Abstract: The present invention relates to a process for the manufacture of hydrogen-based lubricants modified with per(halo)fluorinated aromatic compounds, to the modified lubricants thereby obtained and to the use of the modified lubricants for the preparation of lubricant compositions.
Description

MODIFIED HYDROGEN-BASED LUBRICANTS

[0001] This application claims priority to European patent application no. 13163768.8 - filed on April 15th, 2013 - the whole content of this application being incorporated herein by reference for all purposes.

Technical Field

[0002] The present invention relates to modified lubricants, in particular to modified hydrogen-based lubricants.

Background Art

[0003] It is known that certain hydrogen-based lubricants of natural or synthetic origin, in particular certain lubricant oils, are endowed with remarkable lubricant properties and are available on the market at reasonable costs. Examples of hydrogen-based lubricant oils comprise mineral oils of hydrocarbon type, animal and vegetal hydrogenated oils, synthetic hydrogenated oils including polyalphaolefins (PAOs), dibasic acid esters, polyl esters, phosphate esters, polyesters, alkylated naphthalenes, polyphenyl ethers, polybutenes, multiply-alkylated cyclopentanes, silane hydrocarbons, siloxanes and polyalkylene glycols.

[0004] Such oils are able to form an even, cohesive film on the substrate to be lubrified; cohesiveness is a desirable key property in any lubricant application, especially in automotive applications. However, they possess low thermal and thermo-oxidative stability and low chemical inertness and, therefore, they are not suitable for lubricant applications wherein high temperatures are reached and wherein reactive species form which may lead to degradation of the lubricant film.

[0005] On the contrary, (per)fluoropolyether (PFPE) lubricants, i.e. lubricants comprising a perfluoroxyalkylene chain, that is to say a chain comprising recurring units having at least one ether bond and at least one fluorocarbon moiety, are endowed with high thermal and chemical resistance, so they are useful in cases of applications characterized by harsh conditions (very high temperatures, presence of oxygen, use of aggressive chemicals and radiations, etc.) and the risk of degradation of the lubricant film is high. Nevertheless, PFPE lubricants are less
performing than hydrocarbon oils in terms of adhesion properties and film strength, they are expensive and also outperforming from the standpoint of thermal stability in applications wherein conditions are not harsh, i.e. wherein the lubricant temperature does not exceed 150°C.

[0006] It would therefore be desirable to provide lubricants having intermediate properties between hydrogen-based lubricants and PFPE lubricants. In particular, it would be desirable to provide hydrogen-based lubricants with higher thermal and chemical stability, higher resistance to wear and friction than PFPE lubricants and which are, at the same time, less expensive.

[0007] It is known from KOBRINA, L.S. Some peculiarities of radical reactions of polyfluoroaromatic compounds. *Journal of Fluorine Chemistry*. 1989, vol.142, no.3, p.301-344. that polyfluorinated aromatic compounds undergo addition reactions with (fluoro)organic radicals; this paper discloses in particular the thermal decomposition of pentafluorobenzoyl peroxide in hexafluorobenzene to provide dimers and addition complexes. The paper also reports on the reactions of octafluorotoluene, octafluoronaphthalene and decafluorobiphenyl in the presence of benzyol peroxide as radical source and on the reactions of hexafluorobenzene with alkyl radicals differing in polarity and steric requirements, namely methyl and cyclohexyl radicals generated from tert-butyl peroxide. These reactions are further discussed in KOBRINA, L.S. Radical reactions of polyfluoroarenes. *Fluorine notes*. 2012, vol.2, no.8 1.

[0008] Addition reactions of certain organic radicals on polyfluoroaromatic compounds are also disclosed in BROOKE, G.M. The preparation of polyfluoroaromatic and heteroaromatic compounds. *Journal of Fluorine Chemistry*. 1997, vol.86, no.1, p.1 -76. Nevertheless, these last two prior art documents are concerned only with the addition of low molecular weight (per)fluoroalkyl or (per)fluoroalkanoyl peroxides to certain fluoroaromatic compounds; furthermore, the addition reaction was studied only for mechanistic purposes.

[0009] EP 2100909 A (SOLVAY SOLEXIS S.P.A.) 16.09.2009 discloses a process for the addition of PFPE peroxides onto per(halo)fluorinated aromatic compounds to provide addition compounds comprising at least
one perfluorinated non-aromatic cyclic group having at least two substituents comprising a PFPE chain and, optionally, conjugated or non-conjugated double bonds. The addition compounds are suitable as additives for (per)fluorinated fluids and for (per)fluorinated lubricants or as base materials for the manufacture of gum and/or graft polymer compositions.

[0010] None of the above prior art documents teaches the reaction of perfluorinated aromatic compounds with hydrogen-based lubricants.

[0011] WO 2012/007374 (SOLVAY SOLEXIS S.P.A.) 19.01.2012 discloses a block copolymer comprising one or more PFPE segments, one or more polyalkylene segments and, optionally, at least one per(halo)fluorinated non-aromatic cyclic moiety having chemically bound thereto at least two sp3 hybridized carbon atoms of PFPE segments and, optionally, conjugated or non-conjugated double bonds. This document does not disclose addition compounds obtained by radical addition of a hydrocarbon oil to a per(halo)fluorinated cyclic compound.

