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(54) Titre : COMPOSITIONS LUBRIFIANTES ANTI-USURE POUR UTILISATION DANS DES MOTEURS A COMBUSTION

(54) Title: ANTIWEAR LUBRICANT COMPOSITIONS FOR USE IN COMBUSTION ENGINES

(57) Abrégé/Abstract:
The invention relates to an additive composition, which comprises an additive mixture that essentially consists of a) At least one ammonium phosphate ester; b) At least one thiophosphoric acid ester; and c) At least one dithiophosphoric acid derivative; in combination with sulphur containing oil additives; and a process for the reduction of wear in combustion engines, such as spark ignition or Diesel motor engines.

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(54) Title: ANTIWEAR LUBRICANT COMPOSITIONS FOR USE IN COMBUSTION ENGINES

(57) Abstract: The invention relates to an additive composition, which comprises an additive mixture that essentially consists of a) At least one ammonium phosphate ester; b) At least one thiophosphoric acid ester; and c) At least one dithiophosphoric acid derivative; in combination with sulphur containing oil additives; and a process for the reduction of wear in combustion engines, such as spark ignition or Diesel motor engines.

Antiwear lubricant compositions for use in combustion engines

The present invention relates to a lubricant composition for use in combustion engines, an additive composition, which comprises an additive mixture that essentially consists of

a) At least one ammonium phosphate ester;

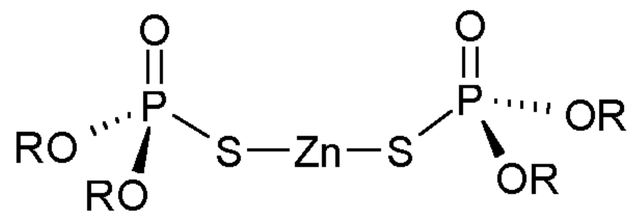
b) At least one thiophosphoric acid ester; and

c) At least one dithiophosphoric acid derivative.

This mixture is combined with sulphur containing oil additives. The invention also relates to a process for the reduction of wear in combustion engines.

It is known that additives improve the performance properties of lubricants, such as mineral oils or synthetic or semi-synthetic oils. Particularly additives are highly desirable which reduce the formation of oxidative degradation products and promote a long shelf life and high performance stability of lubricants.

Zinc dialkyl-/diaryldithiophosphates (ZnDTP)



are additives of first choice. Beside excellent antiwear and extreme pressure properties ZnDTP's are also efficient antioxidants and even metal passivators. These multifunctional properties make them the widest spread cost effective additive group that is used nowadays in huge quantities in engine oils, shock absorber oils and hydraulic fluids, cf. *Ullmann's Encyclopaedia of Industrial Chemistry,* **Lubricants and Lubrication,** Wiley-VCH Verlag, DOI: 10.1002/14356007.a15_423, Article Online Posting Date: January 15, 2002, and C. G. A. von Eberan-Eberhorst, R. S. Hexter, A. C. Clark, B. O'Connor, R. H. Walsh, Aschegebende Extreme-Pressure- und Verschleißschutz-Additive, in: W. J. Bartz (ed.): *Additive für Schmierstoffe,* Expert Verlag, 1994, pp. 53 – 83.

Various regulations issued by environmental government agencies in the European Community (EC), the U.S. and other countries require strict limitations with regard to the composition of exhaust fumes emitted from combustion motor engines that operate with self-ignition (Diesel motor engines) or spark ignition (Otto motor engines). In view of the fact that these exhaust fumes at present do not fulfil the environmental regulations, exhaust fume after treatment devices are installed.

These devices consist of porous membranes (particulate traps) or porous supports for catalysts, which deteriorate by the deposition of undesirable by-products in the form of ash particles produced by the combustion process. The activity of solid catalysts is particularly reduced by the interaction with solid phosphorus compounds as well as acidic sulphur compounds. These by-products, generally classified as ash, partially result from the presence of lubricant additives present in motor fuels and oils.

In order to minimize the negative impact of the lubricant additives, so-called low SAPS (**S**ulfated **A**sh, **P**hosphorus and **S**ulfur) engine oils are developed, e.g. Shigeki Takeshima, Nippon Corp., Development and durability of low SAPS diesel engine oils for passenger cars (JSAE Paper No. 20045277).

There is a tendency that the amount of ash producing detergents, phosphorus additives and ZnDTP is reduced in recently developed lubricant compositions. This invention therefore has for its object to provide substantially metal-free additives or additive combinations of low sulphur and phosphorus content, which approach the good antioxidative and wear protection of the zinc dialkyldithiophosphates used to date.

U.S. Patent Specification No. 5 531 911 describes zinc-free hydraulic fluids that comprise phosphorus- and sulphur-containing additive components. One component is a thiophosphoric acid ester of the triphenylthiophosphate type (IRGALUBE TPPT). This is combined with dithiophosphoric acid esters of the IRGALUBE 63 type and with other optional oil additive components, for example ammonium sulphonates.

WO 02/053687 discloses a lubricating oil composition comprising β–dithiophosphorylated propionic acid (A), 3-(O,O-diisopropyldithiophosphoryl)-2-methylpropionic acid, triaryl (Irgalube®353), triaryl phosphate (B) and base oil comprising mineral oil and/or synthetic oil.

EP-A-903 399 discloses hydraulic fluid compositions comprising thiophosphoric acid esters and dithiophosphoric acid esters or phosphoric acid thio esters and oil additives from the group of the polyol partial esters, amines and epoxides.

It has surprisingly been found that an additive mixture that essentially consists of

a) At least one ammonium phosphate ester;

b) At least one thiophosphoric acid ester; and

c) At least one dithiophosphoric acid derivative, in combination with additional sulphur containing oil additives;

is particularly useful for preparing a lubricant composition that has a low metal content and meets the requirements of low sulphur and phosphorus content.

The present invention relates to a lubricant composition for use in combustion engines comprising

A) An additive mixture that essentially consists of

a) At least one ammonium phosphate ester;

b) At least one thiophosphoric acid ester; and

c) At least one dithiophosphoric acid derivative;

B) At least one additional sulphur containing oil additive;

C) Customary crank case oil additives; and

D) Low sulphur oil of lubricating viscosity;

With the proviso that the total amount of sulphur in the composition is less than 0.3 weight%.

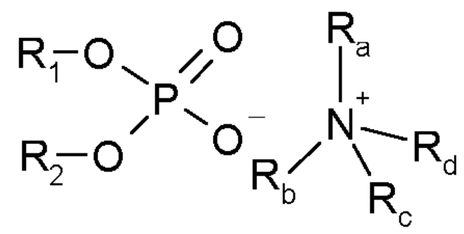
The compositions containing the additive mixture as specified above are characterized by their superior performance as compared with the corresponding compositions containing ZNDTP. This can be demonstrated in various commonly accepted tests, such as C&T P-VW 5106 (developed by VW (VAG)) and **P**ressurized **D**ifferential **S**canning **C**alorimetry (PDSC).

The compositions according to the instant invention are particularly suitable for use as lubricants having excellent antioxidative properties in internal combustion engines, such as spark-ignition internal combustion engines (popularly known as Otto motor engines) or self-ignition internal combustion engines (popularly known as Diesel motor engines).

The compositions are particularly suitable as motor oils which meet the classifications of the API (**A**merican **P**etroleum **I**nstitute: 1120L Str. NW, Washington DC, USA), the S- and C-categories (e.g. SM, CE, as described in ASTM D 4485), the GF-categories defined by ILSAC (**I**nternational **L**ubricant **S**tandardization and **A**pproval **C**ommittee, published by API) and to the A, B, C and E specifications issued by ACEA (European Automobile Manufacturers Association, Rue du Noyer 211, B-1000 Bruxelles BE).

A preferred embodiment of the invention relates to a lubricant composition, wherein the additive mixture A) essentially consists of

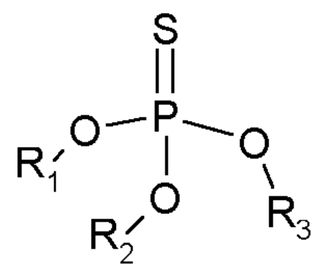
a) At least one ammonium phosphate ester of the formula



one of R_1 and R_2 represents hydrogen and the other one represents a C_1-C_{20}hydrocarbon radical; or

Both R_1 and R_2 represent C_1-C_{20}hydrocarbon radicals; and R_a, R_b, R_c and R_d independently of one another represent hydrogen or C_6-C_{20}hydrocarbon radicals;

b) At least one thiophosphoric acid ester of the formula



A particularly preferred embodiment of the invention relates to a lubricant composition, wherein the additive mixture A) consists essentially of

a) At least one ammonium phosphate ester (I), wherein one of R_1 and R_2 represents hydrogen and the other one represents C_3-C_{18}alkyl; or both R_1 and R_2 represent C_3-C_{18}alkyl; and R_a, R_b, R_c and R_d independently of one another represent hydrogen or C_6-C_{20}alkyl;

b) At least one thiophosphoric acid ester (II), wherein R_1, R_2 and R_3 independently of one another represent phenyl or C_7-C_{24}alkylphenyl; and

c) At least one dithiophosphoric acid derivative selected from the group consisting of a 3-dithiophosphorylpropionic acid (III), wherein R_1 and R_2 represent C_3-C_{18}alkyl and R_3 represents hydrogen or methyl, and an ammonium salt of a dithiophosphoric acid (IV), wherein R_1 and R_2 represent C_3-C_{18}alkyl and R_a, R_b, R_c and R_d independently of one another represent hydrogen or C_6-C_{20}alkyl.

