

Description**Title: LUBRICATING COMPOSITION FOR PREVENTING OR REDUCING ABNORMAL COMBUSTION IN AN ENGINE****5 Field of the invention**

The present invention relates to the field of lubricating oils, in particular for use in engines, in particular gas-powered engines (liquefied natural gas, compressed gas or hydrogen gas). More precisely, the present invention relates to lubricating compositions that can prevent or reduce the abnormal consumption of fuel in an engine, and in particular the phenomenon of pre-ignition and knocking in an engine, in particular in a gas engine.

Prior art

With the aim of improving air quality and of complying with government restrictions in terms of reducing greenhouse gas emissions, many vehicle engine manufacturers are studying the use of gas, in particular hydrogen, as a fuel for internal combustion engines.

However, gases, whether natural gas or hydrogen, have a higher thermal capacity than that of liquid hydrocarbons, and gas-powered engines therefore generate higher combustion temperatures than liquid hydrocarbon-powered engines. This places severe demands on the lubricants used in these engines and therefore on the development of dedicated lubricants.

Hydrogen-powered engines and, more generally, gas engines, are more particularly subject to an undesirable abnormal combustion phenomenon, known as pre-ignition.

This phenomenon may be considered to be an uncontrolled explosion occurring in the combustion chamber following ignition, by a source other than the spark plug, of combustible elements that may derive from the fuel, but also of small quantities of engine lubricant in the combustion chamber.

More recently, low speed pre-ignition, more widely known as “LSPI”, has been identified and generally occurs at low speeds and under high loads.

The phenomenon of pre-ignition potentially has a significant negative impact on the efficiency and overall performances of the engine, or even of causing considerable damage to the cylinders, pistons, spark plugs and valves in the engine, which could lead to a breakdown of the engine or even to breaking of the engine.

As a result, the studies have focused on understanding the origin of LSPI, with the aim of reducing or even of eradicating the occurrence of this phenomenon.

Several studies have therefore demonstrated that the frequency of LSPI is sensitive to the composition of the engine lubricant used. In particular, the calcium deriving from calcium-based detergents has been identified as one of the causes of the appearance of LSPI. Reducing the quantity of calcium-based detergents, for example of calcium sulfonate, phenate, salicylate, and increasing magnesium-based detergents, has therefore been suggested in order to reduce the occurrence of LSPI phenomena (Kocsis *et al.*, "*The Impact of Lubricant Volatility, Viscosity and Detergent Chemistry on Low Speed Pre-Ignition Behavior*", SAE Int. J. Engines, 10(3):1019-1035, 2017; Ritchie *et al.*, "*Controlling Low-Speed Pre-Ignition in Modern Automotive Equipment, Part 3: Identification of Key Additive Component Types and Other Lubricating composition Effects on Low-Speed Pre-Ignition*", SAE Int. J. Engines, 9(2): 832-840, 2016).

In general, calcium-based detergents are present during the formulation of lubricants, in the additive package added to a base oil and dedicated to bringing about the desired performances.

A simple reduction in the calcium-based detergent content is not satisfactory, since it is carried out to the detriment of the detergent capacities and the thermal stability of the engine lubricant, resulting in an increased formation of deposits (or varnish) in the engine, and therefore has a deleterious effect on the lifetime of the engine.

Regarding the proposed solution of replacing calcium-based detergent additives with magnesium-based detergents, this could certainly reduce the LSPI, but here again, to the detriment of the other required properties. In particular, this approach would oblige the formulators to use an extremely high and unstable concentration of these detergents in order to ensure that the formulations were capable of maintaining the required performances (such as the TBN, or total base number, of the detergent). What is more, the advantage in terms of the reduction in LSPI is counterbalanced by the negative impact of the magnesium-based formulations on the vehicle engine fuel consumption reduction properties, also known as "Fuel Eco" properties (Gupta *et al.*, "*Impact of Engine Oil Detergent on Low Speed Pre-Ignition (LSPI) and Fuel Economy Performance*", SAE Technical Paper, 2020-01-1424, 2020).

Knocking is another abnormal combustion phenomenon that may be produced, in particular in a positive ignition engine in vehicles, and more particularly in a positive ignition engine in automotive vehicles, and which is due to self-ignition of the fuel upstream of the flame front in the combustion chamber. This self-ignition propagates at very high speed in the combustion chamber and generates high frequency vibrations in the bulk of the gas and thermal overloads in the engine, which could have severe mechanical consequences. The solutions which are currently used by automotive engineers in order to avoid this phenomenon, such as reducing the spark advance, however, significantly reduce the efficiency of the positive ignition engines.

As a consequence, research has been oriented towards the development of novel lubricating compositions that can be used to reduce the phenomena of abnormal combustion in the engines, such as LSPI and knocking, while preserving the other desired properties for the lubricant.

As an example, the document US 2017/0015933 proposes a lubricating composition comprising a mixture of overbased and neutral or “low-based” detergents, providing the composition with a controlled calcium content. The addition of additives for reducing pre-ignition in the lubricating compositions has also been proposed. An example that may be cited is the document US 2019/0292473, which proposes the use of various nitrogen-containing compounds for this purpose.

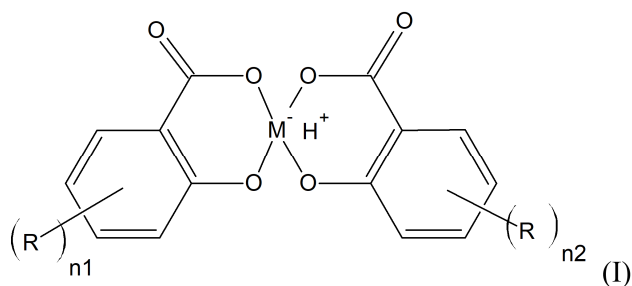
On the other hand, the documents US 2763613 and US 2898359 have described the use of anti-knock compounds selected from organometallic compounds, and more particularly from ferrocene type compounds, in a lubricating composition. It is also possible to cite the document WO 2004/101717, which describes the use of manganese-based organometallic compounds in a lubricating composition in order to reduce the phenomenon of knocking in an engine. However, the use of such organometallic compounds encourages deposits in the combustion chamber and can therefore cause abnormal combustion such as hot spot ignition, which could cause major mechanical failures. In addition, these compounds could present a risk to human health.

Disclosure of the invention

The aim of the present invention is to provide a lubricant that, when it is used for the lubrication of a mobile or stationary motorization system, in particular a gas-powered engine, in particular in an automotive vehicle, can prevent and/or reduce abnormal combustion, in particular pre-ignition, especially low speed pre-ignition (LSPI), or in fact knocking, without affecting the other properties of the lubricant, in particular its detergent capacity.

More particularly, in accordance with a first of these aspects, the invention concerns the use of a lubricating composition comprising one or more base oils and at least one spiro compound with the following formula (I):

[Chem 1]

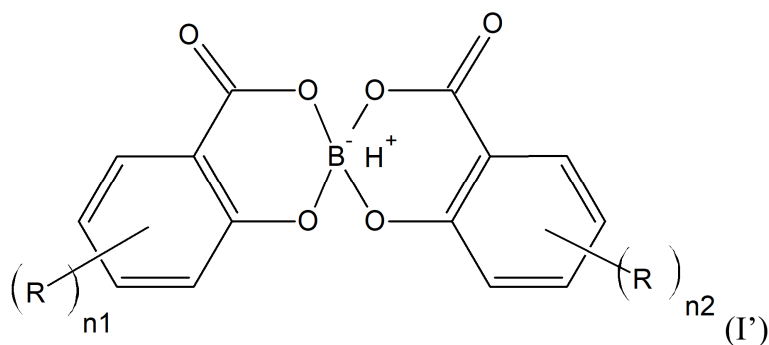


in which:

M is an atom selected from boron (B) and aluminum (Al), in particular a boron atom;
 n1 and n2, independently of one another, equal 0, 1 or 2; and

R, independently of one another, represents a hydrocarbon group comprising from 1 to 50 carbon atoms, in particular from 5 to 20 and more particularly from 5 to 15 carbon atoms; in order to prevent and/or reduce the abnormal consumption of fuel, in particular pre-ignition, especially LSPI and/or knocking, in an engine, in particular in a gas-powered engine, especially a vehicle, lubricated by means of said lubricating composition.

Preferably, the spiro compound used in accordance with the invention has the formula (I) cited above, in which M is a boron atom. In other words, in accordance with this particular embodiment, the spiro compound is a compound known as a “spiroboronate compound”, with the following formula (I’):



in which n1, n2 and R are as defined above.