[0012] US 3720646 (MONTEDISON S.P.A.) 13.03.1973 discloses the reaction product of a PFPE with an optionally halogenated quinone compound; also this document does not disclose addition compounds obtained by radical addition of a hydrocarbon oil, like a polyalphaolefin or a mineral oil, to a per(halo)fluorinated cyclic compound.

[0013] It has now been found that improved hydrogen-based lubricants can be obtained by modifying them with perfluoroaromatic compounds.

[0014] **Summary of invention**

[0015] Accordingly, the present invention relates to a process for the addition of a hydrogen-based lubricant to a per(halo)fluorinated aromatic compound, said process comprising the radical reaction of a hydrogen-based lubricant [lubricant (RH)] with a per(halo)fluorinated aromatic compound [compound (F)] to provide a compound [compound (A)] comprising at least one per(halo)fluorinated cyclic group [group (F')] having at least one lubricant chain [chain (RHC)] bound thereto, said group (F') optionally containing conjugated or non-conjugated double bonds.

[0016] Compounds [A] obtainable according to the present invention will be
herein otherwise referred to as "modified lubricants".

[0017] For the purposes of the present invention, the expression "hydrogen-based lubricants" is intended to denote one or more lubricants (either natural or synthetic or semi-synthetic) whose viscosity ranges from 2 to 1,000,000 cSt, preferably from 2 to 3,000 cSt, and containing straight or branched hydrocarbon moieties. Thus, hydrogen-based lubricants include those which at room temperature (25°C) are in the liquid form, namely lubricant oils, and those which at room temperature are in the semi-solid form like lubricant waxes or greases. Hydrogen-based lubricants suitable for the purposes of the present inventions are lubricant oils including mineral oils of hydrocarbon type, animal or vegetable oils, synthetic oils like polyalphaolefins (PAOs), dibasic acid esters, polyol esters, phosphate esters, polyesters, alkylated naphthalenes, polyphenyl ethers, polybutenes, multiply-alkylated cyclopentanes, silane hydrocarbons, siloxanes and polyalkylene glycols. Preferably, the hydrogen-based lubricant is a mineral oil of hydrocarbon type or a polyalphaolefin.

[0018] For the sake of clarity, the expression "lubricant(s) (RH)" is intended to mean "hydrogen-based lubricant lubricant(s) (RH)".

[0019] Without wishing to be bound to theory, the process typically proceeds via extraction of hydrogen from lubricant (RH) and formation of radical lubricant chain (RHC*) which adds to compound (F) to form radical species (RHC-F**) which reacts with another radical (RHC*) giving rise to disubstituted addition compounds (A) of the type RHC-F'-RHC, wherein lubricant chains (RCH) are linked to sp³ hybridized carbons of group (F'). Radicals (RHC - F') can also react together to form addition compounds of the type RHC-F'-F'-RHC; some radicals (RHC - F') may also combine with a hydrogen atom, thereby forming mono-substituted addition compounds (A) of the type RHC-F'-H, which may undergo re-aromatization to form compounds (A) wherein (F') is an aromatic cyclic group and wherein chain (RCH) is linked to a sp² hybridized carbon of group (F').

[0020] The choice of the per(halo)fluorinated aromatic compound [compound (F)] is not particularly limited, provided that this compound is aromatic and that
is per(halo)fluorinated, that is to say that it is free from hydrogen atoms and comprises at least one fluorine atom.

[0021] For the avoidance of doubt, the term "aromatic compound" is hereby intended to denote a cyclic structure having a delocalized conjugated \( \pi \) system with a number of \( \pi \) delocalized electrons fulfilling the Huckel's rule (number of \( \pi \) electrons equal to \((4n+2)\), with \( n \) being an integer).

[0022] Per(halo)fluorinated aromatic compound (F) can be monocyclic or polycyclic and can comprise one or more than one aromatic ring. Should it comprise more than one aromatic ring, these aromatic rings can be condensed or not condensed. Compound (F) can be a heteroaromatic compound, comprising one or more heteroatoms (e.g. O, S, N) in the ring and can be substituted or not substituted.

[0023] Preferably, compound (F) is perfluorinated, that is to say that all its free valences are saturated with fluorine atoms.

[0024] Non-limitative examples of compounds (F) which are suitable for the purposes of the present invention are notably perfluorobenzene, perfluorobiphenyl, perfluoronaphthalene, perfluoroanthracene, perfluoropyridine, perfluorotoluene and derivatives thereof comprising one or more perfluorinated substituent(s). Preferred examples of compounds (F) are perfluorobenzene (hexafluorobenzene) and perfluorobiphenyl (decafluorobiphenyl).

[0025] The radical reaction according to the present invention can be initiated by contacting lubricant (RH) and compound (F) with organic or inorganic peroxides, with redox systems, with ozone or hydrogen peroxide; it can also be initiated by thermal or photochemical decomposition of lubricant (RH).

