

DESCRIPTION**TITLE OF INVENTION****LUBRICATING OILS FOR WET CLUTCH SYSTEMS**

5

FIELD OF THE INVENTION

The present invention generally relates to lubricating oil compositions useful for industrial machinery, especially transport, construction and agricultural machinery.

10

BACKGROUND OF THE INVENTION

Lubricating oils for automatic transmissions, called automatic transmission fluids, have been used conventionally to assist smooth operation of automatic transmissions which are installed in automobiles, trucks, construction machinery, and other vehicles. They include torque converters, gear mechanisms, wet clutches, and hydraulic systems.

15

It is well known that lubricant additives give effects on the friction properties of wet clutch and steel plates. Additive effects are caused by both their physical and chemical absorption on clutch materials, ex. cellulose, aramid (a natural and synthesized) fibers, silica and steel plate surface.

20

Diesel engine oils are widely used for internal combustion engines, not only automotive heavy duty but also construction machinery diesel engine systems in Asia, and especially in Japan. Some construction machines are equipped with wet-clutch systems in not only the transmission but also the steering, parking brake, and many systems to control moving and power operating torque. The wet clutch (static) friction between the clutch material and steel in lubricant fluids is very important to transmit the engine power efficiently.

25

In addition, the wet clutch static friction coefficient depends on wet clutch torque capacity. Engine oils are widely used for transmission and hydraulic systems in construction machinery, and their wet clutch systems. It is important to maintain a higher (static) friction coefficient of wet clutches to operate safely, and also transmit power efficiently for construction machineries. If a lubricant gives poor friction performance, power loss, slow response of

30

machine operation which can negatively impact safety when operating the machinery, or

uncomfortable vibration with high noise from lock-up of the wet clutch in the transmission would occur.

The present invention finds a solution for maintaining higher static friction coefficient of wet clutches which are not only important in construction equipment but also motorcycle lubricants that are equipped with a transmission and wet clutch.

SUMMARY OF THE INVENTION

In accordance with one embodiment of the present invention, provided is a lubricating oil composition comprising:

- (a) a major amount of oil of lubricating viscosity,
- (b) a calcium containing detergent,
- (c) at least 800 ppm of Mg from a magnesium containing detergent
- (d) less than 600 ppm of N from a nitrogen containing dispersant;

wherein the lubricating oil composition has a phosphorus content of from 0.06 to 0.15 wt. %, a sulfur content of less than 0.5 wt. % and a sulfated ash content of from greater than 0.8 wt. % to 2.0 wt. %, wherein the mass ratio of Ca to Mg is from 1:2 to 4:1, and wherein said lubricating oil composition lubricates the crankcase of an internal combustion engine of a vehicle and at least one of a wet clutch, brakes, torque converters, gear systems, hydro static transmissions and hydraulic systems.

In accordance with another embodiment of the present invention, provided is a method for maintaining friction in a vehicle comprising lubricating said vehicle with a lubricating oil composition comprising:

- (a) a major amount of oil of lubricating viscosity,
- (b) a calcium containing detergent,
- (c) at least 800 ppm of Mg from a magnesium containing detergent
- (d) less than 600 ppm of N from a nitrogen containing dispersant;

wherein the lubricating oil composition has a phosphorus content of from 0.06 to 0.15 wt. %, a sulfur content of less than 0.5 wt. % and a sulfated ash content of from greater than 0.8 wt. % to 2.0 wt. %, wherein the mass ratio of Ca to Mg is from 1:2 to 4:1, and

wherein said lubricating oil composition lubricates the crankcase of an internal combustion engine of said vehicle and at least one of a wet clutch, brakes, torque converters, gear systems, hydro static transmissions and hydraulic systems.

5

DETAILED DESCRIPTION OF THE INVENTION

To facilitate the understanding of the subject matter disclosed herein, a number of terms, abbreviations or other shorthand as used herein are defined below. Any term, abbreviation or shorthand not defined is understood to have the ordinary meaning used by a skilled artisan contemporaneous with the submission of this application.

Definitions

In this specification, the following words and expressions, if and when used, have the meanings given below.

15 A “major amount” means in excess of 50 weight % of a composition.

A “minor amount” means less than 50 weight % of a composition, expressed in respect of the stated additive and in respect of the total mass of all the additives present in the composition, reckoned as active ingredient of the additive or additives.

20 “Active ingredients” or “actives” refers to additive material that is not diluent or solvent.

All percentages reported are weight % on an active ingredient basis (i.e., without regard to carrier or diluent oil) unless otherwise stated.

The abbreviation “ppm” means parts per million by weight, based on the total weight of the lubricating oil composition.

25 High temperature high shear (HTHS) viscosity at 150°C was determined in accordance with ASTM D4683.

Kinematic viscosity at 100°C (KV₁₀₀) was determined in accordance with ASTM D445.

Metal – The term “metal” refers to alkali metals, alkaline earth metals, or mixtures thereof.

Throughout the specification and claims the expression oil soluble or dispersible is used. By oil soluble or dispersible is meant that an amount needed to provide the desired
5 level of activity or performance can be incorporated by being dissolved, dispersed or suspended in an oil of lubricating viscosity. Usually, this means that at least about 0.001% by weight of the material can be incorporated in a lubricating oil composition. For a further discussion of the terms oil soluble and dispersible, particularly “stably dispersible”, see U.S. Pat. No. 4,320,019 which is expressly incorporated herein by reference for relevant teachings
10 in this regard.

