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

(11) **EP 4 585 670 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
16.07.2025 Bulletin 2025/29

(21) Application number: **25150792.7**

(22) Date of filing: **08.01.2025**

(51) International Patent Classification (IPC):
C10M 161/00 *(2006.01)*
C10N 10/04 *(2006.01)*
C10N 10/12 *(2006.01)*
C10N 20/04 *(2006.01)*
C10N 30/04 *(2006.01)*
C10N 30/06 *(2006.01)*
C10N 30/10 *(2006.01)*
C10N 30/00 *(2006.01)*
C10N 40/25 *(2006.01)*

(52) Cooperative Patent Classification (CPC):
C10M 161/00; C10M 2203/1025; C10M 2207/023; C10M 2207/028; C10M 2207/262; C10M 2215/064; C10M 2215/28; C10M 2219/046; C10M 2219/068; C10M 2223/045; C10N 2010/04; C10N 2010/12; C10N 2020/04; C10N 2030/04; C10N 2030/06;
(Cont.)

(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 ME MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA
Designated Validation States:
GE KH MA MD TN

(30) Priority: **09.01.2024 US 202463618975 P**
11.11.2024 US 202418943221

(71) Applicant: **Infineum International Limited**
Abingdon, Oxfordshire OX13 6BB (GB)

(72) Inventors:
- **KILLIAN, Grégory**
  13131 Berre L’Etang (FR)
- **SHEN, Xiaobo**
  Linden, 07036 (US)
- **ACOSTA, Ali**
  Linden, 07036 (US)
- **GUSMAN, Claire**
  Linden, 07036 (US)

(74) Representative: **Hart, Richard Joseph et al**
Infineum UK Ltd.
Milton Hill Business & Technology Centre
Milton Hill
Abingdon, Oxfordshire OX13 6BD (GB)

(54) LUBRICANT COMPOSITIONS CONTAINING LOW PHOSPHORUS AND LOW SULPHATED ASH

(57) This invention relates to a lubricating oil composition, such as a composition having a phosphorus content of less than 800 ppm, such as less than or about 500 ppm, and a SASH content of less than 0.9 %, such as less than or about 0.5 %, comprising a dispersant mixture, the dispersant mixture comprising (1) 0.01-15 mass% based upon the total mass of the dispersant mixture, of an amide, imide, and/or ester functionalized partially or fully saturated polymer comprising C_{4-5} olefins having: i) an Mw/Mn of less than 2, ii) a Functionality Distribution (Fd) value of 3.5 or less, and iii) an Mn of 10,000 g/mol or more (GPC-PS) of the polymer prior to functionalization; and (2) 50-90 mass% based upon the total mass of the dispersant mixture, of one or more poly(alkenyl) succinimide(s), which is derived from a polyalkenyl-substituted succinic anhydride prepared using a chlorine-assisted alkylation process and a polyamine; and (3) 10-30 mass% based upon the total mass of the dispersant mixture, of one or more poly(alkenyl)succinimide(s), which is derived from a polyalkenyl succinic anhydride prepared using a halogen-free thermal alkylation process and a polyamine.

EP 4 585 670 A1

(52) Cooperative Patent Classification (CPC): (Cont.)
C10N 2030/10; C10N 2030/42; C10N 2030/45;
C10N 2040/25

Description

FIELD OF THE INVENTION

[0001] This disclosure relates to the use of a dispersant mixture comprising functionalized polymer, chloro dispersant(s) and thermal dispersant(s) in lubricant compositions providing robust wear, cleanliness, oxidation, and corrosion performance in engine crankcase applications, especially in compression ignited engine and/or spark ignited applications.

BACKGROUND OF THE INVENTION

[0002] The present invention relates to lubricating oil compositions which exhibit improved performance, particularly against turbo charger and piston deposits. More specifically, the present invention relates to automotive crankcase lubricating oil compositions for use in gasoline (spark-ignited) and diesel (compression-ignited) internal combustion engines, such compositions being referred to as crankcase lubricants; and to the use of additives in such lubricating oil compositions for improving the performance of an engine lubricated with the lubricating oil composition, in particular with regard to piston cleanliness, liner wear, wear on gear train wheels, turbocharger housing deposits, and oxidation.

[0003] The emphasis on fuel economy has been increased in recent years. One approach to improve the fuel economy of vehicles is to design new lubricant oils that reduce friction while maintaining a good film thickness for durability and wear protection while also preventing soot-induced viscosity increase. In an attempt to improve fuel economy, the use and stipulation of low viscosity grades by Original Equipment Manufacturers (OEM) is becoming increasingly widespread. One of the challenges for the provision of engine and/or drive train transmission oils having these reduced viscosity grades is maintaining cleanliness and wear protection. Such oils must be able to reduce sludge, provide good soot handling, and provide wear protection, whilst providing desired fuel economy benefits. These targets should be achieved while maintaining low levels of sulphated ash (SASH) and phosphorus, as well as ensuring seal compatibility. There is a need to provide new engine oils having low viscosity grades that meet these requirements.