The term “abnormal combustion” means any phenomenon during which all or a portion of the fuel mixture is ignited in an uncontrolled manner inside the combustion chamber of an engine, in particular a vehicle engine, especially an automotive vehicle. The term “abnormal combustion” as used in accordance with the invention more particularly means the phenomena of pre-ignition, including low speed pre-ignition (LSPI); and knocking, including super knocking or mega knocking which may follow a pre-ignition event.

The term “pre-ignition” as used in accordance with the invention is intended to include the phenomenon of low frequency vibration, producing an acoustic effect (or “rumble”). More particularly, “pre-ignition” is low speed pre-ignition (LSPI).

The term “fuel” in accordance with the invention more particularly means gasoline, diesel fuel and/or gas.

More simply, in the remainder of the text, the term “spiro compound” in accordance with the invention will be used to designate a spiro compound with formula (I) as defined above, in particular a spiroboronate compound with formula (I') as defined above. Examples of spiro compounds under consideration according to the invention are described in more detail in the text below.

In addition, more simply, the term “lubricating composition in accordance with the invention” or “lubricant in accordance with the invention” will be used to define a lubricating composition as defined above, incorporating at least one spiro compound in accordance with the invention.

In particular, the invention concerns the use of a lubricating composition comprising one or more base oils and at least one spiro compound with formula (I) as defined above and detailed in the text below, in particular at least one spiroboronate compound with formula (I'), in order to prevent and/or reduce pre-ignition, in particular LSPI, in an engine, in

particular in a gas-powered engine, especially a vehicle, lubricated by means of said lubricating composition.

The invention also concerns the use of a lubricating composition comprising one or more base oils and at least one spiro compound with formula (I) as defined above and detailed in the text below, in particular at least one spiroboronate compound with formula (I'), in order to prevent and/or reduce knocking in an engine, in particular in a gas-powered engine, especially a vehicle, lubricated by means of said lubricating composition.

In accordance with another of its aspects, the invention further concerns a lubricating composition intended for the lubrication of a gas-powered engine, in particular a vehicle, especially an automotive vehicle, comprising at least:

- one or more base oils;
- at least one spiro compound with formula (I) as defined above and detailed in the text below, in particular at least one spiroboronate compound with formula (I').

In accordance with a particular embodiment, in addition to said spiro compound or spiro compounds in accordance with the invention, a lubricating composition used in accordance with the invention comprises one or more detergent additives, in particular selected from the metallic detergent additives conventionally used in the field of lubricants, in particular based on calcium or magnesium.

As illustrated in the examples below, the inventors have discovered that, by supplementing a lubricant with a spiro compound as defined above, in particular of the spiroboronate type, even in a low quantity, it is possible to significantly reduce the metallic detergent additive content, in particular of calcium-based detergent additives, which are undesirable because of their influence on the occurrence of abnormal combustion phenomena, especially LSPI, while maintaining, and even improving, the detergent capacity of the lubricant.

Advantageously, the use of a spiro compound in accordance with the invention as a lubricant means that the content of metallic detergent additives, especially with calcium, generally used in order to access the desired detergent properties, can be reduced, and therefore the phenomena of abnormal combustion, in particular the phenomenon of pre-ignition, in particular LSPI, in an engine, for example a gas engine lubricated by means of said lubricant can be prevented or reduced.

The use of a lubricating composition in accordance with the invention to lubricate an engine, in particular a gas-powered engine, can therefore both reduce or even prevent the phenomena of abnormal combustion, in particular the phenomenon of pre-ignition, especially LSPI, and provide access to excellent detergent properties.

- 5 As will be illustrated in the examples below, the detergent properties of the lubricant can be appreciated by evaluating the performances of the lubricant in terms of thermal stability using a “MCT” (“Micro Coking Test”) test in accordance with the standard GFC Lu-27-T-07, as described in the examples. This test reveals the tendency of the lubricant to form deposits/varnish under high temperature conditions similar to those encountered in the
10 hottest parts of the engine (from 230°C to 280°C).

Advantageously, the use of a lubricating composition in accordance with the invention to lubricate an engine, in particular an automotive vehicle engine, can also enable the phenomenon of knocking to be reduced or even eliminated, in particular without the need to add anti-knocking additives to the lubricant.

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The reduction in the metallic detergents content, known to be a source of ash, in particular sulfated ash, may also advantageously enable the content of ash generated by the lubricant to be reduced.

- In particular, the or said metallic detergent additives may be present in the lubricating
20 composition in a manner such as to provide a metallic element(s) content, in particular calcium, of less than or equal to 6000 ppm, in particular from 100 ppm to 4000 ppm, preferably from 250 ppm to 3000 ppm.

- A lubricating composition in accordance with the invention may advantageously have a sulfated ash content, measured in accordance with the standard ASTM D874, of less than or
25 equal to 2% by weight, in particular less than or equal to 1.5% by weight, and more particularly less than or equal to 1%, with respect to the total weight of said lubricating composition.

- Advantageously, a lubricating composition in accordance with the invention also has good
30 properties in terms of reducing the fuel consumption of motor vehicles, also known as the “Fuel Eco” properties, and for this reason, contributes to the reduction in CO₂ emissions.

In addition, advantageously, as illustrated in the examples, the use of a spiro compound in accordance with the invention, in particular of the spiroboronate type, can also be used to significantly increase the oxidation stability of the lubricating composition.

Thus, the use of a spiro compound in accordance with the invention, in particular of a
5 spiroboronate compound in accordance with the invention, provides access to a lubricant having excellent detergent properties, a reduced ash content and excellent oxidation stability properties, while reducing or even eliminating abnormal combustion phenomena.

Furthermore, advantageously, as illustrated in the examples below, the spiro compounds in
10 accordance with the invention are not hydrolysable, primarily because of the tetravalent configuration of the boron or of the aluminum atom.

In other words, the spiro compounds in accordance with the invention, in particular the spiroboronate compounds in accordance with the invention, have an excellent stability when they are brought into contact with water (which would, for example, be obtained from the
15 combustion of fuel or from condensation). The absence of decomposition/degradation of the spiro compounds in the presence of water can in particular be used to prevent, during the use of the lubricating composition in accordance with the invention, the formation of boric acid, a product which is classified as CMR (carcinogenic, mutagenic, and reprotoxic).

20 The invention also concerns a process or a method for preventing and/or reducing the abnormal combustion of fuel in an engine, in particular in a gas-powered engine, for example a vehicle engine, comprising lubrication of said engine with a lubricating composition in accordance with the invention as defined above.

In particular, the invention concerns a process or a method for preventing and/or reducing
25 pre-ignition, in particular low speed pre-ignition, in an engine, in particular in a gas-powered engine, for example a vehicle engine, comprising the lubrication of said engine with a lubricating composition in accordance with the invention as defined above.

The invention also concerns a process or a method for preventing and/or reducing knocking in an engine, in particular in a gas-powered engine, for example a vehicle engine, comprising
30 lubrication of said engine with a lubricating composition in accordance with the invention as defined above.

Said processes or said methods more particularly comprise a step for bringing at least one mechanical part of said engine into contact with a lubricating composition in accordance with the invention as defined above.

5 The invention also concerns the use of a lubricating composition in accordance with the invention for the lubrication of an engine, in particular a gas-powered engine, for example a vehicle engine.

In another of its aspects, the invention also concerns a process or a method for the lubrication of an engine, especially in a gas-powered engine, for example a vehicle engine, comprising a step for bringing at least one mechanical part of the engine into contact with a lubricating
10 composition in accordance with the invention as defined above.

The lubricating compositions in accordance with the invention are advantageously used for any type of engine, for mobile or stationary applications which, during their operation, may be subjected to abnormal combustion phenomena, in particular to a pre-ignition
15 phenomenon, in particular LSPI, and/or to knocking.

More particularly, it concerns internal combustion engines of vehicles such as gasoline engines, diesel engines, gas-powered engines.

A “diesel engine” in the context of the invention is a combustion engine for which the fuel is diesel fuel.

20 “Gas-powered engines” designates internal combustion engines for which the fuel comprises at least one gas, including biogases. They include engines which are exclusively powered by gas, termed gas engines, for example engines powered by natural gas (liquefied natural gas, LNG), or compressed natural gas (CNG), and hydrogen engines, but also engines powered by gas and by gasoline (“dual fuel” gas/gasoline engines), engines powered by gas and diesel
25 fuel (“dual fuel” gas/diesel fuel engines).

More particularly, the engines for a mobile application are engines used in vehicles, including heavy goods vehicles, mobile machines known as “off road” vehicles, light vehicles or in fact marine vehicles.