The term “sulfated ash” as used herein refers to the non-combustible residue resulting from detergents and metallic additives in lubricating oil. Sulfated ash may be determined using ASTM Test D874.

The term “Total Base Number” or “TBN” as used herein refers to the amount of base
15 equivalent to milligrams of KOH in one gram of sample. Thus, higher TBN numbers reflect more alkaline products, and therefore a greater alkalinity. TBN was determined using ASTM D 2896 test.

Boron, calcium, magnesium, molybdenum, phosphorus, sulfur, and zinc contents were determined in accordance with ASTM D5185.

20 Nitrogen content was determined in accordance with ASTM D4629.

All ASTM standards referred to herein are the most current versions as of the filing date of the present application.

Unless otherwise specified, all percentages are in weight percent.

While the disclosure is susceptible to various modifications and alternative forms,
25 specific embodiments thereof are herein described in detail. It should be understood, however, that the description herein of specific embodiments is not intended to limit the disclosure to the particular forms disclosed, but on the contrary, the intention is to cover all modifications, equivalents, and alternatives falling within the spirit and scope of the disclosure as defined by the appended claims.

30 Note that not all of the activities described in the general description or the examples are required, that a portion of a specific activity may not be required, and that one or more further activities may be performed in addition to those described. Still further, the order in which activities are listed is not necessarily the order in which they are performed.

Benefits, other advantages, and solutions to problems have been described herein with regard to specific embodiments. However, the benefits, advantages, solutions to problems, and any feature(s) that may cause any benefit, advantage, or solution to occur or become more pronounced are not to be construed as a critical, required, or essential feature of any or
5 all the claims.

The specification and illustrations of the embodiments described herein are intended to provide a general understanding of the structure of the various embodiments.

As used herein, the terms “comprises,” “comprising,” “includes,” “including,” “has,” “having,” or any other variation thereof, are intended to cover a non-exclusive inclusion. For
10 example, a process, method, article, or apparatus that comprises a list of features is not necessarily limited only to those features but may include other features not expressly listed or other features that are inherent to such process, method, article, or apparatus. Further, unless expressly stated to the contrary, “or” refers to an inclusive-or and not to an exclusive-or. For example, a condition A or B is satisfied by any one of the following: A is true (or
15 present) and B is false (or not present), A is false (or not present) and B is true (or present), and both A and B are true (or present).

The use of “a” or “an” is employed to describe elements and components described herein. This is done merely for convenience and to give a general sense of the scope of the embodiments of the disclosure. This description should be read to include one or at least one
20 and the singular also includes the plural, or vice versa, unless it is clear that it is meant otherwise. The term “averaged,” when referring to a value, is intended to mean an average, a geometric mean, or a median value. Group numbers corresponding to columns within the Periodic Table of the elements use the “New Notation” convention as seen in the CRC Handbook of Chemistry and Physics, 81st Edition (2000-2001).

Unless otherwise defined, all technical and scientific terms used herein have the same
25 meaning as commonly understood by one of ordinary skill in the art to which this disclosure belongs. The materials, methods, and examples are illustrative only and not intended to be limiting. To the extent not described herein, many details regarding specific materials and processing acts are conventional and may be found in textbooks and other sources within the
30 lubricants as well as the oil and gas industries.

The specification and illustrations are not intended to serve as an exhaustive and comprehensive description of all the elements and features of formulations, compositions, apparatus and systems that use the structures or methods described herein. Separate

embodiments may also be provided in combination in a single embodiment, and conversely, various features that are, for brevity, described in the context of a single embodiment, may also be provided separately or in any sub-combination. Further, reference to values stated in ranges includes each and every value within that range. Many other embodiments may be apparent to skilled artisans only after reading this specification. Other embodiments may be used and derived from the disclosure, such that a structural substitution, logical substitution, or another change may be made without departing from the scope of the disclosure. Accordingly, the disclosure is to be regarded as illustrative rather than restrictive.

10 In accordance with one embodiment of the present invention, provided is a lubricating oil composition comprising:

- (a) a major amount of oil of lubricating viscosity,
- (b) a calcium containing detergent,
- (c) at least 800 ppm of Mg from a magnesium containing detergent
- (d) less than 600 ppm of N from a nitrogen containing dispersant;

15 wherein the lubricating oil composition has a phosphorus content of from 0.06 to 0.15 wt. %, a sulfur content of less than 0.5 wt. % and a sulfated ash content of from greater than 0.8 wt. % to 2.0 wt. %,

wherein the mass ratio of Ca to Mg is from 1:2 to 4:1, and

20 wherein said lubricating oil composition lubricates the crankcase of an internal combustion engine of a vehicle and at least one of a wet clutch, brakes, torque converters, gear systems, hydro static transmissions and hydraulic systems.

In one embodiment of the present invention, the vehicle is an industrial machinery, an automobile, a truck, or other vehicle. In another embodiment the industrial machinery is a transport, construction, or an agricultural machinery.

25 In one embodiment the transport machinery is a bus or truck equipped with a Diesel Engine and a hydraulic system.

In one embodiment the construction machinery is equipped with a Diesel engine, a Hydro Static Transmission (HST), a Power shift transmission with wet clutches, and a hydraulic system.

30 In one embodiment the agricultural machinery is equipped with a Diesel engine, a Hydro Static Transmission (HST), a Power shift transmission with wet clutches, and a hydraulic system.