[0026] Organic peroxides include, for example, diacyl peroxide, peroxy esters, peroxidcarbonates, dialkyl peroxides, ketone peroxides, peroxy ketals, hydroperoxides, which are soluble in the aforementioned hydrogen-based oils; more preferably, the organic peroxide is selected from benzoyl peroxide and di-ter-butyl peroxide (DTBP).

[0027] Inorganic peroxides include, for example, ammonium peroxydisulfate, potassium peroxydisulfate, sodium peroxydisulfate and potassium
Examples of redox systems include those based on Fe(II) ions in combination with hydrogen peroxide, organic peroxides (including alkyl peroxides, hydroperoxides, acyl peroxides), peroxydisulphates, peroxydiphosphates; Cr (II), V (II), Ti (III), Co (II) and Cu (I) ions can also be employed instead of Fe(II) ions in many of these systems. Redox systems based on organic alcohols and transition metals chosen among Ce (IV), V (V), Cr (VI) and Mn (III) can also be employed.

Thermal decomposition of lubricant (RH) can be achieved by heating a mixture of lubricant (RH) and compound (F) at such a temperature as to generate radicals (RHC*); this temperature depends on the specific lubricant (RH) to be modified and can be determined by the person skilled in the art on a case-by-case basis according to known methods. In any case, this temperature is generally higher than 150°C, typically higher than 200°C.

Photochemical decomposition of lubricant (RH) can be accomplished by submitting a mixture of lubricant (RH) and compound (F) to a radiation source, including UV-rays, X-rays and γ-rays sources. Photochemical decomposition by exposure to UV-rays is typically carried out in the presence of a photo-initiator, including, for example, benzoin ethers, benzyl ketals, a-dialkoxy-acetophenones, a-hydroxy-alkyl-phenones, a-amino-alkyl-phenones, acylphosphine oxides, benzophenones, benzoamines, thio-xanthones, thio-amines, titanocenes. However, the use of photo-initiators can be avoided if the hydrocarbon oil contains functional groups able to generate radicals upon exposure to UV rays; examples of such functional groups are carbonyl groups.

The process of the invention is preferably carried out without solvents; nevertheless, solvents can also be employed, especially if lubricant (RH) is highly viscous, in particular if viscosity is higher than 3,000 cSt, in order to bring lubricant (RH) into intimate contact with compound (F). The solvent will be selected by the person skilled in the art on a case-by-case basis, according to the specific lubricant (RH) and compound (F), in such a way as it does not generate radicals that might interfere with the reaction.
between lubricant (RH) and compound (F). Examples of suitable solvents are organic solvents like alkanes, ketons, esters and aromatics solvents, optionally chlorinated or fluorinated.

[0032] The weight ratio between lubricant (RH) and compound (F) typically ranges from 0.01 to 1.00, more preferentially between 0.05 and 100 and even more preferably between 0.1 and 10.

[0033] The reaction is generally carried out under magnetic or mechanical stirring and under inert atmosphere, for example under nitrogen atmosphere.

[0034] If the radical reaction is initiated by contacting lubricant (RH) and compound (F) with organic or inorganic peroxides, the temperature is typically set in such a way as to range from 20°C to 250°C, preferably from 50°C to 200°C. The reaction temperature will be established by the person skilled in the art on the basis of the decomposition kinetics of the peroxide. Optionally, in order to keep the concentration of lubricant radicals (RHC*) within a defined range over the process, the temperature can be increased, either linearly or step-by-step, with time.

[0035] If the radical reaction is initiated by contacting lubricant (RH) and compound (F) with a redox system, it is typically performed at a temperature ranging from -40°C to 250°C, preferably from 20°C to 100°C.

[0036] If the radical reaction is initiated by photochemical decomposition of lubricant (RH) with photo-initiators or by radiation-induced decomposition of lubricant (RH), it is typically performed at a temperature ranging from -100°C to 200°C, preferably from -40°C to 120°C.

[0037] If the radical reaction is initiated by thermal decomposition of lubricant (RH), it is typically performed at a temperature ranging from 100°C to 350°C, preferably from 150°C to 300°C.

[0038] The reaction can be performed either in batch or in semi-batch or in a continuous stirred-tank reactor.

[0039] At the end the reaction, the excess of compound (F), residues of any organic initiators and any undesired by-products are removed by using techniques known in the art for, example by distillation or solvent extraction. Filtration can also be carried out afterwards to remove any solid impurities. Distillation is typically carried out under reduced pressure at a
temperature lower than that at which thermal decomposition of the lubricant begins. As an alternative, water-vapour phase distillation can be used. Extraction is typically carried out with halogenated solvents which solubilise the excess of compound (F), but not compounds (A); among halogenated solvents, (per)fluoropolyether (PFPE) solvents are preferred.

[0040] Typically, the process of the invention allows obtaining compounds (A) wherein the weight percentage of per(halo)fluorinated cyclic group [group (F')], preferably perfluorinated cyclic group, with respect to the weight of compound (A) ranges from 1 to 15%, preferably from 2 to 12%.