[0004] Engine durability is an important consideration in the choice of a lubricant, especially for heavy duty diesel (HDD) engine applications. Original equipment manufacturers are continuing to increase their oil drain intervals and the average lifetime of vehicles has steadily increased over the last few decades. Likewise, there is a trend towards use of ashless anti-wear agents which have a lower impact on after treatment systems such as diesel particulate filters in heavy duty diesel vehicles.

[0005] In addition, environmental and regulatory requirements are driving a desire to improve the efficiency of the internal combustion engine. Lower viscosity lubricants require less energy to pump around an engine and thus can improve its fuel economy. However, lower viscosity lubricants result in thinner oil films between contacting engine parts (e.g., in the valve train, piston zone and in bearings), which can lead to higher rates of wear, reduced friction modification, etc. Conventionally, zinc dialkyl dithiophosphates (ZDDPs) are often used as lubricant additives to prevent engine wear and or reduce friction in the boundary lubrication regimes.

[0006] Alongside the drive for improved fuel economy, there is also a desire to reduce the emissions from vehicles. Control of exhaust emissions is typically achieved by after-treatment devices, such as catalytic convertors, which generally employ precious metal catalysts to convert combustion products into less undesirable species. However, these catalysts are poisoned by, *inter alia,* phosphorous and sulfur, which impacts their catalytic activity. In particular, SASH and phosphorus accumulate in the diesel after-treatment system of HDD vehicles, specifically in the diesel particulate filter (DPF). The exhaust back pressure due to DPF SASH and phosphorus accumulation can shorten the life of the DPF, reduce fuel economy, and have detrimental effects on the catalyst hindering the overall effectiveness of the after treatment system in HDD vehicles.

[0007] Typically, HDD formulations contain 800 to 1200 ppm phosphorous and more than 0.9 % SASH in order to deliver the required wear and cleanliness performance dictated by the various industry and OEM engine tests and specific requirements. This invention now intends to provide lubricant compositions targeting reduced SASH and phosphorous, in particular of 500 ppm phosphorous and 0.5 % SASH, while still maintain robust wear and cleanliness performance in key engine tests. However, the reduction of SASH and phosphorous translate to reduction of detergent and anti-wear agent in the lubricant composition which have a critical role in delivering robust performance in HDD lubricants.

[0008] During engine operation, oil-insoluble oxidation byproducts, such as soot, are produced. Dispersants help keep these byproducts suspended or in solution, thus diminishing their deposition on metal surfaces. Common dispersants include (poly)alkenylsuccinic derivatives, such as hydrocarbyl-substituted succinic anhydrides, such as polyisobutylene succinic anhydride (PIBSA) and hydrocarbyl-substituted succinimides, such as polyisobutylene succinimides (PIBSA-PAM), such as those derived from reaction of maleated polyisobutylene with N-phenyl-p-phenylenediamine.

[0009] United States Patent Application USSN 18/480,571 filed October 4, 2023 claiming priority to USSN 63/379,006, filed October 11, 2022 discloses the use of amide, imide, and/or ester functionalized polymers comprising specific C_{4-5} olefins as additives in lubricating oil compositions to reduce wear. United States Patent Application USSN 63/584,675 filed

September 22, 2023 further discloses lubricant compositions comprising functionalized polymers comprising a specific olefin homopolymer or copolymer backbone while traditional polyalkenylsuccinimide dispersant(s), in which the polyalkenyl is derived from polyisobutylene and the imide is derived from polyamine (PIBSA-PAMs), are reduced or completely absent.

[0010] It has now surprisingly been found by the present inventors that a dispersant mixture comprising the above-described amide, imide, and/or ester functionalized polymer comprising specific C_{4-5} olefins, as well as poly(alkenyl) succinimide, which is derived from a polyalkenyl-substituted succinic anhydride prepared using a chlorine-assisted alkylation process and a polyamine (chloro dispersant), and poly(alkenyl)succinimide, which is derived from a polyalkenyl succinic anhydride prepared using a halogen-free thermal alkylation process and a polyamine (thermal dispersant) can be used in a lubricant composition, such as in internal combustion engines, to provide improved wear and cleanliness performance. Further, it has surprisingly been found by the present inventors that using said dispersant mixture in a lubricant composition allows passing of the Daimler OM471 FE1 Performance Test even at a phosphorus content of less than 800 ppm, such as less than 500 ppm, and a SASH content of less than 0.9 %, such as less than 0.5 %. In addition, strong performance in the Daimler OM471 FE1 Performance Test is observed in a semi-synthetic basestock system with said invention promoting a more sustainable but effective solution.

SUMMARY OF THE INVENTION

[0011] This invention relates to an additive concentrate or additive package comprising a dispersant mixture, the dispersant mixture comprising

(1) 0.01-15 mass% based upon the total mass of the dispersant mixture, of an amide, imide, and/or ester functionalized partially or fully saturated polymer comprising C_{4-5} olefins having:

i) an Mw/Mn of less than 2,
ii) a Functionality Distribution (Fd) value of 3.5 or less, and
iii) an Mn of 10,000 g/mol or more (GPC-PS) of the polymer prior to functionalization; and

(2) 50-90 mass% based upon the total mass of the dispersant mixture, of one or more poly(alkenyl) succinimide(s), which is derived from a polyalkenyl-substituted succinic anhydride prepared using a chlorine-assisted alkylation process and a polyamine (hereinafter termed "chloro dispersant(s)"); and
(3) 10-30 mass% based upon the total mass of the dispersant mixture, of one or more poly(alkenyl)succinimide(s), which is derived from a polyalkenyl succinic anhydride prepared using a halogen-free thermal alkylation process and a polyamine (hereinafter termed "thermal dispersant(s)").