In another embodiment the vehicle is equipped with an automatic transmission, or a continuously variable transmission.

In another embodiment, provided is a method for maintaining friction in a vehicle comprising lubricating said vehicle with a lubricating oil composition comprising:

- 5 (a) a major amount of oil of lubricating viscosity,
 - (b) a calcium containing detergent,
 - (c) at least 800 ppm of Mg from a magnesium containing detergent
 - (d) less than 600 ppm of N from a nitrogen containing dispersant;
- wherein the lubricating oil composition has a phosphorus content of from 0.06
10 to 0.15 wt. %, a sulfur content of less than 0.5 wt. % and a sulfated ash content of from greater than 0.8 wt. % to 2.0 wt. %, wherein the mass ratio of Ca to Mg is from 1:2 to 4:1, and wherein said lubricating oil composition lubricates the crankcase of an internal combustion engine of said vehicle and at least one of a wet clutch, brakes,
15 torque converters, gear systems, hydro static transmissions and hydraulic systems.

Oil of Lubricating viscosity/Base Oil Component

The oil of lubricating viscosity (sometimes referred to as “base stock” or “base oil”) is
20 the primary liquid constituent of a lubricant, into which additives and possibly other oils are blended, for example to produce a final lubricant (or lubricant composition). A base oil is useful for making concentrates as well as for making lubricating oil compositions therefrom, and may be selected from natural and synthetic lubricating oils and combinations thereof.

Natural oils include animal and vegetable oils, liquid petroleum oils and hydrorefined,
25 solvent-treated mineral lubricating oils of the paraffinic, naphthenic and mixed paraffinic-naphthenic types. Oils of lubricating viscosity derived from coal or shale are also useful base oils.

Synthetic lubricating oils include hydrocarbon oils such as polymerized and
interpolymerized olefins (e.g., polybutylenes, polypropylenes, propylene-isobutylene
30 copolymers, chlorinated polybutylenes, poly(1-hexenes), poly(1-octenes), poly(1-decenes); alkylbenzenes (e.g., dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di(2-ethylhexyl)benzenes; polyphenols (e.g., biphenyls, terphenyls, alkylated polyphenols); and

alkylated diphenyl ethers and alkylated diphenyl sulfides and the derivatives, analogues and homologues thereof.

Another suitable class of synthetic lubricating oils comprises the esters of dicarboxylic acids (e.g., malonic acid, alkyl malonic acids, alkenyl malonic acids, succinic acid, alkyl succinic acids and alkenyl succinic acids, maleic acid, fumaric acid, azelaic acid, suberic acid, sebacic acid, adipic acid, linoleic acid dimer, phthalic acid) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, propylene glycol). Specific examples of these esters include dibutyl adipate, di(2-ethylhexyl) sebacate, di-*n*-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, and the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid.

Esters useful as synthetic oils also include those made from C₅ to C₁₂ monocarboxylic acids and polyols, and polyol ethers such as neopentyl glycol, trimethylolpropane, pentaerythritol, dipentaerythritol and tripentaerythritol.

The base oil may be derived from Fischer-Tropsch synthesized hydrocarbons. Fischer-Tropsch synthesized hydrocarbons are made from synthesis gas containing H₂ and CO using a Fischer-Tropsch catalyst. Such hydrocarbons typically require further processing in order to be useful as the base oil. For example, the hydrocarbons may be hydroisomerized; hydrocracked and hydroisomerized; dewaxed; or hydroisomerized and dewaxed; using processes known to those skilled in the art.

Unrefined, refined and re-refined oils can be used in the present lubricating oil composition. Unrefined oils are those obtained directly from a natural or synthetic source without further purification treatment. For example, a shale oil obtained directly from retorting operations, a petroleum oil obtained directly from distillation or ester oil obtained directly from an esterification process and used without further treatment would be unrefined oil. Refined oils are similar to the unrefined oils except they have been further treated in one or more purification steps to improve one or more properties. Many such purification techniques, such as distillation, solvent extraction, acid or base extraction, filtration and percolation are known to those skilled in the art. Re-refined oils are obtained by processes similar to those used to obtain refined oils applied to refined oils which have been already used in service. Such re-refined oils are also known as reclaimed or reprocessed oils and

often are additionally processed by techniques for approval of spent additive and oil breakdown products.

Hence, the base oil which may be used to make the present lubricating oil composition may be selected from any of the base oils in Groups I-V as specified in the American Petroleum Institute (API) Base Oil Interchangeability Guidelines (API Publication 1509). Such base oil groups are summarized in Table 1 below:

TABLE 1

Group ^(a)	Base Oil Properties		
	Saturates ^(b) , wt. %	Sulfur ^(c) , wt. %	Viscosity Index ^(d)
Group I	<90 and/or	>0.03	80 to <120
Group II	≥90	≤0.03	80 to <120
Group III	≥90	≤0.03	≥120
Group IV	Polyalphaolefins (PAOs)		
Group V	All other base stocks not included in Groups I, II, III or IV		

^(a) Groups I-III are mineral oil base stocks.

^(b) Determined in accordance with ASTM D2007.

^(c) Determined in accordance with ASTM D2622, ASTM D3120, ASTM D4294 or ASTM D4927.

^(d) Determined in accordance with ASTM D2270.

Base oils suitable for use herein are any of the variety corresponding to API Group I, II, Group III, Group IV, and Group V oils and combinations thereof.