[0041] A further object of the present invention is a compound [compound (A)] comprising at least one per(halo)fluorinated cyclic group [group (F')] having at least one lubricant (RH) chain [chain RHC] bound thereto, said group (F') optionally containing conjugated or non-conjugated double bonds. Compounds (A) are obtainable through the process of the invention.

[0042] For the sake of clarity, in the expression "lubricant (RH) chain [chain RHC]." "lubricant (RH)" means a "hydrogen-based lubricant (RH)" as defined above.

[0043] In compounds (A), the at least one lubricant chain can be bound to an sp² hybridized carbon of group (F') (when re-aromatization occurs in the process) or to an sp³ hybridized carbon of group (F'). Typically, compounds (A) comprise at least two lubricant chains, each chain being bound to at least one sp³ hybridized carbon atom of group (F').

[0044] Typically, in compounds (A), the weight percentage of per(halo)fluorinated cyclic group [group (F')], preferably perfluorinated cyclic group, with respect to the weight of compound (A) ranges from 1 to 15%, preferably from 2 to 12%.

[0045] According to a preferred embodiment of the invention, compounds (A) comply with formula (I) below:

\[
\text{RHC}_n \begin{array}{c}
\text{C} \\
\text{NA} \\
\text{C} \\
\text{R'HC}_m
\end{array}
\]

wherein:

- \text{RHC} \text{ and } \text{R'HC} \text{, equal to or different from one another, each represent a}
lubricant chain (RHC) bound to a sp^3 hybridized carbon atom:
- Xf and Xf, equal to or different from one another, are selected from halogen and C\(_1\)-C\(_{12}\) per(halo)fluorocarbon substituents, preferably among -F and C\(_1\)-C\(_{12}\) perfluoroalkyl or perfluoroaryl groups;
- NA represents a per(halo)fluorinated non-aromatic cyclic moiety (NA) optionally condensed with additional aromatic or non-aromatic cycles, optionally having one or more conjugated or non-conjugated double bond(s), optionally having one or more per(halo)fluoro substituents and wherein said cyclic moiety comprises the two sp^3 hybridized carbon bearing RHC and R'HC chains.

[0046] Non limitative examples of structures encompassed by the above general formula of compound (A) as above detailed are notably the followings:
wherein RHC, R’HC are lubricant chains as defined above and Wf is a fluorine atom or a C1-C6 perfluorocarbon group.

[0048] According to a preferred embodiment of the invention, in compounds (A), (RCH) represents a lubricant chain of a mineral oil or of a polyalphaolefin. According to a further preferred embodiment, compounds (A) comprise at least one lubricant chain selected from a mineral oil and a polyalphaolefin and at least one perfluorinated cyclohexyl or bicyclohexyl group (F’) optionally containing conjugated or non-conjugated double bonds.

[0049] Compounds (A) according to the present invention are used as lubricants, in particular, as lubricants for internal combustion engine oils (including car engines, tractor engines, gas engines, marine diesel engine), gears, ballistics systems, compressors (for example screw compressor, roots compressor, turbo compressor, compressor for the production of compressed air), refrigerators, turbines, hydroelectric plants, and wind-mills. Thus, the present invention also relates to a lubrication method comprising using compounds (A).

[0050] Although compounds (A) are preferably used as such, they can also be mixed with further ingredients and additives to form lubricant compositions. Thus, the present invention further comprises a method of manufacturing lubricant compositions comprising using compounds (A), as well as lubricant compositions containing one or more compounds (A) in admixture with further ingredients and additives. Examples of further ingredients are unmodified hydrocarbon oils; however, (per)fluoropolyether oils (PFPE oils) can also be used. Examples of suitable PFPE oils are those identified as compounds (1) - (8) in the above-cited European patent application EP21 00909. Metal detergents, ashless dispersants, oxidation inhibitors, rust inhibitors (otherwise referred to as anti-rust
agents), emulsifiers, extreme pressure agents, friction modifiers, viscosity index improvers, pour point depressants and foam inhibitors can also be used as further ingredients/additives to be added to the modified lubricants of the invention to prepare lubricant compositions. Suitable further ingredients and additives and methods for the manufacture of lubricant compositions will be chosen by the person skilled person according to the compound (A) to be formulated and according to the specific intended use in view of the common general knowledge, for example according to Lubricants and lubrication. 2nd edition. Edited by MANG, Theo, et al. Weinheim: Wiley-VCH Verlag GmbH, 2007.

[0051] Lubricant compositions containing compounds (A) can be, for example, in the form of oil-in water emulsions, oil-in-oil emulsions, greases, pastes, suspensions or powders; the form of the composition will be chosen by the skilled person according to the specific intended use.

[0052] The present invention is advantageous in several aspects. The toxicological risk of the process of the invention is relatively low, since, unlike non-fluorinated aromatic compounds, perfluorinated aromatic compounds are generally not harmful. Furthermore, they are usually soluble in hydrocarbon oils, so the use of solvents can be avoided; this allows reducing not only toxicological risks, but also production costs. Due to the superior oxidative stability of compounds (A), maintenance and service costs are reduced in comparison with those of the corresponding non-modified lubricants.

