(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 2 467 456 B2**

(12) **NEW EUROPEAN PATENT SPECIFICATION**
After opposition procedure

(45) Date of publication and mention of the opposition decision:
09.08.2023 Bulletin 2023/32

(45) Mention of the grant of the patent:
22.10.2014 Bulletin 2014/43

(21) Application number: **10747108.8**

(22) Date of filing: **10.08.2010**

(51) International Patent Classification (IPC):
C10M 159/22 *(2006.01)* ***C10M 159/24*** *(2006.01)*
C10N 10/04 *(2006.01)* ***C10N 30/06*** *(2006.01)*
C10N 40/25 *(2006.01)* ***C10N 40/26*** *(2006.01)*

(52) Cooperative Patent Classification (CPC):
(C-Sets available)
C10M 159/24; C10M 159/22; C10M 2207/027; C10M 2207/028; C10M 2207/042; C10M 2207/262; C10M 2207/281; C10M 2207/289; C10M 2215/08; C10M 2215/224; C10M 2215/28; C10M 2219/046; C10M 2219/088; C10M 2219/089; C10M 2223/043;

(Cont.)

(86) International application number:
PCT/US2010/044968

(87) International publication number:
WO 2011/022245 (24.02.2011 Gazette 2011/08)

(54) **Lubricating method**

Schmiermethode

Procede de lubrification

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO SE SI SK SM TR

(30) Priority: **18.08.2009 US 234727 P**

(43) Date of publication of application:
27.06.2012 Bulletin 2012/26

(73) Proprietor: **The Lubrizol Corporation**
Wickliffe, OH 44092-2298 (US)

(72) Inventor: **DAVIES, Mark C.**
Belper, Derby DE56 1QN (GB)

(74) Representative: **D Young & Co LLP**
120 Holborn
London EC1N 2DY (GB)

(56) References cited:
EP-A1- 2 077 317
EP-A2- 1 041 134
EP-A2- 1 418 353
EP-A2- 1 475 430

- **"Chemistry and Technology of Lubricants", 2nd Edition, edited by R.M.Mortier and S.T. Orszulik, (1997), pp. 82-86**
- **"Nanoscale chemistry and mechanical properties of triboflims on Al-Si alloy (A383): interaction of ZDDP, calcium detergent and molybdenum friction modifier", G. Pereira et al.. Tribology vol. 1, No. 1 (2007), pp 4-17**

Remarks:
The file contains technical information submitted after the application was filed and not included in this specification

EP 2 467 456 B2

(52) Cooperative Patent Classification (CPC): (Cont.)
C10M 2223/045; C10N 2030/06; C10N 2030/42;
C10N 2030/43; C10N 2030/45; C10N 2030/52;
C10N 2040/25; C10N 2040/251; C10N 2040/252;
C10N 2040/253; C10N 2040/255; C10N 2040/26;
C10N 2060/10

C-Sets
C10M 2207/027, C10N 2010/02;
C10M 2207/027, C10N 2010/04;
C10M 2207/028, C10N 2010/02;
C10M 2207/028, C10N 2010/04;
C10M 2219/088, C10N 2010/04;
C10M 2219/089, C10N 2010/04;
C10M 2223/045, C10N 2010/04

Description

FIELD OF INVENTION

[0001] The invention provides a method of lubricating an aluminium-alloy surface of an internal combustion engine comprising supplying to the aluminium-alloy surface a lubricating composition comprising an oil of lubricating viscosity and an alkali or alkaline earth metal phenate detergent. The phenate disclosed herein may further provide antiwear performance on the aluminium-alloy surface.

BACKGROUND OF THE INVENTION

[0002] It is well known for lubricating oils to contain a number of surface active additives (including antiwear agents, dispersants, or detergents) used to protect internal combustion engines from corrosion, wear, soot deposits and acid build up. Often, such surface active additives can have harmful effects on engine component wear (in both iron and aluminium based components), bearing corrosion or fuel economy. A common antiwear additive for engine lubricating oils is zinc dialkyldithiophosphate (ZDDP). It is believed that ZDDP antiwear additives protect the engine by forming a protective film on metal surfaces. ZDDP may also have a detrimental impact on fuel economy and efficiency and copper corrosion. Consequently, engine lubricants may also contain a friction modifier to obviate the detrimental impact of ZDDP on fuel economy and corrosion inhibitors to obviate the detrimental impact of ZDDP on copper corrosion. Other additives may also increase lead corrosion.

[0003] Developments in engine design have resulted in engines that employ ferrous-containing and/or non-ferric components. Typically non-ferric engine components thereof, are based on aluminium-alloy, silicates, oxides, or other ceramic materials. Antiwear additives such as ZDDP are believed to result in poorer engine wear performance in aluminium-alloy based engine compared with ferric based engines.

[0004] Further, engine lubricants containing phosphorus compounds and sulphur have been shown to contribute in part to particulate emissions and emissions of other pollutants. In addition, sulphur and phosphorus tend to poison the catalysts used in catalytic converters, resulting in a reduction in performance of said catalysts.

[0005] Attempts to lubricate engine components with aluminium surfaces have been described in EP 1 624 044 A1 (8 February, 2006 by Oldfield) and International Publication WO 2008/147701 (filed 15 May, 2008, by Davies et al.).

[0006] EP 1624 044 A1 discloses a method of lubricating an aluminium alloy surface with a lubricating composition containing an effective friction reducing amount of an oil soluble tri-nuclear organo-molybdenum compound.

[0007] WO2008/147701. discloses lubricating an aluminium-alloy surface by supplying to the aluminium-alloy surface a lubricating composition comprising an oil of lubricating viscosity and an ashless antiwear agent. The examples disclosed therein also indicate 1.5 wt % of detergent However, there is no specific disclosure of the type of detergent utilised.

[0008] EP 1 041 134 A2 discloses a lubricating oil composition particularly suited for use as a crankcase lubricant. The composition contains an oil-soluble molybdenum compound, a diarylamine and a phenate and is substantially free of reactive sulfur.

[0009] EP 2 077 317 A1 describes a lubricating oil composition comprising a base oil, a fatty acid partial ester compound, an aliphatic amine compound and/or an acid amide compound, a specific benzotriazole derivative and a specific succinimide compound. The composition is used for internal combustion engines.

[0010] EP 1 418 353 A2 discloses a low-friction sliding mechanism involving a lubricant and optionally an aluminium-based alloy material. The lubricant contains a base oil and at least one of an ashless fatty-ester friction modifier.