Engines for stationary applications, or stationary engines, may, for example, have
30 applications in devices for the production of electrical energy. As an example, it may be a stationary gas-powered engine.

In accordance with a particular embodiment, the lubricating composition in accordance with the invention is used for the lubrication of gas engines, in particular hydrogen engines or natural gas (LNG or CNG) engines.

- 5 Other characteristics, variations and advantages of using a lubricating composition in accordance with the invention will become apparent from the following description and examples, given by way of non-limiting illustration of the invention.

10 The expressions “comprised between... and...”, “from ... to ...”, “formed from... to...”, and “varying from... to ...” should be construed as including the limits, unless stated otherwise.

In the description and the examples, unless indicated otherwise, the percentages are percentages by weight. Thus, the percentages are expressed by weight with respect to the total weight of the composition.

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Brief description of the drawings

Figure 1 shows the particle size distribution for the emulsion of spiroboronate in water obtained after stirring using a paddle (Figure 1a) and after Ultra-Turrax® stirring (Figure 1b), as described in Example 4.

- 20 Figure 2 shows the NMR spectra for pure spiroboronate (Figure 2a) and for residue (Figure 2b), obtained as described in Example 4.

Detailed description

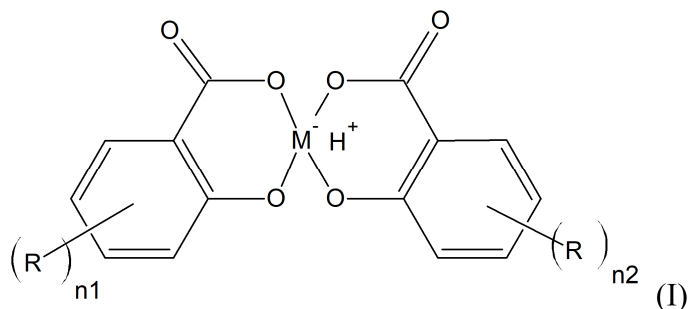
SPIRO COMPOUND

- 25 As indicated above, the invention resides in the use of one or more specific spiro compounds in a lubricant for an engine, in particular for a gas-powered engine.

It should be understood that the invention may use a single spiro compound or a mixture of at least two distinct spiro compounds, in particular three or four distinct spiro compounds, in particular as defined below.

- 30 As mentioned above, the spiro compound under consideration according to the invention has the following formula (I):

[Chem 2]



in which:

M is an atom selected from boron and aluminum, and in particular is a boron atom;
 n1 and n2, independently of one another, equal 0, 1 or 2; and

- 5 R, independently of one another, represents a hydrocarbon group comprising from 1 to 50 carbon atoms, in particular from 5 to 20 and more particularly from 5 to 15 carbon atoms.

The hydrocarbon groups under consideration according to the invention may optionally be interrupted by one or more heteroatoms, for example -O-, -NH-, -N= or -S-, in particular -
 10 O- or -NH-; and/or optionally substituted by one or more -OH, -NH₂ and -SH groups, in particular -OH or -NH₂.

In accordance with a particular embodiment, the R groups are solely compounds of carbon and hydrogen atoms.

The hydrocarbon groups may in particular be alkyl, alkenyl, aryl or aralkyl groups.

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In accordance with a particular embodiment, the R substituents, independently of one another, represent a hydrocarbon group, preferably an aliphatic, linear or branched chain comprising from 3 to 50 carbon atoms, in particular from 3 to 30 carbon atoms, especially from 5 to 25 carbon atoms, especially from 5 to 20 carbon atoms and more particularly from
 20 8 to 15 carbon atoms.

In particular, the R substituents, independently of one another, may represent a linear or branched alkyl chain, in particular a C₁ to C₅₀; in particular C₃ to C₃₀, especially C₅ to C₂₅, especially C₅ to C₂₀ and more particularly C₈ to C₁₅, for example C₁₀ alkyl chain, preferably linear.

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In accordance with a particular embodiment, n1 and n2 equal 0.

In accordance with another particular embodiment, n1 and n2 equal 1 or 2.

When n_1 equals 2 or n_2 equals 2, the R groups carried by the same ring may be identical or different.

In accordance with a particular embodiment, the spiro compound may have formula (I) cited above, in which n_1 and n_2 equal 1; the R substituents possibly being identical or different, preferably identical.

In accordance with a particular embodiment, the spiro compound has formula (I) cited above, in which:

n_1 and n_2 equal 1; and

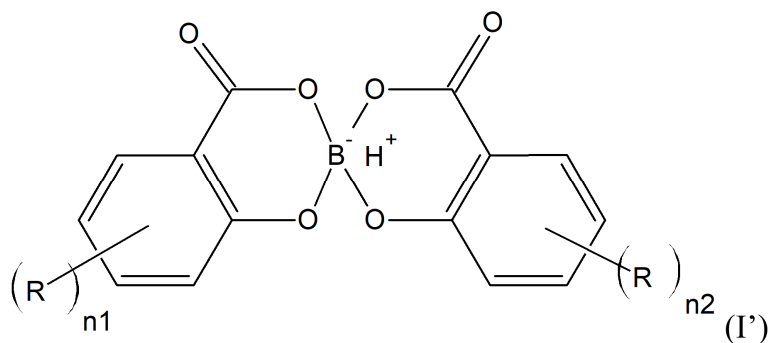
the R groups, which are identical, represent C_1 to C_{50} , in particular C_3 to C_{30} , especially C_5 to C_{25} , especially C_5 to C_{20} and more particularly C_8 to C_{15} , yet more preferably C_{10} , alkyl groups, preferably linear.

In accordance with a particular embodiment, the spiro compound has formula (I) in which

M is a boron atom.

In other words, in accordance with this particular embodiment, the spiro compound may be a compound known as a spiroboronate, with the following formula (I'):

[Chem 3]

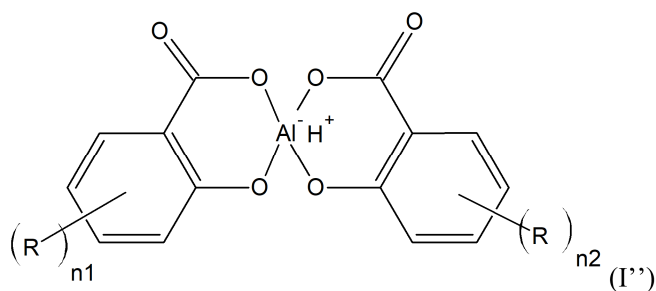


in which n_1 and n_2 and R are as defined above.

In accordance with another particular embodiment, the spiro compound has formula (I) in which M is an aluminum atom.

In other words, in accordance with this particular embodiment, the spiro compound may be a compound known as a spiroaluminate, with formula (I'') as follows:

[Chem 4]



in which $n1$, $n2$ and R are as defined above.

In accordance with another of its aspects, the invention therefore concerns a spiro compound with formula (I) cited above, in which:

- M is an aluminum atom;
- $n1$ and $n2$, independently of one another, equal 0, 1 or 2, at least one of $n1$ and $n2$ being equal to 1 or 2; preferably, $n1$ and $n2$ are equal to 1;
- the R groups, independently of one another, represent a linear or branched aliphatic chain, in particular an alkyl chain, preferably linear, comprising from 5 to 50 carbon atoms, in particular from 6 to 30 carbon atoms, especially from 8 to 25 carbon atoms and more particularly from 10 to 15 carbon atoms.

In other words, the invention concerns a compound of the spiroaluminate type with formula (I'') cited above, in which:

- $n1$ and $n2$, independently of one another, equal 0, 1 or 2, at least one of $n1$ and $n2$ being equal to 1 or 2; preferably, $n1$ and $n2$ are equal to 1; and
- the R groups, independently of one another, represent a linear or branched aliphatic chain, in particular an alkyl chain, preferably linear, comprising from 5 to 50 carbon atoms, in particular from 6 to 30 carbon atoms, especially from 8 to 25 carbon atoms and more particularly from 10 to 15 carbon atoms.

In accordance with a particular embodiment, the compound of the spiroaluminate type in accordance with the invention has formula (I'') in which:

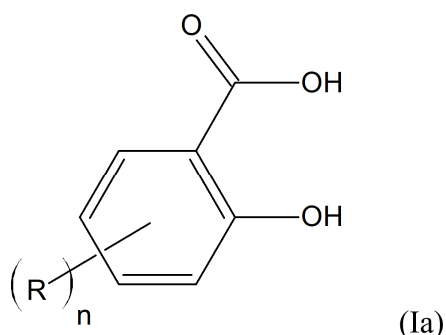
- $n1$ and $n2$ equal 1; and
- the R groups, which may be identical or different, preferably identical, represent alkyl chains, preferably linear, comprising from 5 to 50 carbon atoms, in particular from 6 to 30 carbon atoms, especially from 8 to 25 carbon atoms and more particularly from 10 to 15 carbon atoms.