[0053] The invention is illustrated in greater detail in the following Experimental Section.

[0054] Should the disclosure of any patents, patent applications, and publications which are incorporated herein by reference conflict with the description of the present application to the extent that it may render a term unclear, the present description shall take precedence.

[0055] EXPERIMENTAL SECTION

[0056] Materials and methods

[0057] Mineral oil (Yubase® IV) was purchased from Fuchs Lubricants, polyalphaolefin 400/40 (PAO 400/40), polyalphaolefin 65/40 (PAO 65/40)
were purchased from Kluber^ Lubrication.

[0058] Decafluorobiphenyl (perfluorobiphenyl) and hexafluorobenzene (perfluorobenzene) were purchased from Sigma-Aldrich®.

[0059] Benzoyl peroxide (70% wt in water) and di-\textit{t}-butyl peroxide (DTBP) were purchased from Sigma-Aldrich®.

[0060] All reagents were used as received.

[0061] $^{19}$F-NMR spectra were recorded on a Varian Mercury® 300 MHz spectrometer; samples: 10%wt solutions in n-hexane.

[0062] Dynamic thermogravimetric analyses were carried out with a Perkin Elmer® PYRIS 1 TGA apparatus.

[0063] FT-IR spectra were recorded on a Nicolet Avatar® FT-IR spectrometer. Tribological tests were carried out with an Optimol® SRV III test machine. In the following examples, the expressions "hexafluorobenzene moieties" and "decafluorobiphenyl moieties" are intended to comprise any cyclic group, optionally containing conjugated or non-conjugated double bonds, deriving from the addition of the selected lubricant to hexafluorobenzene and decafluorobiphenyl respectively.

[0064] **Examples**

[0065] **Example 1 - Reaction of polyalphaolefin 400/40 (PAO 400/40) with decafluorobiphenyl**

[0066] 40 g PAO 400/40, 72 g decafluorobiphenyl (216 mmol) and 18 g benzoyl peroxide (52 mmol) were placed in a 250 ml glass flask equipped with magnetic stirrer, under nitrogen atmosphere.

[0067] The mixture was heated to 80°C until it turned to a homogeneous solution, which was then stirred for 4.5 hours at 300 rpm following a heating ramp from 80°C to 120°C with steps of 5°C every 30 minutes.

[0068] At the end, the reaction mixture was distilled under vacuum (10^{-2} mbar) up to 230°C to remove the excess of decafluorobiphenyl (bp = 208°C) and by-products (mainly benzoic acid) to obtain 45.3 modified PAO. $^{19}$F-NMR analysis showed the presence of 8.5% by weight of decafluorobiphenyl moieties.

[0069] **Example 1\textit{bis} - Reaction of polyalphaolefin 400/40 (PAO 400/40) with decafluorobiphenyl**
The same procedure as in example 1 was followed, with the difference that 16 g decafluorobiphenyl (48 mmol) and 5 g benzoyl peroxide (15 mmol) were used. 4 1.2 g modified PAO were obtained and $^{19}$F-NMR analysis confirmed the presence of 2% wt of decafluorobiphenyl moieties.

**Example 2 - Reaction of polyalphaolefin 65/40 (PAO 65/40) with decafluorobiphenyl**

The same procedure as in example 1 was followed, with the difference that 40 g PAO 65/40 instead of 40 g PAO 400/40 was used. 47.98 g modified PAO were recovered and $^{19}$F-NMR analysis confirmed the presence of 10.2% wt of decafluorobiphenyl moieties.

**Example 3 - Reaction of polyalphaolefin 400/40 (PAO 400/40) with decafluorobiphenyl**

A 45 ml stainless steel autoclave, equipped with magnetic stirrer, was charged with 5 g polyalphaolefin (PAO 400/40), 9.2 g decafluorobiphenyl and 0.98 g di-tert-butyl peroxide (DTBP). The autoclave was immersed in liquid nitrogen and three vacuum - nitrogen cycles were applied. At the end, the autoclave was heated to room temperature and pressurized under 2 bars nitrogen.

The reaction was conducted at 130°C for 4.5 hours. At the end, the reaction mixture was cooled to room temperature and the excess of decafluorobiphenyl and by-products were removed by distillation at 230°C at 10⁻² mbar to afford 5.72 g modified PAO. $^{19}$F-NMR analysis confirmed the presence of 7.5% by weight of decafluorobiphenyl moieties.

**Example 4 - Reaction of a mineral oil with decafluorobiphenyl**

10 g mineral oil Yubase® IV, 18 g decafluorobiphenyl (53 mmol) and 4.6 g of benzoyl peroxide (13 mmol) were placed in a 100 ml glass flask equipped with a magnetic stirrer, under nitrogen atmosphere.

The mixture was heated to 80°C until it turned to a homogeneous solution, which was then stirred for 4.5 hours at 300 rpm following a heating ramp from 80°C to 120°C with steps of 5°C every 30 minutes.