[0011] EP 1475 430 A2 discloses a low sulphur, low ash, and low phosphorus oil-soluble lubricant additive package comprising an overbased metal phenate.

SUMMARY OF THE INVENTION

[0012] In one embodiment the present invention provides a method of lubricating an aluminium-alloy surface of an internal combustion engine comprising supplying to the aluminium-alloy surface a lubricating composition comprising an oil of lubricating viscosity and an alkali or alkaline earth metal (including lithium, sodium, calcium, magnesium, or barium) phenate detergent. The phenate detergent is a calcium sulphurised-phenate, in particular an overbased calcium sulphur-ised-phenate.

[0013] The detergent delivers 0.75 wt % to 2 wt % of hydrocarbyl-substituted phenol to the lubricating composition, the aluminium alloy is a eutectic or hyper-eutectic aluminium alloy and the internal combustion engine has part or all of a cylinder bore, cylinder block, or piston ring composed of an aluminium alloy.

[0014] In one embodiment the present invention provides a method of lubricating an aluminium-alloy surface of an internal combustion engine comprising supplying to the aluminium-alloy surface a lubricating composition comprising (a) an oil of lubricating viscosity, (b) an overbased alkali or alkaline earth metal (including lithium, sodium, calcium,

magnesium, or barium, typically calcium) phenate (typically a sulphurised-phenate) detergent having a TBN of 200 to 400 (or 200 to 350), and (c) a neutral phenate (typically a non-sulphur containing calcium phenate) with a TBN of 20 to 170 (such as 155). The non-sulphur containing calcium phenate may include detergents described in European Patent applications EP 1 680 491 A, or EP 1 778 824 A.

[0015] In one embodiment the present invention provides a method of lubricating an aluminium-alloy surface of an internal combustion engine comprising supplying to the aluminium-alloy surface a lubricating composition comprising an oil of lubricating viscosity and an alkali or alkaline earth metal phenate detergent (typically a calcium sulphurised-phenate).

[0016] Also described herein is a method of controlling wear of an aluminium-alloy surface in an internal combustion engine comprising supplying to the aluminium-alloy surface a lubricating composition comprising an oil of lubricating viscosity and an alkali or alkaline earth metal phenate detergent (typically a calcium sulphurised-phenate).

[0017] Also described herein is the use of the Lubricating composition disclosed herein to mitigate wear on an aluminium-alloy surface of an internal combustion engine. In one embodiment the invention provides for the use of an alkali or alkaline earth metal phenate detergent which is a calcium sulphurised-phenate, as an antiwear agent for an aluminium alloy surface of an internal combustion engine wherein the detergent delivers 0.75 wt % to 2 wt % of hydrocarbyl-substituted phenol to the lubricating composition the aluminium alloy is a eutectic or hyper-eutectic aluminium alloy and the internal combustion engine has part or all of a cylinder bore, cylinder block, or piston ring composed of an aluminium alloy.

[0018] In one embodiment the invention provides a method of lubricating an internal combustion engine as disclosed herein, wherein the aluminium alloy is an eutectic or hyper-eutectic aluminium alloy (such as those derived from aluminium silicates, aluminium oxides, or other ceramic materials).

[0019] In one embodiment the invention provides a method of lubricating an Internal combustion engine as disclosed herein, wherein the internal combustion engine has part or all of a cylinder bore, cylinder block, or piston ring composed of an aluminium alloy.

DETAILED DESCRIPTION OF THE INVENTION

[0020] The present invention provides a method for lubricating an engine and the use of an alkali or alkaline earth metal phenate detergent as disclosed above. Also described herein is a lubricating composition as disclosed above.

Phenate Detergent

[0021] The alkali or alkaline earth metal phenate detergent may be described as an overbased material. Overbased materials, otherwise referred to as overbased or superbased salts, are generally single phase, homogeneous Newtonian systems characterised by an amount of excess metal beyond that which would be necessary for neutralisation, according to the stoichiometry of the metal and the particular acidic organic compound reacted with the metaL The amount of excess metal is commonly expressed in terms of substrate to metal ratio. The term "substrate to metal ratio," alternatively expressed as the metal to substrate ratio, or simply "metal ratio," is the ratio of the total equivalents of the metal to the equivalents of the substrate. A more detailed description of the term metal ratio is provided in "Chemistry and Technology of Lubricants", Second Edition, Edited by R. M. Mortier and S. T. Orszulik, pages 85 and 86, 1997.

[0022] The overbased alkali or alkaline earth metal phenate detergent may have a metal ratio of 0.8 to 10, or 1 to 10, or 3 to 9, or 4 to 8, or 5 to 7.

[0023] In different embodiments the alkali or alkaline earth metal phenate detergent may have a total base number (TBN) 50 to 400, or 200 to 350, or 220 to 300. In one embodiment the alkali or alkaline earth metal phenate detergent may have a TBN of about 255. A more detailed description of the alkali or alkaline earth metal phenate detergent is described in for example, US Patent 6,551,965, or European Patent applications EP 1 903 093 A and EP 0 601 721 A.

[0024] The alkali or alkaline earth metal phenate detergent additive may be derived from a hydrocarbyl-substituted phenol, wherein the hydrocarbyl-substituted phenol may be present in range from 10 wt % to 70 wt %, or 25 wt % to 65 wt %, or 30 wt % to 60 wt % of the phenate detergent. When the additive is added to a lubricant the overall percentage reduces due to diluent effect of all the base oil and presence of other additives in the overall lubricating composition.

[0025] The alkali or alkaline earth metal phenate detergent is derived from a hydrocarbyl-substituted phenol, wherein the alkaline earth metal phenate detergent delivers 0.75 wt % to 2 wt %, or 0.9 wt % to 1.75 wt %, or 1 wt % to 1.5 wt % of hydrocarbyl-substituted phenol to the lubricating composition. The hydrocarbyl-substituted phenol content (this includes the phenol and anions thereof) delivered by the alkali or alkaline earth metal phenate detergent is from 0.75 wt % to 2 wt %, or 0.9 wt % to 1.75 wt %, or 1 wt % to 1.5 wt % of the lubricating composition.