[0012] This disclosure further relates to a lubricating oil composition comprising or resulting from the admixing of:

(A) at least 50 mass% of one or more base oil(s), based upon the total mass of the lubricating oil composition; and
(B) an additive concentrate comprising a dispersant mixture, the dispersant mixture comprising

(1) 0.01-15 mass% based upon the total mass of the dispersant mixture, of an amide, imide, and/or ester functionalized partially or fully saturated polymer comprising C_{4-5} olefins having:

i) an Mw/Mn of less than 2,
ii) a Functionality Distribution (Fd) value of 3.5 or less, and
iii) an Mn of 10,000 g/mol or more (GPC-PS) of the polymer prior to functionalization; and

(2) 50-90 mass% based upon the total mass of the dispersant mixture, of one or more poly(alkenyl) succinimide(s), which is derived from a polyalkenyl-substituted succinic anhydride prepared using a chlorine-assisted alkylation process and a polyamine (hereinafter termed "chloro dispersant(s)"); and
(3) 10-30 mass% based upon the total mass of the dispersant mixture, of one or more poly(alkenyl)succinimide(s), which is derived from a polyalkenyl succinic anhydride prepared using a halogen-free thermal alkylation process and a polyamine (hereinafter termed "thermal dispersant(s)").

[0013] Typically, the one or more poly(alkenyl) succinimide dispersant(s) is one or more PIBSA-PAM dispersant(s), i.e. derived from a polyisobutylene-substituted succinic anhydride prepared using either a chlorine-assisted alkylation process or a halogen-free thermal alkylation process, and a polyamine.

[0014] According to another aspect of the present disclosure, there is provided the use of the dispersant mixture described above for increasing the piston cleanliness and/or the wear resistance of a lubricating oil composition.

[0015] According to yet a further aspect of the present invention, there is provided the use of the lubricating oil composition described above, where the lubricating oil composition has:

a) an average piston cleanliness, as determined by Daimler OM471 FE1 (CEC L-118-21), of 70 % or more such as 73 % or more such as 74 % or more, of 75 % or more such as 76 % or more, of 78 % or more such as 80 % or more such as 80.5 % or more, and/or
b) an average wear on gear train wheels, as determined by Daimler OM471 FE1 (CEC L-118-21), of 75 % or more, of 80 % or more such as 81 % or more, of 82 % or more such as 82.5 % or more such as 83 % or more, and/or
c) an average liner wear, as determined by Daimler OM471 FE1 (CEC L-118-21), of 8 μm or less, of 5 μm or less, of 3 μm or less such as 2 μm or less such as 1 μm or less, and/or
d) an oxidation, as determined by Daimler OM471 FE1 (CEC L-118-21), of 65 A/cm or less, of 55 A/cm or less such as 51 A/cm or less such as 49 A/cm or less such as 45 A/cm or less such as 40 A/cm or less.

[0016] According to yet a further aspect of the present invention, there is provided a crankcase lubricating oil composition comprising or made by admixing:

(i) one or more base oils, in a major amount;
(ii) the dispersant mixture described above.

[0017] In another aspect the lubricating oil compositions described herein contain:

1) a phosphorous content of less than 800 ppm, such as less than 550 ppm, such as less than 500 ppm, such as less than 490 ppm based upon the total mass of the lubricating oil composition, and
2) a sulfated ash ("SASH") content of less than 0.9 mass%, such as less than 0.6 mass%, such as less than 0.5 mass% based upon the total mass of the lubricating oil composition.

[0018] This invention also relates to a lubricating oil composition comprising or resulting from the admixing of: (i) one or more base oil(s), (ii) one or more poly(alkenyl) succinimide chloro dispersant(s) and one or more poly(alkenyl) succinimide thermal dispersant(s), (iii) one or more detergent(s), (iv) one or more anti-wear agent(s), (v) one or more antioxidant(s), and (vi) one or more functionalized polymer(s) described herein, where the lubricating oil composition comprises the chloro dispersant(s) and the thermal dispersant(s) at a ratio of at least 4:1, where the lubricating oil composition has:

a) an SAE viscosity grade of 20W-X, 15W-X, 10W-X, 5W-X, or 0W-X (such as 10W-X or 5W-X), where X represents any one of 8, 12, 16, 20, 30, 40, and 50 (such as 30); and
b) an average piston cleanliness, as determined by Daimler OM471 FE1 (CEC L-118-21), of 70 % or more such as 73 % or more such as 74 % or more, of 75 % or more such as 76 % or more, of 78 % or more such as 80 % or more such as 80.5 % or more, and
c) an average wear on gear train wheels, as determined by Daimler OM471 FE1 (CEC L-118-21), of 75 % or more, of 80 % or more such as 81 % or more, of 82 % or more such as 82.5 % or more such as 83 % or more, and
d) an average liner wear, as determined by Daimler OM471 FE1 (CEC L-118-21), of 8 μm or less, of 5 μm or less, of 3 μm or less such as 2 μm or less such as 1 μm or less, and
e) an oxidation, as determined by Daimler OM471 FE1 (CEC L-118-21), of 65 A/cm or less, of 55 A/cm or less such as 51 A/cm or less such as 49 A/cm or less such as 45 A/cm or less such as 40 A/cm or less.