At the end, the reaction mixture was distilled under vacuum (10⁻² mbar) up to 230°C to remove the excess of decafluorobiphenyl (bp = 208°C) and by-products (mainly benzoic acid) to obtain 9.0 g modified oil. $^{19}$F-NMR
analysis showed the presence of 9.5% by weight of decafluorobiphenyl moieties.

**Example 5 - Reaction of a mineral oil with hexafluorobenzene**

10 g mineral oil Yubase® IV, 10 g hexafluorobenzene (54 mmol) and 4.6 g benzoyl peroxide (13 mmol) were placed in a 100 ml glass flask equipped with magnetic stirrer and condenser.

The mixture was heated to 80°C at reflux under nitrogen atmosphere and then stirred for 8 hours at 80°C at 300 rpm.

The reaction mixture was distilled under the same conditions as in Example 1, to afford 8.98 g modified oil. $^{19}$F-NMR confirmed the presence of 3.1% by weight of hexafluorobenzene moieties.

**Example 6 - Reaction of polyalphaolefin 65/40 (PAO 65/40) with hexafluorobenzene**

A 45 ml stainless steel autoclave, supplied with magnetic stirrer, was charged with 5 g polyalphaolefin PAO 65/40 (PAO 65/40), 5 g hexafluorobenzene and 2.3 g benzoyl peroxide. The autoclave was immersed in liquid nitrogen and three cycle of vacuum - nitrogen were applied. At the end, the autoclave was heated to room temperature and pressurized with 2 bars nitrogen and the reaction was conducted from 80 to 120°C, with a heating ramp of 5°C every 30 minutes.

At the end, the reaction mixture was cooled to room temperature and the excess of hexafluorobenzene and by-products were removed by distillation at 150°C at $10^{-2}$ mbar, to afford 4.91 g modified PAO. $^{19}$F-NMR confirmed the presence of 5.7% by weight hexafluorobenzene moieties.

**Example 7 - Reaction of polyalphaolefin 65/40 with hexafluorobenzene**

The same procedure as in example 6 was followed, with the difference that 1.02 g DTBP was used and that after pressurizing the autoclave with 2 bars nitrogen, the reaction was conducted at 130°C for 6 hours. After distillation of the excess of hexafluorobenzene and by-products, 5.29 g modified PAO was recovered. $^{19}$F-NMR analysis confirmed the presence of 8.9% by weight hexafluorobenzene moieties.

**Thermooxidation tests**

**Test 1 - Evaluation of thermal stability**
Dynamic TGA analyses of PAO 400/40 and of the modified PAO of example 1 were carried out in air with a heating rate of 10°C/min. The results are reported in the table below:

<table>
<thead>
<tr>
<th>Weight loss</th>
<th>PAO 400/40 Temperature, °C</th>
<th>Modified PAO of example 1 Temperature, °C</th>
<th>Delta T, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1%</td>
<td>251</td>
<td>291</td>
<td>40</td>
</tr>
<tr>
<td>2%</td>
<td>266</td>
<td>313</td>
<td>47</td>
</tr>
<tr>
<td>10%</td>
<td>309</td>
<td>367</td>
<td>58</td>
</tr>
<tr>
<td>50%</td>
<td>369</td>
<td>434</td>
<td>65</td>
</tr>
</tbody>
</table>

The results show that the same weight loss in the modified PAO of Example 1 as in PAO 400/40 was observed at temperatures 40 - 65°C higher; thus, the modified PAO according to the invention has a higher thermal stability.

Test 2 - Evaluation of thermo-oxidative stability

20 g PAO 400/40 and 20 g modified PAO of example 1 were placed in two 100 ml glass flasks and heated to 200°C for 12 hours under magnetic stirring in the presence of air. The content of carbonyl groups in each PAO (50% wt solution in n-hexane) was measured by FT-IR analysis (the peaks of the carbonyl groups fall in the range of 1719 to 1721 cm⁻¹).

The results are reported in table 2 below:

<table>
<thead>
<tr>
<th>Sample</th>
<th>Intensity of carbonyl peaks at 1719-1721 cm⁻¹, Ht</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 h</td>
</tr>
<tr>
<td>PAO 400/40</td>
<td>0.00</td>
</tr>
<tr>
<td>Modified PAO of</td>
<td>0.20</td>
</tr>
<tr>
<td>Example 1</td>
<td></td>
</tr>
</tbody>
</table>

The results show that in the modified PAO of the invention there is a
significantly lower increase of carbonyl groups content than in PAO 400/40; thus, the modified PAO of the invention is endowed with higher thermooxidation stability.

[0098] **Test 3 - Tribological test**

[0099] Tribological test were carried out in an SRV® test machine according to ASTM D6425 - 05 (2010). Decrease of COF (coefficient of friction) and wear was observed in the modified PAOs of Examples 1 and 2, and in blends of modified PAO of Example 1 with PAO 400/40 in comparison with the corresponding unmodified PAOs.