[0026] The alkali or alkaline earth metal phenate detergent hydrocarbyl-substituted phenol content and sulphated ash may vary. In one embodiment the hydrocarbyl-substituted phenol content delivered by the phenate may be 0.9 wt % to 1.75 wt %; and the sulphated ash content may be at least 0.4 wt % to 1.3 wt % of the lubricating composition. In one

embodiment the hydrocarbyl-substituted phenol content delivered by the phenate may be 0.9 wt % to 1.75 wt %; and the sulphated ash content may be at least 0.4 wt % to 1.2 wt % of the lubricating composition. In one embodiment the hydrocarbyl-substituted phenol content delivered by the phenate may be 1 wt % or higher to 1.5 wt %; and the sulphated ash content may be at least 0.6 wt % to 1.1 wt % of the lubricating composition.

[0027] Each hydrocarbyl group of hydrocarbyl-substituted phenol may contain on average 6 or more, 8 or more, or 10 or more carbon atoms. The maximum number of carbon atoms per hydrocarbyl group may be up to 300, or up to 100, or up to 70, or up to 50, or up to 20. In one embodiment each hydrocarbyl group may 8 to 20, or 10 to 12 carbon atoms (typically each hydrocarbyl group may be dodecyl).

[0028] The amount of sulphated ash delivered by the overbased alkali or alkaline earth metal phenate detergent may be 0.4 wt % to 1.2 wt %, or 0.6 wt % to 1.1 wt % of the lubricating composition.

[0029] The lubricant composition for an internal combustion engine may be suitable for any engine lubricant irrespective of the sulphur, phosphorus or sulphated ash (ASTM D-874) content. The sulphur content of the engine oil lubricant may be 1 wt % or less, or 0.8 wt % or less, or 0.5 wt % or less, or 0.3 wt % or less. In one embodiment the sulphur content may be in the range of 0.001 wt % to 0.5 wt %, or 0.01 wt % to 0.3 wt %.

[0030] The phosphorus content may be 0.2 wt % or less, or 0.12 wt % or less, or 0.1 wt % or less, or 0.085 wt % or less, or 0.08 wt % or less, or even 0.06 wt % or less, 0.055 wt % or less, or 0.05 wt % or less. In one embodiment the phosphorus content may be 100 ppm to 1000 ppm, or 200 ppm to 600 ppm.

[0031] The sulphated ash content of the lubricating composition may be at least 0.3 wt%, or at least 0.4 wt %, at least 0.6 wt % up to 2 wt %, or 1.5 wt %, or 1.3 wt %, or 1.1 wt % of the lubricating composition. The sulphated ash content may in different embodiments range from 0.3 wt % to 2 wt %, or 0.4 wt % to 1.5 wt %, or 0.6 wt % to 1.3 wt %, or 0.6 wt % to 1.1 wt % of the lubricating composition.

[0032] In one embodiment the lubricating composition may be characterised as having (i) a sulphur content of 0.5 wt % or less, (ii) a phosphorus content of 0.06 wt % or less, and (iii) a sulphated ash content of 1.3 wt % or less.

Oils of Lubricating Viscosity

[0033] The lubricating composition comprises an oil of lubricating viscosity. Such oils include natural and synthetic oils, oil derived from hydrocracking, hydrogenation, and hydrofinishing, unrefined, refined, re-refined oils or mixtures thereof. A more detailed description of unrefined, refined and re-refined oils is provided in International Publication WO2008/147704, paragraphs [0054] to [0056]. A more detailed description of natural and synthetic lubricating oils is described in paragraphs [0058] to [0059] respectively of WO2008/147704. Synthetic oils may also be produced by Fischer-Tropsch reactions and typically may be hydroisomerised Fischer-Tropsch hydrocarbons or waxes. In one embodiment oils may be prepared by a Fischer-Tropsch gas-to-liquid synthetic procedure as well as other gas-to-liquid oils.

[0034] Oils of lubricating viscosity may also be defined as specified in April 2008 version of "Appendix E - API Base Oil Interchangeability Guidelines for Passenger Car Motor Oils and Diesel Engine Oils", section 1.3 Sub-heading 1.3. "Base Stock Categories". In one embodiment the oil of lubricating viscosity may be an API Group I, or Group II, or Group III, or Group IV oil. In one embodiment the oil of lubricating viscosity may be an API Group II or Group III oil.

[0035] The amount of the oil of lubricating viscosity present is typically the balance remaining after subtracting from 100 wt % the sum of the amount of the compound of the invention and the other performance additives.

[0036] The lubricating composition may be in the form of a concentrate and/or a fully formulated lubricant. If the lubricating composition (comprising the additives disclosed herein) is in the form of a concentrate which may be combined with additional oil to form, in whole or in part, a finished lubricant, the ratio of the of these additives to the oil of lubricating viscosity and/or to diluent oil include the ranges of 1:99 to 99:1 by weight, or 80:20 to 10:90 by weight

Other Performance Additives

[0037] The composition optionally comprises other performance additives. The other performance additives include at least one of metal deactivators, viscosity modifiers, detergents (in addition to the phenate previously described as part of the invention), friction modifiers, Antiwear agents, corrosion inhibitors, dispersants, dispersant viscosity modifiers, extreme pressure agents, antioxidants, foam inhibitors, demulsifiers, pour point depressants, seal swelling agents and mixtures thereof. Typically, fully-formulated lubricating oil will contain one or more of these performance additives.

[0038] In one embodiment the lubricating composition further includes other additive. In one embodiment the invention provides a lubricating composition further comprising at least one of a dispersant, an antiwear agent, a dispersant viscosity modifier, a friction modifier, a viscosity modifier, an antioxidant, a detergent (in addition to the phenate previously described as part of the invention), or mixtures thereof.

[0039] The dispersant may be a succinimide dispersant, or mixtures thereof. In one embodiment the dispersant may be present as a single dispersant. In one embodiment the dispersant may be present in a mixture of two or three different dispersants, wherein at least one may be a succinimide dispersant.

[0040] The succinimide dispersant may be derived from an aliphatic polyamine, or mixtures thereof. The aliphatic polyamine may be aliphatic polyamine such as an ethylenepolyamine, a propylenepolyamine, a butylenepolyamine, or mixtures thereof. In one embodiment the aliphatic polyamine may be ethylenepolyamine. In one embodiment the aliphatic polyamine may be selected from the group consisting of ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine, polyamine still bottoms, and mixtures thereof.