The spiro compound used in accordance with the invention may be prepared from at least salicylic acid or a salicylic acid derivative and a boron compound or an aluminum compound.

5 More particularly, it may be obtained by the reaction of:

- at least one compound selected from salicylic acid and its derivatives, with formula (Ia) as follows:

[Chem 5]



10 in which R is as defined above and n is as defined above for n1 and n2; and

- at least one boron or aluminum compound, in particular boric acid or aluminum hydroxide.

The preparation of the spiro compound used in the lubricating composition in accordance with the invention does not involve any steps, subsequent to the reaction of salicylic acid or
 15 of one of its derivatives with said boron or aluminum compound, for a reaction with an amine compound, as is the case, for example, in the context of the preparation of the compounds proposed in the applications WO2018/220007 and WO2018/220009.

Salicylic acid and its derivatives with formula (Ia) cited above may be synthesized in
 20 accordance with synthesis methods which are known to the person skilled in the art or are commercially available.

The boron compound (in other words, based on boron) may in particular be selected from boric acid ($B(OH)_3$), boronic acids, boric and boronic esters, boron oxide and boric acid
 25 complexes.

In particular, the boron compound may be selected from boric acid; boron oxide; boric acid complexes; trialkyl borates, in particular in which the alkyl groups, independently of one

another, comprise from 1 to 4 carbon atoms; boronic acids containing a C₁-C₁₂ alkyl group; boric acids substituted by two alkyl groups, in particular C₁ to C₁₂; boric acids substituted by two aryl groups, in particular C₆ to C₁₂; boric acids substituted by one or two aralkyl groups, in particular C₇ to C₁₂, and derivatives of these compounds obtained by substitution of at least one alkyl group by one or more alkoxy groups.

In particular, the boric acid complexes are complexes of boron with one or more molecules comprising one or more alcohol functions.

In accordance with a particular embodiment, the boron compound is boric acid.

- 10 The aluminum compound (in other words, based on aluminum) may, for example, be selected from aluminum hydroxide (Al(OH)₃), aluminum oxide, aluminum sulfate (Al₂SO₄)₃.

The person skilled in the art will be capable of adjusting the reaction conditions between the or said compounds (Ia) and the boron or aluminum compound in order to obtain the desired spiro compound.

In particular, the reaction may be carried out in a solvent medium constituted by one or more apolar solvents and/or polar protic solvents.

- 20 The solvent medium may be constituted by one or more solvents selected from naphtha, polar protic solvents such as water and alcohols, for example methanol, ethanol, propanol, butanol; and their mixtures.

Advantageously, the reaction between the salicylic acid or one of its derivatives with formula (Ia) cited above and the boron or aluminum compound in order to obtain the desired spiro compound, in particular the reaction between salicylic acid or one of its derivatives with formula (Ia) and the boron compound in order to obtain the desired spiroboronate compound, may be carried out in an apolar aprotic solvent, in particular in toluene.

In the context of the invention, the term:

- 30 - "hydrocarbon group" means a radical, which may or may not be saturated, which may be linear, branched or cyclic, which may or may not be aromatic, comprising carbon and hydrogen;

- “aliphatic chain” means a hydrocarbon group exclusively constituted by carbon atoms and hydrogen atoms, which may be linear or branched, saturated or unsaturated, not aromatic. Preferably, an aliphatic chain is an alkyl chain.

- “alkyl” means a saturated aliphatic group, which may be linear or branched; as an example, a C_x to C_z alkyl represents a saturated carbon chain containing x to z carbon atoms, which may be linear or branched;

- “alkenyl” means a monounsaturated or polyunsaturated aliphatic group, which may be linear or branched;

- “cycloalkyl” means a cyclic alkyl group, for example, a C_x to C_z cycloalkyl represents a cyclic carbon-containing group containing x to z carbon atoms, for example a cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl group;

- “aryl” means a monocyclic or polycyclic aromatic group, in particular comprising between 6 and 10 carbon atoms. An example of an aryl group that may be cited is a phenyl or naphthyl group;

- “aralkyl” means an aryl group as defined above, substituted by at least one alkyl group as defined above.

Said spiro compound or spiro compounds are advantageously used in a content that is sufficient to reach the required level for the detergent capacity of the lubricant and/or to prevent abnormal combustion phenomena, in particular the phenomena of pre-ignition and/or knocking.

In particular, the spiro compounds content is adjusted in a manner such that the lubricating composition, even if it comprises a reduced quantity of metallic detergent additives, in particular of detergent additives based on calcium and/or magnesium, has equivalent detergent properties, or even improved properties compared with a lubricating composition for which the detergent capacity is provided solely by the metallic detergent additives.

Advantageously, even a small quantity of spiro compound(s), in particular less than 2% by weight, especially less than or equal to 1% by weight, with respect to the total weight of said lubricating composition, means that good detergent properties can be obtained.

Clearly, the quantity of spiro compound(s) used may be adjusted as a function of the nature of the lubricant, and more particularly taking into account the presence or otherwise and the

quantity of other detergent additive(s) used which are present in the lubricant, in particular metallic detergents, for example based on calcium.

5 In general, said spiro compound or spiro compounds under consideration according to the invention, in particular as defined above, may be used in an amount of 0.1 to 20% by weight, in particular 0.2 to 15% by weight, especially 0.5 to 10% and more particularly 0.5 to 5.0% by weight, with respect to the total weight of said lubricating composition.

LUBRICATING COMPOSITION

10 A lubricating composition such as that under consideration according to the invention comprises one or more base oils and, optionally, other additives considered conventional in the lubricating compositions.

It should be understood that the nature and the quantity of the compounds below are adapted to the destination of the lubricant, and more particularly in respect of the engine for which it
15 is intended.

Base oil

As mentioned above, a lubricating composition in accordance with the invention comprises at least one base oil in addition to at least one spiro compound in accordance with the
20 invention.

These base oils may be selected from base oils in conventional use in the field of lubricating oils for engines, in particular for gas engines, such as mineral oils, synthetic oils or natural, animal or vegetable oils.

It may be a blend of several base oils, for example a blend of two, three or four base oils.

25 The base oils of the lubricating compositions under consideration according to the invention may in particular be oils of mineral or synthetic origins belonging to groups I to V in accordance with the classes defined in the API (or their equivalents in accordance with the ATIEL classification) and shown in Table A below, or their blends.

[Table 1]

	Saturates content	Sulfur content	Viscosity index (VI)
Group I Mineral oils	< 90%	> 0.03%	$80 \leq VI < 120$
Group II Hydrocracked oils	$\geq 90\%$	$\leq 0.03\%$	$80 \leq VI < 120$
Group III Hydrocracked or hydroisomerized oils	$\geq 90\%$	$\leq 0.03\%$	≥ 120
Group IV	Polyalphaolefins (PAO)		
Group V	Esters and other bases not included in groups I to IV		

Table A

Mineral base oils include all types of base oils obtained by atmospheric and vacuum distillation of crude oil, followed by refining operations such as solvent extraction,
5 deasphalting, solvent dewaxing, hydrotreatment, hydrocracking, hydroisomerization and hydrofinishing.

The synthetic base oils may be esters of carboxylic acids and alcohols, polyalphaolefins or in fact polyalkylene glycols (PAG) obtained by polymerization or copolymerization of
10 alkylene oxides comprising 2 to 8 carbon atoms, in particular 2 to 4 carbon atoms. The polyalphaolefins used as base oils are, for example, obtained from monomers comprising 4 to 32 carbon atoms, for example from decene, octene or dodecene, and for which the viscosity at 100°C is comprised between 1.5 and 15 mm².s⁻¹ in accordance with the standard ASTM D445. Their molecular weight average is generally comprised between 250 and 3000
15 in accordance with the standard ASTM D5296.

Blends of synthetic and mineral oils, which may have been biosourced, may also be used.

There is generally no limitation as to the use of different base oils in the lubricating composition, except that it must have properties, in particular those of viscosity, viscosity index, sulfur content or oxidation resistance, which are adapted to a use for gas-powered
20 engines, in particular vehicle engines.

Preferably, a lubricating composition under consideration according to the invention comprises at least one base oil selected from oils from group II, III and IV of the API classification, and their blends.

