US 20160010024A1

(19) **United States**

(12) **Patent Application Publication**

BOUFFET et al.

(10) **Pub. No.: US 2016/0010024 A1**

(43) **Pub. Date: Jan. 14, 2016**

(54) **LUBRICATING COMPOSITIONS FOR TRANSMISSIONS**

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(21) Appl. No.: **14/377,668**

(22) PCT Filed: **Feb. 14, 2013**

(86) PCT No.: **PCT/EP2013/053012**

§ 371 (c)(1),
(2) Date: **Aug. 8, 2014**

(30) **Foreign Application Priority Data**

Feb. 15, 2012 (FR) 1251393

Publication Classification

(51) **Int. Cl.**
C10M 141/10 (2006.01)

(52) **U.S. Cl.**
CPC ***C10M 141/10*** (2013.01)

(57) **ABSTRACT**

A lubricating composition includes at least one base oil, at least one compound including a dithiocarbamate group, at least one compound including a phosphite group and at least one compound including a dithiophosphate group. The lubricating composition simultaneously has good anti-wear and extreme-pressure properties, a low coefficient of friction and good anti-seizing properties. The lubricating composition can be used for lubricating transmissions such as gearboxes, axles, preferably the manual gearboxes of motor vehicles.

LUBRICATING COMPOSITIONS FOR TRANSMISSIONS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is a National Phase Entry of International Application Serial No. PCT/EP2013/053012, filed on Feb. 14, 2013, which claims priority to French Patent Application Serial No. 1251393, filed on Feb. 15, 2012, both of which are incorporated by reference herein.

TECHNICAL FIELD

[0002] The present invention relates to lubricating compositions for transmissions, in particular for manual gearboxes, axles or double clutch transmissions. The lubricating compositions according to the invention simultaneously exhibit, in particular, good extreme-pressure and anti-wear properties and a low coefficient of friction.

BACKGROUND

[0003] It is very difficult to formulate lubricating compositions simultaneously having good extreme-pressure properties, good anti-wear properties and good friction properties, as well as good anti-seizing properties. Thus most lubricating compositions have only two of these properties at once. Moreover, despite the existence of a large number of anti-wear additives, extreme-pressure additives or friction-modifier additives, not all have the same effectiveness, some being able to improve one property and at the same time make a second property worse. Similarly, the chemistry of these additives is complex and the additives can react with each other to form new chemical species the influence of which on the extreme-pressure, wear, friction and seizing properties is ultimately unknown. It is known that additives such as the diphosphites, which can be both friction modifiers and anti-wear components, react with the sulphur used as extreme-pressure agent to form, for example, thiophosphonic derivatives the properties of which are markedly different from those of the original molecules. Thus, a large number of extreme-pressure components react with the anti-wear additives or the friction modifiers in order to produce novel chemical entities. These reactions are not controlled, nor are the precise properties of the final product monitored over time. Interactions can occur between the different extreme-pressure/anti-wear/friction modifier additives and lead to antagonistic effects on the final properties of the compositions containing additives.

[0004] U.S. Patent Publication No. 2009/011964, U.S. Pat. No. 5,674,820 and U.S. Pat. No. 5,872,085 describe a lubricating composition comprising a compound comprising a dithiocarbamate group, a compound comprising a phosphite group and a compound comprising a dithiophosphate group. However, none of these documents specifically demonstrates that such a combination makes it possible to simultaneously obtain good extreme-pressure, anti-wear and friction properties. Furthermore, no indication is given in these documents as to the improvement of the anti-seizing properties of these lubricating compositions.

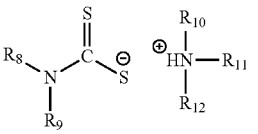
SUMMARY

[0005] The Applicant company has developed a novel lubricating composition comprising at least four essential additives in order to simultaneously obtain good extreme-pressure, anti-wear, friction and anti-seizing properties. This specific combination of additives is based on the presence of at least one compound comprising a metal dithiocarbamate group, at least one compound comprising an amine dithiocarbamate group, at least one compound comprising a phosphite group and at least one compound comprising a dithiophosphate group. The lubricating composition according to the invention, comprising at least one compound comprising a metal dithiocarbamate group, at least one compound comprising an amine dithiocarbamate group, at least one compound comprising a phosphite group and at least one compound comprising a dithiophosphate group, simultaneously have good wear, extreme-pressure, friction and anti-seizing properties. Moreover, this lubricating composition also has good properties in terms of oxidation and corrosion.

[0006] The invention relates to a lubricating composition comprising at least one base oil, at least one compound comprising a dithiocarbamate group, at least one compound comprising a phosphite group and at least one compound comprising a dithiophosphate group, the compound comprising a dithiocarbamate group being a mixture of:

[0007] at least one amine dithiocarbamate of general formula (I-c)

(I-c)



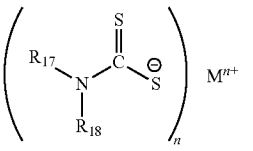
[0008] in which

[0009] R_8 and R_9 represent independently of each other hydrocarbon-containing groups, optionally substituted, comprising from 1 to 30 carbon atoms,

[0010] R_{10}, R_{11} and R_{12} represent independently of each other a hydrogen atom or a hydrocarbon-containing group from 1 to 30 carbon atoms, it being understood that at least one of the R_{10}, R_{11} and R_{12} groups is not a hydrogen atom, and

[0011] at least one metal dithiocarbamate of general formula (I-e),

(I-e)



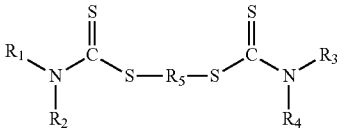
[0012] in which R_{17} and R_{18} represent independently of each other hydrocarbon-containing groups, optionally substituted, comprising from 1 to 30 carbon atoms, M represents a metal cation and n is the valency of this metal cation.

[0013] In an embodiment, the composition according to the invention can also comprise another compound comprising at least one dithiocarbamate group. Preferably, this other compound comprising a dithiocarbamate group is selected from

the group constituted by the bisdithiocarbamates, ammonium dithiocarbamates and dithiocarbamate esters, used alone or in a mixture.

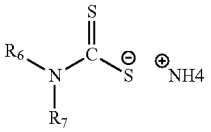
[0014] Preferably, the bisdithiocarbamate has formula (I-a), in which R_1, R_2, R_3 and R_4 represent independently of each other hydrocarbon-containing groups, optionally substituted, comprising from 1 to 30 carbon atoms, R_5 represents a hydrocarbon-containing group from 1 to 8 carbon atoms:

(I-a)



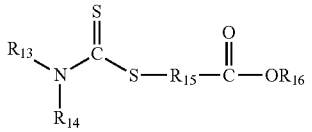
[0015] Preferably, the ammonium dithiocarbamate has formula (I-b), in which R_6 and R_7 represent independently of each other hydrocarbon-containing groups, optionally substituted, comprising from 1 to 30 carbon atoms:

(I-b)



[0016] Preferably, the dithiocarbamate ester has formula (I-d), in which R_{13} and R_{14} represent independently of each other hydrocarbon-containing groups, optionally substituted, comprising from 1 to 30 carbon atoms, R_{15} and R_{16} represent independently of each other a hydrocarbon-containing group from 1 to 18 carbon atoms:

(I-d)



[0017] Preferably, the lubricating composition comprises from 0.1 to 5% by mass of compounds comprising a dithiocarbamate group, relative to the total mass of lubricating composition, preferably from 0.2 to 4%, more preferentially from 0.3 to 2%, even more preferentially from 0.5 to 1%.

[0018] Preferably, the lubricating composition comprises from 0.1 to 3% by mass of the mixture of compounds corresponding to formulae (I-c) and (I-e), preferably from 0.1 to 2% by mass, advantageously from 0.5 to 2% by mass. Preferably, the compound comprising a phosphite group is selected from the phosphite monoesters, phosphite diesters or phosphite triesters, used alone or in a mixture.

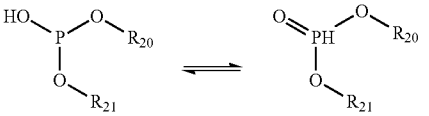
[0019] Preferably, the phosphite monoester has general formula (II-a) in its alcohol and/or ketone form, in which R_{19} represents a hydrocarbon-containing group, optionally substituted, of 1 to 30 carbon atoms:

(II-a)

alcohol form ketone form

[0020] Preferably, the phosphite diester has general formula (II-b) in its alcohol and/or ketone form, in which R_{20} and R_{21} represent independently of each other hydrocarbon-containing groups, optionally substituted, of 1 to 30 carbon atoms:

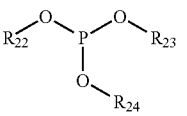
(II-b)



alcohol form ketone form

[0021] Preferably, the phosphite triester has general formula (II-c) in which R_{22}, R_{23} and R_{24} represent independently of each other hydrocarbon-containing groups, optionally substituted, comprising from 1 to 30 carbon atoms:

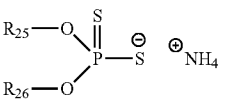
(II-c)



[0022] Preferably, the lubricating composition comprises from 0.1 to 5% by mass of compound comprising a phosphite group, relative to the total mass of lubricating composition, preferably from 0.2 to 4%, more preferentially from 0.3 to 2%, even more preferentially from 0.5 to 1%. Preferably, the compound comprising a dithiophosphate group is selected from the group constituted by the ammonium dithiophosphates, amine dithiophosphates, dithiophosphate esters and metal dithiophosphates, used alone or in a mixture.