A highly preferred embodiment of the invention relates to a lubricant composition, wherein the additive mixture A) consists essentially of

a) At least one ammonium phosphate ester (I), wherein one of R_1 and R_2 represents hydrogen and the other one represents C_3-C_9alkyl; or both R_1 and R_2 represent C_3-C_9alkyl; and R_a, R_b, R_c and R_d independently of one another represent hydrogen or C_{12}-C_{20}alkyl;

b) At least one thiophosphoric acid ester (II), wherein R_1, R_2 and R_3 independently of one another represent phenyl or $(C_1$-C_9alkyl$)_{1-3}$phenyl; and

c) At least one dithiophosphoric acid derivative selected from the group consisting of a 3-dithiophosphorylpropionic acid (III), wherein R_1 and R_2 represent 2-methylpropyl and R_3 represents methyl, and an ammonium salt of a dithiophosphoric acid (IV), wherein R_1 and R_2 represent isopropyl and R_a, R_b, R_c and R_d independently of one another represent hydrogen or C_{12}-C_{20}alkyl.

A highly preferred embodiment of the invention relates to a lubricant composition, wherein the additive mixture A) consists essentially of

a) At least one ammonium phosphate ester (I), wherein one of R_1 and R_2 represents hydrogen and the other one represents C_3-C_9alkyl; or both R_1 and R_2 represent represents C_3-C_9alkyl; and R_a, R_b, R_c and R_d independently of one another represent hydrogen or C_{12}-C_{20}alkyl;

b) At least one thiophosphoric acid ester (II), wherein

R_1, R_2 and R_3 represent phenyl; or

one of R_1, R_2 and R_3 represents phenyl and two of R_1, R_2 and R_3 represent $(C_1\text{-}C_9alkyl)_{1\text{-}3}phenyl$; or

two of R_1, R_2 and R_3 represent phenyl and one of R_1, R_2 and R_3 represents $(C_1\text{-}C_9alkyl)_{1\text{-}3}phenyl$; or

R_1, R_2 and R_3 represent $(C_1\text{-}C_9alkyl)_{1\text{-}3}phenyl$; and

c) At least one 3-dithiophosphorylpropionic acid (III), wherein R_1 and R_2 represent 2-methylpropyl and R_3 represents methyl.

Component A

The additive mixture present in the Component A) consists of at least three different phosphate, thiophosphate or dithiophosphate additives.

The phosphate component a) of that mixture is an ammonium phosphate ester, such as the one represented by the formula (I) of above, wherein one of R_1 and R_2 represents hydrogen and the other one represents a $C_1\text{-}C_{20}$hydrocarbon radical; or both R_1 and R_2 represent $C_1\text{-}C_{20}$hydrocarbon radicals; and R_a, R_b, R_c and R_d independently of one another represent hydrogen or $C_6\text{-}C_{20}$hydrocarbon radicals.

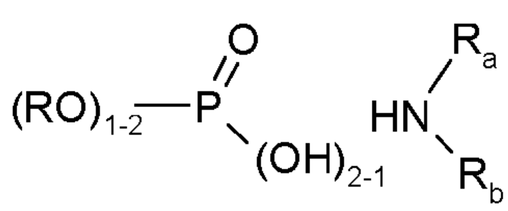
According to a preferred embodiment one of R_1 and R_2 represents hydrogen and the other one represents $C_3\text{-}C_{18}$alkyl; or both R_1 and R_2 represent $C_3\text{-}C_{18}$alkyl; and R_a, R_b, R_c and R_d independently of one another represent hydrogen or $C_6\text{-}C_{20}$alkyl.

According to a particularly preferred embodiment one of R_1 and R_2 represents hydrogen and the other one represents $C_3\text{-}C_9$alkyl; or both R_1 and R_2 represent $C_3\text{-}C_9$alkyl; and R_a, R_b, R_c and R_d independently of one another represent hydrogen or $C_{12}\text{-}C_{20}$alkyl.

A $C_1\text{-}C_{20}$hydrocarbon radical R_1 and R_2 is preferably $C_1\text{-}C_{20}$alkyl, e.g. methyl, ethyl or straight chained or branched $C_3\text{-}C_{30}$alkyl, e.g. n-propyl, isopropyl, n-, iso- or tert-butyl, n-pentyl, isoamyl, neopentyl, 2-ethylbutyl, n-hexyl, 1-methylpentyl, 1,3-dimethylbutyl, n-heptyl, isoheptyl, n-octyl, 1,4,4-trimethyl2-pentyl, 3,4-, 3,5- or 4,5-dimethyl-1-hexyl, 3- or 5-methyl-1-heptyl, 1,1,3,3-tetramethylbutyl, 2-ethylhexyl, branched octyl as obtained from a dimer of isobutylene, n-nonyl, 1,1,3-trimethylhexyl, branched nonyl as obtained from a trimer of tripropylene, 1-methylundecyl, 2-n-butyl-n-octyl, branched dodecyl obtained from a trimer of isobutylene or a tetramer of propylene, branched pentadecyl obtained from a pentamer of propylene, 2-n-hexyl-n-decyl or 2-n-octyl-n-dodecyl.

R_a, R_b, R_c and R_d defined as C_6-C_{20}alkyl have the same meanings as R_1 and R_2 defined above with regard to alkyl groups of 6-20 carbon atoms.

Ammonium phosphate esters as represented by the formula (I) are known compounds and can be prepared by known methods. Many of them are commercially available, such as the product Irgalube® (trade mark of Ciba Specialty Chemicals AG) 349:



Wherein R represents C_3-C_{18}alkyl and R_a and R_b represent C_6-C_{20}alkyl, such as products named as amines, C11-14-branched alkyl, monohexyl and dihexyl phosphates.

Other ammonium phosphate esters present in the composition according to the invention are available commercially by Rheinchemie Rheinau GmbH Mannheim Germany, such as the products Additin® RC 3740, RC 3741 or RC 3760 (amine neutralized phosphoric acid ester of aliphatic alcohols).

The thiophosphate component b) of the additive mixture is a thiophosphoric acid ester, such as the one of the formula (II) of above, wherein R_1, R_2 and R_3 represent C_3-C_{20}hydrocarbon radicals.

According to a preferred embodiment R_1, R_2 and R_3 independently of one another represent phenyl or C_7-C_{20}alkylphenyl.

According to a particularly preferred embodiment, R_1, R_2 and R_3 independently of one another represent phenyl or $(C_1$-C_9alkyl$)_{1-3}$phenyl.

According to a highly preferred embodiment, R_1, R_2 and R_3 independently of one another represent R_1, R_2 and R_3 represent phenyl; or

one of R_1, R_2 and R_3 represents phenyl and two of R_1, R_2 and R_3 represent $(C_1$-C_9alkyl$)_{1-3}$phenyl; or

two of R_1, R_2 and R_3 represent phenyl and one of R_1, R_2 and R_3 represents $(C_1$-C_9alkyl$)_{1-3}$phenyl; or

R_1, R_2 and R_3 represent $(C_1$-C_9alkyl$)_{1-3}$phenyl.

C_3-C_{20}Hydrocarbon radicals R_1, R_2 and R_3 are preferably C_3-C_{20}alkyl, C_5-C_{12}cycloalkyl, C_5-C_{12}cycloalkyl-C_1-C_4alkyl, phenyl, C_7-C_{20}alkylphenyl, C_7-C_{20}alkoxyphenyl, naphthyl and C_7-C_9phenylalkyl.

C_3-C_{20}Alkyl is, e.g., n-nonyl, 1,1,3-trimethylhexyl, n-decyl, n-undecyl, n-dodecyl, 1-methylundecyl, n-tridecyl, n-tetradecyl, n-pentadecyl, n-hexadecyl, n-heptadecyl and n-octadecyl. An especially preferred radical for R_1, R_2 and R_3 is isopropyl. The meanings of R_1, R_2 and R_3 may be the same or different.

Thiophosphoric acid esters of formula II are known, for example from *U.S. Patent Specification 5,531,911*. Many of them are commercially available.

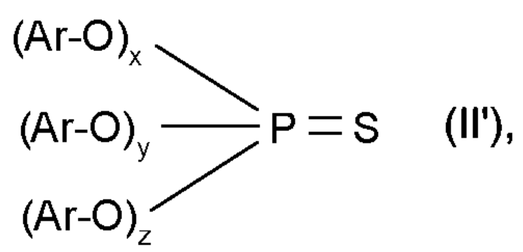
C_5-C_{12}Cycloalkyl is, e.g., cyclopentyl or cyclohexyl. C_5-C_{12}Cycloalkyl-C_1-C_4alkyl is, e.g. cyclopentylmethyl, 2-cyclopentylethyl, cyclohexylmethyl or 2-cyclohexylethyl.

C_7-C_{20}Alkylphenyl is phenyl that is substituted, for example, by from one to three of the C_1-C_4alkyl radicals described above or by one or two C_1-C_6alkyl radicals or one C_1-C_{12}alkyl radical.

C_7-C_{20}Alkoxyphenyl is phenyl that is substituted, for example, by from one to three C_1-C_4-alkoxy radicals, especially methoxy or ethoxy, or by one or two C_1-C_6alkoxy radicals or one C_1-C_{12}alkoxy radical, those radicals being analogous to the alkyl radicals mentioned hereinabove.

C_7-C_9Phenylalkyl is, e.g. benzyl, 1-phenyl-1-ethyl or 2-phenyl-1-ethyl.