In particular, such a lubricating composition may comprise at least one base oil from group III, in particular a blend of at least two base oils from group III.

The base oils which are suitable for the invention may have a kinematic viscosity, measured at 40°C in accordance with the standard ASTM D445 (KV40), of 10 to 100 mm²/s, in particular of 12 to 50 mm²/s, more particularly of 15 to 40 mm²/s.

Suitable base oils for the invention may have a kinematic viscosity, measured at 100°C in accordance with the standard ASTM D445 (KV100), of 1 to 15 mm²/s, in particular of 2 to 10 mm²/s, more particularly of 4 to 8 mm²/s.

The base oil or base oils may be present in a lubricating composition in accordance with the invention in a content of at least 50% by weight, with respect to its total mass, in particular of at least 60% by weight, more particularly of 60 to 99% by weight and preferably of 70% to 90% by weight.

Preferably, the group III oil or oils represent(s) at least 50% by weight, in particular at least 60% by weight, more particularly between 70 and 100% by weight, for example between 80 and 100% by weight, of the total mass of the base oils of the composition.

ADDITIVES

A lubricating composition in accordance with the invention may comprise any type of additive which is adapted to the envisaged use of the lubricant, as detailed in the text below, for example for a use of the lubricant for a gas engine, for example in a vehicle.

These additives may be introduced in isolation and/or in the form of a mixture, or “additive package”, in the same manner as those which are already on sale for commercial lubricant formulations for vehicle engines, with a performance level as defined by the ACEA (European Automobile Manufacturers Association) and/or the API (American Petroleum Institute), which are well known to the person skilled in the art.

These additives, which are distinct from said spiro compound or spiro compounds, may in particular be selected from other detergent additives, which are distinct from said spiro

compound or spiro compounds, in particular metallic detergent additives, friction modifiers, anti-wear additives, extreme pressure additives, antioxidants, viscosity index improvers (VI), pour point depressant additives (PPD), dispersing agents, anti-foaming agents, thickening agents, corrosion inhibitors, and their mixtures.

- 5 Advantageously, a lubricating composition in accordance with the invention comprises one or more additives selected from other detergent additives, which are distinct from said spiro compound or spiro compounds, in particular selected from metallic detergent additives, viscosity index improvers, pour point depressant additives, anti-wear additives, antioxidants and their mixtures.

10

Other detergents

The lubricating composition under consideration according to the invention may comprise one or more other detergent additives, which are distinct from the spiro compounds in accordance with the invention, in particular one or more metallic detergent additives.

- 15 As discussed above, metallic detergents are known to the person skilled in the art for providing high levels of detergency. However, these metallic compounds suffer from the disadvantage of being generators of sulfated ash. Calcium-based detergent additives have also been identified as one of the origins of the phenomenon of pre-ignition, in particular LSPI.

- 20 They are generally anionic compounds comprising a long lipophilic hydrocarbon chain and a hydrophilic head, the associated cation possibly being a metallic cation of an alkali or alkaline earth metal.

- They are generally selected from alkali metal or alkaline earth metal salts of carboxylic acids, in particular sulfonates, salicylates, naphthenates, phenates, carboxylates and mixtures thereof. The alkali and alkaline earth metals are preferably calcium, magnesium, sodium or barium.
- 25

- These metallic salts generally comprise the metal in stoichiometric quantities or in fact in excess, i.e., in a quantity which is above the stoichiometric quantity. They are therefore overbased detergent additives; the excess metal providing the overbased character of the detergent additive is thus generally in the form of a metallic salt that is insoluble in the base oil, for example a carbonate, a hydroxide, an oxalate, an acetate, a glutamate, preferably a carbonate.
- 30

In accordance with a particular embodiment, a lubricating composition in accordance with the invention comprises at least one metallic detergent additive that is distinct from the spiro compounds in accordance with the invention, in particular selected from the salts of alkali
5 metals or alkaline earth metals, which may or may not be overbased, in particular from calcium salts, magnesium salts and their mixtures.

Thus, in accordance with a particular embodiment, a lubricating composition used in accordance with the invention for the lubrication of an engine, in particular a gas-powered engine, especially in a vehicle, comprises at least:

- 10 - one or more base oils;
- at least one spiro compound in accordance with the invention, in particular at least one spiroboronate compound in accordance with the invention; and
- at least one metallic detergent additive that is distinct from said spiro compound, in particular as defined above, especially selected from calcium salts and magnesium salts and
15 their mixtures.

In particular, a lubricating composition used in accordance with the invention may comprise at least one detergent additive based on calcium, such as a sulfonate, a salicylate, a naphthenate, a phenate, a calcium carboxylate or a mixture thereof, in particular a detergent additive based on overbased calcium, for example with calcium carbonate.

20

Advantageously, as indicated above, the use of one or more spiro compounds in accordance with the invention means that the content of metallic detergents as defined above in the lubricating composition, in particular calcium-based detergents, which are undesirable in respect of their impact on pre-ignition, in particular LSPI, can be reduced, while preserving
25 good detergent properties.

In accordance with a particular embodiment, the lubricating composition in accordance with the invention may comprise less than 15% by weight, in particular less than 10% by weight and more particularly 0.1 to 10% by weight, in particular 0.5% to 5% by weight, of metallic detergent additive(s) which are distinct from the spiro compounds in accordance with the
30 invention, with respect to the total weight of said composition.

In particular, the or said metallic detergent additives may be present in the lubricating composition in a manner such as to provide a metallic element(s) content, in particular of

calcium, of less than or equal to 3000 ppm, in particular from 100 ppm to 2000 ppm, preferably from 250 ppm to 1500 ppm.

The reduction in the metallic detergents content, such as the calcium and magnesium salts, can advantageously enable “LOW SAPS” specifications for lubricating compositions to be met.

Advantageously, a lubricating composition used in accordance with the invention therefore has a sulfated ash content, determined in accordance with the standard ASTM D-874, of less than or equal to 2% by weight, in particular less than or equal to 1.5% by weight and more particularly less than or equal to 1% by weight.

In accordance with a particular embodiment, a lubricating composition used in accordance with the invention may comprise:

- from 60 to 99.8% by weight, preferably from 70 to 90% by weight, of one or more base oils;

- from 0.1 to 20% by weight, in particular from 0.2 to 15% by weight and more particularly from 0.5 to 10% by weight, of at least one spiro compound in accordance with the invention, in particular as defined above and more particularly of at least one spiroboronate compound in accordance with the invention; and

- from 0.1 to 10% by weight, in particular from 0.5 to 5% by weight, of one or more metallic detergent additives, distinct from said spiro compound in accordance with the invention, in particular as defined above, especially selected from calcium and magnesium salts and their mixtures;

the contents being expressed with respect to the total weight of said lubricating composition.

Other additives

A lubricating composition in accordance with the invention may also comprise at least one or more other additives, which are distinct from said spiro compound or spiro compounds, selected from friction modifiers, anti-wear additives, extreme pressure additives, antioxidants, viscosity index improvers, pour point depressant additives, dispersing agents, anti-foaming agents, thickening agents, corrosion inhibitors, and their mixtures.

Thus, a lubricating composition in accordance with the invention may also comprise at least one viscosity index improver (VI).

Viscosity index improvers (VI), in particular viscosity index-improving polymers, can guarantee good cold performances and a minimum viscosity at high temperatures. Examples of viscosity index-improving polymers that may be cited are polymeric styrene, butadiene and isoprene esters, homopolymers or copolymers which may be hydrogenated or non-hydrogenated, homopolymers or copolymers of olefins such as ethylene or propylene, polyacrylates and polymethacrylates (PMA).

Advantageously, a lubricating composition in accordance with the invention comprises at least one viscosity index improver selected from polymethacrylates (PMA) and linear, graft, comb or star, preferably star, hydrogenated polyisoprene-styrene (PISH).

In particular, the viscosity index-improving additive(s) may be present in a lubricating composition used in accordance with the invention in a content of 1 to 15% by weight, in particular of 2 to 10% by weight, with respect to the total weight of the lubricating composition.

In accordance with one embodiment, a lubricating composition in accordance with the invention is free from a viscosity index-improving additive.

A lubricating composition under consideration according to the invention may comprise at least one friction modifier.

Friction modifiers may be selected from compounds providing metallic elements and ash-free compounds, preferably from ash-free compounds.

Compounds which provide metallic elements that may be cited are complexes of transition metals such as Mo, Sb, Sn, Fe, Cu, Zn the ligands of which may be hydrocarbon compounds comprising oxygen, nitrogen, sulfur or phosphorus atoms.