[0041] The dispersant may be a N-substituted long chain alkenyl succinimide. Examples of N-substituted long chain alkenyl succinimide include polyisobutylene succinimide. Typically the polyisobutylene from which the polyisobutylene succinic anhydride is derived has a number average molecular weight of 350 to 5000, or 550 to 3000 or 750 to 2500. Succinimide dispersants and their preparation are disclosed, for instance in US Patents 3,172,892, 3,219,666, 3,316,177, 3,340,281, 3,351,552, 3,381,022, 3,433,744, 3,444,170, 3,467,668, 3,501,405, 3,542,680, 3,576,743, 3,632,511, 4,234,435, Re 26,433, and 6,165,235, 7,238,650 and EP Patent Application 0 355 895 A.

[0042] The dispersant may also be post-treated by conventional methods by a reaction with any of a variety of agents. Among these are boron compounds, urea, thiourea, dimercaptothiadiazoles, carbon disulphide, aldehydes, ketones, carboxylic acids, hydrocarbon-substituted succinic anhydrides, maleic anhydride, nitriles, epoxides, and phosphorus compounds.

[0043] The dispersant may be present at 0.01 wt % to 20 wt %, or 0.1 wt % to 15 wt %, or 0.1 wt % to 10 wt %, or 1 wt % to 6 wt % of the lubricating composition.

[0044] In one embodiment the lubricating composition further comprises a dispersant viscosity modifier. The dispersant viscosity modifier may be present at 0 wt % to 5 wt %, or 0 wt % to 4 wt %, or 0.05 wt %to 2 wt % of the lubricating composition.

[0045] The dispersant viscosity modifier may include functionalised polyolefins, for example, ethylene-propylene co-polymers that have been functionalized with an acylating agent such as maleic anhydride and an amine; polymethacrylates functionalised with an amine, or styrene-maleic anhydride copolymers reacted with an amine. More detailed description of dispersant viscosity modifiers are disclosed in International Publication WO2006/015130 or U.S. Patents 4,863,623; 6,107,257; 6,107,258; and 6,117,825. In one embodiment the dispersant viscosity modifier may include those described in U.S. Patent 4,863,623 (see column 2, line 15 to column 3, line 52) or in International Publication WO2006/015130 (see page 2, paragraph [0008] and preparative examples are described paragraphs [0065] to [0073]).

[0046] As used herein the term "fatty" has at least 6 or at least 8 to 30, or 20 carbon atoms.

[0047] In one embodiment the friction modifier may be selected from the group consisting of fatty acid derivatives of amines, fatty esters, or fatty epoxides; fatty imidazolines; amine salts of alkylphosphoric acids. The friction modifier may be present at 0 wt % to 6 wt %, or 0.05 wt % to 4 wt %, or 0.1 wt % to 2 wt % of the lubricating composition

[0048] In one embodiment: the lubricating composition further includes a. zinc dialkyldithiophosphate, or mixtures thereof.. Zinc dialkyldithiophosphates are known in the art. The zinc dialkyldithiophosphate may be present at 0 wt % to 5 wt %, or 0.1 wt % to 3 wt %, or 0.5 wt % to 2 wt % of the lubricating composition.

[0049] In one embodiment the lubricating composition further comprises a molybdenum compound. The molybdenum compound may be selected from the group consisting of molybdenum dialkyldithiophosphates, molybdenum dithiocarbamates, amine salts of molybdenum compounds, and mixtures thereof. The molybdenum compound may provide the lubricating composition with 0 to 1000 ppm, or 5 to 1000 ppm, or 10 to 750 ppm 5 ppm to 300 ppm, or 20 ppm to 250 ppm of molybdenum.

[0050] In one embodiment the lubricating composition further comprises a neutral or an overbased detergent in addition to the phenate previously described as part of the invention. The neutral or overbased detergent may be selected from the group consisting of sulphonates, salixarates, salicylates, saligenins and mixtures thereof. Typically the neutral or overbased detergent may be a sodium, calcium or magnesium salt of the sulphonates, salixarates and salicylates.

[0051] Neutral detergents may have a TBN of less than 200, or typically less than 170. For example a "neutral" or "slightly overbased" sulphonate detergent may have a TBN of 0 to 100 or 20 to 100 (such as 80 or 85). The lubricating composition may contain 0 wt % to 5 wt % or 0.5 to 3 wt % of a neutral sulphonate detergent (typically calcium sulphonate) with a TBN of 80 or 85. The lubricating composition may contain 0 wt % to 3 wt %, or 0.5 to 2 wt % of a calcium phenate detergent with a TBN of 155. (A neutral phenate detergent, i.e., not overbased, will typically still exhibit a measurable TBN.)

[0052] Overbased phenates and salicylates, typically have a total base number of 200 to 450 TBN. Overbased sulphonates typically have a total base number of 250 to 600, or 300 to 500 (typically 300 or 400). Overbased detergents are known in the art. In one embodiment the sulphonate detergent may be a predominantly linear alkylbenzene sulphonate detergent having a metal ratio of at least 8 to 40 as is described in paragraphs [0026] to [0037] of US Patent Application 2005065045 (and granted as US 7,407,919) having a TBN of 400. The predominantly lineal alkylbenzene sulphonate detergent may be particularly useful for assisting in improving fuel economy. The total amount of neutral and overbased detergent in addition to the claimed phenate may be present at 0 wt % to 15 wt %, or 0.1 wt % to 10 wt %, or 0.2 wt % to 8 wt % of the lubricating composition (including amounts of diluent oil known to be conventionally associated with detergents. This may for instance be 30 to 50 wt % of the ranges quoted).

[0053] In one embodiment the lubricating composition includes an antioxidant, or mixtures thereof. The antioxidant

may be present at 0 wt % to 15 wt 5, or 0.1 wt % to 10 wt %, or 0.5 wt % to 5 wt % of the lubricating composition.

[0054] Antioxidants include sulphurised olefins, alkylated diphenylamines (typically dinonyl diphenylamine, octyl diphenylamine, dioctyl diphenylamine), hindered phenols, molybdenum compounds (such as molybdenum dithiocarbamates), or mixtures thereof.

[0055] The hindered phenol antioxidant often contains a secondary butyl and/or a tertiary butyl group as a sterically hindering group. The phenol group may be further substituted with a hydrocarbyl group (typically linear or branched alkyl) and/or a bridging group linking to a second aromatic group. Examples of suitable hindered phenol antioxidants include 2,6-di-tert-butylphenol, 4-methyl-2,6-di-tert-butylphenol, 4-ethyl-2,6-di-tert-butylphenol, 4-propyl-2,6-di-tertbutylphenol or 4-butyl-2,6-di-tert-butylphenol, or 4-dodecyl-2,6-di-tertbutylphenol. In one embodiment the hindered phenol antioxidant may be an ester and may include, e.g., Irganox™ L-135 from Ciba. A more detailed description of suitable ester-containing hindered phenol antioxidant chemistry is found in US Patent 6,559,105.