The base oil constitutes the major component of the present lubricating oil composition and is present in an amount ranging from greater than 50 to 99 wt. % (e.g., 70 to 95 wt. %, or 85 to 95 wt. %).

In general, the level of sulfur in the lubricating oil compositions of the present invention is less than or equal to about 0.7 wt. %, based on the total weight of the lubricating oil composition, e.g., a level of sulfur of about 0.01 wt. % to about 0.70 wt. %, 0.01 to 0.6 wt.%, 0.01 to 0.5 wt.%, 0.01 to 0.4 wt.%, 0.01 to 0.3 wt.%, 0.01 to 0.2 wt.%, 0.01 wt. % to 0.10 wt. %. In one embodiment, the level of sulfur in the lubricating oil compositions of the present invention is less than or equal to about 0.60 wt. %, less than or equal to about 0.50

wt. %, less than or equal to about 0.40 wt. %, less than or equal to about 0.35 wt. %, less than or equal to about 0.34 wt. %, less than or equal to about 0.33 wt. %, less than or equal to about 0.32 wt. %, less than or equal to about 0.31 wt. %, less than or equal to about 0.30 wt. % based on the total weight of the lubricating oil composition.

5 In one embodiment, the levels of phosphorus in the lubricating oil compositions of the present invention is less than or equal to about 0.15 wt. %, based on the total weight of the lubricating oil composition. In one embodiment, the levels of phosphorus in the lubricating oil compositions of the present invention is about 0.06 wt. % to about 0.15 wt. %. In one embodiment, the levels of phosphorus in the lubricating oil compositions of the present invention is less than or equal to about 0.14 wt. %, based on the total weight of the lubricating oil composition, e.g., a level of phosphorus of about 0.06 wt. % to about 0.14 wt. %. In one embodiment, the levels of phosphorus in the lubricating oil compositions of the present invention is less than or equal to about 0.13 wt. %, based on the total weight of the lubricating oil composition, e.g., a level of phosphorus of about 0.06 wt. % to about 0.13 wt. %. In one embodiment, the levels of phosphorus in the lubricating oil compositions of the present invention is less than or equal to about 0.12 wt. %, based on the total weight of the lubricating oil composition, e.g., a level of phosphorus of about 0.06 wt. % to about 0.12 wt. %.

20 In one embodiment, the level of sulfated ash produced by the lubricating oil compositions of the present invention is less than or equal to about 1.60 wt. % as determined by ASTM D 874, e.g., a level of sulfated ash of from about 0.80 to about 1.60 wt. % as determined by ASTM D 874. In one embodiment, the level of sulfated ash produced by the lubricating oil compositions of the present invention is less than or equal to about 1.50 wt. % as determined by ASTM D 874, e.g., a level of sulfated ash of from about 0.80 to about 1.50 wt. % as determined by ASTM D 874. In one embodiment, the level of sulfated ash produced by the lubricating oil compositions of the present invention is less than or equal to about 1.40 wt. % as determined by ASTM D 874, e.g., a level of sulfated ash of from about 0.80 to about 1.40 wt. % as determined by ASTM D 874

30

Suitably, the present lubricating oil composition may have a total base number (TBN) of 8 to 16 mg KOH/g. In some embodiments, the lubricating oil composition may have a total

base number (TBN) of 10 to 16 mg KOH/g, 10 to 14 mg KOH/g, 10 to 13 mg KOH/g, or 10 to 12 mg KOH/g.

In some embodiments for example, the desired grade of oil, is of SAE Viscosity Grade 0W-30, 0W-40, 5W-30, 10W-30, 10W-40, 10W-50, 15W-30, 15W-40, 20W-50, 30, 40 and the like.

Detergent Mixture

The detergent mixture comprises at least one calcium-containing detergent and at least one magnesium-containing detergent.

A typical detergent is an anionic material that contains a long chain hydrophobic portion of the molecule and a smaller anionic or oleophobic hydrophilic portion of the molecule. The anionic portion of the detergent is typically derived from an organic acid such as a sulfur acid, carboxylic acid, phosphorous acid, phenol, or mixtures thereof. The counterion is typically an alkaline earth or alkali metal.

Salts that contain a substantially stoichiometric amount of the metal are described as neutral salts and have a total base number (TBN) of from 0 to 80 mg KOH/g. Many compositions are overbased, containing large amounts of a metal base that is achieved by reacting an excess of a metal compound (e.g., a metal hydroxide or oxide) rich an acidic gas (e.g., carbon dioxide). Useful detergents can be neutral, mildly overbased, or highly overbased.

It is desirable for at least some detergent used in the detergent mixture to be overbased. Overbased detergents help neutralize acidic impurities produced by the combustion process and become entrapped in the oil. Typically, the overbased material has a ratio of metallic ion to anionic portion of the detergent of 1.05:1 to 50:1 (e.g., 4:1 to 25:1) on an equivalent basis. The resulting detergent is an overbased detergent that will typically have a TBN of 150 mg KOH/g or higher (e.g., 250 to 450 mg KOH/g or more). A mixture of detergents of differing TBN can be used.

In some embodiments, the overbased detergents may be low overbased, e.g., an overbased salt having a TBN below 100 on an actives basis. In one embodiment, the TBN of a low overbased salt may be from about 30 to about 100. In another embodiment, the TBN of a low overbased salt may be from about 30 to about 80. In some embodiments, the overbased detergents may be medium overbased, e.g., an overbased salt having a TBN from about 100 to about 250. In one embodiment, the TBN of a medium overbased salt may be from about

100 to about 200. In another embodiment, the TBN of a medium overbased salt may be from about 125 to about 175. In some embodiments, the overbased detergents may be high overbased, e.g., an overbased salt having a TBN above 250. In one embodiment, the TBN of a high overbased salt may be from about 250 to about 800 on an active basis.