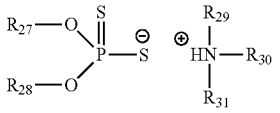
[0023] Preferably, the ammonium dithiophosphate has general formula (III-a), in which R_{25} and R_{26} represent independently of each other hydrocarbon-containing groups, optionally substituted, comprising from 1 to 30 carbon atoms:

(III-a)



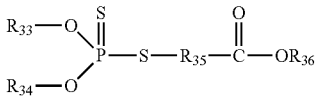
[0024] Preferably, the amine dithiophosphate has general formula (III-b), in which R_{27} and R_{28} represent independently of each other hydrocarbon-containing groups, optionally substituted, comprising from 1 to 30 carbon atoms, R_{29}, R_{30} and R_{31} represent independently of each other a hydrogen atom or a hydrocarbon-containing group from 1 to 30 carbon atoms, it being understood that at least one of the R_{29}, R_{30} and R_{31} groups is not a hydrogen atom:

(III-b)



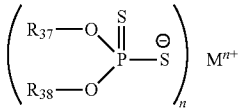
[0025] Preferably, the dithiophosphate ester has general formula (III-c), in which R_{33} and R_{34} represent independently of each other hydrocarbon-containing groups, optionally substituted, comprising from 1 to 30 carbon atoms, R_{35} and R_{36} represent independently of each other hydrocarbon-containing groups comprising from 1 to 18 carbon atoms:

(III-c)



[0026] Preferably, the metal dithiophosphate has general formula (III-d), in which R_{37} and R_{38} represent independently of each other hydrocarbon-containing groups, optionally substituted, comprising from 1 to 30 carbon atoms, M represents a metal cation and n is the valency of this metal cation:

(III-d)



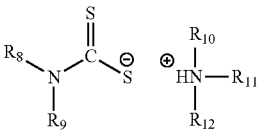
[0027] Preferably, the lubricating composition comprises from 0.1 to 5% by mass of compound comprising a dithiophosphate group, relative to the total mass of lubricating composition, preferably from 0.2 to 4%, more preferentially from 0.3 to 2%, even more preferentially from 0.5 to 1%. Preferably, the lubricating composition also comprises an antioxidant selected from the group formed by the aromatic amines or phenol derivatives. By phenol derivatives within the meaning of the present invention, is meant any compound comprising at least one phenol or phenoxy group. Preferably, the lubricating composition also comprises a dispersant derived from polyisobutene. Preferably, the lubricating composition also comprises a polymethacrylate-type polymer. Preferably, the lubricating composition has a kinematic viscosity at 100° C. according to the standard ASTM D445 comprised between 4 and 40 cSt, preferably between 4.1 and 32.5 cSt, preferably between 6 and 18.5 cSt.

[0028] The invention also relates to the use of a lubricating composition as defined above for lubricating transmissions such as gearboxes, axles, preferably the manual gearboxes of motor vehicles. Preferably, the lubricating composition is used in order to reduce the fuel consumption of vehicles, in particular motor vehicles.

[0029] The invention also relates to the use of at least one compound comprising a dithiocarbamate group, at least one compound comprising a phosphite group and at least one compound comprising a dithiophosphate group in a base oil for improving the wear, extreme-pressure, friction and anti-seizing properties of a lubricating composition, the compound comprising a dithiocarbamate group being a mixture of:

[0030] at least one amine dithiocarbamate of general formula (I-c):

(I-c)



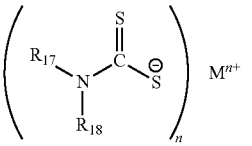
[0031] in which:

[0032] R_8 and R_9 represent independently of each other hydrocarbon-containing groups, optionally substituted, comprising from 1 to 30 carbon atoms,

[0033] R_{10}, R_{11} and R_{12} represent independently of each other a hydrogen atom or a hydrocarbon-containing group from 1 to 30 carbon atoms, it being understood that at least one of the R_{10}, R_{11} and R_{12} groups is not a hydrogen atom, and

[0034] at least one metal dithiocarbamate of general formula (I-e):

(I-e)

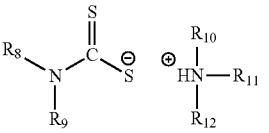


[0035] in which R_{17} and R_{18} represent independently of each other hydrocarbon-containing groups, optionally substituted, comprising from 1 to 30 carbon atoms, M represents a metal cation and n is the valency of this metal cation.

[0036] In an embodiment of the invention, the lubricating composition essentially consists of at least one base oil, at least one compound comprising a dithiocarbamate group, at least one compound comprising a phosphite group and at least one compound comprising a dithiophosphate group, the compound comprising a dithiocarbamate group being a mixture of:

[0037] at least one amine dithiocarbamate of general formula (I-c):

(I-c)



[0038] in which:

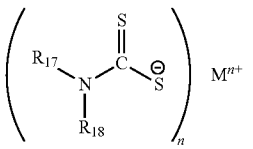
[0039] R_8 and R_9 represent independently of each other hydrocarbon-containing groups, optionally substituted, comprising from 1 to 30 carbon atoms,

[0040] R_{10}, R_{11} and R_{12} represent independently of each other a hydrogen atom or a hydrocarbon-containing

group from 1 to 30 carbon atoms, it being understood that at least one of the R_{10}, R_{11} and R_{12} groups is not a hydrogen atom, and

[0041] at least one metal dithiocarbamate of general formula (I-e):

(I-e)



[0042] in which R_{17} and R_{18} represent independently of each other hydrocarbon-containing groups, optionally substituted, comprising from 1 to 30 carbon atoms, M represents a metal cation and n is the valency of this metal cation.

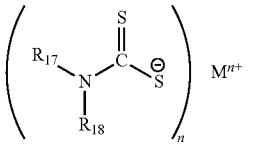
DETAILED DESCRIPTION

[0043] Dithiocarbamate

[0044] The lubricating composition according to the invention comprises at least one compound comprising a metal dithiocarbamate group and at least one compound comprising an amine dithiocarbamate group. With a view to simplification of the description, the compound comprising a metal dithiocarbamate group is called "metal dithiocarbamate" and the compound comprising an amine dithiocarbamate is called "amine dithiocarbamate" in the remainder of the present description.

[0045] The metal dithiocarbamate is a metal dithiocarbamate of general formula (I-e), in which R_{17} and R_{18} represent independently of each other hydrocarbon-containing groups, optionally substituted, comprising from 1 to 30 carbon atoms, M represents a metal cation and n is the valency of this metal cation:

(I-e)



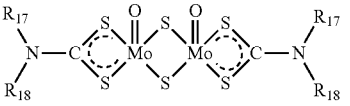
[0046] Preferably, the metal is selected from the group constituted by zinc, aluminium, copper, iron, mercury, silver, cadmium, tin, lead, antimony, bismuth, thallium, chromium, molybdenum, cobalt, nickel, tungsten, sodium, calcium, magnesium, manganese and arsenic. The preferred metals are zinc, molybdenum and antimony, preferably zinc and molybdenum, preferably zinc. Mixtures of metals can be used. The metal dithiocarbamates are neutral as represented in formula (I-e) or basic when a stoichiometric excess of metal is present.

[0047] Preferably, R_{17} and R_{18} represent independently of each other hydrocarbon-containing groups, optionally substituted, comprising from 2 to 24 carbon atoms, more preferentially from 3 to 18 carbon atoms, even more preferentially from 5 to 12 carbon atoms. Preferably, R_{17} and R_{18} represent independently of each other unsubstituted hydrocarbon-containing groups, said hydrocarbon-containing groups being able to be alkyl, alkenyl, alkynyl groups, comprising from 2 to 24 carbon atoms, more preferentially from 3 to 18 carbon atoms, even more preferentially from 5 to 12 carbon atoms, phenyl or benzyl. Preferably, R_{17} and R_{18} represent independently of each other linear or branched alkyl hydrocarbon-containing groups, more preferentially linear alkyl hydrocarbon-containing groups, comprising from 2 to 24 carbon atoms, more preferentially from 3 to 18 carbon atoms, even more preferentially from 5 to 12 carbon atoms. Preferably, R_{17} and R_{18} represent independently of each other hydrocarbon-containing groups optionally substituted with one or more heteroatoms such as the oxygen atom, nitrogen atom, sulphur atom, phosphorus atom, preferably with one or more oxygen atoms.

