable of being perhalogenated - preferably perfluorinated - by using the process according to the invention:

$$Me_3SiO(SiMe_2O)_{-8}(SiHMeO)_{-4}SiMe_3$$

$$Me_3SiO(SiMeHO)_{-50}SiMe_3$$

The POS according to the invention can take the form of pure oils or else aqueous emulsions.

Thus the invention further relates to an aqueous emulsion which contains:

- at least one POS obtained by the process as defined above;
- water; and
- at least one surfactant.

According to yet another of its features, the invention relates to:

→ the application of the perhalogenated (perfluorinated) silicon compounds *per se*, as described above, or those obtained by the perhalogenation process disclosed above, as:

- lubricants
- agents for lowering surface tension
- dirt repellents
- antiadhesives
- antifoams
- oleophobic and/or hydrophobic agents and
- raw materials for the production of elastomers or films for resisting chemical attack and solvents; and

→ a film and/or coating possessing at least one of the above-mentioned properties.

Finally the invention further relates to a dirt-repelling composition comprising:

- at least one POS obtained by the process as defined above,
- and/or at least one emulsion as defined above,
- said POS used preferably carrying:
  * grafts bifunctionalized by perhalogenated - perfluorinated - radicals as defined above,
  * optionally grafts monofunctionalized by perhalogenated - perfluorinated - radicals also as defined above, and
  * optionally other grafts functionalized by groups other than bis- or mono-perhalogenated - perfluorinated - groups.

EXAMPLES

EXAMPLE I: SYNTHESIS OF SILICONES GRAFTED WITH PERFLUORINATED UNITS - CATALYSIS WITH COBALT

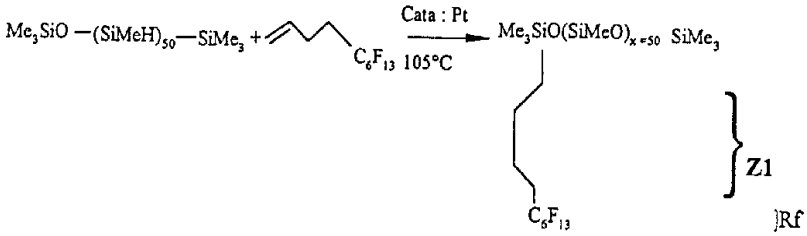
20 g (0.058 mol of Si-H units) of the following resin:

$(MeHSiO)_{0.5}(MeSiO_{3/2})_{0.5}(O_{1/2}Et)_2$

in which the molar ratios are D'/T = 1 and Si-O-Et/Si = 2 and the functionality is 288.5 meq/100 g of resin, 33.1 g (0.074 mol, 30 mol% excess) or propenyl-C_8F_{17} and 0.2734 g (0.0008 mol, 0.5 wt.%/resin) of Co_2CO_8 are introduced into a 100 ml reactor under nitrogen.

The medium is homogeneous. It is heated to 47°C in a bath. Exothermicity is observed and the temperature of the reaction mixture reaches 80°C. The reaction is allowed to proceed for 30 min. The degree of conversion of the Si-H units is of the order of 98%. After 16 h of reaction at 45°C, the degree of conversion of the Si-H units is quantitative. The mixture is allowed to return to room temperature and 150 ml of methanol are added. There is no evolution of CO coming from the catalyst. 5 washes are carried out with methanol. The functionalized resin is soluble in methanol. After devolatilization (90°C, 1 h, 6 mm Hg), 16 g of a resin are recovered. The extraction residue is solubilized in trichlorotrifluoroethane. The mixture of devolatilized resin and residue is filtered to give a yellowish liquid, which yields 20 g of a clear, light yellow resin on devolatilization.

EXAMPLE II: SYNTHESIS OF SILICONES CONTAINING PERFLUORINATED UNITS Gf_1 WHERE m > 2 / CATALYSIS BY ORGANOMETALLIC PLATINUM COMPLEXES



177.9 g (0.47 mol, 20% molar excess/Si-H units) of CH_2=CH-$(CH_2)_2$-C_6F_{13} (4-perfluorohexylbut-1-ene), *i.e.* Gf_1 where m = 4 in Z_1, 10.5 µl of a KARSTEDT catalyst (11.9 wt.%) and 12 mg of sodium acetate (Aldrich, 99.995% pure) are introduced into a reactor. The mixture is stirred at 370 rpm. It is heated to 110°C and 25 g of a silicone oil containing Si-H units of the type RHODORSIL® H68 (RHONE POULENC), corresponding to an α,ω-(trimethylsiloxy)polymethylhydrogenosiloxane oil = $MeSiO(SiMeHO)_{50}SiMe_3$, containing 0.015 eq of SiH per gram of H68 and having the formula $Me_3SiO(SiOMeH)_{50}$-$SiMe_3$, are run in over 1 h 20 min. When the introduction has ended, the degree of conversion of the Si-H units is >99%. After 3 h of reaction the degree of conversion of the Si-H units is >99.5%. IR analysis shows that Si-H units are no longer present. The reaction mixture is constantly homogeneous throughout the hydrosilylation reaction. 168.2 g of a light yellowish oil are recovered by devolatilization at 100°C under 1 mm Hg. The amount of volatile material is 32 g. The structure of this oil is confirmed my structural analyses.