[0056] Examples of suitable friction modifiers include fatty acid derivatives of amines, fatty esters, or fatty epoxides; fatty imidazolines such as condensation products of carboxylic acids and polyalkylene-polyamines; amine salts of alkylphosphoric acids; fatty alkyl tartrates; fatty alkyl tartrimides; or fatty dialkyl tartramides.

[0057] Friction modifiers may also encompass materials such as sulphurised fatty compounds and olefins, molybdenum dialkyldithiophosphates, molybdenum dithiocarbamates, sunflower oil or monoester of a polyol and an aliphatic carboxylic acid.

[0058] In one embodiment the friction modifier may be selected from the group consisting of fatty acid derivatives of amines, fatty esters, or fatty epoxides; fatty alkyl tartrates; fatty alkyl tartrimides; and fatty alkyl tartramides. The fatty alkyl tartrates; fatty alkyl tartrimides; and fatty alkyl tartramides may be the same or different to the amide, ester or imide derivative of a hydroxycarboxylic acid described above.

[0059] In one embodiment the friction modifier may be a fatty acid ester. In another embodiment the fatty acid ester may be a mono-ester and in another embodiment the fatty acid ester may be a (tri)glyceride.

[0060] Other performance additives such as corrosion inhibitors include those described in paragraphs 5 to 8 of US Application US05/038319, published as WO2006/047486, octylamine octanoate, or condensation products of dodecenyl succinic acid or anhydride and a fatty acid such as oleic acid with a polyamine. In one embodiment the corrosion inhibitors include the Synalox® corrosion inhibitor. The Synalox® corrosion inhibitor may be a homopolymer or copolymer of propylene oxide. The Synalox® corrosion inhibitor is described in more detail in a product brochure with Form No. 118-01453-0702 AMS, published by The Dow Chemical Company. The product brochure is entitled "SYNALOX Lubricants, High-Performance Polyglycols for Demanding Applications."

[0061] Metal deactivators including derivatives of benzotriazoles (typically tolyltriazole), dimercaptothiadiazole derivatives, 1,2,4-triazoles, benzimidazoles, 2-alkyldithiobenzimidazoles, or 2-alkyldithiobenzothiazoles; foam inhibitors including copolymers of ethyl acrylate and 2-ethylhexyl acrylate and optionally vinyl acetate; demulsifiers including trialkyl phosphates, polyethylene glycols, polyethylene oxides, polypropylene oxides and (ethylene oxide-propylene oxide) polymers; pour point depressants including esters of maleic anhydride-styrene, polymethacrylates, polyacrylates or polyacrylamides may be useful. Foam inhibitors that may be useful in the compositions of the invention include copolymers of ethyl acrylate and 2-ethylhexyl acrylate and optionally vinyl acetate; demulsifiers including trialkyl phosphates, polyethylene glycols, polyethylene oxides, polypropylene oxides and (ethylene oxide-propylene oxide) polymers.

[0062] Pour point depressants that may be useful in the compositions of the invention include polyalphaolefins, esters of maleic anhydride-styrene, poly(meth)acrylates, polyacrylates or polyacrylamides.

[0063] In different embodiments the lubricating composition may in addition to the detergent of the invention have a composition further containing additive in ranges described in the following table:

Additive	Embodiments (wt %)		
	A	B	C
Phenate of the Invention	0.01 to 5	0.1 to 3	0.25 to 1.5
Dispersant	0.05 to 12	0.75 to 8	0.5 to 6
Dispersant Viscosity Modifier	0 to 5	0 to 4	0.05 to 2
Additional Overbased Detergent	0 to 15	0.1 to 10	0.2 to 8
Antioxidant	0 to 15	0.1 to 10	0.5 to 5
Antiwear Agent	0 to 15	0.1 to 10	0.3 to 5
Friction Modifier	0 to 6	0.05 to 4	0.1 to 2
Viscosity Modifier	0 to 10	0.5 to 8	1 to 6

(continued)

Additive	Embodiments (wt %)		
	A	B	C
Any Other Performance Additive	0 to 10	0 to 8	0 to 6
Oil of Lubricating Viscosity	Balance to 100 %	Balanceto 100 %	Balance to 100 %
Footnote: Ranges quoted above are on an oil free basis i.e., amount of active ingredient with diluent oil factored out.			

Industrial Application

[0064] The lubricating composition is utilised in an internal combustion engine. The internal combustion engine may or may not have an Exhaust Gas Recirculation system. The internal combustion engine may be fitted with an emission control system or a turbocharger. Examples of the emission control system include diesel particulate filters (DPF), or systems employing selective catalytic reduction (SCR).

[0065] In one embodiment the internal combustion engine may be a diesel fuelled engine (typically a heavy duty diesel engine), a gasoline fuelled engine, a natural gas fuelled engine or a mixed gasoline/alcohol fuelled engine. In one embodiment the internal combustion engine may be a diesel fuelled engine and in another embodiment a gasoline fuelled engine.

[0066] The internal combustion engine may be a 2-stroke or 4-stroke engine. Suitable internal combustion engines include marine diesel engines, aviation piston engines, low-load diesel engines, and automobile and truck engines.

[0067] The following examples provide illustrations of the invention. These examples are non-exhaustive and are not intended to limit the scope of the invention.

EXAMPLES

[0068] Comparative Lubricant Examples 1 to 5 (CE1 to CE5) are prepared by blending a mixture of succinimide dispersants (total amount of succinimide dispersants 8.3 wt % including 40 wt % diluent oil), 3 wt % of a dispersant viscosity modifier commercially sold as Hitec®5777 (including diluent oil), 4 wt % of a mixture of antioxidants (including amine and phenolic antioxidants), and 1.2 wt % of glycerol monooleate friction modifier. In addition, CE1 to CE5 contain overbased detergent as is described in the table below. Also included is the charactisation data for each lubricant indicating sulphated ash content and total base number (TBN mg KOH/g).

	Overbased Detergent		Lubricant Characterisation	
	Type	wt %	Sulphated Ash (wt %)	TBN
CE1	calcium salixarate	2.4	0.45	6.63
CE2	calcium salicylate	2.16	0.44	6.59
CE3	magnesium saligenin	6	0.44	7.17
CE4	calcium sulphonate	1.06	0.44	6.27
CE5	calcium sulphurised-phenate	1.41	0.45	6.63
Footnote: Amount of each detergent quoted includes conventional amounts of diluent oil (typically ranging from 30 to 50 wt %).				