[0048] The metal dithiocarbamates that can be used are compounds well known to a person skilled in the art. One of the processes for preparing these compounds is described in the U.S. Pat. No. 2,492,314. Suppliers of such additives are for example Vanderbilt, Rhein Chemie, Adeka, King Industries. Commercial compounds are for example Vanlube® AZ, Vanlube® EZ, Vanlube® 73, Vanlube® 73 Super Plus, Molyvan® A, Molyvan® 807, Molyvan® 822, Additin® RC 6301, Additin® RC 6320, Sakura-Lube® 200, Sakura-Lube® 165, Sakura-Lube® 525, Sakura-Lube® 600, Na-Lube® ADTC.

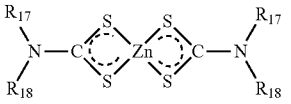
[0049] Preferably, the metal dithiocarbamate is a molybdenum dithiocarbamate of formula (I-e-1), in which R_{17} and R_{18} have the same meaning as in formula (I-e):

(I-e-1)



[0050] Preferably, the metal dithiocarbamate is a zinc dithiocarbamate of formula (I-e-2), in which R_{17} and R_{18} have the same meaning as in formula (I-e):

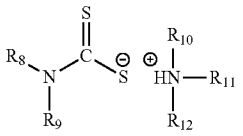
(I-e-2)



[0051] Particularly preferred compounds corresponding to formula (I-e-2) are such that R_{17} and R_{18} represent independently of each other linear alkyl hydrocarbon-containing groups comprising from 5 to 12 carbon atoms and are for example, zinc diamyldithiocarbamate and zinc dibutyldithiocarbamate.

[0052] The amine dithiocarbamate is an amine dithiocarbamate of general formula (I-c), in which R_8 and R_9 represent independently of each other hydrocarbon-containing groups, optionally substituted, comprising from 1 to 30 carbon atoms, R_{10}, R_{11} and R_{12} represent independently of each other a hydrogen atom or a hydrocarbon-containing group from 1 to 30 carbon atoms, it being understood that at least one of the R_{10}, R_{11} and R_{12} groups is not a hydrogen atom:

(I-c)



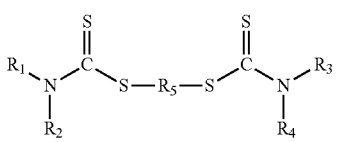
[0053] Preferably, R_8 and R_9 represent independently of each other hydrocarbon-containing groups, optionally substituted, comprising from 2 to 24 carbon atoms, more preferentially from 3 to 18 carbon atoms, even more preferentially from 5 to 12 carbon atoms. Preferably, R_8 and R_9 represent independently of each other unsubstituted hydrocarbon-containing groups, said hydrocarbon-containing groups being able to be alkyl, alkenyl, alkynyl groups comprising from 2 to 24 carbon atoms, more preferentially from 3 to 18 carbon atoms, even more preferentially from 5 to 12 carbon atoms, phenyl or benzyl. Preferably, R_8 and R_9 represent independently of each other linear or branched alkyl hydrocarbon-containing groups, more preferentially linear alkyl hydrocarbon-containing groups comprising from 2 to 24 carbon atoms, more preferentially from 3 to 18 carbon atoms, even more preferentially from 5 to 12 carbon atoms.

[0054] Preferably, R_8 and R_9 represent independently of each other hydrocarbon-containing groups optionally substituted with one or more heteroatoms such as the oxygen atom, nitrogen atom, sulphur atom, phosphorus atom, preferably with one or more oxygen atoms. Preferably, R_{10}, R_{11} and R_{12} represent independently of each other a hydrocarbon-containing group from 2 to 24 carbon atoms, more preferentially from 3 to 18 carbon atoms, even more preferentially from 5 to 12 carbon atoms. Particularly preferred compounds are diamyl amine diamyldithiocarbamate and diamyl amine dibutyldithiocarbamate. Commercial compounds are for example Vanlube® EZ.

[0055] Preferably, the dithiocarbamate is a mixture of the dithiocarbamates of formulae (I-c) and (I-e-2) described above. Advantageously, the dithiocarbamate is a mixture of zinc dithiocarbamate and diamyl ammonium diamyldithiocarbamate. In an embodiment, the composition according to the invention can also comprise another compound comprising a dithiocarbamate group.

[0056] In a first embodiment, this other dithiocarbamate compound is a bisdithiocarbamate of general formula (I-a), in which R_1, R_2, R_3 and R_4 represent independently of each other hydrocarbon-containing groups, optionally substituted, comprising from 1 to 30 carbon atoms, R_5 represents a hydrocarbon-containing group from 1 to 8 carbon atoms:

(I-a)

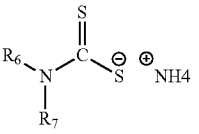


[0057] Preferably, R_1, R R_3 and R_4 represent independently of each other hydrocarbon-containing groups, optionally substituted, comprising from 2 to 24 carbon atoms, more preferentially from 3 to 18 carbon atoms, even more preferentially from 5 to 12 carbon atoms. Preferably, R_1, R_2, R_3 and R_4 represent independently of each other unsubstituted hydrocarbon-containing groups, said hydrocarbon-containing groups being able to be alkyl, alkenyl, alkynyl, phenyl or benzyl groups. Preferably, R_1, R_2, R_3 and R_4 represent independently of each other hydrocarbon-containing groups, linear or branched alkyl groups, more preferentially linear alkyl hydrocarbon-containing groups.

[0058] Preferably, R_1, R_2, R_3 and R_4 represent independently of each other hydrocarbon-containing groups optionally substituted with oxygen, nitrogen, sulphur and/or phosphorus atoms, preferably oxygen atoms. Preferably, R_5 represents a hydrocarbon-containing group of 2 to 6 carbon atoms. Commercial compounds are for example Vanlube® 7723 or Additin® RC 6340.

[0059] In a second embodiment, this other dithiocarbamate compound is an ammonium dithiocarbamate of general formula (I-b), in which R_6 and R_7 represent independently of each other hydrocarbon-containing groups, optionally substituted, comprising from 1 to 30 carbon atoms:

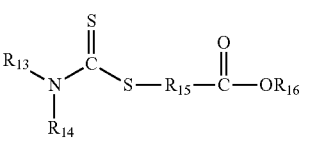
(I-b)



[0060] Preferably, R_6 and R_7 represent independently of each other hydrocarbon-containing groups, optionally substituted, comprising from 2 to 24 carbon atoms, more preferentially from 3 to 18 carbon atoms, even more preferentially from 5 to 12 carbon atoms. Preferably, R_6 and R_7 represent independently of each other unsubstituted hydrocarbon-containing groups, said hydrocarbon-containing groups being able to be alkyl, alkenyl, alkynyl, phenyl or benzyl groups. Preferably, R_6 and R_7 represent independently of each other linear or branched alkyl hydrocarbon-containing groups, more preferentially linear alkyl hydrocarbon-containing groups. Preferably, R_6 and R_7 represent independently of each other hydrocarbon-containing groups optionally substituted with oxygen, nitrogen, sulphur and/or phosphorus atoms, preferably with oxygen atoms.

[0061] In a third embodiment, this other dithiocarbamate compound is a dithiocarbamate ester of general formula (I-d), in which R_{13} and R_{14} represent independently of each other hydrocarbon-containing groups, optionally substituted, comprising from 1 to 30 carbon atoms, R_{15} and R_{16} represent independently of each other hydrocarbon-containing groups comprising from 1 to 18 carbon atoms:

(I-d)



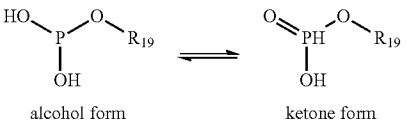
[0062] Preferably, R_{13} and R_{14} represent independently of each other hydrocarbon-containing groups, optionally substituted, comprising from 2 to 24 carbon atoms, more preferentially from 3 to 18 carbon atoms, even more preferentially from 5 to 12 carbon atoms. Preferably, R_{13} and R_{14} represent independently of each other unsubstituted hydrocarbon-con-

taining groups, said hydrocarbon-containing groups being able to be alkyl, alkenyl, alkynyl, phenyl or benzyl groups. Preferably, R_{13} and R_{14} represent independently of each other linear or branched alkyl hydrocarbon-containing groups, more preferentially linear alkyl hydrocarbon-containing groups. Preferably, R_{13} and R_{14} represent independently of each other hydrocarbon-containing groups optionally substituted with oxygen, nitrogen, sulphur and/or phosphorus atoms, preferably with oxygen atoms. Preferably, R_{15} and R_{16} represent independently of each other hydrocarbon-containing groups of 2 to 6 carbon atoms.