DEFINITIONS

[0019] For purposes of this specification and all claims to this invention, the following words and expressions, if and when used, have the meanings ascribed below.

[0020] For purposes herein, the new numbering scheme for the Periodic Table of the Elements is used as set out in CHEMICAL AND ENGINEERING NEWS, 63(5), 27 (1985), *i.e.,* **Alkali metals** are group 1 metals (*e.g.*, Li, Na, K, etc.) and **Alkaline earth metals** are group 2 metals (*e.g.,* Mg, Ca, Ba, etc.).

[0021] The term **"absent"** (or "free of") as it relates to components or active ingredients included within the lubricating oil compositions described herein and the claims thereto means that the particular component or active ingredient is present at 0.000 wt%, based upon the weight of the lubricating oil composition, or if **"substantially absent,"** the component or active ingredient is present at levels that do not impact the lubricating oil composition properties, such as at less than 100 ppm, such as 10 ppm, or less than 1 ppm or less than 0.001 ppm. When the term "absent" is used in relation to monomer reactants and/or to repeat units in (co)polymers described herein, it means present at 0 wt%, based upon the weight of all (co)monomers in the (co)polymer, or, if present at all, at levels so low that they do not substantially impact the physical properties of the (co)polymer, such as at 0.2 wt% or less or at 0.1 wt% or less.

[0022] The term **"about"** means approximately, which includes values obtain by rounding. As used herein, the term "about" modifying the quantity of an ingredient, component, or reactant of the invention employed refers to variation in the numerical quantity that can occur, for example, through typical measuring and liquid handling procedures used for making concentrates or lubricating oil compositions. Furthermore, variation can occur from inadvertent error in measuring procedures, differences in the manufacture, source, or purity of the ingredients employed to make the compositions or carry out the methods, and the like. In one aspect, the term "about" means within 10% of the reported numerical value. In another aspect, the term "about" means within 5% of the reported numerical value. Yet, in another aspect, the term "about" means within 10, 9, 8, 7, 6, 5, 4, 3, 2, or 1% of the reported numerical value.

[0023] The term **"LOC"** means lubricating oil composition (which term is interchangeably used herein with the term "lubricant oil composition", or "lubricating composition", or "lubricant composition").

[0024] The term **"major amount"** means more than 50 mass% of a composition, such as more than 60 mass% of a composition, such as more than 70 mass% of a composition, such as from 80 to 99.009 mass% of a composition, such as from 80 to 99.9 from 80 to 99.009 mass% of a composition, of a composition based upon the mass of the composition.

[0025] The term **"minor amount"** means 50 mass% or less of a composition; such as 40 mass% or less of a composition; such as 30 mass% or less of a composition, such as from 20 to 0.001 mass%, such as from 20 to 0.1 mass%, based upon the mass of the composition.

[0026] The term **"mass%"** means mass percent of a component, based upon the mass of the composition as measured in grams, unless otherwise indicated, and is alternately referred to as weight percent ("weight %", "wt%", or "%w/w").

[0027] The term **"active ingredient"** (also referred to as "a.i." or "A.I.") refers to additive material that is neither diluent nor solvent. Unless otherwise indicated, amounts herein are described as active ingredient. By way of example, a certain component in a lubricating oil composition may contain a functionalized polymer as described herein and diluent oil. The content of the functionalized polymer itself is the active ingredient content (expressed e.g. in mass% based on the mass of the entire component including diluent oil). Unless otherwise indicated, all amounts, ranges and ratios in the present specification and claims refer to active ingredient, unless indicated otherwise.

[0028] The terms **"oil-soluble"** and **"oil-dispersible,"** or cognate terms, used herein do not necessarily indicate that the compounds or additives are soluble, dissolvable, miscible, or are capable of being suspended in the oil in all proportions. These do mean, however, that they are, for example, soluble or stably dispersible in oil to an extent sufficient to exert their intended effect in the environment in which the oil is employed. Moreover, the additional incorporation of other additives may also permit incorporation of higher levels of a particular additive, if desired.

[0029] The terms **"group"** and **"radical"** are used interchangeably herein.

[0030] The term **"hydrocarbon"** means a compound of hydrogen and carbon atoms. A "heteroatom" is an atom other than carbon or hydrogen. When referred to as "hydrocarbons," particularly as "refined hydrocarbons," the hydrocarbons may also contain one or more heteroatoms or heteroatom-containing groups (such as halo, especially chloro and fluoro, amino, alkoxyl, mercapto, alkylmercapto, nitro, nitroso, sulfoxy, etc.) in minor amounts (*e.g.*, where the heteroatom(s) do not substantially alter the hydrocarbon properties of the hydrocarbon compound).