[0069] Each lubricant is then evaluated in a 4-ball wear test using steel balls (i.e., the ball composition includes iron). The procedure is the same that described in Institute of Petroleum Method IP239. The results obtained are as follows:

Lubricant	Detergent Type	4-Ball Wear Scar (microns) (steel)
CE1	calcium salixarate	433
CE2	calcium salicylate	483
CE3	magnesium saligenin	482

(continued)

Lubricant	Detergent Type	4-Ball Wear Scar (microns) (steel)
CE4	calcium sulphonate	511
CE5	calcium sulphurised-phenate	603

[0070] The results indicate that, on steel, calcium sulphurised-phenate is the least effective at controlling wear. The wear scar obtained for calcium sulphurised phenate is 18 % higher than that obtained for calcium sulphonate.

[0071] Comparative Lubricant Examples 6 to 7 (CE6 to CE7) are prepared by blending a mixture of succinimide dispersants (total amount of succinimide dispersants 7.9 wt % including 40 wt % diluent oil), a mixture of antioxidants (including amine and phenolic antioxidants), and 0.57 wt % of a zinc dialkyldithiophosphate. CE6 and CE7 contain 2 wt % (including diluent oil) and 2.7 wt % (including diluent oil) of overbased calcium sulphonate respectively.

[0072] Invention Lubricant Examples 1 and 2 (EX1 and EX2) are similar to CE6 and CE7, except EX1 contains 1.9 wt % (including 39 wt % diluent oil) and EX2 contains 2.75 wt % (including 39 wt % diluent oil) of overbased calcium sulphurised-phenate respectively in place of overbased calcium sulphonate.

[0073] CE6, CE7, EX1 and EX2 are characterised as follows:

Lubricant	Sulphated Ash (wt %)	Hydrocarbyl-Substituted Phenol Content (wt %)	Soap Content from Sulphonate (wt %)
CE6	0.5	0	1
EX1	0.5	1	0
CE7	1.0	0	1
EX2	1.0	1	0

Test: HFRR Wear

[0074] The lubricants are evaluated for wear in a programmed temperature high frequency reciprocating rig (HFRR) available from PCS Instruments. HFRR conditions for the evaluations were 500g load, 75 minute duration, 1000 micrometer stroke, 20 Hertz frequency, and temperature profile of 15 minutes at 40 °C followed by an increase in temperature to 160 °C at a rate of 2 °C per minute. The upper test piece was a 6 mm diameter aluminium silicate piece cut from a commercially available engine. Both the upper and lower specimens are available together from PCS Instruments (Part Number HFRSSP). The wear scar data obtained for aluminium based engine component is measured and presented in the following table:

	EX1	CE6	EX2	CE7
Wear Scan (microns)	218	303	212	267

[0075] Overall the data presented indicates that the lubricating composition containing overbased calcium sulphurised-phenate has reduced wear on aluminium components compared with similar lubricants containing overbased calcium sulphonate. The data indicates that the lubricating composition containing overbased calcium sulphurised-phenate has at least 20 % less wear than the lubricating composition containing overbased calcium sulphonate.

[0076] It is known that some of the materials described above may interact in the final formulation, so that the components of the final formulation may be different from those that are initially added. The products formed thereby, including the products formed upon employing lubricant composition of the present invention in its intended use, may not be susceptible of easy description. Nevertheless, all such modifications and reaction products are included within the scope of the present invention; the present invention encompasses lubricant composition prepared by admixing the components described above.

[0077] Except in the Examples, or where otherwise explicitly indicated, all numerical quantities in this description specifying amounts of materials, reaction conditions, molecular weights, number of carbon atoms, and the like, are to be understood as modified by the word "about." Unless otherwise indicated, each chemical or composition referred to herein should be interpreted as being a commercial grade material which may contain the isomers, by-products, derivatives, and other such materials which are normally understood to be present in the commercial grade. However, the amount of each chemical component is presented exclusive of any solvent or diluent oil, which may be customarily

present in the commercial material, unless otherwise indicated. It is to be understood that the upper and lower amount, range, and ratio limits set forth herein may be independently combined. Similarly, the ranges and amounts for each element of the invention may be used together with ranges or amounts for any of the other elements.

[0078] As used herein, the term "hydrocarbyl substituent" or "hydrocarbyl group" is used in its ordinary sense, which is well-known to those skilled in the art. Specifically, it refers to a group having a carbon atom directly attached to the remainder of the molecule and having predominantly hydrocarbon character. Examples of hydrocarbyl groups include: hydrocarbon substituents, including aliphatic, alicyclic, and aromatic substituents; substituted hydrocarbon substituents, that is, substituents containing non-hydrocarbon groups which, in the context of this invention, do not alter the predominantly hydrocarbon nature of the substituent; and hetero substituents, that is, substituents which similarly have a predominantly hydrocarbon character but contain other than carbon in a ring or chain. A more detailed definition of the term "hydrocarbyl substituent" or "hydrocarbyl group" is described in paragraphs [0118] to [0119] of International Publication WO2008147704.

[0079] While the invention has been explained in relation to its preferred embodiments, it is to be understood that various modifications thereof will become apparent to those skilled in the art upon reading the specification. Therefore, it is to be understood that the invention disclosed herein is intended to cover such modifications as fall within the scope of the appended claims.

Claims

1. A method of lubricating an aluminium-alloy surface of an internal combustion engine comprising supplying to the aluminium-alloy surface a lubricating composition comprising an oil of lubricating viscosity and an alkali or alkaline earth metal phenate detergent,

   wherein the alkali or alkaline earth metal phenate detergent delivers 0.75 wt % to 2 wt % of hydrocarbyl-substituted phenol to the lubricating composition;
   wherein the aluminium alloy is a eutectic or hyper-eutectic aluminium alloy;
   wherein the internal combustion engine has part or all of a cylinder bore, cylinder block, or piston ring composed of an aluminium alloy; and
   wherein the phenate detergent is a calcium sulphurised-phenate.

2. The method of claim 1, wherein the phenate detergent is an overbased calcium sulphurised-phenate.

3. The method of any preceding claim 1 to 2, wherein the lubricating composition comprises (a) an oil of lubricating viscosity, (b) an overbased alkali or alkaline earth metal phenate detergent having a TBN of 200 to 400, and further comprises (c) a neutral phenate with a TBN of 20 to 170.