[0063] Phosphite

[0064] The lubricating composition according to the invention comprises at least one compound comprising a phosphite group. With a view to simplification of the description, the compound comprising a phosphite group is called "phosphite" in the remainder of the present description. By phosphite, is meant a phosphite ester, which may be a phosphite monoester, a phosphite diester or a phosphite triester, used alone or in a mixture. The phosphite monoesters are found in two forms in equilibrium, a "ketone" form and an "alcohol" form. The same is true of the phosphite diesters.

[0065] A useable phosphite can be a phosphite monoester of general formula (III-a) in its alcohol and/or ketone form, in which R_{19} represents a hydrocarbon-containing group, optionally substituted, of 1 to 30 carbon atoms:

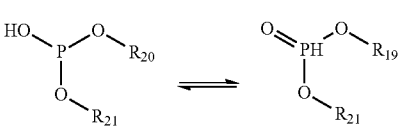


(II-a)

alcohol form ketone form

[0066] Preferably, R_{19} represents a hydrocarbon-containing group, optionally substituted, comprising from 2 to 24 carbon atoms, more preferentially from 3 to 20 carbon atoms, even more preferentially from 4 to 18 carbon atoms, even more preferentially from 6 to 16 carbon atoms, even more preferentially from 8 to 12 carbon atoms. Preferably, R_{19} represents an unsubstituted hydrocarbon-containing group, said hydrocarbon-containing group being able to be an alkyl, alkenyl, alkynyl, phenyl or benzyl group. Preferably, R_{19} represents a linear or branched alkyl hydrocarbon-containing group, more preferentially a linear alkyl hydrocarbon-containing group. Preferably, R_{19} represents a hydrocarbon-containing group substituted with oxygen, nitrogen, sulphur and/or phosphorus atoms, preferably oxygen atoms. As examples of phosphite monoesters, alkyl (C_{10}) bisphenol A phosphite and alkyl (C_{12}-C_{15}) bisphenol A phosphite may be mentioned.

[0067] A useable phosphite can also be a phosphite diester of general formula (III-b) in its alcohol and/or ketone form, in which R_{20} and R_{21} represent independently of each other hydrocarbon-containing groups, optionally substituted, of 1 to 30 carbon atoms:

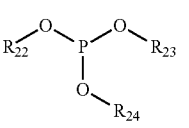


(II-b)

alcohol form ketone form

[0068] Preferably R_{20} and R_{21} represent hydrocarbon-containing groups, optionally substituted, comprising from 2 to 24 carbon atoms, more preferentially from 3 to 20 carbon atoms, even more preferentially from 4 to 18 carbon atoms, even more preferentially from 6 to 16 carbon atoms, even more preferentially from 8 to 12 carbon atoms. Preferably, R_{20} and R_{21} represent independently of each other unsubstituted hydrocarbon-containing groups, said hydrocarbon-containing groups being able to be alkyl, alkenyl, alkynyl, phenyl or benzyl groups. Preferably, R_{20} and R_{21} represent independently of each other linear or branched alkyl hydrocarbon-containing groups, more preferentially linear alkyl hydrocarbon-containing groups. Preferably, R_{20} and R_{21} represent hydrocarbon-containing groups substituted with oxygen, nitrogen, sulphur and/or phosphorus atoms, preferably oxygen atoms. As examples of phosphite diesters, dimethyl phosphite, diethyl phosphite, diisopropyl phosphite, dibutyl phosphite, dihexyl phosphite, dicylohexyl phosphite, diisodecyl phosphite, di-n-octyl phosphite, dibenzyl phosphite, diphenyl phosphite, and dioleyl phosphite may be mentioned.

[0069] A useable phosphite can also be a phosphite triester of general formula (III-c) in which R_{22}, R_{23} and R_{24} represent independently of each other hydrocarbon-containing groups, optionally substituted, comprising from 1 to 30 carbon atoms:



(II-c)

[0070] Preferably R_{22}, R_{23} and R_{24} represent hydrocarbon-containing groups, optionally substituted, comprising from 2 to 24 carbon atoms, more preferentially from 3 to 20 carbon atoms, even more preferentially from 4 to 18 carbon atoms, even more preferentially from 6 to 16 carbon atoms, even more preferentially from 8 to 12 carbon atoms. Preferably, R_{22}, R_{23} and R_{24} represent independently of each other unsubstituted hydrocarbon-containing groups, said hydrocarbon-containing groups being able to be alkyl, alkenyl, alkynyl, phenyl or benzyl groups. Preferably, R_{22}, R_{23} and R_{24} represent independently of each other linear or branched alkyl hydrocarbon-containing groups, more preferentially linear alkyl hydrocarbon-containing groups. Preferably, R_{22}, R_{23} and R_{24} represent hydrocarbon-containing groups substituted with oxygen, nitrogen, sulphur and/or phosphorus atoms, preferably oxygen atoms.

[0071] As examples of phosphite triesters, diphenyl isodecyl phosphite, diphenyl isooctyl phosphite, tridimethylphenyl phosphite, diphenyl ethylhexyl phosphite, phenyl diisodecyl phosphite, triisodecyl phosphite, trilauryl phosphite, triphenyl phosphite, tris(dipropyleneglycol)phosphite, tris (nonylphenyl)phosphite, tris(2,4-di-t-butylphenyl)phosphite, tris(5-norbornene-2-methyl)phosphite, tris(tridecyl)

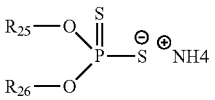
phosphite, trimethyl phosphite, triethyl phosphite, triisopropyl phosphite, tributyl phosphite, triisoctyl phosphite, tribenzylphosphite, triphenyl phosphite, poly(dipropyleneglycol)phenyl phosphite and tris(dipropylene glycol) phosphite may be mentioned. Commercial compounds are for example Duraphos® AP230, Duraphos® AP240L, Duraphos® DBHP, Doverphos® 4, Doverphos® 10, Doverphos® 213, Doverphos® 6, Doverphos® 7, Doverphos® 8, Doverphos® 9, Doverphos® 11, Doverphos® 12, Doverphos® 613, Doverphos® 675, Doverphos® 49, Doverphos® 53, Doverphos® 72, Doverphos® 253, Doverphos® 271, Irgaphos® OPH, or the Rhodaphos® range products marketed by the company Rhodia. The lubricating composition according to the invention comprises from 0.1 to 5% by mass of phosphite, relative to the total mass of the lubricating composition, preferably from 0.2 to 4%, more preferentially from 0.3 to 2%, even more preferentially from 0.5 to 1%.

[0072] Dithiophosphate

[0073] The lubricating composition according to the invention comprises at least one compound comprising a dithiophosphate group. With a view to simplification of the description, the compound comprising a dithiophosphate group is called "dithiophosphate" in the remainder of the present description. A useable dithiophosphate is a dithiophosphate selected from the group constituted by the ammonium dithiophosphates, amine dithiophosphates, dithiophosphate esters and metal dithiophosphates, used alone or in a mixture. The ammonium dithiophosphates, amine dithiophosphates and dithiophosphate esters have the advantage of being ashless dithiophosphates, in particular zinc-free.

[0074] In a first embodiment, the dithiophosphate is an ammonium dithiophosphate of general formula (III-a), in which R_{25} and R_{26} represent independently of each other hydrocarbon-containing groups, optionally substituted, comprising from 1 to 30 carbon atoms:

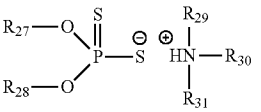
(III-a)



[0075] Preferably, R_{25} and R_{26} represent independently of each other hydrocarbon-containing groups, optionally substituted, comprising from 2 to 24 carbon atoms, more preferentially from 3 to 18 carbon atoms, even more preferentially from 5 to 12 carbon atoms. Preferably, R_{25} and R_{26} represent independently of each other unsubstituted hydrocarbon-containing groups, said hydrocarbon-containing groups being able to be alkyl, alkenyl, alkynyl, phenyl or benzyl groups. Preferably, R_{25} and R_{26} represent independently of each other linear or branched alkyl hydrocarbon-containing groups, more preferentially linear alkyl hydrocarbon-containing groups. Preferably, R_{25} and R_{26} represent independently of each other hydrocarbon-containing groups optionally substituted with oxygen, nitrogen, sulphur and/or phosphorus atoms, preferably oxygen atoms. Examples of commercial products are the ammonium dimethyl dithiophosphates, ammonium diethyl dithiophosphates, ammonium dibutyl dithiophosphates.