EXAMPLE III:

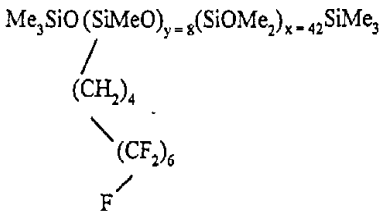
The same process as that described in Example no. II is used, but the operating conditions are slightly changed (introduction of the Si-H fluid in 60 minutes, reaction temperature and time: 80°C and 6 hours) and the following reactants and amounts are used:

- 10 mg of sodium acetate

- 80 g (0.214 mol) of 4-perfluorohexylbut-1-ene (Gf_1, m = 2 in Z_1)
- 130 microliters of a 1% (w/w) solution of KARSTEDT platinum
- 50 g (0.105 eq of Si-H) of an oil of the structure

$$Me_3SiO(SiMeHO)_8(SiMe_2O)_{42}SiMe_3$$

82.2 g of an oil of the structure



are obtained after devolatilization.

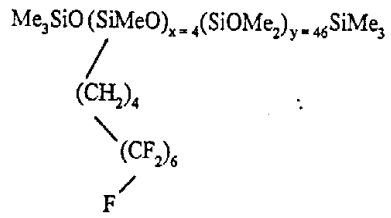
EXAMPLE IV:

The same process as that described in Example no. II is used, but the operating conditions are slightly changed (introduction of the Si-H fluid in 15 minutes, reaction temperature and time: 95°C and 3 h 20 min) and the following reactants and amounts are used:

- 16.5 g (0.044 mol) of 4-perfluorohexylbut-1-ene (Gf_1, m = 2 in Z_1)
- 11 microliters of a 13.6% (w/w) solution of KARSTEDT platinum
- 33.7 g (0.04 eq of Si-H) of an oil of the structure

$$Me_3SiO(SiMeHO)_4(SiMe_2O)_{46}SiMe_3$$

42.3 g of an oil of the structure



are obtained after devolatilization.

EXAMPLE V: PROPERTIES OF THE PERFLUORINATED POS ACCORDING TO THE INVENTION IN RESPECT OF SURFACE ENERGY LOWERING

The surface energies γ_L of the oils according to Examples II to IV and of a POS of the polydimethylsiloxane (PDMS) type are collated in Table 1 below (c = 4 and d = 6):

TABLE 1

Oil	x	y	γ_L (mN/m)
Example II	50	0	19.6
Example III	8	42	18.2
Example IV	4	46	18.9
PDMS	0	50	21

By way of comparison, the surface energies of polytrifluoropropylmethylsiloxane measured under the same conditions are 24.2 mN/m for FL 100 SHINETSU and 23.7 mN/m for FS 1265 DOW CORNING.

This ability to lower surface energies opens up avenues for the perfluorinated POS according to the invention as active ingredients in antifoams, lubricants, mold release agents and antiadhesives (paper or the like and concrete or stone).

Each liquid has a corresponding number and the perfluorinated oil is assigned a grade corresponding to the liquid of highest number which remains on the surface of the mat for at least 30 seconds.

* Treatment of the mat:

The oil KP 307 is deposited in different amounts on a polyamide-6 mat from a solution in 1,1,2-trifluorotrichloroethane; the mat is first placed in an oven for 14 hours at 30°C and then placed in an oven for 6 minutes at 80°C and 4 minutes at 140°C.

* Results:

TABLE 2

Amount of fluorine/ PA 6 (ppm)	t with liquid no. 1 (seconds)	t with liquid no. 2 (seconds)	t with liquid no. 3 (seconds)	t with liquid no. 4 (seconds)	t with liquid no. 5 (seconds)
700	>50	>50	1	1	1
1400	>50	>50	39	1	1
2800	>50	>50	>50	36	1
4200	>50	>50	>50	17	2
5600	>50	>50	>50	>50	7
7000	>50	>50	>50	>50	7

The compositions of the standard grading liquids used are as follows:

liquid 1: NUJOL (liquid paraffin)

liquid 2: NUJOL/n-hexadecane, 65/35 by volume, at 21°C

liquid 3: n-hexadecane

liquid 4: n-tetradecane

liquid 5: n-dodecane

Thus the oil of VI.1 has corresponding grades of 2 at 700 ppm of fluorine, 3 at 1400 and 4200 ppm of fluorine and 4 at 2800, 5600 and 7000 ppm of fluorine.

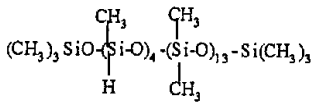
EXAMPLE VI:

87.6 g of allylsuccinic anhydride (*i.e.* 0.626 mol) are introduced into a four-necked 500 ml reactor provided with a central mechanical stirrer, a thermometer, a vertical bulb condenser and a septum.

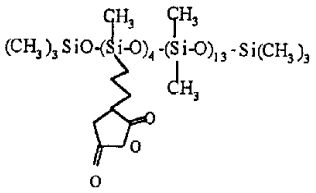
The medium is stirred, rendered inert with nitrogen and heated to a temperature of 90°C and 30 µl (*i.e.* 20 ppm/weight of Si-H oil) of a divinyltetramethyldisiloxane solution of a platinum complex containing 9.5% by weight of platinum with a divinyltetramethyldisiloxane ligand (Karstedt catalyst) are then introduced.

140 g (*i.e.* 0.525 eq of Si-H) of a poly(dimethyl,methylhydrogenosiloxane) oil are then run in over 3 h 45 minutes, the characteristics of said oil being as follows:

* Mn = 1364 g
* 0.375 eq of Si-H per 100 g of oil
* average structure:



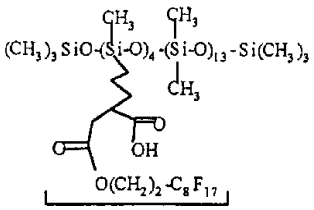
7 h after the start of the reaction, the degree of conversion of the Si-H groups is 99.3%; a devolatilization under vacuum (130°C for 6 hours under 0.05 mbar) is then carried out to remove the excess allylsuccinic anhydride and give 210 g of an oil of the structure



The following are introduced into a four-necked 250 ml reactor provided with a central mechanical stirrer, a thermometer, a vertical bulb condenser and a septum:

- 43.5 g of the previous oil, *i.e.* 0.1056 eq of anhydride groups,
- 54.1 g of 1-perfluorooctyl-2-hydroxyethane, $C_8F_{17}CH_2CH_2OH$ (*i.e.* 0.1166 mol),
- 36.6 g of toluene and
- 0.65 g of triethylamine.