In a preferred embodiment of the invention, component b) consists of a mixture of thiophosphoric acid esters of formula:

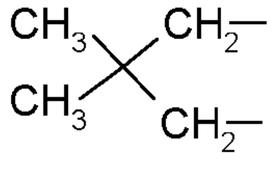


(II'),

wherein x is from 0 to 2.7, y is 3 - (x + z), z is from 0 to 3 - (x + y) and x + y + z = 3, and Ar is phenyl, C_7-C_{18}alkylphenyl, C_7-C_{18}alkoxyphenyl, naphthyl or C_7-C_9phenylalkyl as defined above. The preparation of those thiophosphoric acid esters is described in *EP-A-368 803*. Preferred thiophosphoric acid esters of formula I' are triarylthiophosphate mixtures of the IRGALUBE 211 type comprising substances, such as n-decylphenyl-n-nonylphenyl-phenylthiophosphate, o-tert-butylphenyl-o-isopropylphenyl-phenylthiophosphate, or n-hexylphenylphenylthiophosphate mixtures.

In a further preferred embodiment of the invention, component b) consists of a thiophosphoric acid ester of the triphenylthiophosphate type (IRGALUBE TPPT), such as O,O,O-tris(2(or4)-C9-10-isoalkylphenyl)phosphorothioate.

The dithiophosphate component c) of the additive mixture is a dithiophosphoric acid derivative, such as the one of the formula (III) or (IV). In a compound (III) R_1 and R_2 independently of one another represent C_3-C_{18}alkyl, C_5-C_{12}cycloalkyl, C_9-C_{10}bicycloalkylmethyl, C_9-C_{10}tricycloalkylmethyl, phenyl or C_7-C_{24}alkylphenyl; or R_1 and R_2 together represent the group:



; and

R_3 represents hydrogen or methyl, preferably hydrogen.

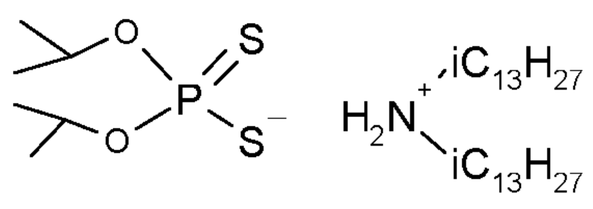
R_1 and R_2 defined as C_3-C_{18}alkyl are, with preference, isopropyl, isobutyl or 2-ethylhexyl. Other groups include n-propyl, n- or tert-butyl, n-pentyl, isoamyl, neopentyl, 2-ethylbutyl, n-hexyl, 1-methylpentyl, 1,3-dimethylbutyl, n-heptyl, isoheptyl, n-octyl, 1,4,4-trimethyl-2-pentyl, 3,4-, 3,5- or 4,5-dimethyl-1-hexyl, 3- or 5-methyl-1-heptyl, 1,1,3,3-tetramethylbutyl, branched octyl as obtained from a dimer of isobutylene, n-nonyl, 1,1,3-trimethylhexyl, branched nonyl as obtained from a trimer of tripropylene.

The groups C_5-C_{12}cycloalkyl, C_9-C_{10}bicycloalkylmethyl, C_9-C_{10}tricycloalkylmethyl, C_7-C_{24}alkylphenyl are the ones as specified in *U.S. Patent Specification No.5,922,657*.

Compounds (III) are known, e.g. from *U.S. 5,922,657*.

In ammonium salt of a dithiophosphoric acid of the formula (IV) R_1 and R_2 are as defined with regard to the formula (III) and R_a, R_b, R_c and R_d independently of one another represent hydrogen or C_6-C_{20}hydrocarbon radicals. R_a, R_b, R_c and R_d defined as C_6-C_{20}alkyl have the same meanings as R_a, R_b, R_c and R_d defined above with regard to the ammonium phosphates (I) and the alkyl groups of 6-20 carbon atoms.

A particularly preferred embodiment relates to the ammonium salt of a dithiophosphoric acid of the formula:



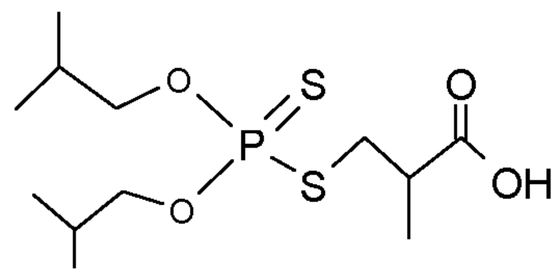
(XPDL 613),

such as O,O-diisopropyl hydrogen dithiophosphate alkyl amine.

According to a particularly preferred embodiment, the dithiophosphoric acid derivative is selected from the group consisting of a 3-dithiophosphorylpropionic acid (III), wherein R_1 and R_2 represent C_3-C_{18}alkyl and R_3 represents hydrogen or methyl, and an ammonium salt of a dithiophosphoric acid (IV), wherein R_1 and R_2 represent C_3-C_{18}alkyl and R_a, R_b, R_c and R_d independently of one another represent hydrogen or C_6-C_{20}alkyl.

According to a highly preferred embodiment, the dithiophosphoric acid derivative is selected from the group consisting of a 3-dithiophosphorylpropionic acid (III), wherein R_1 and R_2 represent C_3-C_{18}alkyl and R_3 represents hydrogen or methyl, and an ammonium salt of a dithiophosphoric acid (IV), wherein R_1 and R_2 represent C_3-C_{18}alkyl and R_a, R_b, R_c and R_d independently of one another represent hydrogen or C_6-C_{20}alkyl.

A highly preferred embodiment relates to 3-dithiophosphoryl-2-methylpropionic acid (III), such as 3-[[bis(2-methylpropoxy)phosphinothioyl]thio]-2-methylpropanoic acid:



This compound is commercially available and marketed under the trademark IRGALUBE 353.

In a preferred embodiment of the invention, the phosphorus content of components a), b) and c) in the additive mixture defined, based on the composition is less than 800 ppm. In an especially preferred embodiment, the phosphorus content is from 400 to 800 ppm, especially from 300 to 700 ppm. The ratio by weight of component b) to component c) may vary within the ranges of approximately from 10 : 10 : 80 and 80 : 10: 10 to 10 : 80 : 10% by weight.

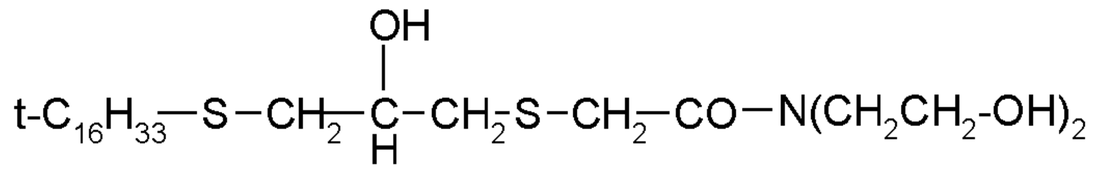
Although the total content of the Component A) in the composition is not critical, the preferred total content of component A) in the composition is in the range between 1.0 and 0.001, preferably 0.1 and 0.01 percent by weight, based on the total weight of the composition, or, preferably, between 0.01 and 0.1%, as expressed by the total phosphorus content in the composition.

Component B

The lubricant composition according to the invention, which is suitable for use in combustion engines comprises the Component A) defined above, wherein an additive mixture is present that essentially consists of

a) At least one ammonium phosphate ester;
b) At least one thiophosphoric acid ester; and
c) At least one dithiophosphoric acid derivative.

This additive mixture is combined with at least one additional sulphur containing oil additive. Various sulphur containing oil additives are suitable. Preferred is a dithioglycidyl ether selected from the group consisting of



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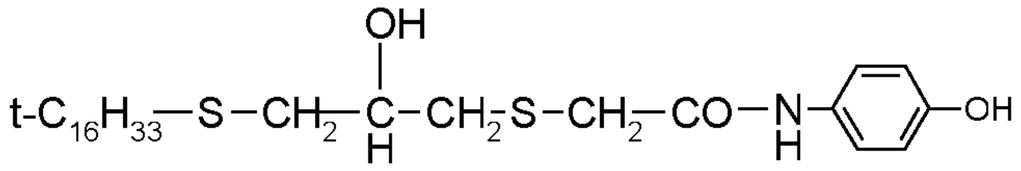

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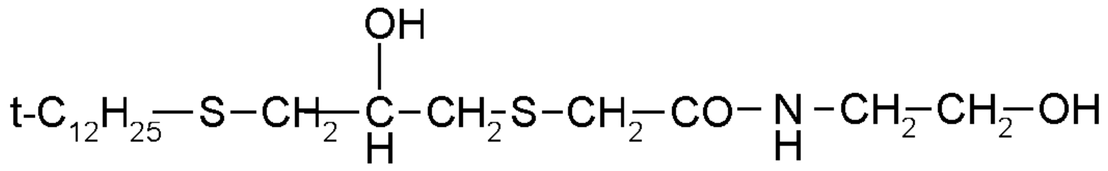

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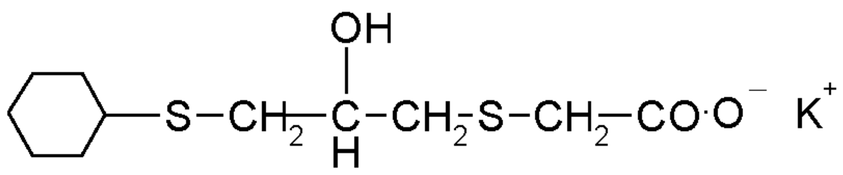