[0076] In a second embodiment, the dithiophosphate is an amine dithiophosphate of general formula (III-b), in which R_{27} and R_{28} represent independently of each other hydrocarbon-containing groups, optionally substituted, comprising from 1 to 30 carbon atoms, R_{29}, R_{30} and R_{31} represent independently of each other a hydrogen atom or a hydrocarbon-containing group from 1 to 30 carbon atoms, it being understood that at least one of the R_{29}, R_{30} and R_{31} groups is not a hydrogen atom:

(III-b)

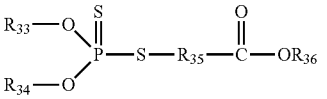


[0077] Preferably, R_{27} and R_{28} represent independently of each other hydrocarbon-containing groups, optionally substituted, comprising from 2 to 24 carbon atoms, more preferentially from 3 to 18 carbon atoms, even more preferentially from 5 to 12 carbon atoms. Preferably, R_{27} and R_{28} represent independently of each other unsubstituted hydrocarbon-containing groups, said hydrocarbon-containing groups being able to be alkyl, alkenyl, alkynyl, phenyl or benzyl groups. Preferably, R_{27} and R_{28} represent independently of each other linear or branched alkyl hydrocarbon-containing groups, more preferentially linear alkyl hydrocarbon-containing groups. Preferably, R_{27} and R_{28} represent independently of each other hydrocarbon-containing groups optionally substituted with oxygen, nitrogen, sulphur and/or phosphorus atoms, preferably with oxygen atoms.

[0078] Preferably, R_{29}, R_{30} and R_{31} represent independently of each other a hydrocarbon-containing group from 2 to 24 carbon atoms, more preferentially from 3 to 18 carbon atoms, even more preferentially from 5 to 12 carbon atoms. Commercial compounds are for example Additin® RC 3880.

[0079] In a third embodiment, the dithiophosphate is a dithiophosphate ester of general formula (III-c), in which R_{33} and R_{34} represent independently of each other hydrocarbon-containing groups, optionally substituted, comprising from 1 to 30 carbon atoms, R_{35} and R_{36} represent independently of each other hydrocarbon-containing groups comprising from 1 to 18 carbon atoms:

(III-c)



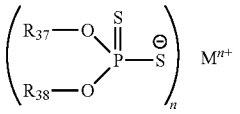
[0080] Preferably, R_{33} and R_{34} represent independently of each other hydrocarbon-containing groups, optionally substituted, comprising from 2 to 24 carbon atoms, more preferentially from 3 to 18 carbon atoms, even more preferentially from 5 to 12 carbon atoms. Preferably, R_{33} and R_{34} represent independently of each other unsubstituted hydrocarbon-containing groups, said hydrocarbon-containing groups being able to be alkyl, alkenyl, alkynyl, phenyl or benzyl groups. Preferably, R_{33} and R_{34} represent independently of each other linear or branched alkyl hydrocarbon-containing groups, more preferentially linear alkyl hydrocarbon-containing groups. Preferably, R_{33} and R_{34} represent independently of each other hydrocarbon-containing groups optionally substituted with oxygen, nitrogen, sulphur and/or phosphorus atoms, preferably oxygen atoms. Preferably, R_{33} and R_{34}

represent independently of each other, a hydrocarbon-containing group of 2 to 6 carbon atoms.

[0081] Preferably, R_{35} and R_{36} represent independently of each other hydrocarbon-containing groups of 2 to 6 carbon atoms. Commercial compounds are for example Irgalube® 63.

[0082] In a fourth embodiment, the dithiophosphate is a metal dithiophosphate of general formula (III-d), in which R_{37} and R_{38} represent independently of each other hydrocarbon-containing groups, optionally substituted, comprising from 1 to 30 carbon atoms, M represents a metal cation and n is the valency of this metal cation:

(III-d)



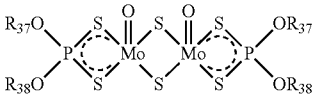
[0083] Preferably, the metal is selected from the group constituted by zinc, aluminium, copper, iron, mercury, silver, cadmium, tin, lead, antimony, bismuth, thallium, chromium, molybdenum, cobalt, nickel, tungsten, sodium, calcium, magnesium, manganese and arsenic. The preferred metals are zinc, molybdenum, antimony, preferably zinc and molybdenum, preferably zinc. Mixtures of metals can be used. The metal dithiophosphates are neutral as exemplified in formula (III-d) or basic when a stoichiometric excess of metal is present.

[0084] Preferably, R_{37} and R_{38} represent independently of each other hydrocarbon-containing groups, optionally substituted, comprising from 2 to 24 carbon atoms, more preferentially from 3 to 18 carbon atoms, even more preferentially from 5 to 12 carbon atoms. Preferably, R_{37} and R_{38} represent independently of each other unsubstituted hydrocarbon-containing groups, said hydrocarbon-containing groups being able to be alkyl, alkenyl, alkynyl, phenyl or benzyl groups. Preferably, R_{37} and R_{38} represent independently of each other linear or branched alkyl hydrocarbon-containing groups, more preferentially linear alkyl hydrocarbon-containing groups. Preferably, R_{37} and R_{38} represent independently of each other hydrocarbon-containing groups optionally substituted with oxygen, nitrogen, sulphur and/or phosphorus atoms, preferably with oxygen atoms.

[0085] The useable metal dithiophosphates are compounds well known to a person skilled in the art. Commercial compounds are for example Additin® RC 3038, Additin® RC 3045, Additin® RC 3048, Additin® RC 3058, Additin® RC 3080, Additin® RC 3180, Additin® RC 3212, Additin® RC 3580, Kikulube® Z112, Lubrizol® 1371, Lubrizol® 1375, Lubrizol® 1395, Lubrizol® 5179, Oloa® 260, Oloa® 267.

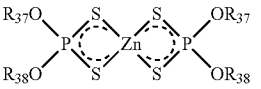
[0086] Preferably, the metal dithiophosphate is a molybdenum dithiophosphate of formula (III-d-1), in which R_{37} and R_{38} have the same meaning as in formula (III-d):

(III-d-1)



[0087] Preferably, the metal dithiophosphate is a zinc dithiophosphate of formula (III-d-2), in which R_{37} and R_{38} have the same meaning as in formula (III-d):

(III-d-2)



The lubricating composition according to the invention comprises from 0.1 to 5% by mass of dithiophosphate, relative to the total mass of the lubricating composition, preferably from 0.2 to 4%, more preferentially from 0.3 to 2%, even more preferentially from 0.5 to 1%.

[0088] Base Oil

[0089] The lubricating compositions according to the invention can contain any type of lubricating base, synthetic or natural mineral, animal or vegetable, suited to their use. The base oil or oils used in the lubricating compositions according to the present invention can be oils of mineral or synthetic origin of groups I to V according to the classes defined in the API classification (or their equivalents according to the ATIEL classification) as summarized below, alone or in a mixture.

	Saturates content	Sulphur content	Viscosity Index (VI)
Group I Mineral oils	<90%	>0.03%	80 ≤ VI < 120
Group II Hydrocracked oils	≥90%	≤0.03%	80 ≤ VI < 120
Group III Hydrocracked or hydroisomerized oils	≥90%	≤0.03%	≥120
Group IV	Polyalphaolefins (PAO)		
Group V	Esters and other bases not included in bases of groups I to IV		

[0090] The mineral base oils according to the invention include all types of bases obtained by atmospheric and vacuum distillation of crude oil, followed by refining operations such as solvent extraction, deasphalting, solvent dewaxing, hydrotreatment, hydrocracking and hydroisomerization, hydrofinishing. The base oils of the compositions according to the present invention can also be synthetic oils, such as certain esters of carboxylic acids and alcohols, or polyalphaolefins. The polyalphaolefins used as base oils, are for example obtained from monomers having 4 to 32 carbon atoms (for example octene, decene), and a viscosity at 100° C. comprised between 1.5 and 15 cSt according to the standard ASTM D445. Their weight-average molecular weight is typically comprised between 250 and 3000 according to the standard ASTM D5296. Mixtures of synthetic oils and minerals can also be used.

[0091] There is no limitation as regards the use of a specific lubricating base for producing the lubricating compositions according to the invention, except that they must have properties, in particular in terms of viscosity, viscosity index, sulphur content, oxidation resistance, suitable for use in a gearbox, in particular a motor vehicle gearbox, in particular in a manual gearbox. Preferentially, the lubricating bases represent at least 50% by mass, relative to the total mass of the lubricating composition, preferentially at least 60%, or also at least 70%. Typically, they represent between 75 and 90% by

mass, relative to the total mass of the lubricating compositions according to the invention.

[0092] Preferentially, the lubricating compositions according to the invention comprise mineral bases of group I and/or III, or synthetic bases of group IV according to the API classification. Preferentially, the lubricating compositions according to the invention have a kinematic viscosity at 100° C. measured according to the standard ASTM D445 comprised between 4 and 41 cSt, according to the SAE J 306 classification, preferably between 4.1 and 32.5 cSt.

[0093] The preferred grades are all the grades comprised between grades 75W and 140, in particular grades 75W, 75W80 and 75W90. Preferentially, the lubricating compositions according to the invention have a viscosity index (VI) greater than 120 (standard ASTM 2270).