- 5 Suitable detergents include metal salts of sulfonates, phenates, carboxylates, phosphates, and salicylates.

 Sulfonates may be prepared from sulfonic acids which are typically obtained by the sulfonation of alkyl-substituted aromatic hydrocarbons such as those obtained from the fractionation of petroleum or by the alkylation of aromatic hydrocarbons. Examples included
10 those obtained by alkylating benzene, toluene, xylene, naphthalene, diphenyl or their halogen derivatives. The alkylation may be carried out in the presence of a catalyst with alkylating agents having from about 3 to more than 70 carbon atoms. The alkaryl sulfonates usually contain from about 9 to 80 or more carbon atoms (e.g., about 16 to 60 carbon atoms) per alkyl substituted aromatic moiety.

- 15 Phenates can be prepared by reacting an alkaline earth metal hydroxide or oxide (e.g., CaO, Ca(OH)₂, MgO, or Mg(OH)₂) with an alkyl phenol or sulfurized alkylphenol. Useful alkyl groups include straight or branched chain C₁ to C₃₀ (e.g., C₄ to C₂₀) alkyl groups, or mixtures thereof. Examples of suitable phenols include isobutylphenol, 2-ethylhexylphenol, nonylphenol, dodecyl phenol, and the like. It should be noted that starting alkylphenols may
20 contain more than one alkyl substituent that are each independently straight chain or branched chain. When a non-sulfurized alkylphenol is used, the sulfurized product may be obtained by methods well known in the art. These methods include heating a mixture of alkylphenol and sulfurizing agent (e.g., elemental sulfur, sulfur halides such as sulfur dichloride, and the like) and then reacting the sulfurized phenol with an alkaline earth metal
25 base.

 Salicylates may be prepared by reacting a basic metal compound with at least one carboxylic acid and removing water from the reaction product. Detergents made from salicylic acid are one class of detergents prepared from carboxylic acids. Useful salicylates include long chain alkyl salicylates.

- 30 Hydrocarbyl-substituted salicylic acids may be prepared from phenols by the Kolbe reaction (see U.S. Patent No. 3,595,791). The metal salts of the hydrocarbyl-substituted

salicylic acids may be prepared by double decomposition of a metal salt in a polar solvent such as water or alcohol.

Alkaline earth metal phosphates are also used as detergents and are known in the art.

Preferred calcium-containing detergents include calcium sulfonates, calcium phenates,
5 and calcium salicylates, especially calcium sulfonates, calcium salicylates, and mixtures thereof.

Calcium Detergent

In one embodiment, the calcium-containing detergents include calcium sulfonates,
10 calcium phenates, and calcium salicylates.

The calcium-containing detergent may be used in an amount that provides at least 1000 ppm, at least 1050 ppm, at least 1100 ppm, at least 1150 ppm, at least 1200 ppm, at least 1250 ppm, at least 1300 ppm, at least 1350 ppm, at least 1400 ppm, at least 1450 ppm, at least 1500 ppm, at least 1550 ppm, at least 1600 ppm, at least 1650 ppm, at least 1700 ppm,
15 at least 1750 ppm, at least 1800 ppm, at least 1850 ppm, at least 1900 ppm, at least 1950 ppm, at least 2000 ppm by weight of calcium to the lubricating oil composition. In one embodiment, the calcium content is not greater than 4000 ppm, not greater than 3500 ppm, not greater than 3000 ppm by weight of calcium to the lubricating oil composition.

In some embodiments, the calcium-containing detergents can be high overbased,
20 medium overbased, or low overbased detergents.

Magnesium Detergent

Preferred magnesium-containing detergents include magnesium sulfonates, magnesium phenates, and magnesium salicylates, especially magnesium sulfonates.

The magnesium-containing detergent may be used in an amount that provides at least 800 ppm, at least 850 ppm, at least 900 ppm, at least 950 ppm, at least 1000 ppm, at least 1050 ppm, at least 1100 ppm, at least 1150 ppm, at least 1200 ppm, at least 1250 ppm, at least 1300 ppm, at least 1350 ppm, at least 1400 ppm, at least 1450 ppm, at least 1500 ppm, at least 1550 ppm, at least 1600 ppm, at least 1650 ppm, at least 1700 ppm, at least 1750 ppm,
25 at least 1800 ppm, at least 1850 ppm, at least 1900 ppm, at least 1950 ppm, at least 2000 ppm by weight of magnesium in the lubricating oil composition. In one embodiment, the magnesium content is not greater than 4000 ppm, not greater than 3500 ppm, not greater than 3000 ppm, not greater than 2500 ppm, by weight of magnesium in the lubricating oil
30

composition. In one embodiment, the magnesium content is from 800 to 2500 ppm, from 900 to 2300 ppm, from 1100 to 2300 ppm, 1300 to 2300 ppm, 1500 to 2300 ppm by weight of magnesium in the lubricating oil composition.