4. The method of any preceding claim 1 to 3, wherein the alkali or alkaline earth metal phenate detergent has a metal ratio of 0.8 to 10 or 3 to 9, or 4 to 8, or 5 to 7.

5. The method of any preceding claim 1 to 4, wherein the alkali or alkaline earth metal phenate detergent delivers 0.9 wt % to 1.75 wt %, or 1 wt % to 1.5 wt % of hydrocarbyl-substituted phenol to the lubricating composition.

6. The method of any preceding claim 1 to 4, wherein the alkali or alkaline earth metal phenate detergent delivers 0.9 wt % to 1.75 wt % of hydrocarbyl-substituted phenol and anions thereof to the lubricating composition; and the sulphated ash content is at least 0.4 wt % to 1.3 wt % of the lubricating composition.

7. The method of any preceding claim 1 to 4, wherein the alkali or alkaline earth metal phenate detergent delivers 1 wt % or higher to 1.5 wt % of hydrocarbyl-substituted phenol to the lubricating composition; and the sulphated ash is at least 0.6 wt % to 1.1 wt % of the lubricating composition.

8. The method of any preceding claim 1 to 4, wherein the lubricating composition is characterised as having (i) a sulphur content of 0.5 wt % or less, (ii) a phosphorus content of 0.06 wt % or less, and (iii) a sulphated ash content of 1.3 wt % or less.

9. The method of any preceding claim 1 to 8, wherein the aluminium alloy is a eutectic or hyper-eutectic aluminium alloy which is derived from aluminium silicates or aluminium oxides.

10. The use of an alkali or alkaline earth metal phenate detergent as an antiwear agent for an aluminium alloy surface of an internal combustion engine, wherein the alkali or alkaline earth metal phenate detergent delivers 0.75 wt % to 2 wt % of hydrocarbyl-substituted phenol to a lubricating composition;

wherein the aluminium alloy is a eutectic or hyper-eutectic aluminium alloy;
wherein the internal combustion engine has part or all of a cylinder bore, cylinder block, or piston ring composed of an aluminium alloy; and
wherein the phenate detergent is a calcium sulphurised-phenate.

Patentansprüche

1. Verfahren zum Schmieren einer Aluminiumlegierungsoberfläche eines Verbrennungsmotors, umfassend das Zuführen einer Schmiermittelzusammensetzung, die ein Öl von Schmierviskosität und ein Alkali- oder Alkalinerdmetallphenat-Reinigungsmittel umfasst, zu der Aluminiumlegierungsoberfläche,

wobei das Alkali- oder Alkalinerdmetallphenat-Reinigungsmittel 0,75 Gew.-% bis 2 Gew.-% kohlenwasserstoffrestsubstituiertes Phenol an die Schmiermittelzusammensetzung abgibt;
wobei die Aluminiumlegierung eine eutektische oder hypereutektische Aluminiumlegierung ist;
wobei der Verbrennungsmotor einen Teil oder alle von Zylinderbohrung, Zylinderblock oder Kolbenring aus einer Aluminiumlegierung aufweist; und

wobei das Phenatreinigungsmittel ein calciumgeschwefeltes Phenat ist.

2. Verfahren nach Anspruch 1, wobei das Phenatreinigungsmittel ein überbasisches calciumgeschwefeltes Phenat ist.

3. Verfahren nach einem der Ansprüche 1 bis 2, wobei die Schmiermittelzusammensetzung (a) ein Öl mit Schmiermittelviskosität, (b) ein überbasisches Alkali- oder Alkalinerdmetallphenat-Reinigungsmittel mit einem TBN von 200 bis 400 umfasst und weiterhin (c) ein neutrales Phenat mit einem TBN von 20 bis 170 umfasst.

4. Verfahren nach einem der Ansprüche 1 bis 3, wobei das Alkali- oder Alkalinerdmetallphenat-Reinigungsmittel ein Metallverhältnis von 0,8 bis 10 oder 3 bis 9 oder 4 bis 8 oder 5 bis 7 aufweist.

5. Verfahren nach einem der Ansprüche 1 bis 4, wobei das Alkali- oder Alkalinerdmetallphenat-Reinigungsmittel 0,9 Gew.-% bis 1,75 Gew.-% oder 1 Gew.-% bis 1,5 Gew.-% kohlenwasserstoffrestsubstituiertes Phenol an die Schmiermittelzusammensetzung abgibt.

6. Verfahren nach einem der vorherigen Ansprüche 1 bis 4, wobei das Alkali- oder Alkalinerdmetallphenat-Reinigungsmittel 0,9 Gew.-% bis 1,75 Gew.-% des kohlenwasserstoffrestsubstituierten Phenols und Anionen davon an die Schmiermittelzusammensetzung abgibt; und wobei der Sulfataschegehalt mindestens 0,4 Gew.-% bis 1,3 Gew.-% der Schmiermittelzusammensetzung beträgt.

7. Verfahren nach einem der vorherigen Ansprüche 1 bis 4, wobei das Alkali- oder Alkalinerdmetallphenat-Reinigungsmittel 1 Gew.-% oder mehr bis 1,5 Gew.-% des kohlenwasserstoffrestsubstituierten Phenols an die Schmiermittelzusammensetzung abgibt; und wobei die Sulfatasche mindestens 0,6 Gew.-% bis 1,1 Gew.-% der Schmiermittelzusammensetzung beträgt.

8. Verfahren nach einem der vorherigen Ansprüche 1 bis 4, wobei die Schmiermittelzusammensetzung **dadurch gekennzeichnet ist, dass** sie (i) einen Schwefelgehalt von 0,5 Gew.-% oder weniger, (ii) einen Phosphorgehalt von 0,06 Gew.-% oder weniger und (iii) einen Schwefelaschegehalt von 1,3 Gew.-% oder weniger aufweist.

9. Verfahren nach einem der vorherigen Ansprüche 1 bis 8, wobei die Aluminiumlegierung eine eutektische oder hypereutektische Aluminiumlegierung ist, die aus Aluminiumsilikaten oder Aluminiumoxiden abgeleitet wird.