[0100]

<table>
<thead>
<tr>
<th>Sample</th>
<th>Load, N</th>
<th>Temperature, °C</th>
<th>COF</th>
<th>∆ COF, %</th>
<th>∆ wear, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAO 400/40</td>
<td>300</td>
<td>50</td>
<td>0.15</td>
<td>-</td>
<td>0.74</td>
</tr>
<tr>
<td>Modified PAO of Example 1</td>
<td>300</td>
<td>50</td>
<td>0.11</td>
<td>29.5</td>
<td>0.60</td>
</tr>
<tr>
<td>Modified PAO of Example 1 b/s</td>
<td>300</td>
<td>50</td>
<td>0.11</td>
<td>29.1</td>
<td>0.62</td>
</tr>
<tr>
<td>Blend 25% w/w of modified PAO (example 1) 75% w/w of PAO 400/40</td>
<td>300</td>
<td>50</td>
<td>0.10</td>
<td>31.6</td>
<td>0.63</td>
</tr>
<tr>
<td>PAO 400/40</td>
<td>50</td>
<td>80</td>
<td>0.18</td>
<td>-</td>
<td>0.46</td>
</tr>
<tr>
<td>Modified PAO of Example 1</td>
<td>50</td>
<td>80</td>
<td>0.12</td>
<td>33.1</td>
<td>0.25</td>
</tr>
<tr>
<td>Modified PAO of Example 1 b/s</td>
<td>50</td>
<td>80</td>
<td>0.11</td>
<td>36.5</td>
<td>0.28</td>
</tr>
<tr>
<td>Blend 25% w/w of modified PAO</td>
<td>50</td>
<td>80</td>
<td>0.11</td>
<td>37.0</td>
<td>0.27</td>
</tr>
</tbody>
</table>
Test 4 - Evaluation of the thermal stability of the product of Example 7

Dynamic TGA analyses of PAO 65/40 and of the modified PAO of example 7 were carried out in air with a heating rate of 10°C/min. The results are reported in the table below:

<table>
<thead>
<tr>
<th>Weight loss</th>
<th>PAO 65/40</th>
<th>Delta T, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1%</td>
<td>241</td>
<td>10</td>
</tr>
<tr>
<td>2%</td>
<td>252</td>
<td>14</td>
</tr>
<tr>
<td>10%</td>
<td>286</td>
<td>22</td>
</tr>
<tr>
<td>50%</td>
<td>333</td>
<td>35</td>
</tr>
</tbody>
</table>

The results show that the same weight loss in the modified PAO of Example 1 as in PAO 400/40 was observed at temperatures 10-35°C higher; thus, the modified PAO according to the invention has a higher thermal stability.

Test 5 - Evaluation of thermo-oxidative stability of the product of Example 7

20 g PAO 65/40 and 20 g modified PAO of Example 7 were placed in two 100 ml glass flasks and heated to 200°C for 12 hours under magnetic stirring in the presence of air. The content of carbonyl groups in each PAO (50% wt solution in n-hexane) was measured by FT-IR analysis (the peaks
of the carbonyl groups fall in the range of 1719 to 1721 cm$^{-1}$).

[0107] The results are reported in the table below:

[0108]

<table>
<thead>
<tr>
<th>Compound</th>
<th>Intensity of carbonyl peaks at 1719-1721 cm$^{-1}$, Ht</th>
<th>$\Delta$ peak at 1719-1721 cm$^{-1}$, Ht</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAO 65/40</td>
<td>0.00</td>
<td>2.00</td>
</tr>
<tr>
<td>Modified PAO of</td>
<td>0.60</td>
<td>0.75</td>
</tr>
<tr>
<td>Example 7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Claims
1. A process for the addition of a hydrogen-based lubricant to a per(halo)fluorinated aromatic compound, said process comprising the radical reaction of a hydrogen-based lubricant [lubricant (RH)] with a per(halo)fluorinated aromatic compound [compound (F)] to provide a compound [compound (A)] comprising at least one per(halo)fluorinated cyclic group (F') having at least one lubricant chain (RH) [chain (RHC)] bound thereto, said group (F') optionally containing conjugated or non-conjugated double bonds.
2. The process according to claim 1 wherein lubricant (RH) is one or more lubricant whose viscosity ranges from 2 to 1,000,000 cSt and containing straight or branched hydrocarbon moieties.
3. The process according to claim 2 wherein lubricant (RH) is in the liquid or in the semi-solid form at room temperature.
4. The process according to claim 3 wherein lubricant (RH) is in the liquid form and is selected from one or more mineral oils of hydrocarbon type, animal or vegetable oils, synthetic oils like polyalphaolefins (PAOs), dibasic acid esters, polyol esters, phosphate esters, polyesters, alkylated naphthalenes, polyphenyl ethers, polybutenes, multiply-alkylated cyclopentanes, silane hydrocarbons, siloxanes and polyalkylene glycols.
5. The process according to claim 4 wherein oil (RH) is a mineral oil of hydrocarbon type or a polyalphaolefin.
6. The process according to any one of claims 1 to 5 wherein the radical reaction is initiated by contacting lubricant (RH) and compound (F) with organic or inorganic peroxides, redox systems, ozone, hydrogen peroxide or by thermal or photochemical decomposition of lubricant (RH).
7. The process according to claim 6 wherein the organic peroxide is benzoyl peroxide or di-ter-butyl peroxide.
8. The process according to any one of claims 1 - 7 which is carried out in the absence of solvents.
9. The process according to any one of claims 1 - 8 wherein compound (F) is selected from perfluorobenzene, perfluorobiphenyl, perfluoronaphthalene, perfluoroanthracene, perfluoropyridine, perfluorotoluene and derivatives.
thereof comprising one or more perfluorinated substituent(s).