In some embodiments, the magnesium-containing detergents can be high overbased, medium overbased, or low overbased detergents. In one embodiment, the mass ratio of calcium to magnesium in the lubricating oil composition is from 0.5:1 to 4:1. In other embodiments, the mass ratio of calcium to magnesium in the lubricating oil composition is from 0.6:1 to 3.5:1, 0.6:1 to 3.0:1, 0.6:1 to 2.5:1, 0.6:1 to 2.0:1, 0.6:1 to 1.7:1, 0.6:1 to 1.5:1, 0.6:1 to 1.3:1.

Nitrogen Containing Dispersant

Dispersants maintain in suspension materials resulting from oxidation during engine operation that are insoluble in oil, thus preventing sludge flocculation and precipitation or deposition on metal parts. Dispersants useful herein include nitrogen-containing, ashless (metal-free) dispersants known to be effective to reduce formation of deposits upon use in gasoline and diesel engines.

Suitable dispersants include hydrocarbyl succinimides, hydrocarbyl succinamides, mixed ester/amides of hydrocarbyl-substituted succinic acid, hydroxyesters of hydrocarbyl-substituted succinic acid, and Mannich condensation products of hydrocarbyl-substituted phenols, formaldehyde and polyamines. Also suitable are condensation products of polyamines and hydrocarbyl-substituted phenyl acids. Mixtures of these dispersants can also be used.

Basic nitrogen-containing ashless dispersants are well-known lubricating oil additives and methods for their preparation are extensively described in the patent literature. Preferred dispersants are the alkenyl succinimides and succinamides where the alkenyl-substituent is a long-chain of preferably greater than 40 carbon atoms. These materials are readily made by reacting a hydrocarbyl-substituted dicarboxylic acid material with a molecule containing amine functionality. Examples of suitable amines are polyamines such as polyalkylene polyamines, hydroxy-substituted polyamines and polyoxyalkylene polyamines.

Particularly preferred ashless dispersants are the polyisobutenyl succinimides formed from polyisobutenyl succinic anhydride and a polyalkylene polyamine such as a polyethylene polyamine of formula:



wherein z is 1 to 11. The polyisobutenyl group is derived from polyisobutene and preferably has a number average molecular weight (Mn) in a range of 700 to 3000 Daltons (e.g., 900 to 2500 Daltons). For example, the polyisobutenyl succinimide may be a bis-succinimide derived from a polyisobutenyl group having a Mn of 900 to 2500 Daltons.

As is known in the art, the dispersants may be post-treated (e.g., with a boronating agent or a cyclic carbonate).

Nitrogen-containing ashless (metal-free) dispersants are basic, and contribute to the TBN of a lubricating oil composition to which they are added, without introducing additional sulfated ash.

Dispersants may be present at an amount to provide less than 600 ppm nitrogen to the lubricating oil composition, less than 550 ppm, less than 500 ppm, less than 450 ppm, less than 400 ppm of nitrogen by weight of nitrogen to the lubricating oil composition.

Other Lubricating Oil Additives

In addition to the additives compound described herein, the lubricating oil composition can comprise additional lubricating oil additives.

The lubricating oil compositions of the present disclosure may also contain other conventional additives that can impart or improve any desirable property of the lubricating oil composition in which these additives are dispersed or dissolved. Any additive known to a person of ordinary skill in the art may be used in the lubricating oil compositions disclosed herein. Some suitable additives have been described in Mortier et al., "Chemistry and Technology of Lubricants", 2nd Edition, London, Springer, (1996); and Leslie R. Rudnick, "Lubricant Additives: Chemistry and Applications", New York, Marcel Dekker (2003), both of which are incorporated herein by reference. For example, the lubricating oil compositions can be blended with antioxidants, anti-wear agents, metal detergents, rust inhibitors, dehazing agents, demulsifying agents, metal deactivating agents, friction modifiers, pour point depressants, antifoaming agents, co-solvents, corrosion-inhibitors, ashless dispersants, multifunctional agents, dyes, extreme pressure agents and the like and mixtures thereof. A variety of the additives are known and commercially available. These additives, or their analogous compounds, can be employed for the preparation of the lubricating oil compositions of the disclosure by the usual blending procedures.

The lubricating oil composition of the present invention can contain one or more anti-wear agents that can reduce friction and excessive wear. Any anti-wear agent known by a person of ordinary skill in the art may be used in the lubricating oil composition. Non-limiting examples of suitable anti-wear agents include zinc dithiophosphate, metal (e.g., Pb, Sb, Mo and the like) salts of dithiophosphates, metal (e.g., Zn, Pb, Sb, Mo and the like) salts of dithiocarbamates, metal (e.g., Zn, Pb, Sb and the like) salts of fatty acids, boron compounds, phosphate esters, phosphite esters, amine salts of phosphoric acid esters or thiophosphoric acid esters, reaction products of dicyclopentadiene and thiophosphoric acids and combinations thereof. The amount of the anti-wear agent may vary from about 0.01 wt. % to about 5 wt. %, from about 0.05 wt. % to about 3 wt. %, or from about 0.1 wt. % to about 1 wt. %, based on the total weight of the lubricating oil composition.

In certain embodiments, the anti-wear agent is or comprises a dihydrocarbyl dithiophosphate metal salt, such as zinc dialkyl dithiophosphate compounds. The metal of the dihydrocarbyl dithiophosphate metal salt may be an alkali or alkaline earth metal, or aluminum, lead, tin, molybdenum, manganese, nickel or copper. In some embodiments, the metal is zinc. In other embodiments, the alkyl group of the dihydrocarbyl dithiophosphate metal salt has from about 3 to about 22 carbon atoms, from about 3 to about 18 carbon atoms, from about 3 to about 12 carbon atoms, or from about 3 to about 8 carbon atoms. In further embodiments, the alkyl group is linear or branched.