[0031] The term **"hydrocarbyl"** means a radical that contains hydrogen and carbon atoms. Preferably, the group consists essentially of, more preferably consists only of, hydrogen and carbon atoms, unless specified otherwise. Preferably, the hydrocarbyl group comprises an aliphatic hydrocarbyl group. The term "hydrocarbyl" includes "alkyl," "alkenyl," "alkynyl," and "aryl" as defined herein. Hydrocarbyl groups may contain one or more atoms/groups other than carbon and hydrogen provided they do not affect the essentially hydrocarbyl nature of the hydrocarbyl group. Those skilled in the art will be aware of such atoms/groups (*e.g.*, halo, especially chloro and fluoro, amino, alkoxyl, mercapto, alkylmercapto, nitro, nitroso, sulfoxy, etc.).

[0032] The term **"alkyl"** means a radical of carbon and hydrogen (such as a C_1 to C_{30}, such as a C_1 to C_{12} group). Alkyl groups in a compound are typically bonded to the compound directly via a carbon atom. Unless otherwise specified, alkyl groups may be linear (*i.e.*, unbranched) or branched, be cyclic, acyclic, or part cyclic/acyclic. Preferably, the alkyl group comprises a linear or branched acyclic alkyl group. Representative examples of alkyl groups include, but are not limited to, methyl, ethyl, n-propyl, iso-propyl, n-butyl, sec-butyl, iso-butyl, tert-butyl, n-pentyl, iso-pentyl, neo-pentyl, hexyl, heptyl, octyl, dimethyl hexyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, icosyl and triacontyl.

[0033] The term **"alkenyl"** means a radical of carbon and hydrogen (such as a C_2 to C_{30} radical, such as a C_2 to C_{12} radical) having at least one double bond. Alkenyl groups in a compound are typically bonded to the compound directly via a carbon atom. Unless otherwise specified, alkenyl groups may be linear (i.e., unbranched) or branched, be cyclic, acyclic or part cyclic/acyclic.

[0034] The term **"alkylene"** means a C_1 to C_{20}, preferably a C_1 to C_{10}, bivalent saturated aliphatic radical, which may be linear or branched. Representative examples of alkylene include methylene, ethylene, propylene, butylene, pentylene, hexylene, heptylene, octylene, nonylene, decylene, 1-methyl ethylene, 1-ethyl ethylene, 1-ethyl-2-methyl ethylene, 1,1-

dimethyl ethylene and 1-ethyl propylene.

[0035] An **"olefin",** alternatively referred to as **"alkene,"** is a linear, branched, or cyclic compound of carbon and hydrogen having at least one double bond. For purposes of this specification and the claims appended thereto, when a polymer or copolymer is referred to as comprising an olefin, the olefin present in such polymer or copolymer is the polymerized form of the olefin. For example, when a copolymer is said to have an "isoprene" content of 55 wt% to 95 wt%, it is understood that the mer unit in the copolymer is derived from isoprene in the polymerization reaction and said derived units are present at 55 wt% to 95 wt%, based upon the weight of the copolymer. A **"polymer"** has two or more of the same or different mer units. A **"homopolymer"** is a polymer having mer units that are the same. A **"copolymer"** is a polymer having two or more mer units that are different from each other. "Different" as used to refer to mer units indicates that the mer units differ from each other by at least one atom or are different isomerically. An "isoprene polymer" or "isoprene copolymer" is a polymer or copolymer comprising at least 50 mol % isoprene derived units, a "butadiene polymer" or "butadiene copolymer" is a polymer or copolymer comprising at least 50 mol % butadiene derived units, and so on. Likewise, when a polymer is referred to as a "partially or fully saturated polymer comprising C_{4-5} olefins," the C_{4-5} olefin(s) present in such polymer or copolymer are the polymerized form of the olefin(s), and the polymer has been partially or fully saturated (such as by hydrogenation) after polymerization of the monomers. A polymer **"backbone"** is the polymer main chain containing the mer units of the monomer(s), without/prior to any (subsequent) functionalization.

[0036] The term **"alkynyl"** means a C_2 to C_{30} (such as a C_2 to C_{12}) radical, which includes at least one carbon-to-carbon triple bond.

[0037] The term **"aryl"** means a group containing at least one aromatic ring, such a cyclopentadiene, phenyl, naphthyl, anthracenyl, and the like. Aryl groups are typically C_5 to C_{40} (such as C_5 to C_{18}, such as C_6 to C_{14}) aryl groups, optionally substituted by one or more hydrocarbyl groups, heteroatoms, or heteroatom-containing groups (such as halo, hydroxyl, alkoxy and amino groups). Preferred aryl groups include phenyl and naphthyl groups and substituted derivatives thereof, especially phenyl, and alkyl substituted derivatives of phenyl.

[0038] The term **"substituted"** means that a hydrogen atom has been replaced with hydrocarbon group, a heteroatom, or a heteroatom-containing group. An alkyl substituted derivative means a hydrogen atom has been replaced with an alkyl group. An "alkyl substituted phenyl" is a phenyl group where a hydrogen atom has been replaced by an alkyl group, such as a C_1 to C_{20} alkyl group, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, sec-butyl, iso-butyl, tert-butyl, n-pentyl, iso-pentyl, neo-pentyl, hexyl, heptyl, octyl, dimethyl hexyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, icosyl and/or triacontyl.