[0094] Other Additives

[0095] The lubricating compositions according to the invention can also contain all types of additives suitable for use in the formulations of oils for transmissions, for example one or more additives selected from the polymers, antioxidants, corrosion inhibitors, and dispersants, present at the usual levels required for the application. The polymers are selected from the group of shear-stable polymers, preferably from the group constituted by the ethylene and alpha-olefin copolymers, the polyacrylates such as the polymethacrylates, olefin copolymers (OCP), Ethylene Propylene Diene Monomers (EPDM), polybutenes, styrene and olefin copolymers, hydrogenated or not, styrene and acrylate copolymers. The preferred polymers are the polymethacrylates (PMA).

[0096] The preferred dispersants are the polyisobutylenes (PIB), polyisobutylene succinic anhydride and the amine derivatives of polyisobutylene succinic anhydride (PIB succinimides). The preferred antioxidants are for example amine antioxidants, preferably diphenylamines, in particular dialkylphenylamines, such as the octadiphenylamines, phenyl-alpha-naphthyl amines, or phenolic antioxidants (dibutylhydroxytoluene BHT and derivatives) or sulphur-containing antioxidants (sulphurized phenates). The preferred anti-corrosion additives are phenol derivatives, in particular ethoxylated phenol derivatives substituted with alkyl groups in the ortho position. The corrosion inhibitors may be dimercaptothiadiazole derivatives.

[0097] In an embodiment of the invention, the lubricating composition comprises:

[0098] from 80 to 98.5% of a base oil,

[0099] from 0.5 to 3% of a compound comprising a phosphite group,

[0100] from 0.5 to 3% of a compound comprising a dithiophosphate group,

[0101] from 0.5 to 3% of a compound comprising a dithiocarbamate group, this compound being a mixture of at least one amine dithiocarbamate of general formula (I-c) as described above and a metal dithiocarbamate of general formula (I-e) as described above.

[0102] In an embodiment of the invention, the lubricating composition comprises:

[0103] from 80 to 98.5% of a base oil,

[0104] from 0.5 to 3% of a compound comprising a phosphite group,

[0105] from 0.5 to 3% of a compound comprising a dithiophosphate group,

[0106] from 0.5 to 3% of a compound comprising a dithiocarbamate group, this compound being a mixture of at least one amine dithiocarbamate of general formula (I-c) as described above and a metal dithiocarbamate of general formula (I-e-2) as described above.

[0107] In an embodiment of the invention, the lubricating composition comprises:

[0108] from 80 to 98% of a base oil,

[0109] from 0.5 to 3% of a compound comprising a phosphite group,

[0110] from 0.5 to 3% of a compound comprising a dithiophosphate group,

[0111] from 0.5 to 3% of a compound comprising a dithiocarbamate group, this compound being a mixture of at least one amine dithiocarbamate of general formula (I-c) as described above and a metal dithiocarbamate of general formula (I-e) as described above,

[0112] from 0.5 to 3% of at least one other additive.

[0113] The additional additive can be selected from the other additives described above. Preferably, the other additive can be selected from the group formed by the polymers, antioxidants, corrosion inhibitors, dispersants and mixtures thereof. Preferably, the other additive is a mixture of at least one antioxidant and at least one dispersant. Preferably, the other additive is a mixture of at least one polysiobutylene succinimide and at least one dialkylphenylamine.

[0114] In an embodiment of the invention the lubricating composition essentially consists of:

[0115] from 80-98.5% of a base oil,

[0116] from 0.5 to 3% of a compound comprising a phosphite group,

[0117] from 0.5 to 3% of a compound comprising a dithiophosphate group,

[0118] from 0.5 to 3% of a compound comprising a dithiocarbamate group, this compound being a mixture of at least one amine dithiocarbamate of general formula (I-c) as described above and a metal dithiocarbamate of general formula (I-e) as described above.

[0119] In an embodiment of the invention the lubricating composition essentially consists of:

[0120] from 80-98.5% of a base oil,

[0121] from 0.5 to 3% of a compound comprising a phosphite group,

[0122] from 0.5 to 3% of a compound comprising a dithiophosphate group,

[0123] from 0.5 to 3% of a compound comprising a dithiocarbamate group, this compound being a mixture of at least one amine dithiocarbamate of general formula (I-c) as described above and a metal dithiocarbamate of general formula (I-e-2) as described above.

[0124] In an embodiment of the invention, the lubricating composition essentially consists of:

[0125] from 80 to 98% of a base oil,

[0126] from 0.5 to 3% of a compound comprising a phosphite group,

[0127] from 0.5 to 3% of a compound comprising a dithiophosphate group,

[0128] from 0.5 to 3% of a compound comprising a dithiocarbamate group, this compound being a mixture of at least one amine dithiocarbamate of general formula (I-c) as described above and a metal dithiocarbamate of general formula (I-e) as described above,

[0129] from 0.5 to 3% of at least one other additive.

[0130] The additional additive can be selected from the other additives described above. Preferably, the other additive can be selected from the group formed by the polymers, the antioxidants, the corrosion inhibitors, the dispersants and

mixtures thereof. Preferably, the other additive is a mixture of at least one antioxidant and at least one dispersant. Preferably, the other additive is a mixture of at least one polysiobutylene succinimide and at least one dialkylphenylamine.

[0131] The invention also relates to a method for lubricating transmissions such as gearboxes, axles, preferably the manual gearboxes of motor vehicles, said method comprising a step of bringing the lubricating composition as defined above into contact with transmissions such as gearboxes. Preferably, this method makes it possible to simultaneously reduce wear, to improve the extreme-pressure properties, reduce friction and improve the anti-seizing properties of the lubricating composition. Advantageously, this method makes it possible to reduce the fuel consumption of vehicles, in particular motor vehicles. The use of these four additives in a lubricating composition makes it possible to simultaneously reduce wear, improve the extreme-pressure properties, reduce the coefficient of friction and improve the anti-seizing properties of the lubricating composition.

[0132] In a preferred embodiment, the lubricating composition comprises at least one base oil, at least one compound comprising a metal dithiocarbamate group of formula (I-e), at least one compound comprising an amine dithiocarbamate group of formula (I-c), at least one compound comprising a phosphite group at least one compound comprising a dithiophosphate group, at least one antioxidant and at least one dispersant. The presence of an antioxidant and a dispersant, and in particular the presence of the dispersant, does not adversely affect the extreme-pressure, wear, friction and anti-seizing properties which are still very good, and at the same time makes it possible to ensure excellent oxidation resistance. It is surprising to note that the use of the dispersant makes it possible to clearly improve the oxidation resistance.

EXAMPLES

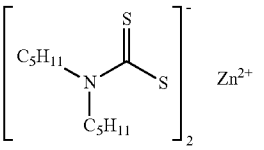
Example 1

[0133] Lubricating compositions 1 to 7 are prepared from:

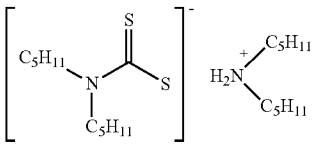
[0134] a group IV base oil of PAO type having a viscosity at 100° C. of 6 cSt according to the standard ASTM D445, and viscosity index equal to 125 according to the standard ASTM 2270,

[0135] a dithiocarbamate (Vanlube EZ) which is a mixture of:

[0136] zinc diamyldithiocarbamate of formula



[0137] and diamyl amine diamyldithiocarbamate of formula,



[0138] a phosphite P_1 which is di-n-octyl phosphite,

[0139] a dithiophosphate, 3-[(bis-isopropyloxyphosphinothioyl)thio]propionic acid ethyl ester.

TABLE I

Mass composition (%) of the lubricating compositions 1 to 7

Lubricating composition	1	2	3	4	5	6	7
Base oil PAO6	99	99	99	98	98	98	97
Dithiocarbamate	1	—	—	1	1	—	1
Phosphite P_1	—	1	—	1	—	1	1
Dithiophosphate	—	—	1	—	1	1	1

The wear, extreme-pressure and friction properties of these lubricating compositions 1 to 7 are then measured.