The amount of the dihydrocarbyl dithiophosphate metal salt including the zinc dialkyl dithiophosphate salts in the lubricating oil composition disclosed herein is measured by its phosphorus content. In some embodiments, the phosphorus content of the lubricating oil composition is as disclosed herein.

The lubricating oil composition of the invention preferably contains an organic oxidation inhibitor in an amount of 0.01-5 wt. %, preferably 0.1-3 wt. %. The oxidation inhibitor can be a hindered phenol oxidation inhibitor or a diarylamine oxidation inhibitor. The diarylamine oxidation inhibitor is advantageous in giving a base number originating from the nitrogen atoms. The hindered phenol oxidation inhibitor is advantageous in producing no NOx gas.

Examples of the hindered phenol oxidation inhibitors include 2,6-di-*t*-butyl-*p*-cresol, 4,4'-methylenebis(2,6-di-*t*-butylphenol), 4,4'-methylenebis(6-*t*-butyl-*o*-cresol), 4,4'-isopropylidenebis(2,6-di-*t*-butylphenol), 4,4'-bis(2,6-di-*t*-butylphenol), 2,2'-

methylenebis(4-methyl-6-t-butylphenol), 4,4'-thiobis(2-methyl-6-t-butylphenol), 2,2-thio-diethylenebis[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate], octyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate, octadecyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate, and octyl 3-(3,5,4-t-butyl-4-hydroxy-3-methylphenyl)propionate, and commercial products such as, but not limited to, Irganox L135® (BASF), Naugalube 531® (Chemtura), and Ethanox 376® (SI Group).

Examples of the diarylamine oxidation inhibitors include alkyldiphenylamine having a mixture of alkyl groups of 4 to 9 carbon atoms, p,p'-dioctyldiphenylamine, phenyl-naphthylamine, phenyl-naphthylamine, alkylated-naphthylamine, and alkylated phenyl-naphthylamine.

Each of the hindered phenol oxidation inhibitor and diarylamine oxidation inhibitor can be employed alone or in combination. If desired, other oil soluble oxidation inhibitors can be added.

In the preparation of lubricating oil formulations, it is common practice to introduce the additives in the form of 10 to 80 wt. % active ingredient concentrates in hydrocarbon oil, e.g. mineral lubricating oil, or other suitable solvent.

Usually these concentrates may be diluted with 3 to 100, e.g., 5 to 40, parts by weight of lubricating oil per part by weight of the additive package in forming finished lubricants, e.g. crankcase motor oils. The purpose of concentrates, of course, is to make the handling of the various materials less difficult and awkward as well as to facilitate solution or dispersion in the final blend.

Processes of Preparing Lubricating Oil Compositions

The lubricating oil compositions disclosed herein can be prepared by any method known to a person of ordinary skill in the art for making lubricating oils. In some embodiments, the base oil can be blended or mixed with the zirconium-containing compounds described herein. Optionally, one or more other can be added. The additives may be added to the base oil individually or simultaneously. In some embodiments, the additives are added to the base oil individually in one or more additions and the additions may be in any order. In other embodiments, the additives are added to the base oil simultaneously, optionally in the form of an additive concentrate. In some embodiments, the solubilizing of the additives in the base oil may be assisted by heating the mixture to a

temperature from about 25 °C to about 200 °C, from about 50 °C to about 150 °C or from about 75 °C to about 125 °C.

Any mixing or dispersing equipment known to a person of ordinary skill in the art may be used for blending, mixing or solubilizing the ingredients. The blending, mixing or solubilizing may be carried out with a blender, an agitator, a disperser, a mixer (*e.g.*, planetary mixers and double planetary mixers), a homogenizer (*e.g.*, Gaulin homogenizers and Rannie homogenizers), a mill (*e.g.*, colloid mill, ball mill and sand mill) or any other mixing or dispersing equipment known in the art.

Application of the Lubricating Oil Compositions

The lubricating oil composition disclosed herein may be suitable for use as motor oils (that is, engine oils or crankcase oils), in a spark-ignited internal combustion engine, particularly direct injected and boosted engines.

The following examples are presented to exemplify embodiments of the invention but are not intended to limit the invention to the specific embodiments set forth. Unless indicated to the contrary, all parts and percentages are by weight. All numerical values are approximate. When numerical ranges are given, it should be understood that embodiments outside the stated ranges may still fall within the scope of the invention. Specific details described in each example should not be construed as necessary features of the invention.

EXAMPLES

The following examples are intended for illustrative purposes only and do not limit in any way the scope of the present invention.

EXAMPLE 1

A lubricating oil composition was prepared by blending together the following components:

- (a) a mixture of primary and secondary zinc dialkyldithiophosphate;
- (b) a mixture of an overbased phenate, an overbased borated sulfonate, and a low overbased calcium sulfonate detergent;

- (c) a highly overbased magnesium sulfonate detergent (Mg Sulfonate with TBN of 402 and 9.4%wt of Mg content);
- (d) an ethylene carbonate treated and a borated succinimide dispersant;
- (e) an alkylated diphenylamine antioxidant,
- (f) conventional amounts of pour point depressant,
- (g) an ethylene propylene based viscosity index improvers,
- (h) a molybdenum succinimide anti-oxidant,
- (i) foam inhibitor; and
- (j) the balance a Group I base oil.