[0039] The term **"halogen"** or **"halo"** means a group 17 atom or a radical of group 17 atom, such as fluoro, chloro, bromo, and iodo.

[0040] The term **"ashless"** in relation to an additive means the composition does not include a metal.

[0041] The term **"ash-containing"** in relation to an additive means the composition includes a metal.

[0042] The term **"ppm"** means parts per million by mass, based on the total mass of the lubricating oil composition, unless otherwise indicated.

[0043] The term **"metal content"** of a lubricating oil composition or of an additive component, for example, magnesium content, molybdenum content or total metal content (*i.e.,* the sum of all individual metal contents), is measured by ASTM D5185.

[0044] The term **"aliphatic hydrocarbyl fatty acid"** means a monocarboxylic acid having an aliphatic C_7 to C_{29}, preferably a C_9 to C_{27}, most preferably a C_{11} to C_{23} hydrocarbyl chain. Such compounds may be referred to herein as aliphatic (C_7 to C_{29}), more preferably (C_9 to C_{27}), most preferably (C_{11} to C_{23}), hydrocarbyl monocarboxylic acid(s) or hydrocarbyl fatty acid(s) (wherein Cx to Cy designates the total number of carbon atoms in the aliphatic hydrocarbyl chain of the fatty acid, the fatty acid itself due to the presence of the carboxyl carbon atom includes a total of Cx+1 to Cy+1 carbon atoms). Preferably, the aliphatic hydrocarbyl fatty acid, inclusive of the carboxyl carbon atom, has an even number of carbon atoms. The aliphatic hydrocarbyl chain of the fatty acid may be saturated or unsaturated (*i.e.,* includes at least one carbon-to-carbon double bond); preferably, the aliphatic hydrocarbyl chain is unsaturated and includes at least one carbon-to-carbon double bond - such fatty acids may be obtained from natural sources (*e.g.*, derived from animal or vegetable oils) and/or by reduction of the corresponding saturated fatty acid. It will be appreciated that a proportion of the aliphatic hydrocarbyl chain(s) of the corresponding aliphatic hydrocarbyl fatty acid ester(s) is unsaturated (*i.e.*, includes at least one carbon-to-carbon double bond) to permit reaction with other agents, such as sulfur, to form the corresponding functionalized, such as sulfurized, aliphatic hydrocarbyl fatty acid ester(s).

[0045] The term **"aliphatic hydrocarbyl fatty acid ester"** means an ester obtainable by converting the monocarboxylic acid functional group of the corresponding aliphatic hydrocarbyl fatty acid into an ester group. Suitably, the monocarboxylic acid functional group of the aliphatic hydrocarbyl fatty acid is converted to a hydrocarbyl ester, preferably a C_1 to C_{30} aliphatic hydrocarbyl ester, such as an alkyl ester, preferably a C_1 to C_6 alkyl ester, especially a methyl ester. Alternatively, or additionally, the monocarboxylic acid functional group of the aliphatic hydrocarbyl fatty acid may be in the form of the natural glycerol ester. Accordingly, the term "aliphatic hydrocarbyl fatty acid ester" embraces aliphatic hydrocarbyl fatty acid glycerol ester(s) and aliphatic hydrocarbyl fatty acid C_1 to C_{30} aliphatic hydrocarbyl ester(s), [*e.g.*, aliphatic hydrocarbyl fatty acid alkyl ester(s), more preferably aliphatic hydrocarbyl fatty acid C_1 to C_6 alkyl ester(s), especially aliphatic hydrocarbyl fatty acid methyl ester(s)]. Suitably, the term "aliphatic hydrocarbyl fatty acid ester" embraces aliphatic (C_7 to C_{29}) hydrocarbyl, more preferably aliphatic (C_9 to C_{27}) hydrocarbyl, most preferably aliphatic (C_{11} to C_{23}) hydrocarbyl fatty acid glycerol ester(s) and aliphatic (C_7 to C_{29}) hydrocarbyl, more preferably aliphatic (C_9 to C_{27}) hydrocarbyl, most preferably aliphatic (C_{11} to C_{23}) hydrocarbyl fatty acid C_1 to C_{30} aliphatic hydrocarbyl ester(s). Suitably, to permit functionalization, such as sulfurization, of the aliphatic hydrocarbyl fatty acid ester(s) a proportion of the aliphatic hydrocarbyl chain(s) of the fatty acid ester(s) is unsaturated and includes at least one carbon-to-carbon double bond.

[0046] The term **"sulfurized aliphatic hydrocarbyl fatty acid ester"** means a compound obtained by sulfurizing an aliphatic hydrocarbyl fatty acid ester as defined herein.

[0047] As used herein, **Mn** is number average molecular weight, **Mw** is weight average molecular weight, and **Mz** is z average molecular weight. **Molecular weight distribution** (MWD), also referred to as **polydispersity index** (PDI), is defined to be Mw divided by Mn. Unless otherwise noted, all molecular weight units (*e.g.*, Mw, Mn, Mz) are reported in g/mol.

[0048] **Total Base Number** also referred to as "TBN," in relation to an additive component or of a lubricating oil composition (*i.e.*, unused lubricating oil composition) means total base number as measured by ASTM D2896 and reported in units of mgKOH/g.