Advantageously, the friction modifiers are selected from ash-free compounds, generally of organic origin and possibly more particularly being selected from monoesters of fatty acids and polyols, alkoxylated amines, alkoxylated fatty amines, fatty epoxides, fatty borate epoxides, fatty amines or fatty acid glycerol esters. In accordance with the invention, the fatty compounds comprise at least one hydrocarbon group comprising from 10 to 24 carbon atoms.

In accordance with an advantageous variation, a lubricating composition comprises at least one friction modifier, in particular based on molybdenum.

In particular, the compounds based on molybdenum may be selected from molybdenum dithiocarbamates (Mo-DTC), molybdenum dithiophosphates (Mo-DTP), and their mixtures.

5 Advantageously, a lubricating composition under consideration according to the invention may comprise from 0.01 to 5% by weight, preferably from 0.01 to 5% by weight, more particularly from 0.1 to 2% by weight or yet more particularly from 0.1 to 1.5% by weight, with respect to the total weight of the lubricating composition, of friction modifiers.

10 A lubricating composition in accordance with the invention may comprise at least one anti-wear and/or extreme pressure additive.

Anti-wear additives and extreme pressure additives protect friction surfaces by forming a protective film adsorbed onto these surfaces.

A wide variety of anti-wear additives exists. Preferably, for the lubricating composition in
15 accordance with the invention, anti-wear additives are selected from phospho-sulfur additives such as metallic alkylthiophosphates, in particular zinc alkylthiophosphates, and more specifically zinc dialkyldithiophosphates or ZnDTP. Preferred compounds have formula $Zn((SP(S)(OR^3)(OR^4))_2$, in which R^3 and R^4 , which may be identical or different, independently represent an alkyl group, preferably an alkyl group comprising from 1 to 18
20 carbon atoms.

Amine phosphates are also anti-wear additives which may be used in the lubricating composition in accordance with the invention. However, the phosphorus provided by these additives could act as a poison on the catalytic systems of automobiles, because these additives generate ash. These effects may be minimized by partially substituting the amine
25 phosphates by additives which do not provide phosphorus, such as polysulfides, for example, in particular sulfur-containing olefins. Advantageously, the extreme pressure and/or anti-wear additive or additives may be present in a lubricating composition in accordance with the invention in a content from 0.01 to 6% by weight, preferably from 0.05 to 4% by weight, more preferably from 0.1 to 2% by weight with respect to the total weight of lubricating
30 composition.

A lubricating composition under consideration according to the invention may comprise at least one antioxidant additive. Antioxidant additives are essentially dedicated to retarding the degradation of the lubricating composition when in service. This degradation may in particular result in the formation of deposits, in the presence of sludge or in an increase in the viscosity of the lubricating composition. In particular, they act as radical inhibitors or hydroperoxide destroyers.

Antioxidant additives in current use that may be cited include antioxidant additives of the phenolic type, antioxidant additives of the amine type, phosphosulfur-containing antioxidant additives. Certain of these antioxidant additives, for example phosphosulfur-containing antioxidant additives, may be ash generators. Phenolic antioxidant additives may be free from ash, or in fact be in the form of neutral or basic metallic salts. The antioxidant additives may in particular be selected from sterically hindered phenols, sterically hindered phenol esters and sterically hindered phenols comprising a thioether bridge, diphenylamines, diphenylamines substituted by at least one C₁-C₁₂ alkyl group, N,N'-dialkyl-aryl diamines, and their mixtures.

Preferably, the sterically hindered phenols are selected from compounds comprising a phenol group wherein at least one carbon is vicinal to the carbon carrying the alcohol function is substituted by at least one C₁-C₁₀ alkyl group, preferably a C₁-C₆ alkyl group, preferably a C₄ alkyl group, preferably by the tert-butyl group.

Amine compounds are another class of antioxidant additives that may be used, optionally in combination with phenolic antioxidant additives. Examples of amine compounds are aromatic amines, for example aromatic amines with formula NR⁵R⁶R⁷ in which R⁵ represents an aliphatic group or an aromatic group, optionally substituted, R⁶ represents an aromatic group, optionally substituted, R⁷ represents a hydrogen atom, an alkyl group, an aryl group or a group with formula R⁸S(O)_zR⁹ in which R⁸ represents an alkylene group or an alkenylene group, R⁹ represents an alkyl group, an alkenyl group or an aryl group, and z represents 0, 1 or 2.

Sulfurized alkyl phenols or their salts of alkali metals and alkaline earth metals may also be used as antioxidant additives.

A lubricating composition under consideration according to the invention may contain any type of antioxidant additive known to the person skilled in the art. Advantageously, the lubricating composition comprises at least one antioxidant additive that is free from ash.

Advantageously again, a lubricating composition under consideration according to the invention may comprise 0.1 to 2% by weight, with respect to the total weight of the composition, of at least one antioxidant additive.

- 5 A lubricating composition under consideration according to the invention may comprise at least one pour point depressant additive (known as “PPD” agents). By slowing down the formation of paraffin crystals, pour point depressant additives generally improve the cold performance of the lubricating composition.

Examples of pour point depressant agents that may be cited are alkyl polymethacrylates, polyacrylates, polyarylamides, polyalkylphenols, polyalkylnaphthalenes and alkylated polystyrenes.

A lubricating composition under consideration according to the invention may also comprise at least one dispersing agent. Dispersing agents ensure that the suspension is maintained and ensure the evacuation of insoluble solid contaminants constituted by the secondary oxidation products that are formed when the lubricating composition is in service. They may be selected from Mannich bases, succinimides and their derivatives.

In particular, a lubricating composition under consideration according to the invention may comprise from 0.2 to 10% by weight of dispersing agent(s), with respect to the total weight of the composition.

A lubricating composition under consideration according to the invention may also comprise at least one anti-foaming additive. The anti-foaming additives may be selected from polar polymers such as polymethylsiloxanes or polyacrylates.

25 In particular, a lubricating composition under consideration according to the invention may comprise from 0.01 to 3% by weight of anti-foaming additive(s), with respect to the total weight of the lubricating composition.

As mentioned above, the ensemble of the additives detailed above may be introduced in the form of a mixture or “package” of additives.

In accordance with this embodiment, the additive package may represent from 1% to 30% by weight with respect to the total weight of the composition, in particular from 1 to 20% by

weight, especially from 3% to 15% by weight and more particularly from 5 to 15% by weight.

In accordance with a particular embodiment, a lubricating composition used in accordance with the invention may comprise, or even be constituted by:

- a base oil or a mixture of base oils;
- one or more spiro compounds in accordance with the invention, in particular as defined above, and more particularly one or more spiroboronate compounds in accordance with the invention; and

- optionally, one or more additives, which are distinct from said spiro compound or spiro compounds, selected from the other detergent additives, in particular metallic detergent additives, friction modifying agents, anti-wear additives, extreme pressure additives, antioxidants, viscosity index improvers (VI), pour point depressant additives (PPD), dispersing agents, anti-foaming agents, thickening agents, corrosion inhibitors, and their mixtures.

In accordance with one embodiment of the invention, a lubricating composition used in accordance with the invention comprises, or even is constituted by:

- from 60 to 98.9% by weight, in particular from 70 to 90% by weight, of one or more base oils;

- from 0.1 to 20% by weight, preferably from 0.5 to 10% by weight, of one or more spiro compounds in accordance with the invention, in particular as defined above and more particularly of one or more spiroboronate compounds in accordance with the invention; and

- from 1% to 30% by weight, preferably from 3% to 20% by weight, of one or more additive(s) selected from the other detergent additives, which are distinct from said spiro compound or spiro compounds, in particular selected from metallic detergent additives; anti-wear agents; antioxidants; dispersing agents; viscosity index-improving agents and their mixtures;

the contents being expressed with respect to the total weight of said lubricating composition.

In particular, a lubricating composition used in accordance with the invention may comprise, or even be constituted by:

- from 60 to 99.8% by weight, in particular from 70 to 90% by weight, of one or more base oils;
 - from 0.1 to 20% by weight, preferably from 0.5 to 10% by weight, of one or more spiro compounds in accordance with the invention as defined above, in particular of the spiroboronate type;
 - from 0.1% to 10% by weight, preferably from 0.5% to 5% by weight, of one or more metallic detergent additives, which are distinct from said spiro compound or spiro compounds, in particular as defined above, especially selected from calcium and magnesium salts and their mixtures; and
 - optionally, from 1% to 30% by weight, preferably from 3% to 20% by weight, of one or more other additives selected from anti-wear agents, antioxidants, viscosity index-improving agents and their mixtures,
- the contents being expressed with respect to the total weight of said lubricating composition.
- In accordance with a particular embodiment, a lubricating composition in accordance with the invention may have a kinematic viscosity, measured at 40°C in accordance with the standard ASTM D445, comprised between 20 mm²/s and 50 mm²/s, preferably between 25 mm²/s and 40 mm²/s.
- Advantageously again, a lubricating composition in accordance with the invention has a kinematic viscosity, measured at 100°C in accordance with the standard ASTM D445, comprised between 2 mm²/s and 20 mm²/s, preferably between 4 mm²/s and 15 mm²/s.