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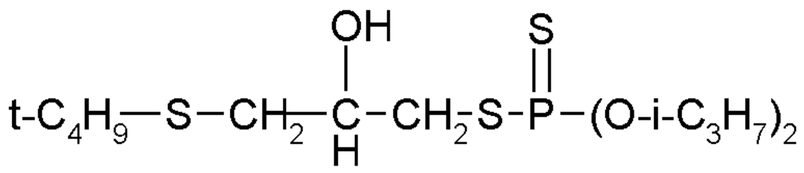

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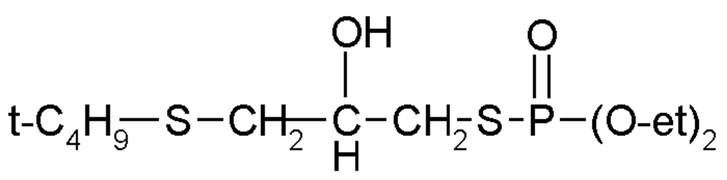

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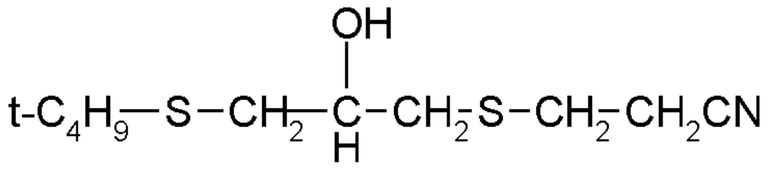

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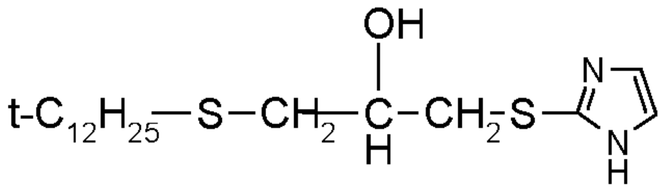

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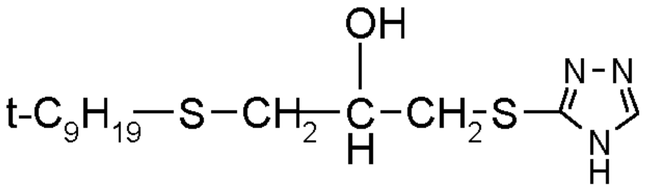

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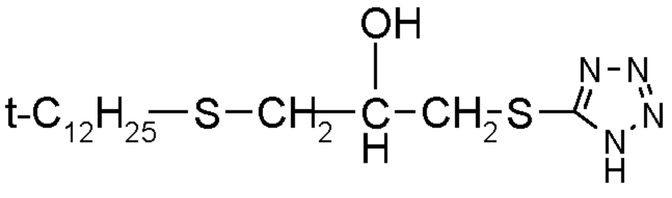

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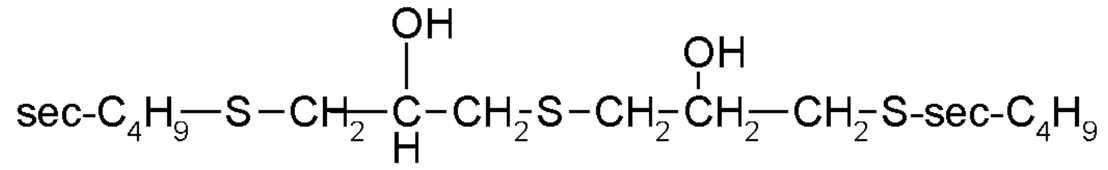

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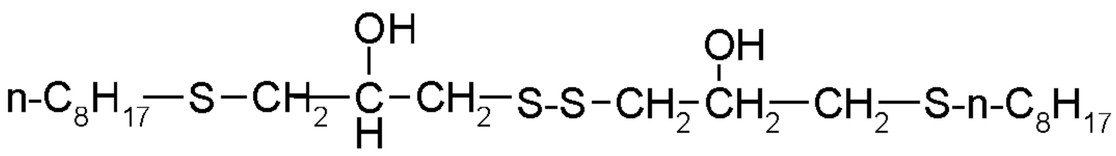

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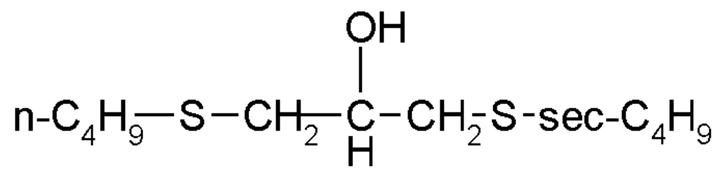

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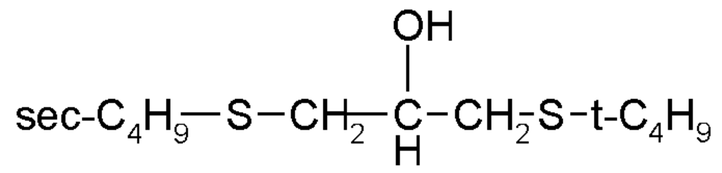

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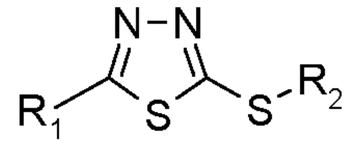
These compounds are known. Their preparation is described in the published *European Patent Application No. 0 166 696*. According to another embodiment the additional sulphur containing oil additive B) is a polyalkylated 1,3,4-thiadiazole compound of the formula



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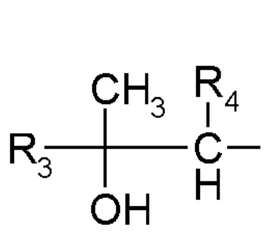
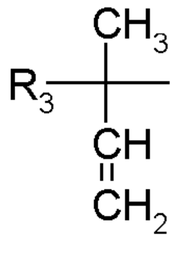
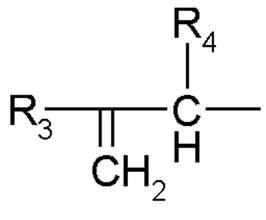
Wherein R_1 represents hydroxy, amino, mercapto, alkylthio, 2-hydroxyalkylthio or the R_2-S group and R_2 represents a polyolefin residue represented by the partial formulae:

 or isomeric  and  , wherein R_3 represents alkyl having 50 to 400 carbon atoms and R_4 represents hydrogen or methyl.

The polyalkylated 1,3,4-thiadiazole compounds described above are known compounds. Their preparation is described in the published *European Patent Application No. 0 406 517*.

A particularly preferred compound is C9-alkyldithiothiadiazole, which is commercially available marketed under the trademark Hitec® 4313.

Environmental regulations issued by various government agencies prescribe that the total amount of sulphur in the composition is less than 0.3%, preferably 0.2% by weight. The additive combination described above is added to the fuel that a content of less than 0.10%, preferably less than 0.05% and particularly less than 0.01%, by weight of sulphur is present.

Component C

The composition according to the invention comprises at least one additional customary oil additive in addition to the components A) and B). Such additives include: further antioxidants, metal passivators, rust inhibitors, viscosity index enhancers, pour-point depressants, dispersants, detergents, further extreme-pressure additives and anti-wear additives. Such additives are added in the amounts customary for each of them, which range in each case approximately from 0.01 to 10.0 %, preferably 0.1 to 1.0 %, by weight. Examples of further additives are given below:

1. Phenolic/ aminic antioxidants:

1.1 Alkylated monophenols: 2,6-di-tert-butyl-4-methylphenol, 2-butyl-4,6-dimethylphenol, 2,6-di-tert-butyl-4-ethylphenol, 2,6-di-tert-butyl-4-n-butylphenol, 2,6-di-tert-butyl-4-iso-butylphenol, 2,6-dicyclopentyl-4-methylphenol, 2-(α-methylcyclohexyl)-4,6-dimethyl-phenol, 2,6-dioctadecyl-4-methylphenol, 2,4,6-tricyclohexylphenol, 2,6-di-tert-butyl-4-methoxymethylphenol, linear nonylphenols or nonylphenols branched in the side chain, such as, for example, 2,6-dinonyl-4-methylphenol, 2,4-dimethyl-6-(1'-methyl-undec-1'-yl)-phenol, 2,4-dimethyl-6-(1'-methylheptadec-1'-yl)-phenol, 2,4-dimethyl-6-(1'-methyl-tridec-1'-yl)-phenol and mixtures thereof

1.2 Alkylthiomethylphenols: 2,4-dioctylthiomethyl-6-tert-butylphenol, 2,4-dioctylthiomethyl-6-methylphenol, 2,4-dioctylthiomethyl-6-ethylphenol, 2,6-didodecylthiomethyl-4-nonyl-phenol

1.3 Hydroquinones and alkylated hydroquinones: 2,6-di-tert-butyl-4-methoxyphenol, 2,5-di-tert-butylhydroquinone, 2,5-di-tert-amylhydroquinone, 2,6-diphenyl-4-octadecyloxy-phenol, 2,6-di-tert-butylhydroquinone, 2,5-di-tert-butyl-4-hydroxyanisole, 3,5-di-tert-butyl-4-hydroxyanisole, 3,5-di-tert-butyl-4-hydroxyphenyl stearate, bis(3,5-di-tert-butyl-4-hydroxyphenyl)adipate

1.4 Tocopherols: α-, β-, γ- or δ-tocopherol and mixtures thereof (vitamin E)

1.5 Hydroxylated thiodiphenyl ethers: 2,2'-thio-bis(6-tert-butyl-4-methylphenol), 2,2'-thio-bis(4-octylphenol), 4,4'-thio-bis(6-tert-butyl-3-methylphenol), 4,4'-thio-bis(6-tert-butyl-2-methylphenol), 4,4'-thio-bis(3,6-di-sec-amylphenol), 4,4'-bis(2,6-dimethyl-4-hydroxy-phenyl)disulphide