[0049] **Total Acid Number** ("TAN") is determined by ASTM D664.

[0050] **Phosphorus, Boron, Calcium, Zinc, Molybdenum, Sodium, Silicon,** and **Magnesium** content are measured by ASTM D5185.

[0051] **Sulfur content in oil** formulations is measured by ASTM D5185.

[0052] **Sulfated ash** ("SASH") content is measured by ASTM D874.

[0053] **Kinematic viscosity** (KV100, KV40) is determined pursuant to ASTM D445-19a and reported in units of cSt, unless otherwise specified.

[0054] **Viscosity index** is determined according to ASTM D2270.

[0055] **Saponification number** is determined by ASTM D94, and reported in units of mgKOH/g.

[0056] **"HTCBT,** high temperature corrosion bench test, is determined pursuant to ASTM D6594.

[0057] **Average functionality** [also referred to as Average Functionality Value (Fv)] **and Functionality Distribution** (Fd) value are determined by Gel Permeation Chromatography using polystyrene standards as described in the Experimental section of USSN 18/480,571 filed October 4, 2023 claiming priority to USSN 63/379,006, filed October 11, 2022, and in the Experimental section herein.

[0058] Unless otherwise indicated, all percentages reported are mass% on an active ingredient basis, *i.e.,* without regard to carrier or diluent oil, unless otherwise indicated. Unless otherwise indicated, "mass%" herein has the same meaning as "weigth %" or "wt%".

[0059] Also, it will be understood that various components used, essential as well as optimal and customary, may react under conditions of formulation, storage or use and that the disclosure also provides the product obtainable or obtained as a result of any such reaction.

[0060] Further, it is understood that any upper and lower quantity, range and ratio limits set forth herein may be independently combined.

[0061] Also, it will be understood that the preferred features of each aspect of the present disclosure are regarded as preferred features of every other aspect of the present disclosure. Accordingly, preferred and more preferred features of one aspect of the present disclosure may be independently combined with other preferred and/or more preferred features of the same aspect or different aspects of the present disclosure.

DETAILED DESCRIPTION OF THE INVENTION

[0062] The features of the disclosure relating, where appropriate, to each and all aspects of the disclosure, will now be described in more detail as follows.

[0063] The lubricating oil compositions and additive concentrates of the disclosure comprise components that may or may not remain the same chemically before and after mixing with an oleaginous carrier (such as a base oil) and/or other additives. This disclosure encompasses compositions which comprise the components before mixing, or after mixing, or both before and after mixing.

Lubricating Oil Compositions

[0064] This disclosure relates to lubricating oil compositions (also referred to as "LOC", "lubricant compositions", "lubricating compositions", or "lubricant oil compositions") comprising or resulting from the admixing of:

(a) from 1 to 99 mass% (alternately 30 to 95 mass%, alternately 50 to 90 mass%, alternately 60 to 95 mass%, alternately 70 to 85 mass%) of one or more **base oil(s),** based upon the weight of the lubricating composition; or alternately 50 mass% or more of one or more **base oil(s),** based upon the weight of the lubricating composition;

(b) from 0.1 to 20 mass% (in particular 0.15 to 10 mass%, alternately 0.2 to 5 mass%, alternately 0.25 to 2 mass%, alternately 0.5 to 1 mass%), based upon the weight of the lubricating composition, of a **functionalized polymer** comprising a partially or fully saturated olefin homopolymer or copolymer backbone and at least one functional group (such as a group derived from an amine or a hydroxyl group), having: an Mn of 10,000 g/mol or more (GPC-PS) of the polymer prior to functionalization, and preferably having been functionalized with an acylating agent and subsequently reacted with a compound containing amino and/or hydroxyl groups, (such as one or more amide, imide, and/or ester functionalized partially or fully saturated polymers comprising C_{2-5} olefins) having: i) an Mw/Mn of less than 2, ii) optionally, a Functionality Distribution (Fd) value of 3.5 or less (GPC-PS), and iii) an Mn of 10,000 g/mol or more (GPC-PS) of the polymer(s) prior to functionalization, provided that, if the polymer(s) prior to functionalization is (are) a copolymer of isoprene and butadiene, then the Mn of the copolymer is greater than 25,000 g/mol (GPC-PS));

c) from 0.1 to 20 mass% (alternately 0.1 to 12 mass%, alternately 0.25 to 10 mass%, alternately 0.5 to 8 mass%, alternately 1 to 7 mass%, alternately 3 to 6 mass%), based upon the weight of the lubricating composition, of one or more poly(alkenyl) succinimide dispersant(s) (such as blends of poly(alkenyl) succinimide dispersants), derived from a polyalkenyl-substituted succinic anhydride prepared using a chlorine-assisted alkylation process and a polyamine **("chloro dispersant(s)");** and

d) from 0.1 to 10 mass% (alternately 0.1 to 6 mass%, alternately 0.25 to 4 mass%, alternately 0.5 to 3 mass%, alternately 0.8 to 1.5 mass%, alternately 1 to 1.25 mass%), based upon the weight of the lubricating composition, of one or more poly(alkenyl) succinimide dispersant(s) (such as blends of poly(alkenyl) succinimide dispersants), derived from a polyalkenyl succinic anhydride prepared using a halogen-free thermal alkylation process and a polyamine **("thermal dispersant(s)"),** which is present in an amount such that the weight ratio of the chloro dispersant(s) (c) to said thermal dispersant(s) is at least 4:1;