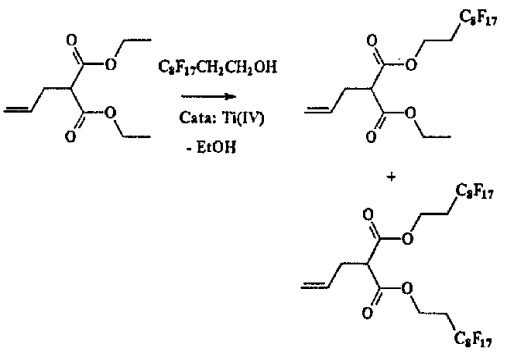
The medium is stirred, rendered inert with nitrogen and heated at a temperature of 70°C for 3 h. A devolatilization under vacuum (130°C for 5 h under 2 mbar) is then carried out to remove the toluene, triethylamine and excess 1-perfluorooctyl-2-hydroxyethane and give 83.85 g of an oil of the structure



Gf

EXAMPLE VII: SYNTHESIS OF MONO- AND BIS-PERFLUOROALKYL MONOMERS WHICH ARE PRECURSORS Gf_p OF BIFID GRAFTS Gf

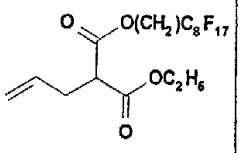
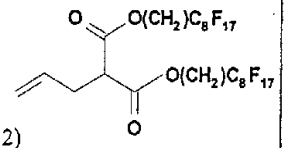
Reaction:



2018 g (10.09 mol) of diethyl allylmalonate, 2340 g (5.04 mol) of the alcohol $C_8F_{17}CH_2CH_2OH$, 3.8 g (0.016 mol) of $Ti(OEt)_4$ and 1000 g of dry toluene are introduced into a 5 l reactor under nitrogen. The temperature in the reaction mixture is raised to 95°C and the reaction takes place under partial vacuum (≈ 500 mm Hg) to favor elimination of the ethanol. After 5 h of reaction, a further 7.3 g (0.032 mol) of $Ti(OEt)_4$ are added. The reaction is left to proceed for 120 h. Analysis by gas chromatography indicates that the degree of conversion of the perfluorinated alcohol is 100%. 60 g of neutral alumina (50-200 μm) are added and the mixture is filtered on board. The light materials are devolatilized under a pump vacuum (5 mm Hg, 3 h 40 min).

A vacuum distillation is then carried out to separate the two mono-

and bis-perfluoroalkyl monomers.

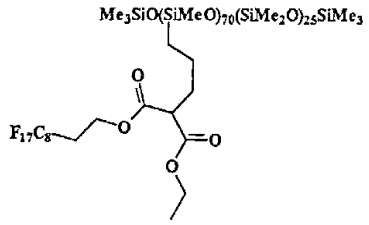
Compound	Results/Purity/Characteristics
 1)	716 g >97.5% 95°C/0.05 mm Hg
 2)	760 g >97% White solid, m.p. = 38°C

IR and NMR analyses confirm the structure of these two monomers.

EXAMPLE VIII: SYNTHESIS OF POS SUBSTITUTED BY MONOPERFLUORINATED BIFID GRAFTS Gf

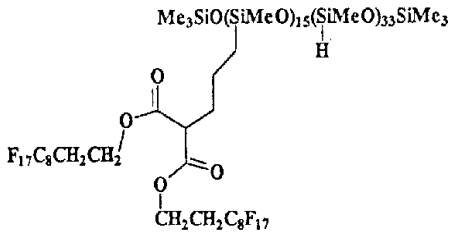
20 g of dry toluene, 2.15 μl of a KARSTEDT catalyst (11.5% of Pt) and 42 g (61.7 meq) of monomer (1) containing monoperfluoroalkyl units of Example VII are introduced into a 250 ml reactor under nitrogen. The reaction mixture is heated to 91-93°C. 4.76 g (53.6 meq of Si-H units) of a silicone oil containing Si-H units of the structure $Me_3SiO(SiMe_2O)_{25}(SiMeHO)_{70}SiMe_3$ are then run in. The introduction time is 45 min. The degree of conversion of the Si-H units is 99% after 48 h. This silicone oil is devolatilized at 130°C under 2 mbar for 2 h. 43.6 g of a clear oil are recovered. IR and NMR analyses confirm the structure of this silicone oil.

The Mn of this oil is 49,500 and the % of fluorine is 45.7.



EXAMPLE IX: SYNTHESIS OF POS SUBSTITUTED BY BISPERFLUORINATED BIFID GRAFTS Gf

86 g of dry toluene and 3 μl of a KARSTEDT catalyst (11.5% of Pt) are introduced into a 250 ml reactor under nitrogen. This reaction mixture is heated to 90°C. A mixture consisting of 435.6 g of bisperfluorinated monomer (2) described in Example VII and 80 g of a silicone oil containing Si-H units of the structure $Me_3SiO(SiMeHO)_{50}SiMe_3$ (1268 meq of Si-H units) is then run in over 2 h 30 min. The reaction is allowed to proceed for 12 h at 90°C. The degree of conversion of the Si-H units is 34.4%. The mixture is filtered on board at 90°C to give a colorless liquid, which is devolatilized at 110°C under 1 mm Hg for 3 h 30 min. 485.4 g of a white solid melting at 58°C are recovered. IR and NMR analyses confirm the structure of this silicone oil.