1.6 Alkylidene bisphenols: 2,2'-methylene-bis(6-tert-butyl-4-methylphenol), 2,2'-methyl-ene-bis(6-tert-butyl-4-ethylphenol), 2,2'-methylene-bis[4-methyl-6-(α-methylcyclo-hexyl)phenol], 2,2'-methylene-bis(4-methyl-6-cyclohexylphenol), 2,2'-methylene-bis(6-nonyl-4-methylphenol), 2,2'-methylene-bis(4,6-di-tert-butylphenol), 2,2'-ethylidene-bis(4,6-di-tert-butylphenol), 2,2'-ethylidene-bis(6-tert-butyl-4-isobutylphenol), 2,2'-me-thylene-bis[6-(α-methylbenzyl)-4-nonylphenol], 2,2'-methylene-bis[6-(α,α-dimethylben-zyl)-4-nonylphenol], 4,4'-methylene-bis(2,6-di-tert-butylphenol), 4,4'-methylene-bis(6-tert-butyl-2-methylphenol), 1,1-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)butane, 2,6-bis(3-tert-butyl-5-methyl-2-hydroxybenzyl)-4-methylphenol, 1,1,3-tris(5-tert-butyl-4-hy-droxy-2-methylphenyl)butane, 1,1-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)-3-n-do-decylmercaptobutane, ethylene glycol bis[3,3-bis(3'-tert-butyl-4'-hydroxyphenyl)bu-tyrate], bis(3-tert-butyl-4-hydroxy-5-methylphenyl)dicyclopentadiene, bis[2-(3'-tert-butyl-

2'-hydroxy-5'-methylbenzyl)-6-tert-butyl-4-methylphenyl]terephthalate, 1,1-bis(3,5-dimethyl-2-hydroxyphenyl)butane, 2,2-bis(3,5-di-tert-butyl-4-hydroxyphenyl)propane, 2,2-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)-4-n-dodecylmercaptobutane, 1,1,5,5-tetra(5-tert-butyl-4-hydroxy-2-methylphenyl)pentane

1.7 O-, N- and S-benzyl compounds: 3,5,3',5'-tetra-tert-butyl-4,4'-dihydroxydibenzyl ether, octadecyl-4-hydroxy-3,5-dimethylbenzyl-mercaptoacetate, tridecyl-4-hydroxy-3,5-di-tert-butylbenzyl-mercaptoacetate, tris(3,5-di-tert-butyl-4-hydroxybenzyl)amine, bis(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)dithioterephthalate, bis(3,5-di-tert-butyl-4-hydroxybenzyl)sulphide, isooctyl-3,5-di-tert-butyl-4-hydroxybenzyl-mercaptoacetate

1.8 Hydroxybenzylated malonates: dioctadecyl-2,2-bis(3,5-di-tert-butyl-2-hydroxybenzyl)malonate, dioctadecyl-2-(3-tert-butyl-4-hydroxy-5-methylbenzyl)malonate, didodecylmercaptoethyl-2,2-bis(3,5-di-tert-butyl-4-hydroxybenzyl)malonate, di[4-(1,1,3,3-tetramethylbutyl)-phenyl]-2,2-bis(3,5-di-tert-butyl-4-hydroxybenzyl)malonate

1.9 Hydroxybenzyl aromatic compounds: 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)-2,4,6-trimethylbenzene, 1,4-bis(3,5-di-tert-butyl-4-hydroxybenzyl)-2,3,5,6-tetramethylbenzene, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)phenol;

1.10 Triazine compounds: 2,4-bis-octylmercapto-6-(3,5-di-tert-butyl-4-hydroxyanilino)-1,3,5-triazine, 2-octylmercapto-4,6-bis(3,5-di-tert-butyl-4-hydroxyanilino)-1,3,5-triazine, 2-octylmercapto-4,6-bis(3,5-di-tert-butyl-4-hydroxyphenoxy)-1,3,5-triazine, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxyphenoxy)-1,2,3-triazine, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)isocyanurate, 1,3,5-tris(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)isocyanurate, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxyphenylethyl)-1,3,5-triazine, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hexahydro-1,3,5-triazine, 1,3,5-tris(3,5-dicyclohexyl-4-hydroxybenzyl)isocyanurate

1.11 Acylaminophenols: 4-hydroxylauric acid anilide, 4-hydroxystearic acid anilide, N-(3,5-di-tert-butyl-4-hydroxyphenyl)-carbamic acid octyl ester

1.12 Esters of β-(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid: with mono- or polyhydric alcohols, e.g. with methanol, ethanol, n-octanol, isooctanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl)isocyanurate, N,N'-bis(hydroxyethyl)oxalic acid diamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane

1.13 Esters of β-(5-tert-butyl-4-hydroxy-3-methylphenyl)propionic acid: with polyhydric

alcohols, e.g. with 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl)isocyanurate, N,N'-bis(hydroxyethyl)oxalic acid diamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane

1.14 Esters of β-(3,5-dicyclohexyl-4-hydroxyphenyl)propionic acid: with mono- or polyhydric alcohols, e.g. with methanol, ethanol, octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl)isocyanurate, N,N'-bis(hydroxyethyl)oxalic acid diamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]-octane

1.15 Esters of 3,5-di-tert-butyl-4-hydroxyphenylacetic acid: with mono- or polyhydric alcohols, e.g. with methanol, ethanol, octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl)isocyanurate, N,N'-bis(hydroxyethyl)oxalic acid diamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane

1.16 Amides of β-(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid: N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hexamethylenediamine, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)trimethylenediamine, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hydrazine

1.17 Ascorbic acid (vitamin C)

1.18 Aminic antioxidants: N,N'-diisopropyl-p-phenylenediamine, N,N'-di-sec-butyl-p-phenylenediamine, N,N'-bis(1,4-dimethylpentyl)-p-phenylenediamine, N,N'-bis(1-ethyl-3-methylpentyl)-p-phenylenediamine, N,N'-bis(1-methylheptyl)-p-phenylenediamine, N,N'dicyclohexyl-p-phenylenediamine, N,N'-diphenyl-p-phenylenediamine, N,N'-di(naphth-2-yl)-p-phenylenediamine, N-isopropyl-N'-phenyl-p-phenylenediamine, N-(1,3dimethylbutyl)-N'-phenyl-p-phenylenediamine, N-(1-methylheptyl)-N'-phenyl-p-phenylenediamine, N-cyclohexyl-N'-phenyl-p-phenylenediamine, 4-(p-toluenesulphonamido)-diphenylamine, N,N'-dimethyl-N,N'-di-sec-butyl-p-phenylenediamine, diphenylamine, N-allyldiphenylamine, 4-isopropoxydiphenylamine, 4-n-butylaminophenol, 4-butyrylaminophenol, 4-nonanoylaminophenol, 4-dodecanoylaminophenol, 4-octadecanoylaminophenol, di(4-methoxyphenyl)amine, 2,6-di-tert-butyl-4-dimethylami-

nomethyl phenol, 2,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylmethane, N,N,N',N'-tetramethyl-4,4'-diaminodiphenylmethane, 1,2-di[(2-methylphenyl)amino]-ethane, 1,2-di(phenylamino)propane, (o-tolyl)biguanide, di[4-(1',3'-dimethylbutyl)-phenyl]amine, tert-octylated N-phenyl-1-naphthylamine, mixture of mono- and di-alkylated tert-butyl/tert-octyl-diphenylamines, mixture of mono- and di-alkylated nonyldiphenylamines, mixture of mono- and di-alkylated dodecyldiphenylamines, mixture of mono- and di-alkylated isopropyl/isohexyl-diphenylamines, mixtures of mono- and di-alkylated tert-butyldiphenylamines, 2,3-dihydro-3,3-dimethyl-4H-1,4-benzothiazine, phenothiazine, mixture of mono- and di-alkylated tert-butyl/tert-octyl-phenothiazines, mixtures of mono- and di-alkylated tert-octylphenothiazines, N-allylphenothiazine, N,N,N',N'-tetraphenyl-1,4-diaminobut-2-ene, N,N-bis(2,2,6,6-tetramethylpiperidin-4-yl)hexamethylenediamine, bis(2,2,6,6-tetramethylpiperidin-4-yl)sebacate, 2,2,6,6-tetramethylpiperidin-4-one, 2,2,6,6-tetramethylpiperidin-4-ol

2. <u>Further Antioxidants</u>

2.1 Aliphatic or aromatic phosphites, esters of thiodipropionic acid or thiodiacetic acid or salts of dithiocarbamic acid, 2,2,12,12-tetramethyl-5,9-dihydroxy-3,7,11-trithiatridecane and 2,2,15,15-tetramethyl-5,12-dihydroxy-3,7,10,14-tetrathiahexadecane

2.2 <u>Sulphur-containing heterocyclic compounds:</u> 2-mercaptobenzothiazole, 2,5-dimercapto-1,3,4-thiadiazole, 2,5-dimercaptobenzothiadiazole and derivatives thereof; 3,5-bis[di(2-ethylhexyl)aminomethyl]-1,3,4-thiadiazolin-2-one

2.3 <u>Amino compounds:</u> salicylidene-propylenediamine, salicylaminoguanidine and salts thereof