EXAMPLE 2

Example 1 was repeated except that a highly overbased magnesium sulfonate with a TBN of 397 and 9.6 %wt of Mg content.

EXAMPLE 3

Example 1 was repeated except that a highly overbased calcium sulfonate and additional highly overbased magnesium sulfonate were added to the formulation to give the values shown below in Table 2.

COMPARATIVE EXAMPLE 1

Overbased magnesium sulfonate was taken out of Example 1 and replaced with an amount of highly overbased calcium sulfonate to give the values shown below in Table 2.

COMPARATIVE EXAMPLE 2

Overbased magnesium sulfonate level was adjusted and highly overbased calcium sulfonate was added to Example 1 to give the values shown below in Table 2.

COMPARATIVE EXAMPLE 3

Overbased magnesium sulfonate level was adjusted and highly overbased calcium sulfonate was added to Example 1 to give the values shown below in Table 2.

COMPARATIVE EXAMPLE 4

Overbased magnesium sulfonate level was adjusted and highly overbased calcium sulfonate was added to Example 1 to give the values shown below in Table 2.

COMPARATIVE EXAMPLE 5

Overbased magnesium sulfonate level was adjusted and highly overbased calcium sulfonate was added to Example 1 to give the values shown below in Table 2.

5

Microclutch Test

As a means of evaluating the wet friction characteristics, measurements were carried out on the basis of the Test Method for Friction Characteristics (JCMAS P 047 4) of the Hydraulic Fluids for Construction Machinery (JCMAS P 047:2004) of the Japan Construction Machinery Association. The details of the method for the micro-clutch tests are shown below.

10

- a) Operate the test apparatus at room temperature for 5 min with conditions given in following test condition, while measuring friction coefficients and temperature.
- b) Operate the test apparatus at the surface pressure and peripheral speed until reaching a next test temperature controlled by electric heater of the Micro clutch test rig.
- c) Measure temperatures and friction coefficients while maintaining the test temperature for 5 min.

15

Test conditions

Test specimen material: Clutch disc facing material: SD1795-S

20

Plate material: SS400 steel

(Detail of test piece dimension is shown in JACMAS P 047)

Test conditions: Temperatures: 40, 60, 80, 100, 120, 140 °C

Surface pressure: 392 kPa, Peripheral speed: 3.0×10^{-2} m/s (Rotating speed: 20 min⁻¹)

Volume of the Test Fluid: 20 ml

25

For a new test clutch, a break-in operation is required to get a stable friction data before measurements. The condition of beak-in operation is as follows.

Temperatures: Room temperature

Surface pressure: 392 kPa, Peripheral speed: 3.0×10^{-2} m/s (Rotating speed: 20 min⁻¹)

Friction time: 60min. or more

30

The present invention is explained below by means of examples and comparative examples under the aforementioned microclutch test conditions, but these are only representative examples and the Invention is in no way limited by them.

5

TABLE 2

	Ex. 1	Ex. 2	Ex. 3	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4	Comp. Ex. 5
Kinematic Viscosity (100°C), mm ² /s	10.5	10.4	10.5	10.5	10.4	10.2	10.6	10.6
CCS Viscosity (-25°C), cP	6780	6880	6980	6800	6840	6870	6880	6920
Zn, wt. %	1370	1370	1370	1370	1370	1370	1370	1370
P, wt. %	1200	1200	1200	1200	1200	1200	1200	1200
Ca, wt. %	1210	1190	2840	4070	3350	3710	2840	2840
Mg, wt. %	1750	1750	2210	0	440	230	595	750
Mo, wt. %	50	50	50	50	50	50	50	50
B, wt. %	190	190	190	190	190	190	190	190
S, wt. %	3220	3270	3200	3190	3190	3190	3200	3200
N, wt. %	300	300	300	300	1370	1370	1370	1370
TBN (D4739)	10.9	10.4	11.5	10.8	10.6	10.7	10.7	10.8
Ca/Mg mass ratio	0.69	0.68	1.29	> 40	7.61	16.13	4.77	3.79
Komatsu Micro Clutch Test (JCMAS P047)								
40 °C	0.168	0.176	0.172	0.155	0.160	0.159	0.159	0.159
60 °C	0.161	0.171	0.168	0.147	0.149	0.148	0.148	0.148
80 °C	0.155	0.165	0.163	0.137	0.139	0.139	0.139	0.139
100 °C	0.149	0.158	0.156	0.129	0.131	0.131	0.131	0.131
120 °C	0.145	0.151	0.149	0.123	0.127	0.128	0.128	0.128
140 °C	0.149	0.143	0.149	0.117	0.122	0.122	0.125	0.125
Sulfate ash (ASTM D874), wt%	1.3	1.3	2.0	1.6	1.6	1.6	1.5	1.5

Diesel engine oils having JASO DH-1, API CG-4, CH-4 or CI-4, are widely used not only for internal combustion engines, but also hydraulic and transmission systems in industrial machinery, especially transport, construction, and agricultural machinery. To obtain a higher

static friction coefficient of wet clutches in their machinery is important to enable safe operation of the machinery, and also to give an excellent power transmit efficiency for the machinery, because of showing a good response and fuel efficiency. Friction coefficient must be greater than 0.13 (0.125) for the oils at every test temperature. It is evident that Ex.1, Ex.2
5 and Ex.3 shows excellent wet clutch friction in micro clutch test.