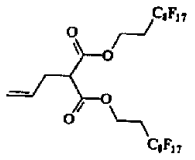
EXAMPLE X: DETERMINATION OF THE DEGREE OF CRYSTALLINITY

The degree of crystallinity measured by X-rays on monomer (2) of Example VII (precursor Gf_p of bisperfluorinated bifid grafts **Gf**) is given below.

These results show the organization resulting from the particular

crystal structure of said monomer.

Differential thermal analysis performed on the same product also shows a crystallization peak.

Structure	Degree of crystallinity/Crystallization temperature
	68.9% (on sample as such at room temperature) 36°C (maximum of the crystallization peak)

EXAMPLE XI: PRODUCTION OF AN AQUEOUS EMULSION FROM THE POS CARRYING MONOPERFLUORINATED BIFID GRAFTS Gf (1) OF EXAMPLE VIII

XI.1 Preparation

The following ingredients are mixed:

POS of Example VIII:	2.5 g
AD33:	0.2 g
Imbentin 33:	0.05 g
Butyl digol:	0.05 g
BRIJ 72:	0.5 g

Water is added gradually and the ingredients are mixed by hand. A further 5.6 g of H_2O are then added and the ingredients are emulsified using a SILVERSTON mixer.

A white emulsion (dry extract = 37%) is obtained.

AD33 (SEPPIC):	ethoxylated nonylphenol with SO_3 groups
BRIJ 72 (ICI):	ethoxylated stearyl alcohol (2 EO)
GENAPOL X 080 (HOECHST):	C_{13} fatty alcohol with 8 EO

XI.2 Application

Two series of tests are performed:

- application in a solvent

Deposition of 700 ppm of fluorine (impregnation of a 15 g disk of polyamide (PA) mat) from solutions diluted to 1% in trichlorotrifluoroethane.

Drying for 6 minutes at 80°C, followed by heat treatment for 4 minutes at 140°C.

- application in an emulsion

Deposition of 700 ppm of fluorine (application with a gun to a 15 g disk of PA mat) from the emulsions described above.

Drying for 6 minutes at 80°C, followed by heat treatment for 4 minutes at 140°C.

The hydrophobicity and oleophobicity properties are evaluated by the penetration or non-penetration of liquids of decreasing surface tension (on three drops of liquid).

The POS is assigned the number corresponding to the liquid of lowest surface tension which does not penetrate after 30 seconds in the oleophobicity test and after 3 minutes in the hydrophobicity test.

TABLE 3

Hydrophobicity index	Composition: isopropanol/H_2O
0	0/100
1	10/90
2	20/80
3	30/70
4	40/60
5	50/50
6	60/40
7	70/30
8	80/20
9	90/10
10	100/0

TABLE 4

AATCC oleophobicity index	Composition
1	Nujol
2	Nujol (65)/n-hexadecane (35)
3	n-hexadecane
4	n-tetradecane
5	n-dodecane
6	n-decane
7	n-octane
8	n-heptane

The compositions are given by volume at 20°C.

XI.3 Results

TABLE 5

	Oleophobicity index	Hydrophobicity index
POS VIII (solvent)	4	1
POS VIII (emulsion)	4	2

EXAMPLE XII: PHYSICOCHEMICAL STUDY OF THE POS CARRYING MONOPERFLUORINATED BIFID GRAFTS Gf (1) OF EXAMPLE VIII

XII.1 Wetting of the deposits

The utility as a "dirt repellent" in terms of physicochemical properties can be summed up by the behavior of the deposit towards liquids (wetting) and its stability over time in contact with a liquid.

XII.1.1 Methodology of the study

The following simple physicochemical study is carried out:

1* Deposition of the treatment polymer by plate whirler from 0.25% solutions of polymer. FC 396 (perfluorinated polyacrylate) (Scotchgard®), a reference treatment, was also studied.

6 families of samples are studied on this basis - the sample "as such" or **initial** sample and a sample **baked** at 140°C for 4 min. These 2 samples are then taken and subjected to:

either a "leaching" test consisting in allowing drops of water to fall from a height of 1 meter for 10 min (**initial and washed, baked and washed**),

or an "immersion" test in demineralized water for 30 min (**initial and immersed, baked and immersed**).

The object of these 2 tests is obviously to find out the permanency of the treatment.

2* Measurement of the angle and its change over time (0 to 60 seconds) in contact with reference liquids (water and CH_2I_2).

Although it is easy to do, we did not recalculate the surface energy

of the deposits or its change. The angle between the test liquid and the surface is in fact sufficient as far as the oleophobicity and hydrophobicity properties are concerned.

The experiments were performed on the following products: the grafted POS of Example VIII, FC 396 and the untreated PA66 control.

XII.1.2 Results

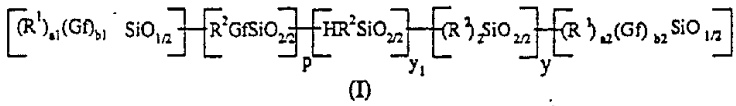
Table 6 shows the angles obtained after 60 seconds.