<u>3. Corrosion Inhibitors</u>

<u>3.1 Organic acids, their esters, metal salts, amine salts and anhydrides:</u> alkyl- and alkenyl-succinic acids and their partial esters with alcohols, diols or hydroxycarboxylic acids, partial amides of alkyl- and alkenyl-succinic acids, 4-nonylphenoxyacetic acid, alkoxy- and alkoxyethoxy-carboxylic acids, such as dodecyloxyacetic acid, dodecyloxy(ethoxy)acetic acid and amine salts thereof, and also N-oleoyl-sarcosine, sorbitan monooleate, lead naphthenate, alkenylsuccinic acid anhydrides, e.g. dodecenylsuccinic acid anhydride, 2-(2-carboxyethyl)-1-dodecyl-3-methylglycerol and salts thereof, especially sodium and triethanolamine salts thereof

<u>3.2 Nitrogen-containing compounds</u>:

<u>3.2.1</u> Tertiary aliphatic or cycloaliphatic amines and amine salts of organic and inorganic acids, e.g. oil-soluble alkylammonium carboxylates, and 1-[N,N-bis(2-hy-

droxyethyl)amino]-3-(4-nonylphenoxy)propan-2-ol

3.2.2 Heterocyclic compounds: substituted imidazolines and oxazolines, e.g. 2-heptadecenyl-1-(2-hydroxyethyl)-imidazoline

3.2.3 Sulphur-containing compounds: barium dinonylnaphthalene sulphonates, calcium petroleum sulphonates, alkylthio-substituted aliphatic carboxylic acids, esters of aliphatic 2-sulphocarboxylic acids and salts thereof

4. Viscosity Index Increasers

Polyacrylates, polymethacrylates, vinylpyrrolidone/methacrylate copolymers, polyvinylpyrrolidones, polybutenes, olefin copolymers, styrene/acrylate copolymers, polyethers

5. Pour point Depressants

Poly(meth)acrylates, ethylene/vinyl acetate copolymers, alkylpolystyrenes, fumarate copolymers, alkylated naphthalene derivatives

6. Dispersants/Surfactants

Succinic acid amides or imides, polybutenylphosphonic acid derivatives, basic magnesium, calcium and barium sulphonates and phenolates

7. Extreme-pressure and anti-wear additives

Sulphur- and halogen-containing compounds, e.g. chlorinated paraffins, sulphurated olefins or vegetable oils (soybean oil, rape oil), alkyl- or aryl-di- or -tri-sulphides, benzotriazoles or derivatives thereof, such as bis(2-ethylhexyl)aminomethyl tolutriazoles, dithiocarbamates, such as methylene-bis-dibutyldithiocarbamate, derivatives of 2-mercaptobenzothiazole, such as 1-[N,N-bis(2-ethylhexyl)aminomethyl]-2-mercapto-1H-1,3-benzothiazole, derivatives of 2,5-dimercapto-1,3,4-thiadiazole, such as 2,5-bis(tert-nonyldithio)-1,3,4-thiadiazole

8. Examples of coefficient of friction reducers

Lard oil, oleic acid, tallow, rape oil, sulphurated fats, amides, amines. Further examples are given in EP-A-0 565 487.

9. Special additives

Emulsifiers: petroleum sulphonates, amines, such as polyoxyethylated fatty amines, nonionic surface-active substances; buffers: such as alkanolamines; biocides: triazines, thia-

zolinones, tris-nitromethane, morpholine, sodium pyridenethiol; processing speed improvers: calcium and barium sulphonates.

An example of a mixture of additional additives to be added as Component C) is given below:

Additive	*Mass % Broad Range*	*Mass % Preferred Range*
Ashless Dispersant	0.1-20.0	1.0-8.0
Metal Detergents	0.1-15.0	0.2-9.0
Corrosion Inhibitor	0.0-5.0	0.0-1.5
Metal dihydrocarbyl dithiophosphate	0.1-6.0	0.1-4.0
Supplemental Anti-oxidant	0.0-5.0	0.01-1.5
Pour Point Depressant	0.01-5.0	0.01-1.5
Anti-Foaming Agent	0.0-5.0	0.001-0.15
Supplemental Anti-wear Agents	0.0-0.5	0.0-0.2
Friction Modifier	0.0-5.0	0.0-1.5
Viscosity Modifier	0.01-6.0	0.0-4.0
Synthetic and/or Mineral Oil Base	Balance	Balance

The above-mentioned additives may be admixed with the above-mentioned components A) and B) in a manner known *per se*. It is also possible to prepare a concentrate or a so-called "additive pack", which can be diluted to give the working concentrations for the intended

lubricant. In a preferred embodiment, components A), B) and C) are liquid at room temperature in the concentrate. The concentrate may further be diluted by the addition of the base oil according to Component D).

Component D

A low sulphur oil of lubricating viscosity can be used for the preparation of combustion engine oils. The total sulphur content in the low sulphur oil should not exceed the limit of more than 0.3 weight% with regard to the total weight of the composition.

Suitable combustion engine oils are based, for example, on mineral oils, natural oils, synthetic oils or mixtures thereof. These oils are known and familiar to the person skilled in the art and are described in standard reference books, such as in *Chemistry and Technology of Lubricants; Mortier, R.M. and Orszulik, S.T. (Editors); 1992 Blackie and Son Ltd. for GB, VCH-Publishers N.Y. for U.S., ISBN 0-216-92921-0, pages 208 et seq. and 269 et seq.; in Kirk-Othmer Encyclopedia of Chemical Technology, Fourth Edition 1969, J. Wiley & Sons, New York, Vol. 13, page 533 et seq. (Hydraulic Fluids); Performance Testing of Hydraulic Fluids; R. Tourret and E.P. Wright, Hyden & Son Ltd. GB, on behalf of The Institute of Petroleum London, ISBN 0 85501 317 6; Ullmann's Encyclopedia of Ind. Chem., Fifth Completely Revised Edition, Verlag Chemie, DE-Weinheim, VCH-Publishers for U.S., Vol. A 15, page 423 et seq. (lubricants), Vol. A 13, page 165 et seq. (hydraulic fluids)*.

The base oil of lubricating viscosity is preferably a mineral oil derived lubricating base oil containing 80% by mass or more of a saturated hydrocarbon component. Various methods for producing the mineral oil derived lubricating base oil are available. For example, the lubricating base oil may be a paraffin oil or a naphthenic oil obtainable by subjecting a lubricating oil fraction derived from an atmospheric or vacuum distillation of crude oil to refining processes, such as deasphalting, solvent refining, such as solvent extraction with furfural, hydrocracking, solvent or catalytic dewaxing, such as solvent or catalytic dewaxing, hydrotreating, such as hydrocracking or hydrofinishing, clay treatment, such as washing with acid treated or activated clay, or chemical refining, such as washing with caustic soda or sulphuric acid and the like. Combinations of these methods are also available for producing the mineral oil derived lubricating base oil.

Preferred methods for producing the mineral oil derived lubricating base oil consists of the following technical procedures, wherein one of the following oils is used as feedstock oil:

1) A distillate derived from the atmospheric distillation of a paraffin crude oil and/or a mixed crude oil;

2) A whole vacuum gas oil (WVGO) of a paraffin crude oil and/or a mixed crude oil;

3) An oil obtained by subjecting the product obtained according to 1) and/or 2) to mild hydrocracking (MHC);

4) A mixture of two or more selected from products obtained according to 1) to 3);

5) A deasphalted oil (DAO) from products obtained according to 1), 2), 3) or 4);

6) An oil obtained by subjecting the product obtained according to 5) to mild hydrocracking; and

7) A mixture of two or more oils selected from the group of oils obtained according to 1) through 6).

Either the feedstock oil itself or a lubricating oil fraction recovered there from is refined by conventional refining processes, such as the ones mentioned above, to obtain a lubricating oil fraction which is useful as the component a) of the claimed composition. The base oil may be present in the composition as an individual component or in a combination of two or more of the above-mentioned base oils.

Base oils obtained from gaseous feedstocks by the so-called gas to liquid process (GTL oils) or any other process can be used as the major or minor component of the claimed lubricants.

Other base oils of lubricating viscosity can be used, for example oils based on vegetable and animal oils, fats, tallow, wax and mixtures thereof. Vegetable and animal oils, fats, tallow and wax are, for example, palm-kernel oil, palm oil, olive oil, rapeseed oil, rape oil, linseed oil, soybean oil, cottonseed oil, sunflower oil, coconut oil, maize oil, castor oil, low-grade olive oil and mixtures thereof, fish oils, and also the chemically modified, for example epoxidised and sulphoxidised, forms thereof, or forms thereof produced by genetic engineering, for example genetically engineered soybean oil.

Examples of synthetic oils include lubricants based on aliphatic or aromatic carboxy esters, polymeric esters, polyalkylene oxides, phosphoric acid esters, poly-α-olefins or silicones, the diester of a divalent acid with a monohydric alcohol, such as, for example, dioctyl sebacate or dinonyl adipate, a triester of trimethylolpropane with a monovalent acid or with a mixture of such acids, such as, for example, trimethylolpropane tripelargonate, trimethylolpropane tricaprylate or mixtures thereof, a tetra ester of pentaerythritol with a monovalent acid or with a mixture of such acids, such as pentaerythritol tetracaprylate, or a complex ester of monovalent and divalent acids with polyhydric alcohols, for example a complex ester of trimethylolpropane with caprylic and sebacic acid, or a mixture thereof. Apart from mineral oils, poly-α-olefins, ester-based lubricants, phosphates, glycols, polyglycols and polyalkylene glycols, and also mixtures thereof with water are especially suitable.

An organic or inorganic thickener (base fat) may also be added to the above-mentioned lubricants or mixtures thereof.

A further embodiment of the invention relates to an additive composition, which comprises

A) An additive mixture that essentially consists of

a) At least one ammonium phosphate ester;

b) At least one thiophosphoric acid ester; and

c) At least one dithiophosphoric acid derivative; and

B) Sulphur containing oil additives.