APPLICATIONS

As indicated above, a lubricating composition in accordance with the invention is intended for the lubrication of an engine, for mobile or stationary applications, which may be subjected to abnormal combustion phenomena, in particular to the phenomenon of pre-ignition, in particular LSPI and/or knocking.

The LSPI problem in particular arises for reduced size engines, termed “downsized” engines. A composition in accordance with the invention may in particular be used for the lubrication of engines powered by gas, including biogases.

The gas may be selected from hydrogen (H₂), methane (CH₄), or compressed or liquefied natural gas.

The gas-powered engines may be gas engines, for example engines powered by natural gas (LNG or CNG) and hydrogen engines, but also dual fuel gas/gasoline, dual fuel gas/diesel fuel engines.

- 5 In accordance with a particular embodiment, a lubricating composition in accordance with the invention may be used for an engine of a vehicle, in particular a gas engine of a vehicle. It may be used for any type of vehicle, for example for a heavy goods vehicle, for example a truck, an off-road vehicle, or a light vehicle.

The term “engine” also encompasses 4-stroke engines, and more particularly 4-stroke marine engines, preferably gas-powered 4-stroke marine engines.

- 10 In accordance with a variation of application, a lubricating composition in accordance with the invention may be used for the lubrication of an engine, in particular a gas engine, and of the transmission in a vehicle engine. These uses comprise bringing at least one element of the engine and the transmission, in particular the gear box or the axle, into contact with a
15 lubricating composition in accordance with the invention.

A lubricating composition in accordance with the invention may also be used for the lubrication of stationary engines, in particular stationary gas engines.

- Thus, the invention concerns the use of a lubricating composition comprising one or more
20 base oils and at least one spiro compound with formula (I), as defined above, in order to prevent and/or reduce abnormal combustion in a gas-powered engine, which may be mobile or stationary, in particular in a compressed or liquid natural gas engine, hydrogen engine, dual fuel gas/gasoline or dual fuel gas/diesel fuel engine.

- More precisely, it concerns such a use in order to prevent and/or reduce pre-ignition, in
25 particular low speed pre-ignition (LSPI), and/or knocking.

The ensemble of features and particular embodiments relating to the spiro compound with formula (I) and to the lubricating composition comprising it is also applicable to the uses, processes and methods envisaged according to the invention.

30

The invention will now be described with the aid of the following examples, given by way of non-limiting illustration of the invention.

Example

Thermal stability measurement

The performances of the compositions in terms of thermal stability were evaluated by MCT (“Micro Coking Test”), in accordance with the standard GFC Lu-27-T-07.

The MCT test evaluates the tendency of a composition to form deposits (or varnish) on a hot surface (coking). It reveals the thermal stability of a composition in a thin layer, subjected to temperature conditions similar to those encountered in the hottest parts of an engine (230 to 280°C). The deposits and varnish are measured by a video rater. The result is expressed in the form of a rating out of 10, termed a grade, in accordance with the CEC M-02-A-78 method. The higher the value for the MCT, the better is the thermal stability of the lubricating composition.

The test conditions were as follows:

- 600 μ L of oil;
- duration: 90 minutes;
- plate inclined by 1.5%;
- temperature gradient from 230 to 280°C;
- video rating of varnish on the plate: rating from 0 to 10, best result 10.

Furthermore, the temperature beyond which the varnish is deposited was also determined. The higher this temperature, the better is the thermal stability of the lubricating composition.

Measurement of stability to oxidation

The stability to oxidation was evaluated by pressure differential scanning calorimetry, which determines the oxidation induction time, termed OIT, for the lubricating compositions. It is a standard procedure in the lubricating oil industry based on the standard CEC L-85 T-99.

According to this protocol, the lubricating composition to be tested is heated to a high temperature (in the present case, isothermally at 50°C for 5 minutes, then raised to 210°C at 40°C/min, oxidation occurring at 210°C), and the moment at which the lubricant starts to decompose is measured. The longer the duration of the test, expressed in minutes, the better is the stability of the lubricant to oxidation.

Example 1

Preparation of lubricating compositions

Three lubricating compositions were formulated:

- a reference lubricant, not in accordance with the invention, denoted CC1, using a conventional quantity of calcium-based detergent additives provided by an additive package.

5 The calcium content in lubricant CC1 was 1340 ppm;

- a lubricant which was not in accordance with the invention, denoted CC2, using the same compounds as those of reference formulation 1, but in which the content of said additive package was reduced by half; and

- a lubricant in accordance with the invention, denoted I1, corresponding to the formulation

10 CC2 supplemented by a spiroboronate compound in accordance with the invention in an amount of 1% by weight with respect to the lubricant.

The components and quantities (expressed as a percentage by weight) for the three lubricants are indicated in the table below. The lubricants were formulated simply by mixing the various components at 60°C.

15 [Table 2]

	CC1	CC2	I1
Base oil 1 ⁽¹⁾ [%]	62.7	68.95	67.95
Base oil 2 ⁽²⁾ [%]	20	20	20
Additive package ⁽³⁾ [%]	12.5	6.25	6.25
PISH polymer [%]	4.8	4.8	4.8
Spiroboronate compound ⁽⁴⁾ [%]	-	-	1

⁽¹⁾ Group III base oil (KV100 = 6.3-6.7 mm²/s, KV40 = 37 mm²/s, VI more than 125), commercially available from SK Lubricants, for example, under the commercial name “Yubase[®] 6”.

20 ⁽²⁾ Group III base oil (KV100 = 4.2 mm²/s, KV40 = 19.1 mm²/s, VI of 126), commercially available from SK Lubricants, for example, under the commercial name “Yubase[®] 4”.

⁽³⁾ Mixture of various additives that are usual in the lubricants field and commercially available. It comprised zinc dithiophosphate type anti-wear agents, calcium-based detergents and PIBSI type dispersing agents.

25 ⁽⁴⁾ Spiro compound with formula (I), in which M is a boron atom, R each representing a decyl group and n₁ and n₂ equaling 1.

Example 2

Evaluation of lubricants

The properties in terms of the thermal stability of the various lubricants prepared in Example 1 were evaluated in accordance with the MCT protocol described above.

The rating results are presented in the table below. The values for the temperature beyond which the formation of deposits occurs (T_{deposit}) are also summarized in the table below.

[Table 3]

	CC1	CC2	I1
MCT at 90 min ^(*)	8	5.9	9.4
T_{deposit} (°C)	249	234	271

^(*) The values are expressed with a standard deviation of $\pm 1\%$.

- 10 The composition I1 in accordance with the invention, comprising a spiroboronate compound in accordance with the invention, had an excellent rating, which was higher than that obtained for the comparative compositions CC1 and CC2.

15 These results demonstrate that adding a spiroboronate compound in accordance with the invention, even in a small proportion (1% by weight), can significantly reduce (a reduction by half) the metallic detergent additives content, in particular of calcium-based detergent additives, while preserving excellent thermal stability properties in the lubricant, and therefore excellent detergent properties, and even with better detergent properties compared with a lubricant using only metallic detergent additives.

- 20 These results are confirmed by the deposit formation temperatures for the compositions in accordance with the invention, which are far better than those obtained with the reference lubricants.

25 A composition in accordance with the invention, using a spiroboronate compound in accordance with the invention, can therefore be used to at least partially dispense with metallic detergents, in particular based on calcium, and moreover, reducing the risk of premature ignition, and therefore reducing the incidence of abnormal combustion phenomena, in particular the phenomena of LSPI and knocking.

Example 3

Evaluation of the oxidation stability properties of the lubricants

The effect of adding a spiroboronate compound on the oxidation stability properties was evaluated for two lubricants, denoted CC3 and CC4, details of the composition of which are given in Table 4 below.

Two lubricating compositions in accordance with the invention, denoted I3 and I4, were prepared on the basis of the comparative lubricants CC3 and CC4, in which 2% by weight of base oil was replaced by 2% by weight of spiroboronate compound in accordance with the invention.

The lubricants were formulated simply by mixing the various components at 60°C.