TABLE 6: Change in the angles of test liquids on treated or untreated surfaces

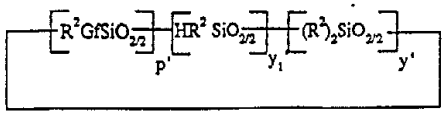
Sample	Control	POS VIII	FC 396
Initial H_2O CH_2I_2	50° 30°	80° 90°	100° 50°
Baked H_2O CH_2I_2	50° 50°	100° 80°	110° or 75° 50°
Initial and washed H_2O CH_2I_2			103° 45°
Baked and washed H_2O CH_2I_2		110° 55°	110° or 80° 60°
Initial and immersed H_2O CH_2I_2			112° 50°
Baked and immersed H_2O CH_2I_2			112° 60° or 90°

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:-

1. A (per)halogenated polyorgano-siloxane (POS) comprising species of the following general formulae **(I)** and **(II)**:



(I)



(II)

in which:

- a1 + b1 = 3, a2 + b2 = 3; a, a2 = 2 or 3; b1, b2 = 0 or 1;

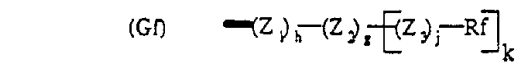
  $1 \leq p \leq 200$;

  $0 \leq y_1 \leq 10$;

  $0 \leq y \leq 100$;

  where $5 \leq p + y_1 + y \leq 200$, and

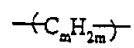
  $[p/(p + y + y_1 + 2)].100 \geq 3$;
- $1 \leq p' \leq 9$;
- $0 \leq y'_1 \leq 1$;
- $0 \leq y' \leq 5$;
- each radical R^1, R^2 on the one hand is identical to or different from like radicals of the same exponent and the other radical of different exponent, and on the other hand is a linear or branched C_1-C_{12}-(cyclo)alkyl - group or a hydrocarbon group, optionally being substituted; and
- **Gf**:
  - is an optionally halogenated functional monovalent radical of identical or different type in the p or p' siloxy units D and/or the two siloxy units M in which it is present,
  - and has the following average formula:

(Gf) 

- where h = 0, 1; g = 0, 1; j = 0, 1 and k = 1 or 2;

Legend: The free valences shown in bold ▬ throughout the present disclosure are those attached directly or indirectly to the silicon of the POS and located closest to said silicon.

- **with the proviso** that at least one radical Gf in which k ≠ 0 is present in said POS (I) or (II);
- Z_1 being a divalent radical of the formula



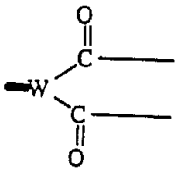
where m ≥ 2,

with the proviso that if m = 2, then at least some of the radicals Gf are radicals in which g ≠ 0,

and it optionally being possible for at least one of the hydrogens substituting the carbons of Z_1 to be replaced by a linear or branched C_1-C_6-lower alkyl;

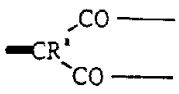
- Z_2 being a mono-, di- or tri-valent radical of one of the following formulae:

.α.



- one or both of the free valences of the carbonyl(s) being joined to $-Z_3Rf$ and, in the case where only one of said free valences is joined to $-Z_3Rf$, the other then being joined to a hydroxyl;

.β.

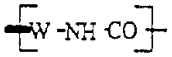


- at least one of the free valences of the carbonyls being joined to $-Z_3$-Rf and, in the case where only one of these free valences is joined to $-Z_3$-Rf, the other then being joined to a linear or branched C_1-C_6-alkoxy; and
- R^1 = H, aryl or linear or branched C_1-C_6-lower alkyl ;

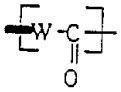
.γ.



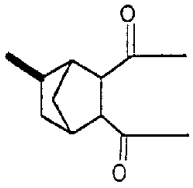
.δ.



.ε.

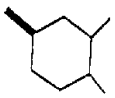


.η.



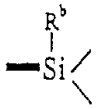
- h = 0 in Gf;
- one or both of the free valences of the carbonyl(s) being joined to $-Z_3$-Rf and, in the case where only one of said free valences is joined to $-Z_3$Rf, the other then being joined to a hydroxyl or to a linear or branched C_1-C_6-alkoxy;

.9.



- one or both of the two free valences other than the valence ▬ being joined to $-Z_3$-Rf and, in the case where only one of these two valences is joined to $-Z_3$-Rf, the other then being joined to OH or to a linear or branched C_1-C_5-alkoxy; or

.λ.



- one or both of the two free valences other than the valence ▬ being joined to $-Z_3$-Rf and, in the case where only one of these two valences is joined to $-Z_3$-Rf, the other then being joined to OH or to a linear or branched C_1-C_6-alkoxy;
- R^b = H or linear or branched C_1-C_5-lower alkyl;

→ W being a cyclic or non-cyclic hydrocarbon radical,
and W also being devoid of an ether link -O-;

△ Z_3 is a divalent radical of the formula

▬ U-C_nH_{2n} -

•where n ≥ 1 and U = O, S, NH or $NHSO_2$; and
△ and Rf being a perhalogenated - radical

2. A POS according to claim 1 wherein the POS is (per)fluorinated.

3. A POS according to claim 1 or 2 wherein $1 \leq p \leq 90$.

4. A POS according to any one of claims 1 to 3 wherein $0 \leq y_1 \leq 5$.

5. A POS according to any one of claims 1 to 4 wherein $0 \leq y \leq 50$.

6. A POS according to any one of claims 1 to 5 wherein $10 \leq p + y_1 + y \leq 100$.

7. A POS according to any one of claims 1 to 6 wherein $[p/(p + y + y_1 + 2)].100 \geq 5$.

8. A POS according to any one of claims 1 to 7 wherein $1 \leq p' \leq 4.5$.

9. A POS according to any one of claims 1 to 8 wherein $0 \leq y_1 \leq 0.25$.

10. A POS according to any one of claims 1 to 9 wherein $0 \leq y^1 \leq 0.5$.

11. A POS according to any one of claims 1 to 10 wherein the linear or branched C_1-C_{12}-(cyclo)alkyl is a C_1-C_6(cyclo)alkyl group.