The additive composition is prepared by conventional mixing techniques. The compositions according to the invention preferably comprise 0.01 to 5.0% by weight, in particular 0.02 to 1.0% by weight, of the additive composition of above comprising the components A) and B), based on the weight of the base oil component D).

A further embodiment of the invention relates to the additive mixture that essentially consists of

a) At least one ammonium phosphate ester;

b) At least one thiophosphoric acid ester; and

c) At least one dithiophosphoric acid derivative

For use in combustion engines, particularly spark-ignition or Diesel motor engines.

A further embodiment of the invention relates to process for the reduction of wear in combustion engines, which comprises adding to the engine the lubricant composition as defined above, wherein the total amount of sulphur in that composition is less than 0.3%, particularly 0.2%, by weight and that of phosphorus less than 0.08% by weight.

The following Examples illustrate the invention.

Application Examples

Test matrix: Anti-wear activity. The target is to show that the Zn–free compositions according to the invention have the same protection against wear as corresponding compositions comprising Zn-dithiophosphate.

TABLE 1 (Compositions Tested)

Components [weight%]	**Ex. 1**	**Ex. 2**	**Ex. 3**	**Ex. 4**	**Ex. 5**	**Target**
Base oil[1)]	100	98.8	99.9	98.65	98.8	
O,O,O-tris(2(or4)-C9-10-isoalkylphenyl)phosphoro-thioate					0.20	
3-[[bis(2-methylpropoxy)phosphinothioyl]thio]-2-methylpropanoic acid				0.25	0.40	
O,O-diisopropyl hydrogen dithiophosphate alkyl amine				0.50		
Amines, C11-14-branched alkyl, monohexyl and Dihexyl phosphates			-	0.50	0.50	
C9-alkyldithiothiadiazole			0.10	0.10	0.10	
ZnDTP		1.2				
Viscosity 40°C [mm^2/s]	81.20	86.80	79.90	81.00	81.60	
Content P [ppm]	0	993	0	760	730	< 800

[1)] Group III oil PAO (poly-alpha-olefin) + customary oil additives

TABLE 2 (Results)

C&T P-VW 5106[1)]	**Ex. 1**	**Ex. 2**	**Ex. 3**	**Ex. 4**	**Ex. 5**	**Target**
Cam						
- Wear average [µ]	1584	101	723	120	59	≤ 75
- Pitting average [µ]		11.4		11.1	10.1	≤ 20
Tappet						
- Wear average [µ]		83.3		53	50	≤ 100
- Pitting average [µ]		8.3		18.6	10.0	≤ 20

[1)] VW-test; published by ISP GmbH, Neuenkirchener Str. 7, D-48499 Salzbergen, Germany

CA 02600587 2007-08-31

TABLE 3 (Compositions Tested)

Components [weight%]	**Ex. 6**	**Ex. 7**	**Ex. 8**	**Ex. 9**
Base oil[1)]	99.5	99.15	98.45	98.0
O,O,O-tris(2(or4)-C9-10-isoalkylphenyl)phosphoro-thioate			0.20	0.20
3-[[bis(2-methylpropoxy)phosphinothioyl]thio]-2-methylpropanoic acid		0.25	0.25	0.20
O,O-diisopropyl hydrogen dithiophosphate alkyl amine			0.50	1.00
Amines, C11-14-branched alkyl, monohexyl and Dihexyl phosphates		0.50	0.50	0.50
C9-alkyldithiothiadiazole		0.10	0.10	0.10
ZnDTP	0.045			
P-calculated [ppm]	450	472	732	992

[1)] Group III oil PAO (poly-alpha-olefin) + customary oil additives

TABLE 4 (Results)

PDSC IL 85[1)]	Ex. 6	Ex. 7	Ex. 8	Ex. 9	Target
Oxidation induction time [min]	110	135	150	145	> 80
VIT[2)] [hours]	40	65	70	45	> 40
P-losses [ppm] - initial - after 48 h at 160°C	 456 451	 490 461	 855 760	 984 986	

[1)] Assessment of oxidation stability by Pressurized Differential Scanning Calorimetry (PDSC) according to ACEA specifications for engine oils 2004, pg. 13, row 1.11 (www.acea.be)

[2)] Bulk oil oxidation, time to 375 viscosity increase

TABLE 5 (OM611* Test Results)

	Ex. 10	Ex. 11	DB 228.5 Limit
Kinematic viscosity at 100°C [mm^2/sec]	14.3	13.2	--
Camshaft intake wear [µm]	155	91	120 max.
Camshaft exhaust wear [µm]	208	134	140 max.
Cylinder liner wear [µm]	2.3	2.1	5.2 max.
Fresh oil [P content in ppm]	647	701	--
Oil at end of test [P content in ppm]	680	770	--
Oil at end of test [Fe content in ppm]	740	701	--
Oil at end of test [Cu content in ppm]	23	30	--

Comments:

Example Nos. 10 and 11 are two engine oil tests formulated with phosphorothioate, dithiophosphate alkyl amine, amines monohexyl and dihexyl phosphates and thiadiazoles, as shown in Table 3 with approximately equimolar quantities of each type of phosphorus. However, Example 10 has only 170 ppm P from dithiophosphate. Example 11 has 250 ppm P from dithiophosphate. The oils are tested in the OM 611 Diesel engine.

This test measures camshaft wear at intake and exhaust positions as well as cylinder liner wear, among several other parameters. The OM611 is considered by the European lubricant industry to be the best replacement for the OM602A wear test.

Claims

1. A lubricant composition for use in combustion engines comprising

A) An additive mixture that essentially consists of

a) At least one ammonium phosphate ester;

b) At least one thiophosphoric acid ester; and

c) At least one dithiophosphoric acid derivative;

B) At least one sulphur containing oil additive;

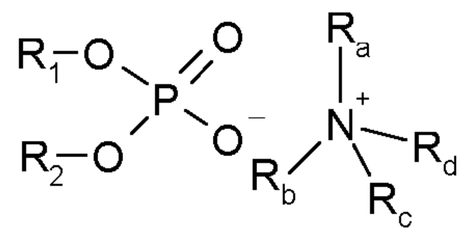
C) Customary crank case oil additives; and

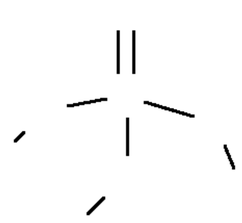
D) Low sulphur oil of lubricating viscosity;

With the proviso that the total amount of sulphur in the composition is less than 0.3 weight%.

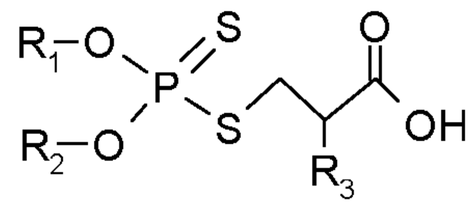
2. A lubricant composition according to claim 1, wherein the additive mixture A) essentially consists of

a) At least one ammonium phosphate ester of the formula





c) At least one dithiophosphoric acid derivative selected from the group consisting of a 3-dithiophosphorylpropionic acid of the formula



4. A lubricant composition according to claim 1, wherein the additive mixture A) consists essentially of

a) At least one ammonium phosphate ester (I), wherein one of R_1 and R_2 represents hydrogen and the other one represents C_3-C_9alkyl; or both R_1 and R_2 represent C_3-C_9alkyl; and R_a, R_b, R_c and R_d independently of one another represent hydrogen or C_{12}-C_{20}alkyl;

b) At least one thiophosphoric acid ester (II), wherein R_1, R_2 and R_3 independently of one another represent phenyl or $(C_1$-C_9alkyl$)_{1-3}$phenyl; and

c) At least one dithiophosphoric acid derivative selected from the group consisting of a 3-dithiophosphorylpropionic acid (III), wherein R_1 and R_2 represent 2-methylpropoxy and R_3 represents methyl, and an ammonium salt of a dithiophosphoric acid (IV), wherein R_1 and R_2 represent isopropyl and R_a, R_b, R_c and R_d independently of one another represent hydrogen or C_{12}-C_{20}alkyl.

5. A lubricant composition according to claim 1, wherein the additive mixture A) consists essentially of

a) At least one ammonium phosphate ester (I), wherein one of R_1 and R_2 represents hydrogen and the other one represents C_3-C_9alkyl; or both R_1 and R_2 represent represents C_3-C_9alkyl; and R_a, R_b, R_c and R_d independently of one another represent hydrogen or C_{12}-C_{20}alkyl;

b) At least one thiophosphoric acid ester (II), wherein

R_1, R_2 and R_3 represent phenyl; or

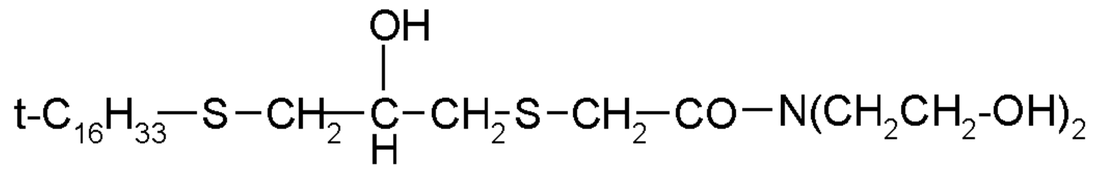
one of R_1, R_2 and R_3 represents phenyl and two of R_1, R_2 and R_3 represent $(C_1$-C_9alkyl$)_{1-3}$phenyl; or

two of R_1, R_2 and R_3 represent phenyl and one of R_1, R_2 and R_3 represents $(C_1$-C_9alkyl$)_{1-3}$phenyl; or

R_1, R_2 and R_3 represent $(C_1$-C_9alkyl$)_{1-3}$phenyl; and

c) At least one 3-dithiophosphorylpropionic acid (III), wherein R_1 and R_2 represent 2-methylpropoxy and R_3 represents methyl.