10. Verwendung eines Alkali- oder Alkalinerdmetallphenat-Reinigungsmittels als Antiverschleißmittel für eine Aluminiumlegierungsoberfläche eines Verbrennungsmotors, wobei das Alkali- oder Alkalinerdmetallphenat-Reinigungsmittel 0,75 Gew.-% bis 2 Gew.-% des kohlenwasserstoffrestsubstituierten Phenols an die Schmiermittelzusammensetzung abgibt;

wobei die Aluminiumlegierung eine eutektische oder hypereutektische Aluminiumlegierung ist;
wobei der Verbrennungsmotor einen Teil oder alle von Zylinderbohrung, Zylinderblock oder Kolbenring aus einer Aluminiumlegierung aufweist; und
wobei das Phenatreinigungsmittel ein calciumgeschwefeltes Phenat ist.

Revendications

1. Procédé de lubrification d'une surface en alliage d'aluminium d'un moteur à combustion interne comprenant le fait d'amener sur la surface en alliage d'aluminium une composition lubrifiante comprenant une huile de viscosité lubrifiante et un détergent de type phénate de métal alcalin ou alcalino-terreux,

   dans lequel le détergent de type phénate de métal alcalin ou alcalino-terreux apporte 0,75 % en poids à 2 % en poids de phénol à substitution hydrocarbyle à la composition lubrifiante ;
   dans lequel l'alliage d'aluminium est un alliage d'aluminium eutectique ou hyper-eutectique ;
   dans lequel le moteur à combustion interne possède une partie ou la totalité d'un alésage, d'un bloc-cylindres ou d'un segment de piston composé d'un alliage d'aluminium ; et
   dans lequel le détergent de type phénate est un phénate de calcium sulfuré.

2. Procédé selon la revendication 1, dans lequel le détergent de type phénate est un phénate de calcium sulfuré surbasique.

3. Procédé selon l'une quelconque des revendications 1 à 2 précédentes, dans lequel la composition lubrifiante comprend (a) une huile de viscosité lubrifiante, (b) un détergent de type phénate de métal alcalin ou alcalino-terreux surbasique possédant un indice de base total de 200 à 400, et comprend en outre (c) un phénate neutre ayant un indice de base total de 20 à 170.

4. Procédé selon l'une quelconque des revendications 1 à 3 précédentes, dans lequel le détergent de type phénate de métal alcalin ou alcalino-terreux possède un taux de métal de 0,8 à 10 ou de 3 à 9, ou de 4 à 8, ou de 5 à 7.

5. Procédé selon l'une quelconque des revendications 1 à 4 précédentes, dans lequel le détergent de type phénate de métal alcalin ou alcalino-terreux apporte 0,9 % en poids à 1,75 % en poids, ou 1 % en poids à 1,5 % en poids, de phénol à substitution hydrocarbyle à la composition lubrifiante.

6. Procédé selon l'une quelconque des revendications 1 à 4 précédentes, dans lequel le détergent de type phénate de métal alcalin ou alcalino-terreux apporte 0,9 % en poids à 1,75 % en poids de phénol à substitution hydrocarbyle et de ses anions à la composition lubrifiante ; et la teneur en cendres sulfatées représente au moins 0,4 % en poids à 1,3 % en poids de la composition lubrifiante.

7. Procédé selon l'une quelconque des revendications 1 à 4 précédentes, dans lequel le détergent de type phénate de métal alcalin ou alcalino-terreux apporte 1 % en poids ou plus à 1,5 % en poids de phénol à substitution hydrocarbyle à la composition lubrifiante ; et les cendres sulfatées représentent au moins 0,6 ô en poids à 1,1 % en poids de la composition lubrifiante.

8. Procédé selon l'une quelconque des revendications 1 à 4 précédentes, dans lequel la composition lubrifiante est **caractérisée en ce qu'**elle possède (i) une teneur en soufre de 0,5 % en poids ou moins, (ii) une teneur en phosphore de 0,06 % en poids ou moins, et (iii) une teneur en cendres sulfatées de 1,3 % en poids ou moins.

9. Procédé selon l'une quelconque des revendications 1 à 8 précédentes, dans lequel l'alliage d'aluminium est un alliage d'aluminium eutectique ou hyper-eutectique qui est dérivé de silicates d'aluminium ou d'oxydes d'aluminium.

10. Utilisation d'un détergent de type phénate de métal alcalin ou alcalino-terreux comme agent anti-usure pour une surface en alliage d'aluminium d'un moteur à combustion interne, dans laquelle le détergent de type phénate de métal alcalin ou alcalino-terreux apporte 0,75 % en poids à 2 % en poids de phénol à substitution hydrocarbyle à une composition lubrifiante ;

    dans laquelle l'alliage d'aluminium est un alliage d'aluminium eutectique ou hyper-eutectique ;
    dans laquelle le moteur à combustion interne possède une partie ou la totalité d'un alésage, d'un bloc-cylindres

ou d'un segment de piston composé d'un alliage d'aluminium ; et
dans laquelle le détergent de type phénate est un phénate de calcium sulfuré.

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- EP 1624044 A1, Oldfield **[0005] [0006]**
- WO 2008147701 A, Davies **[0005] [0007]**
- EP 1041134 A2 **[0008]**
- EP 2077317 A1 **[0009]**
- EP 1418353 A2 **[0010]**
- EP 1475430 A2 **[0011]**
- EP 1680491 A **[0014]**
- EP 1778824 A **[0014]**
- US 6551965 B **[0023]**
- EP 1903093 A **[0023]**
- EP 0601721 A **[0023]**
- WO 2008147704 A **[0033] [0078]**
- US 3172892 A **[0041]**
- US 3219666 A **[0041]**
- US 3316177 A **[0041]**
- US 3340281 A **[0041]**
- US 3351552 A **[0041]**
- US 3381022 A **[0041]**
- US 3433744 A **[0041]**
- US 3444170 A **[0041]**
- US 3467668 A **[0041]**
- US 3501405 A **[0041]**
- US 3542680 A **[0041]**
- US 3576743 A **[0041]**
- US 3632511 A **[0041]**
- US 4234435 A **[0041]**
- US RE26433 A **[0041]**
- US 6165235 A **[0041]**
- US 7238650 A **[0041]**
- EP 0355895 A **[0041]**
- WO 2006015130 A **[0045]**
- US 4863623 A **[0045]**
- US 6107257 A **[0045]**
- US 6107258 A **[0045]**
- US 6117825 A **[0045]**
- US 2005065045 A **[0052]**
- US 7407919 B **[0052]**
- US 6559105 B **[0055]**
- US 05038319 A **[0060]**
- WO 2006047486 A **[0060]**

Non-patent literature cited in the description

- Chemistry and Technology of Lubricants. 1997, 85, , 86 **[0021]**