[Table 4]

	CC3	I3	CC4	I4
Base oil 1 ⁽¹⁾ [%]	59.6	57.6	-	
Base oil 2 ⁽²⁾ [%]	20	20	-	
Base oil 3 ⁽³⁾ [%]			79.2	77.2
Additive package ⁽⁴⁾ [%]	13.2	13.2	13.2	13.2
OCP polymer [%]	7.2	7.2	7.6	7.6
Spiroboronate compound ⁽⁵⁾ [%]	0	2	-	2

⁽¹⁾ Group III base oil (KV100 = 6.3-6.7 mm²/s, KV40 = 37 mm²/s, VI more than 125), commercially available from SK Lubricants, for example, under the commercial name “Yubase[®] 6”;

⁽²⁾ Group III base oil (KV100 = 4.2 mm²/s, KV40 = 19.1 mm²/s, VI of 126), commercially available from SK Lubricants, for example, under the commercial name “Yubase[®] 4”;

⁽³⁾ Group I base oil (KV100 = 5.0-5.5 mm²/s, KV40 = 30.0-31.54 mm²/s, VI of 90-92), commercially available from DANA, for example, under the commercial name “SN 150”;

⁽⁴⁾ Mixture of various additives that are usual in the lubricants field and commercially available. It comprised an overbased calcium-based detergent additive and did not contain a zinc dithiophosphate type anti-wear additive;

⁽⁵⁾ Spiro compound with formula (I), in which M is a boron atom, R each representing a decyl group and n₁ and n₂ equaling 1.

The oxidation stability properties were evaluated using the protocol based on the standard CEC L-85 T-99, described above.

The oxidation induction time (OIT) results are summarized in the table below.

[Table 5]

Lubricant	CC3	I3	CC4	I4
Oxidation induction time (in min)	73	213	118	>250

5

These results demonstrate that adding a spiroboronate compound in accordance with the invention can significantly improve the oxidation stability of the lubricant.

Engine cleanliness test

- 10 Finally, the lubricants CC3 and I3 were evaluated using the TDI3 engine test in accordance with the CEC L-117-20 method which in particular measures the cleanliness of the pistons. The results are summarized in Table 6 below.

[Table 6]

Lubricant	CC3	I3
TDI CEC L-117-20	52	58

- 15 It can be seen that the lubricating composition in accordance with the invention can also improve the cleanliness of the engine.

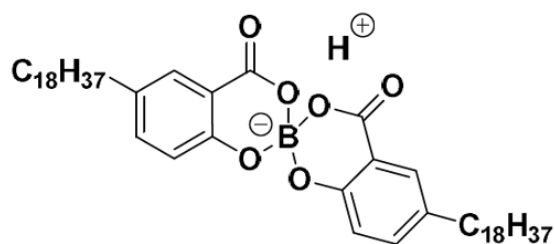
Example 4

Evaluation of the stability of the spiroboronate compound in the presence of water

- 20 The stability of a spiroboronate compound in accordance with the invention with respect to water was evaluated as described below.

The spiroboronate compound that was tested was a spiro compound with formula (I) in which M is a boron atom, R each representing an octadecyl chain (C18) and n_1 and n_2 equaling 1, in other words has the following formula:

25



The spiroboronate compound was prepared from a previously synthesized salicylic acid derivative (2-hydroxy-5-octadecylbenzoic acid) and boric acid.

- 5 The 2-hydroxy-5-octadecylbenzoic acid (8.9 g, 22.8 mmol, 2 eq) and boric acid (0.70 g, 11.4 mmol, 1.0 eq) in toluene (65 mL) were introduced into a 250 mL three-necked flask provided with a Dean-Stark apparatus to eliminate water and a mechanical stirrer, under nitrogen. The mixture was heated under reflux until the reaction was complete, and the spiroboronate compound was recovered.

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The spiroboronate compound was dispersed in an amount of 5% by weight in water. The emulsion underwent vigorous stirring with a paddle, followed by strong stirring with the aid of an Ultra-Turrax[®] stirrer.

The emulsions obtained after each stir were stable. They were analyzed by laser granulometry using a Malvern Mastersizer 2000 granulometer.

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Figure 1 shows the particle size distribution for the emulsion obtained after paddle stirring (Figure 1a) and after Ultra-Turrax[®] stirring (Figure 1b).

The emulsion of spiroboronate in water was then passed to a vacuum rotary evaporator in order to evaporate off the water. The residue when evaporation of the water was complete was recovered and analyzed by ¹H NMR.

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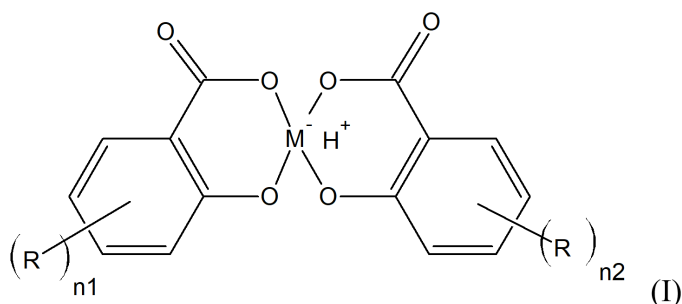
The NMR spectrum of the residue was compared with that of pure spiroboronate compound. Figure 2 shows the NMR spectra for pure spiroboronate (Figure 2a) and for the residue obtained as described above (Figure 2b).

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The comparison of the two spectra shows that the residue obtained corresponded to the starting spiroboronate. Thus, the spiroboronate compound had not undergone hydrolysis in the presence of water.

Claims

1. Use of a lubricating composition comprising one or more base oils and at least one spiro compound with the following formula (I)



in which:

M is an atom selected from boron and aluminum;

n1 and n2, independently of one another, equal 0, 1 or 2, and

10 R, independently of one another, represents a hydrocarbon group comprising from 1 to 50 carbon atoms, especially from 5 to 20 carbon atoms and preferably from 5 to 15 carbon atoms;

in order to prevent and/or reduce the abnormal consumption of fuel in an engine lubricated by means of said lubricating composition.

15 2. The use as claimed in the preceding claim, said spiro compound having formula (I) in which the R substituents, independently of one another, represent a linear or branched aliphatic chain, in particular a C₁ to C₅₀; in particular C₃ to C₃₀, especially C₅ to C₂₅, especially C₅ to C₂₀ and more particularly C₈ to C₁₅, more preferably C₁₀ alkyl chain, preferably linear.

20 3. The use as claimed in claim 1 or claim 2, said spiro compound having formula (I) in which n1 and n2 equal 1, the R substituents being identical.

4. The use as claimed in any one of the preceding claims, said spiro compound having formula (I) in which M is a boron atom.

5. The use as claimed in any one of the preceding claims, said spiro compound or spiro compounds being used in a content comprised between 0.1 and 20% by weight with respect
25 to the total weight of said lubricating composition, in particular comprised between 0.2 and 15% by weight, especially between 0.5 and 10% by weight and more particularly between 0.5 and 5.0% by weight.

6. The use as claimed in any one of the preceding claims, said lubricating composition further comprising at least one metallic detergent additive, which is distinct from the spiro compound with formula (I), selected from the salts of alkali metals or alkaline earth metals, which may or may not be overbased, in particular from calcium salts, magnesium salts and their mixtures.

7. The use as claimed in the preceding claim, said metallic detergent additive or metallic detergent additives being present in a content of less than or equal to 15% by weight, in particular less than or equal to 10% by weight and more particularly from 0.5% to 5% by weight, with respect to the total weight of said lubricating composition.

8. The use as claimed in any one of the preceding claims, the base oil or base oils being present in a content of at least 50% by weight, with respect to the total weight of said lubricating composition, in particular of at least 60% by weight, more particularly from 60 to 99% by weight and preferably from 70 to 90% by weight.

9. The use as claimed in any one of the preceding claims, said lubricating composition comprising one or more other additives, which are distinct from said spiro compound or spiro compounds, selected from friction modifiers, anti-wear additives, extreme pressure additives, antioxidants, viscosity index improvers, pour point depressant additives, dispersing agents, anti-foaming agents, thickening agents, corrosion inhibitors, and their mixtures.

10. The use as claimed in any one of the preceding claims, in order to prevent and/or reduce abnormal combustion in a gas-powered engine, which may be mobile or stationary, in particular in a compressed or liquefied natural gas engine, hydrogen engine, dual fuel gas/gasoline engine or dual fuel gas/diesel fuel engine.

11. The use as claimed in any one of the preceding claims, in order to prevent and/or reduce pre-ignition, in particular low speed pre-ignition (LSPI), and/or knocking.