6. A lubricant composition according to claim 1, wherein the sulphur containing oil additive B) is a dithioglycidyl ether selected from the group consisting of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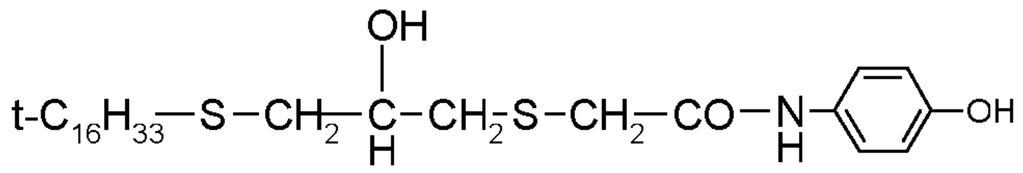
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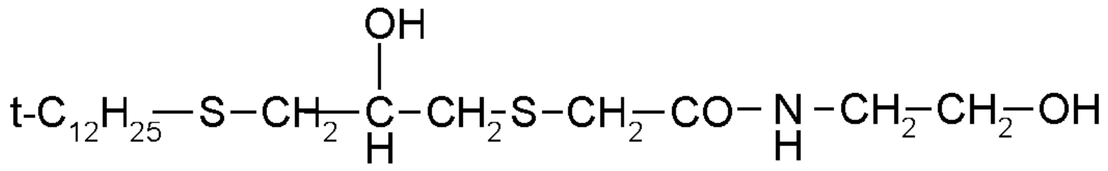
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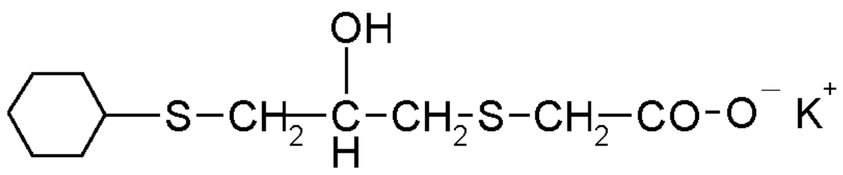
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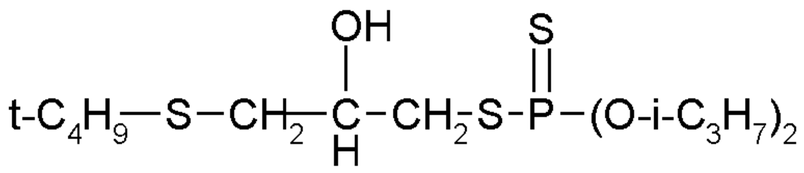
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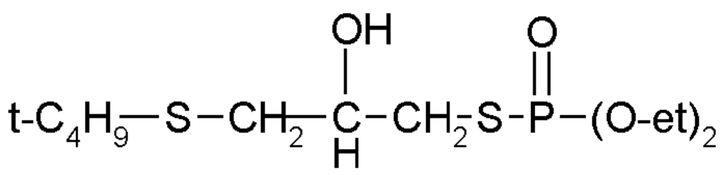
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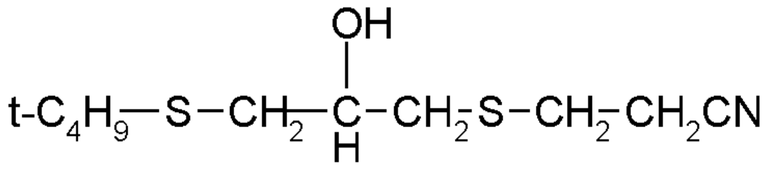
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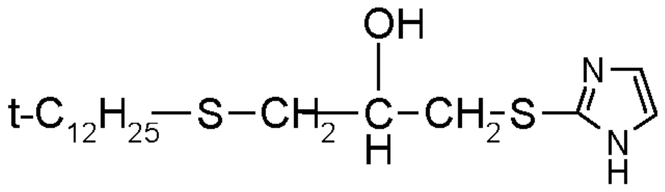
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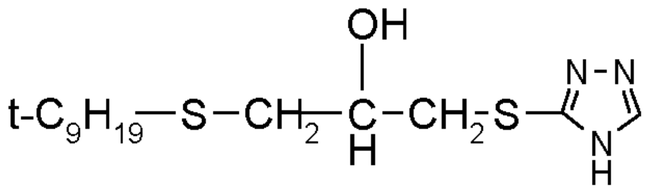
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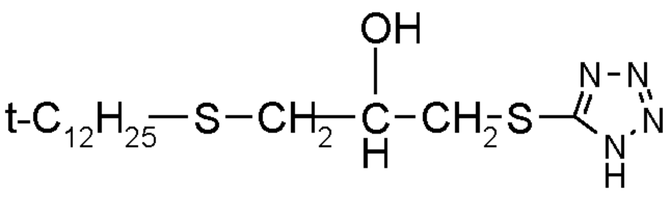
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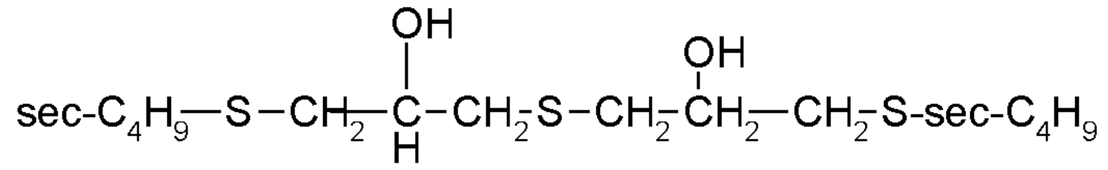
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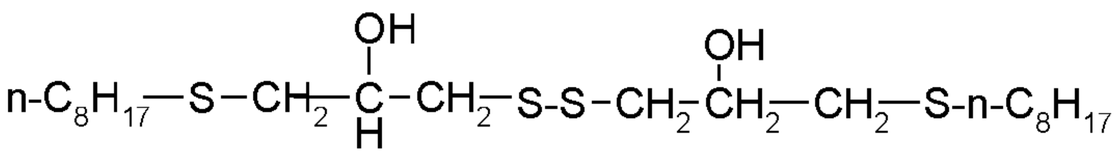
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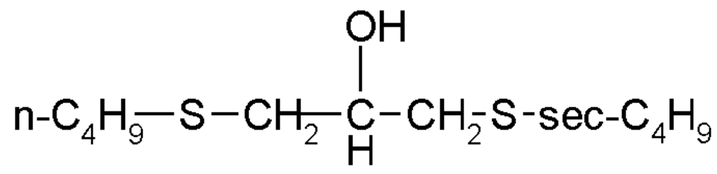

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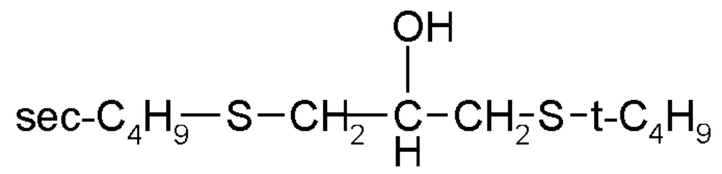

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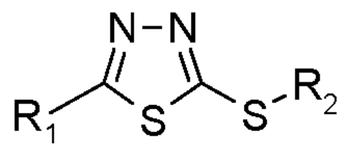
7. A lubricant composition according to claim 1, wherein the sulphur containing oil additive B) is a polyalkylated 1,3,4-thiadiazole compound of the formula



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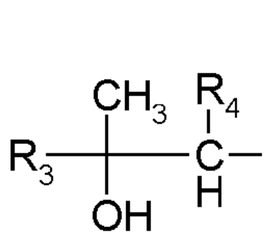
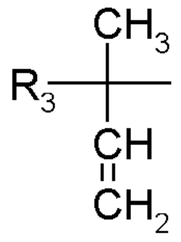
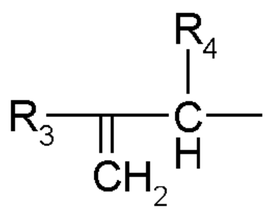
Wherein R_1 represents hydroxy, amino, mercapto, alkylthio, 2-hydroxyalkylthio or the R_2-S group and R_2 represents a polyolefin residue represented by the partial formulae:

 or isomeric  and  , wherein R_3 represents alkyl having 50 to 400 carbon atoms and R_4 represents hydrogen or methyl.

8. A lubricant composition according to claim 1, wherein the low sulphur oil of lubricating viscosity D) is a mineral oil, synthetic oil, natural oil or a mixture thereof.

9. A lubricant composition according to claim 1, wherein the total amount of sulphur in the composition is less than 0.2% by weight.

10. An additive composition, which comprises

A) An additive mixture that essentially consists of

a) At least one ammonium phosphate ester;

b) At least one thiophosphoric acid ester; and

c) At least one dithiophosphoric acid derivative; and

B) Sulphur containing oil additives.

11. An additive mixture that essentially consists of

a) At least one ammonium phosphate ester;

b) At least one thiophosphoric acid ester; and

c) At least one dithiophosphoric acid derivative;

for use in combustion engines.

12. A process for the reduction of wear in combustion engines, which comprises adding to the engine the lubricant composition according to claim 1, wherein the total amount of sulphur in that composition is less than 0.3% by weight and that of phosphorus less than 0.08% by weight.