TABLE II

Properties of lubricating compositions 1 to 7

Lubricating composition	1	2	3	4	5	6	7
Wear (mm) [1]	0.63	0.54	0.65	0.43	0.56	0.51	0.42
Extreme-pressure, welding load (daN) [2]	80	90	100	90	120	110	110
Coefficient of friction [3]	0.346	0.125	0.052	0.084	0.113	0.080	0.067

[1] 4B (4-ball) wear test D55 1078

[2] 4B (4-ball) EP (Extreme-Pressure) D55 1136

[3] The friction properties of the formulae were evaluated using a Cameron-Plint TE-77 reciprocating tribometer. The operating principle is for example described in the publication "Friction Force Measurement in Reciprocating Tribometers", by A G Plint, published by STLE (Society of Tribologists and Lubrication Engineers) in 2011. The procedure used measures the coefficient of friction of a roller on a plane, all immersed in the test lubricant, under conditions of temperature (60° C., 100° C. and 140° C.), load (50, 100, 150 and 200N) and frequency (5, 10, 20 and 40 Hz) that can be varied in order to reproduce the friction conditions encountered in the control mechanisms of gearboxes during use. The course of the roller on the plane, i.e. the reciprocating stroke movement, is fixed at 7 mm. The test duration is 10 minutes. The reduction of the friction under these test conditions makes it possible to indicate a reduction in the gear-changing stresses and in the friction losses in the gears of the gearbox operating with the type of lubricant studied. The value of the coefficient of friction measured in μmin, taken at different temperatures, corresponds to the minimum value of the coefficient of friction taken over the average of the 4 loads during the last minute of the test.

[0140] Lubricating compositions 1 to 6 are control lubricating compositions comprising only one or two of the three additives essential to the invention. The lubricating compositions 1 to 6 do not simultaneously have good anti-wear, extreme-pressure and friction properties. Only the lubricating composition 7, which is a lubricating composition according to the invention, simultaneously has good anti-wear, extreme-pressure and friction properties.

Example 2

[0141] Lubricating compositions 8 to 9 according to the invention are then prepared from:

[0142] a group IV base oil of PAO type having a viscosity at 100° C. of 6 cSt according to the standard ASTM D445, and viscosity index equal to 125 according to the standard ASTM 2270,

[0143] a dithiocarbamate (Vanlube® EZ) which is a mixture of zinc diamyldithiocarbamate and diamyl amine diamyldithiocarbamate,

[0144] a phosphite P_1 which is di-n-octyl phosphite,

[0145] a dithiophosphate, 3-[(bis-isopropyloxyphosphinothioyl)thio]propionic acid ethyl ester.

[0146] an amine antioxidant, a dialkylated diphenylamine with C_4 and C_8 groups,

[0147] a dispersant which is a polyisobutylene derivative, in particular a polyisobutylene succinimide derivative.

TABLE III

Mass composition (%) of lubricating compositions 7 to 9

Lubricating composition	7	8	9
Base oil PAO6	97	96.5	96
Dithiocarbamate	1	1	1
Phosphite	1	1	1
Dithiophosphate	1	1	1
Antioxidant	—	0.5	0.5
Dispersant	—	—	0.5

The extreme-pressure, oxidation and corrosion properties of these lubricating compositions 7 to 9 are then measured (by means of the FZG test).

TABLE IV

Properties of lubricating compositions 7 to 9

Lubricating composition	7	8	9
FZG test (damage load stage) [4]	12	12	10
Oxidation			
Viscosity increase at 100° C. (%) [5]	+1.1	−0.7	+1.1
Content of insolubles (% by mass) [5]	0.045	0.175	0.055
Content of deposits (% by mass) [6]	*	*	0.11

TABLE IV-continued

Properties of lubricating compositions 7 to 9

Lubricating composition	7	8	9
Steel corrosion rating [7]	10	10	10
Copper corrosion rating 4 h [8]	1b	1b	1b
Copper corrosion rating 24 h [8]	1b	1b	1b

[4] CEC L84 (A/16, 6R/120)
[5] GFC T-021-A-90
[6] GFC T-022-A-90
[7] ASTM D665
[8] ASTM D130 to 150° C.
* content of deposits too high to be measured

[0148] It is noted that compositions 7 to 9 have a very satisfactory extreme-pressure level. Compositions 7 and 8 give a damage load stage of 12, composition 9 gives a damage load stage of 10. These results are comparable (and better in the case of compositions 7 and 8) to the results obtained with a reference oil H which has a damage load stage of 9. This reference oil H comprises 72% by mass of group I base oil, relative to the mass of oil, 11% by mass of polymethacrylate-type polymer, 8% by mass of PAO, 8% by mass of a package comprising a zinc dialkyldithiophosphate, a dibutyl phosphite, an aryl phosphite and a diphenylamine as antioxidant. Lubricating compositions 7 to 9 therefore exhibit better extreme-pressure behaviour than this reference oil H since their failure occurs at higher loads. Similarly, lubricating compositions 7 to 9 and especially composition 9 have low susceptibility to corrosion (copper or steel) and to oxidation.

Example 3

[0149] Control lubricating compositions 10 to 15 are then prepared from:

[0150] a group IV base oil of PAO type having a viscosity at 100° C. of 6 cSt according to the standard ASTM D445, and viscosity index equal to 125 according to the standard ASTM 2270,

[0151] a dithiocarbamate which is a mixture of zinc diamyldithiocarbamate and diamyl amine diamyldithiocarbamate. This mixture is identical to that used in Example 1,

[0152] a phosphite P_2 which is triphenyl phosphite,

[0153] a sulphur-containing olefin known for its extreme-pressure properties, Additin® RC 2545.

TABLE V

Mass composition (%) of lubricating compositions 1 and 10 to 15

Lubricating composition	1	10	11	12	13	14	15
Base oil PAO6	99	99	99	98	98	98	97
Dithiocarbamate	1	—	—	1	1	—	1
Phosphite P_2	—	1	—	1	—	1	1
Sulphur-containing olefin	—	—	1	—	1	1	1

The wear and extreme-pressure properties of these lubricating compositions 10 to 15 are then measured.

TABLE VI

Properties of lubricating compositions 10 to 15

Lubricating composition	1	10	11	12	13	14	15
Wear (mm) [1]	0.63	0.46	0.63	0.50	0.59	0.75	0.71
Extreme-pressure, welding load (daN) [2]	80	70	100	70	120	80	100

[1] 4B (4-ball) wear test D55 1078
[2] 4B (4-ball) EP (Extreme-Pressure) test D55 1136

[0154] Additin® RC 2545 is an extreme-pressure additive; it has the same function as the compound comprising a dithiophosphate group used in the compositions according to the invention. However, it is noted that the combination of a dithiocarbamate, a phosphite with a sulphur-containing olefin rather than a dithiophosphate does not make it possible to simultaneously obtain good anti-wear and extreme-pressure properties. Thus, when at least one compound is selected with a chemical structure different from one of the compounds constituting the lubricating composition according to the invention but having the same function (therefore a compound belonging to another family of additives), no simultaneous improvement in the three properties anti-wear, extreme pressure and friction is observed.

Example 4

[0155] Comparative lubricating composition 16 is prepared based on the above composition according to the invention 7, in which the mixture of metal dithiocarbamate and amine dithiocarbamate (Vanlube EZ) is replaced with a zinc diamyl dithiocarbamate (Vanlube AZ).

TABLE VII

Mass composition of lubricating compositions 7 and 16

Lubricating composition	7	16
Base oil PAO6	97	97
Metal dithiocarbamate + amine dithiocarbamate	1	
Metal dithiocarbamate (Vanlube AZ)		1
Phosphite	1	1
Dithiophosphate	1	1

TABLE VIII

Properties of lubricating compositions 7 and 16

Lubricating composition	7	16
Wear[1]	0.42	0.43
FZG test (damage load stage) [4]	12	9

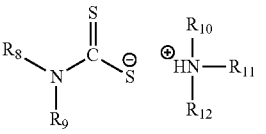
[1]4B (4-ball) wear test D55 1078
[4] CEC L84 (A/16, 6R/120)

[0156] The results show that the combination of a metal dithiocarbamate of formula (I-e) and an amine dithiocarbamate of formula (I-c) makes it possible to very significantly improve the anti-seizing properties of a lubricating composition, while having completely satisfactory anti-wear properties. It should be noted that the presence of a metal dithiocarbamate of formula (I-e) alone in a lubricating composition does not make it possible to obtain good anti-seizing properties.

1. A lubricating composition comprising at least one base oil, at least one compound comprising a dithiocarbamate group, at least one compound comprising a phosphite group and at least one compound comprising a dithiophosphate group, the compound comprising a dithiocarbamate group being a mixture of:

(a) at least one amine dithiocarbamate of general formula (I-c)

(I-c)



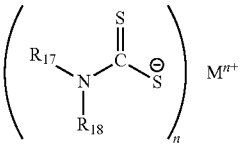
in which:

R_8 and R_9 represent independently of each other hydrocarbon-containing groups, optionally substituted, comprising from 1 to 30 carbon atoms,

R_{10}, R_{11} and R_{12} represent independently of each other a hydrogen atom or a hydrocarbon-containing group from 1 to 30 carbon atoms, it being understood that at least one of the R_{10}, R_{11} and R_{12} groups is not a hydrogen atom; and

(b) at least one metal dithiocarbamate of general formula (I-e),

(I-e)

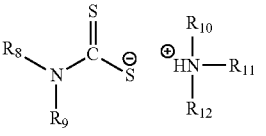


in which R_{17} and R_{18} represent independently of each other hydrocarbon-containing groups, optionally substituted, comprising from 1 to 30 carbon atoms, M represents a metal cation and n is the valency of this metal cation.