10. The process according to claim 9 wherein compound (F) is selected from perfluorobenzene and perfluorobiphenyl.

11. An additional compound [compound (A)] comprising at least one per(halo)fluorinated cyclic group [group (F')] having at least one hydrogen-based lubricant (RH) chain [chain RHC] bound thereto, said group (F') optionally containing conjugated or non-conjugated double bonds.

12. A method for lubricating comprising the use of compound (A) as claimed in claim 11.

13. A method for manufacturing a lubricant composition comprising the use of compound (A) as claimed in claim 12.

14. A lubricant composition comprising compound (A) as claimed in claim 11 in admixture with further ingredients and additives.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
INV. C10M105/50  C10M105/54  C10M107/38  C10M177/00
ADD. C10N30/06  C10N30/08  C10N30/10  C10N40/04  C10N40/25
C10N40/30  C10N50/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
CIOM

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>EP 2 100 909 AI (SOLVAY SOLEXIS SPA [IT] ) 16 September 2009 (2009-09-16) cited in the applications on the whole document</td>
<td>1-14</td>
</tr>
<tr>
<td>A</td>
<td>Wo 2012/007374 AI (SOLVAY SOLEXIS SPA [IT] ; FANTONI MATTEO [IT] ; APOSTOL0 MARCO [IT] ; AVA) 19 January 2012 (2012-01-19) cited in the applications on paragraphs [0024] - [0030] , [0036] , [0044] - [0050] ; claims 1,2,11; examples 1; table e 1</td>
<td>1-14</td>
</tr>
<tr>
<td>A</td>
<td>US 3 720 646 A (SIANESI D ET AL) 13 March 1973 (1973-03-13) cited in the applications on column 2, line 22 - column 6, line 66; claims 1,6-10; examples 1-6,8</td>
<td>1-14</td>
</tr>
</tbody>
</table>

Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:

**A** document defining the general state of the art which is not considered to be of particular relevance

**E** earlier application or patent but published on or after the international filing date

**L** document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

**O** document referring to an oral disclosure, use, exhibition or other means

**P** document published prior to the international filing date but later than the priority date claimed

**Y** later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

**X** document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

**V** document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

**U** document member of the same patent family

Date of the actual completion of the international search 20 June 2014

Date of mailing of the international search report 03/07/2014

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL-2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Renoth, Heinz

Form PCT/ISA/210 (second sheet) (April 2005)
<table>
<thead>
<tr>
<th>Patent document cited in search report</th>
<th>Publication date</th>
<th>Patent family member(s)</th>
<th>Publication date</th>
</tr>
</thead>
<tbody>
<tr>
<td>EP 2100909</td>
<td>16-09-2009</td>
<td>CN 102015828 A</td>
<td>13-04-2011</td>
</tr>
<tr>
<td>EP 2100909</td>
<td>16-09-2009</td>
<td>EP 2254930 A</td>
<td>01-12-2010</td>
</tr>
<tr>
<td>US 2011015107</td>
<td>20-01-2011</td>
<td>W0 2009112577 A</td>
<td>17-09-2009</td>
</tr>
<tr>
<td>W0 2012007374</td>
<td>19-01-2012</td>
<td>CN 103108912 A</td>
<td>15-05-2013</td>
</tr>
<tr>
<td>KR 20130094796</td>
<td>26-08-2013</td>
<td>US 2013109797 A</td>
<td>02-05-2013</td>
</tr>
<tr>
<td>W0 2012007374</td>
<td>19-01-2012</td>
<td>W0 2012007374 A</td>
<td>19-01-2012</td>
</tr>
<tr>
<td>US 3720646</td>
<td>13-03-1973</td>
<td>BE 763731 Al</td>
<td>03-09-1971</td>
</tr>
<tr>
<td>CA 962794</td>
<td>11-02-1975</td>
<td>CH 515466 A</td>
<td>15-11-1971</td>
</tr>
<tr>
<td>DE 2109758</td>
<td>23-09-1971</td>
<td>ES 388785 Al</td>
<td>16-05-1973</td>
</tr>
<tr>
<td>FR 2081667</td>
<td>10-12-1971</td>
<td>GB 1302649 A</td>
<td>10-01-1973</td>
</tr>
<tr>
<td>NL 7102586</td>
<td>07-09-1971</td>
<td>US 3720646 A</td>
<td>13-03-1973</td>
</tr>
<tr>
<td>US 3720646</td>
<td>13-03-1973</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>