12. A POS according to any one of claims 1 to 11 wherein the hydrocarbon group is an aryl, an aralkyl or an alkylaryl group. these groups optionally being substituted.

13. A POS according to any one of claims 1 to 12 wherein Gf is (per)fluorinated.

14. A POS according to any one of claims 1 to 13 wherein the linear or branched C_1-C_6 lower alkyl which replaces the hydrogen substituted carbon of Z_1 is methyl.

15. A POS according to any one of claims 1 to 14 wherein R^a is CH_3.

16. A POS according to any one of claims 1 to 15 wherein R^b is methyl.

17. A POS according to any one of claims 1 to 16 wherein W is an aliphatic and/or alkenyl and/or alkynyl and/or aromatic radical.

18. A POS according to any one of claims 1 to 17 wherein U is O.

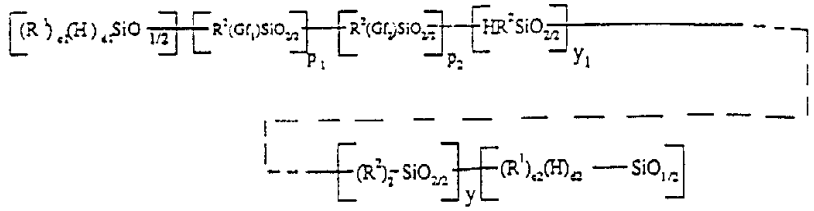
19. A POS according to any one of claims 1 to 18 wherein Rf is perfluorinated.

20. A POS according to any one of claims 1 to 19 wherein Rf is a linear or branched perfluoroalkyl radical having one of the following formulae:

- $Cq\ F_2q - CF_3$ where $q \geq 0$;
- $Cq\ F_2q - H$ where $q \geq 1$;
- $NR^{rf}SO_2\ Cq\ F_2q\text{-}CF_3$ where $q \geq 0$ and R^{rf} = H, aryl or linear or branched C_1-C_6 lower alkyl; and
- $NR^{rf}SO_2\ Cq\ F_2q - H$ where $q \geq 1$ and R^{rf} is as defined above.

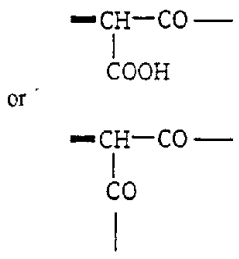
21. A POS according to claim 20 wherein R^{rf} is CH_3.

22. A POS according to claim 1 of the following formula (I.1):



(I.1)

where
- R^1, R^2 = methyl, propyl or butyl;
- c1 + d1 = 3
  c2 + d2 = 3;
- p_1, $p_2 \geq 0$; $p_1 + p_2 \geq 1$;
- $0 \leq y_1 \leq 100$, **with the proviso that if** $y_1 = 0$, then d1 and/or d2 = 1;
- $0 \leq y \leq 500$;
- $Gf_1 = Gf$, where h = k = 1 and g = j = 0;
- $Gf_2 = Gf$, where h = g = 1, k = 1 or 2 and Z_2 =



or

23. A POS according to claim 22 wherein c1 = 2 and d1 = 1.

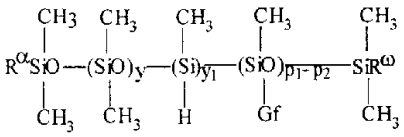
24. A POS according to claim 22 or claim 23 wherein c2 = 2 and d2 = 1.

25. A POS according to any one of claims 22 to 24 wherein $0 \leq y_1 \leq 50$.

26. A POS according to any one of claims 22 to 25 wherein $0 \leq y \leq 500$.

27. A POS according to any one of claims 22 to 25 of the following formula **(I.1.1)**:

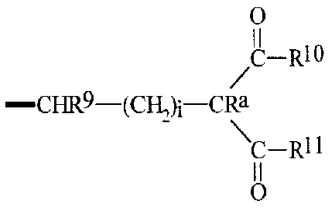
(I.1.1)



where y, y_1, p_1, p_2 and **Gf** = $\mathbf{Gf_1}$ or $\mathbf{Gf_2}$ are as defined in claim 22 and R^{α} and R^{ω}, which are identical or different, are H or C_1-C_6-alkyl.

28. A POS according to any one of claims 1 to 27 which comprises at least one species **(I)** and/or **(II)** substituted by at least one perhalogenated radical **Gf** selected from the following subgroup of radicals:

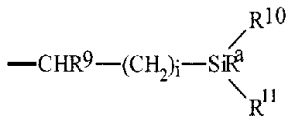
(i)



where:

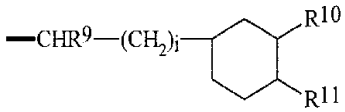
- R^a and R^9 independently are H or linear or branched C_1-C_6-lower alkyl,
- R^{10} and R^{11} independently are OH, linear or branched C_1-C_6-alkoxy or Z_3-Rf, at least one of the radicals R^{10} and R^{11} being -Z_3Rf; and
- i = 0 to 10;

(ii)



where R^9, R^a. R^{10}, R^{11} and i are as defined above;

(iii)



where R^9, R^{10}, R^{11} and i are as defined above, it optionally being possible for the hexyl ring to be substituted; and

mixtures of the above-mentioned radicals.