2. The lubricating composition according to claim **1** in which the compound comprising a dithiocarbamate group is a mixture of:

(a) at least one amine dithiocarbamate of general formula (I-c)

(I-c)



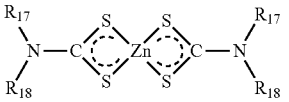
in which:

R_8 and R_9 represent independently of each other hydrocarbon-containing groups, optionally substituted, comprising from 1 to 30 carbon atoms,

R_{10}, R_{11} and R_{12} represent independently of each other a hydrogen atom or a hydrocarbon-containing group from 1 to 30 carbon atoms, it being understood that at least one of the R_{10}, R_{11} and R_{12} groups is not a hydrogen atom; and

(b) at least one metal dithiocarbamate of general formula (I-e-2),

(I-e-2)



in which R_{17} and R_{18} represent independently of each other linear alkyl hydrocarbon-containing groups.

3. The lubricating composition according to claim **2** in which R_{17} and R_{18} represent independently of each other linear alkyl groups comprising from 5 to 12 carbon atoms.

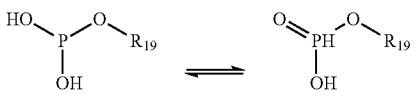
4. The lubricating composition according to claim **1** comprising from 0.1 to 5% by mass of compounds comprising a dithiocarbamate group, relative to the total mass of lubricating composition.

5. The lubricating composition according to claim **1** comprising from 0.1 to 3% by mass of the mixture of amine dithiocarbamate corresponding to formula (I-c) and metal dithiocarbamate corresponding to formula (I-e).

6. The lubricating composition according to claim **1** in which the compound comprising a phosphite group is selected from the phosphite monoesters, phosphite diesters or phosphite triesters, used alone or in a mixture.

7. The lubricating composition according to claim **6** in which the phosphite monoester has general formula (II-a) in its alcohol and/or ketone form, in which R_{19} represents a hydrocarbon-containing group, optionally substituted, of 1 to 30 carbon atoms:

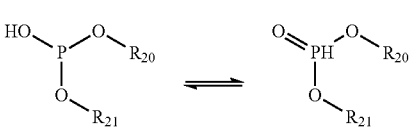
(II-a)



alcohol form ketone form

8. The lubricating composition according to claim **6** in which the phosphite diester has general formula (II-b) in its alcohol and/or ketone form, in which R_{20} and R_{21} represent independently of each other hydrocarbon-containing groups, optionally substituted, of 1 to 30 carbon atoms:

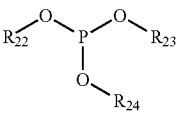
(II-b)



alcohol form ketone form

9. The lubricating composition according to claim **6** in which the phosphite triester has general formula (III-c) in which R_{22}, R_{23} and R_{24} represent independently of each other hydrocarbon-containing groups, optionally substituted, comprising from 1 to 30 carbon atoms:

(II-c)

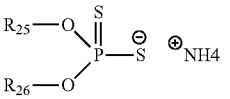


10. The lubricating composition according to claim **1** comprising from 0.1 to 5% by mass of compound comprising a phosphite group, relative to the total mass of lubricating composition.

11. The lubricating composition according to claim **1** in which the compound comprising a dithiophosphate group is selected from the group constituted by the ammonium dithiophosphates, amine dithiophosphates, dithiophosphate esters and metal dithiophosphates, used alone or in a mixture.

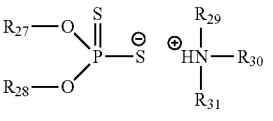
12. The lubricating composition according to claim **11** in which the ammonium dithiophosphate has general formula (III-a), in which R_{25} and R_{26} represent independently of each other hydrocarbon-containing groups, optionally substituted, comprising from 1 to 30 carbon atoms:

(III-a)



13. The lubricating composition according to claim **11** in which the amine dithiophosphate has general formula (III-b), in which R_{27} and R_{28} represent independently of each other hydrocarbon-containing groups, optionally substituted, comprising from 1 to 30 carbon atoms, R_{29}, R_{30} and R_{31} represent independently of each other a hydrogen atom or a hydrocarbon-containing group from 1 to 30 carbon atoms, it being understood that at least one of the R_{29}, R_{30} and R_{31} groups is not a hydrogen atom:

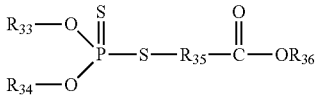
(III-b)



14. The lubricating composition according to claim **11** in which the dithiophosphate ester has general formula (III-c),

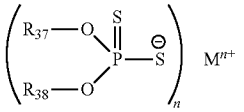
in which R_{33} and R_{34} represent independently of each other hydrocarbon-containing groups, optionally substituted, comprising from 1 to 30 carbon atoms, R_{35} and R_{36} represent independently of each other hydrocarbon-containing groups comprising from 1 to 18 carbon atoms:

(III-c)



15. The lubricating composition according to claim **11** in which the metal dithiophosphate has general formula (III-d), in which R_{37} and R_{38} represent independently of each other hydrocarbon-containing groups, optionally substituted, comprising from 1 to 30 carbon atoms, M represents a metal cation and n is the valency of this metal cation:

(III-d)



16. The lubricating composition according to claim **1** comprising from 0.1 to 5% by mass of compound comprising a dithiophosphate group, relative to the total mass of lubricating composition.

17. The lubricating composition according to claim **1** also comprising an antioxidant selected from the group formed by the aromatic amines or phenol derivatives.

18. The lubricating composition according to claim **1** also comprising a dispersant derived from polyisobutene.

19. The lubricating composition according to claim **1** also comprising a polymethacrylate-type polymer.

20. The lubricating composition according to claim **1** having a kinematic viscosity at 100° C. according to the standard ASTM D445 comprised between 4 and 40 cSt.

21. (canceled)

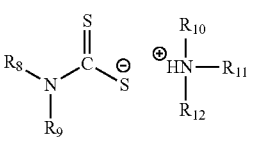
22. A method of using a lubricating composition according to claim **1** in order to reduce the fuel consumption of vehicles.

23. A method for lubricating a transmission of a motor vehicle, the method comprising a step of bringing a lubricating composition into contact with the motor vehicle transmission, the lubricating composition comprising:

at least one base oil, at least one compound comprising a dithiocarbamate group, at least one compound comprising a phosphite group and at least one compound comprising a dithiophosphate group, the compound comprising a dithiocarbamate group being a mixture of:

(a) at least one amine dithiocarbamate of general formula (I-c)

(I-c)



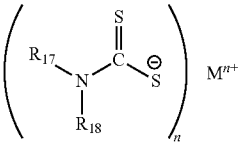
in which:

R_8 and R_9 represent independently of each other hydrocarbon-containing groups, optionally substituted, comprising from 1 to 30 carbon atoms,

R_{10}, R_{11} and R_{12} represent independently of each other a hydrogen atom or a hydrocarbon-containing group from 1 to 30 carbon atoms, it being understood that at least one of the R_{10}, R_{11} and R_{12} groups is not a hydro en atom; and

(b) at least one metal dithiocarbamate of general formula (I-e),

(I-e)

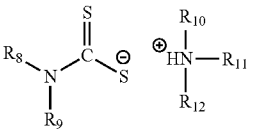


in which R_{17} and R_{18} represent independently of each other hydrocarbon-containing groups, optionally substituted, comprising from 1 to 30 carbon atoms, M represents a metal cation and n is the valency of this metal cation.

24. At least one compound comprising a dithiocarbamate group, at least one compound comprising a phosphite group and at least one compound comprising a dithiophosphate group in a base oil, at least one of the compounds comprising a dithiocarbamate group being a mixture of:

(a) at least one amine dithiocarbamate of general formula (I-c)

(I-c)



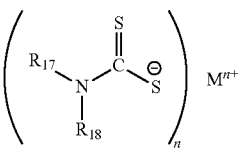
in which

R_8 and R_9 represent independently of each other hydrocarbon-containing groups, optionally substituted, comprising from 1 to 30 carbon atoms,

R_{10}, R_{11} and R_{12} represent independently of each other a hydrogen atom or a hydrocarbon-containing group from 1 to 30 carbon atoms, it being understood that at least one of the R_{10}, R_{11} and R_{12} groups is not a hydrogen atom; and

(b) at least one metal dithiocarbamate of general formula (I-e),

(I-e)



in which R_{17} and R_{18} represent independently of each other hydrocarbon-containing groups, optionally substituted,

comprising from 1 to 30 carbon atoms, M represents a metal cation and n is the valency of this metal cation; the compound improving wear, extreme-pressure, friction and anti-seizing properties of a lubricating composition.

* * * * *