29. A POS according to claim 28 wherein the radical Gf is perfluorinated.

30. A POS according to claim 28 or claim 29 wherein R^a and/or R^9 are CH_3.

31. A POS according to any one of claims 28 to 30 wherein i is 0 to 3.

32. A POS according to any one of claims 28 to 31 wherein i is 1.

33. A POS according to any one of claims 28 to 32 which comprises at least one species (I) and/or (II) substituted by:

- at least one perhalogenated radical **Gf** of formula **(i), (ii)** or **(iii)** according to claim 28, the radicals R^{10} and R^{11} in the formula in question corresponding to Z_3Rf
- and optionally at least one radical **Gf (i), (ii)** or **(iii)** in which one of the radicals R^{10} or R^{11} is Z_3Rf and the other radical R^{10} or R^{11} is different from Z_3Rf.

34. A POS according to claim 33 wherein the **Gf** radical is perfluorinated.

35. A POS according to claim 33 or claim 34 where Z_3Rf corresponds to

— 0 - C_nH_{2n} -Cq F_{2q} - CF_3 ($q \geq 0$) or

— 0 - C_nH_{2n} - Cq F_{2q} - H ($q \geq 1$).

36. A POS according to any one of claims 33 to 35 wherein R^{10} or R^{11} is different from Z_3Rf and is OH or linear or branched C_1-C_6 alkoxy.

37. A POS according to any one of claims 1 to 36 which also comprises:

- siloxy units T = -[R^8-$SiO_{3/2}$]-, where the radicals R^8 of the different units are identical or different and are defined in the same way as R^1, R^2 and **Gf** above; and
- optionally units Q = [$SiO_{4/2}$].

38. A process for the preparation of (per)halogenated POS according to any one of claims 1 to 37, which comprises reacting:

- A → at least one polyalkylhydrogenosiloxane oil
- B → with at least one (per)halogenated olefin which is a precursor of Gf_1 as defined in claim 22 and has the formula Gf_{1p}:

$$Z_{1p}Rf$$

in which:

- Z_{1p} = olefinic precursor of Z_1,
- Rf is as defined in claim 1 and
- m > 2 in Z_1,

- C → in the presence of an effective amount of a metal hydrosilylation catalyst.

39. A process according to claim 38 wherein the polyalkylhydrogenosiloxane oil is polymethylhydrogenosiloxane oil.

40. A process according to claim 38 or 39 wherein the olefin is perfluorinated.

41. A process according to any one of claims 38 to 40 wherein the catalyst is based on platinum.

42. A process according to any one of claims 38 to 41 wherein the oil A is reacted:

- B' → with at least one (per)halogenated olefin which is a precursor of Gf_1 as defined in claim 22 and has the formula Gf_{1p}:

$$Z_{1p}Rf$$

in which:

- Z_{1p} = olefinic precursor of Z_1,
- Rf is as defined above and
- m = 2 in Z_1,

- D → with at least one olefin of the formula

$$Z_{1p}Z_{2p}$$

in which Z_{1p} = olefinic precursor of Z_1 and Z_{2p} = precursor of Z_2,

- B → and/or with reactant B according to claim 38,
- C → in the presence of an effective amount of a metal hydrosilylation catalyst, the reaction product A + B' + D and/or B optionally being brought into contact with a reactant E:
- E → of the type $Z_{3p}Rf$, where Z_{3p} = precursor of Z_3 and Rf is as defined above, to form one or more radicals $\mathbf{Gf_2}$.

43. A process according to claim 42 wherein the catalyst is based on cobalt and/or platinum.

44. A process according to any one of claims 38 to 43 wherein the oil A is reacted:

- D' → with at least one olefin of the formula

$$Z_{1p}Z_{2p}$$

in which:

- Z_{1p} = olefinic precursor of Z_1 and
- Z_{2p} = olefinic precursor of Z_2,

- C → in the presence of an effective amount of a metal hydrosilylation catalyst, the reaction product A + D' optionally being brought into contact with a reactant
- E' → of the type $Z_{3p}Rf$, where Z_{3p} = precursor of Z_3 and Rf is as defined above, to form one or more radicals $\mathbf{Gf_2}$.

45. A process according to claim 44 wherein the catalyst C is based on platinum.

46. A process for the preparation of cyclic or linear halogenated POS according to any one of claims 1 to 37, comprising reacting:

- A → at least one polyalkylhydrogenosiloxane oil
- F → with at least one halogenated olefin which is a precursor of **Gf** and has the formula $(\mathbf{Gf_p})$:

$$(Z_1p)h—(Z_2)g—[(Z_3)j—Rf]k$$

in which:

- Z_{1p} is the olefinic precursor of the radical Z_1 as defined above in claim 1, and
- Z_2, Z_3, Rf, h, g, j and k are also as defined in said claim 1,
- with the provisos that:
  * if h = 0, then g = 1 and Z_2 becomes an olefinic precursor Z_{2p},
  * if k = h = 1 and m = 2, then g = 1 and $Z_2 = Z_{2p}$,
- C → in the presence of an effective amount of a metal hydrosilylation catalyst.

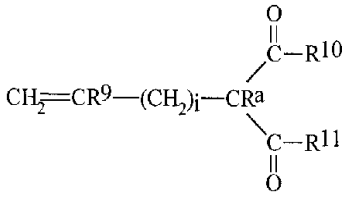
47. A process according to claim 46 wherein the polyalkylhydrogenosiloxane oil is polymethylhydrogenosiloxane oil.

48. A process according to claim 46 or 47 where the olefin is perfluorinated.

49. A process according to any one of claims 46 to 48 wherein the catalyst is based on platinum.

50. A process according to any one of claims 46 to 49 wherein the precursor Gf_p of **Gf** has one of the following formulae:

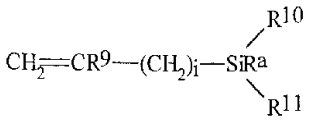
(i_p)



where:

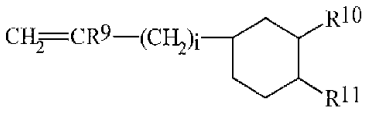
- R^a and R^9 independently are H or linear or branched C_1-C_6-lower alkyl,
- R^{10} and R^{11} independently are OH, linear or branched C_1-C_6-alkoxy or Z_3-Rf, at least one of the radicals R^{10} and R^{11} being Z_3Rf; and
- i = 0 to 10,

(ii_p)



where R^9, R^a, R^{10}, R^{11} and i are as defined above; and

(iii_p)



where R^9, R^{10}, R^{11} and i are as defined above, it optionally being possible for the hexyl ring to be substituted.

51. A process according to claim 50 wherein R^a and/or R^9 are CH_3.

52. A process according to claim 50 or 51 wherein i is 0 to 3.

53. A process according to any one of claims 50 to 52 wherein i is 1.

54. A process according to any one of claims 50 to 53 wherein the precursors **Gf_p** of the grafts **Gf** have one or two perfluorinated groups R^{10}, R^{11} (R^{10} and/or $R^{11} = Z_3Rf$) and are obtained by reacting:

→ at least one compound with a mobile hydrogen, consisting of the hydrogenated radical Z_3Rf, according to claim 1,

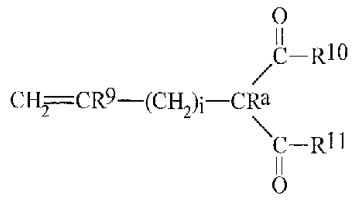
→ with starting materials formed by compounds of formula (i_p), (ii_p) or (iii_p) as defined in claim 50, in which at least one of the radicals R^{10} and R^{11} is a linear or branched C_1-C_6-alkoxy,

according to a transterification mechanism.

55. A process according to claim 54 where the compound with a mobile hydrogen is an alcohol or thiol.

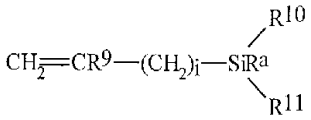
56. A reaction intermediate (synthon) used in the process according to any one of claims 46 to 55 and having one of the following formulae:

(i_p)



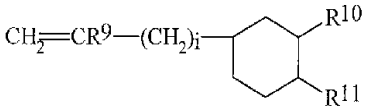
where R^a and R^9 independently are H or linear or branched C_1-C_6-lower alkyl, at least one of the radicals R^{10} and R^{11} corresponds to a linear or branched C_1-C_6-alkoxy, and i = 0 to 10

(ii_p)



where R^9, R^a, R^{10}, R^{11} and i are as defined above; and

(iii_p)



where R^9, R^{10}, R^{11} and i are as defined above, it optionally being possible for the hexyl ring to be substituted.

57. A reaction intermediate according to claim 56 wherein R^a and/or R^9 are CH_3.

58. A reaction intermediate according to claim 56 or 57 wherein R^{10} and/or R^{11} are methoxy, ethoxy or propoxy.

59. A process according to any one of claims 42 to 45 wherein:

- at least some of the precursors Z_{2p} of Z_2 grafted to the oil A are acid anhydrides,
- at least some of these anhydride groups are hydrolyzed so as to generate free carboxyl ends, and
- at least some of said carboxyl ends are esterified with reactants of the type Z_{3p} - Rf, Z_{3p} being a precursor of Z_3, and Z_3 and Rf being as defined in claim 1.

60. A process according to any one of claims 38 to 55 and 59 wherein the reaction between the radicals Z_{2p} and Z_{3p} is an esterification.

61. A process according to claim 60 wherein the Z_{2p} is of the acid type and Z_{3p} is of the ester type.

62. An aqueous emulsion which contains:

- at least one POS according to any one of claims 1 to 37 or obtained by the process according to any one of claims 38 to 55, 59 and 60;
- water; and

- at least one surfactant.

63. Application of the POS according to any one of claims 1 to 37, or obtained by the process according to any one of claims 38 to 55, 59 and 60, as:

- antifoams
- lubricants
- antiadhesives
- agents for lowering surface tension
- dirt repellents
- oleophobic and/or hydrophobic agents and
- raw materials for the production of elastomers or films for resisting chemical attack and solvents.

64. A dirt-repelling composition which comprises:

- at least one POS according to any one of claims 1 to 37 or obtained by the process according to any one of claims 38 to 55, 59 and 60,
- and/or at least one emulsion according to claim 62,

65. A dirt-repelling composition according to claim 64 wherein the POS used carries:

- grafts bifunctionalized by perhalogenated - perfluorinated - radicals as defined in claim 33,
- optionally grafts monofunctionalized by perhalogenated - perfluorinated - radicals also as defined in claim 33, and
- optionally other grafts functionalized by groups other than bis- or mono-perhalogenated - perfluorinated - groups.

66. A (per)halogenated polyorganosiloxane, substantially as herein described with reference to any one of the Examples but excluding any comparative examples therein.

67. A process for the preparation of (per)halogenated polyorganosiloxane, substantially as herein described with reference to any one of the Examples but excluding any comparative examples therein.

DATED this 31st Day of Augsut 1998

RHONE POULENC CHIMIE

Attorney: RUTH M. CLARKSON
Fellow Institute of Patent Attorneys of Australia
of BALDWIN SHELSTON WATERS