e) optionally 0 to 20 mass% (such as absent or substantially absent from the lubricating oil composition, alternately 0.1 to 12 mass%, alternately 0.25 to 8 mass%, alternately 0.5 to 6 mass%, alternately 0.05 to 5 mass%, alternately 3.5 to 5 mass%), based upon the weight of the lubricating composition, of one or more **antioxidant(s)** (such as blends of antioxidants), where if present, optionally the one or more antioxidant(s) is a mixture of one or more amine antioxidant(s) and one or more phenol antioxidant(s), preferably at a ratio of at least 2:1;

where the lubricating oil composition may preferably exhibit:

1) an SAE viscosity grade of 20W-X, 15W-X, 10W-X, 5W-X, or 0W-X (such as 10W-X or 5W-X), where X represents any one of 8, 12, 16, 20, 30, 40, and 50 (such as 30); and

2) optionally, an average piston cleanliness, as determined by Daimler OM471 FE1 (CEC L-118-21), of 70 % or more such as 73 % or more such as 74 % or more, of 75 % or more such as 76 % or more, of 78 % or more such as 80 % or more such as 80.5 % or more, and/or

3) optionally, an average wear on gear train wheels, as determined by Daimler OM471 FE1 (CEC L-118-21), of 75 % or more, of 80 % or more such as 81 % or more, of 82 % or more such as 82.5 % or more such as 83 % or more, and/or

4) optionally, an average liner wear, as determined by Daimler OM471 FE1 (CEC L-118-21), of 8 μm or less, of 5 μm or less, of 3 μm or less such as 2 μm or less such as 1 μm or less, and/or

5) optionally, an oxidation, as determined by Daimler OM471 FE1 (CEC L-118-21), of 65 A/cm or less, of 55 A/cm or less such as 51 A/cm or less such as 49 A/cm or less such as 45 A/cm or less such as 40 A/cm or less.

[0065] This disclosure also relates to lubricating oil compositions comprising or resulting from the admixing of:

(i) from 1 to 99 mass% (alternately 30 to 95 mass%, alternately 50 to 90 mass%, alternately 60 to 95 mass%, alternately 70 to 85 mass%) of one or more **base oil(s),** based upon the weight of the lubricating composition; or alternately the lubricating oil composition comprises 50 mass% of more of one or more **base oil(s),** based upon the weight of the lubricating composition;

(ii) from 0.1 to 20 mass% (in particular 0.1 to 12 mass%, alternately 0.1 to 10 mass%, alternately 1 to 8 mass%), based upon the weight of the lubricating composition, of one or more **poly(alkenyl) succinimide dispersant(s)** (such as blends of poly(alkenyl) succinimide dispersants), comprising one or more poly(alkenyl) succinimide dispersant(s) (such as blends of poly(alkenyl) succinimide dispersants), derived from a polyalkenyl-substituted succinic anhydride prepared using a chlorine-assisted alkylation process and a polyamine ("chloro dispersant(s)"), and one or more poly(alkenyl) succinimide dispersant(s) (such as blends of poly(alkenyl) succinimide dispersants), derived from a polyalkenyl succinic anhydride prepared using a halogen-free thermal alkylation process and a polyamine ("thermal dispersant(s)"), and the thermal dispersant(s) is present in an amount such that the weight ratio of the chloro dispersant(s) to said thermal dispersant(s) is at least 4:1; and

(iii) from 0.01 to 20 mass% (in particular 0.1 to 10 mass%, alternately 0.15 mass% to 5 mass%, alternately 0.2 to 2 mass%), based upon the weight of the composition, of one or more **detergent(s)** (such as blends of detergents);
(iv) from 0.001 to 10 mass% (in particular, 0.01 to 5 wt%, alternately 0.1 to 3 mass%, alternately 0.15 to 1.5 mass%, alternately 0.2 to 1 mass%), based upon the weight of the lubricating composition, of one or more **anti-wear agent(s)** (such as blends of anti-wear agents, such as zinc dialkyl dithio phosphate);
v) from 0.1 to 20 mass% (in particular 0.1 to 12 mass%, alternately 0.25 to 8 mass%, alternately 0.5 to 6 mass%, alternately 0.05 to 5 mass%, alternately 3.5 to 5 mass%), based upon the weight of the lubricating composition, of one or more **antioxidant(s)** (such as blends of antioxidants, such as a mixture of one or more amine antioxidant(s) and one or more phenol antioxidant(s), preferably at a ratio of at least 2:1);
(vi) from 0.10 to 20 mass% (in particular 0.15 to 10 mass%, alternately 0.20 mass% to 5 mass%, alternately 0.25 to 2 mass%, alternately 0.5 to 1 mass%), based upon the weight of the lubricating composition, of one or more **amide, imide, and/or ester functionalized partially or fully saturated polymer(s)** comprising C_{4-5} olefins having:

i) an Mw/Mn of less than 2,
ii) a Functionality Distribution (Fd) value of 3.5 or less (GPC-PS), and
i) an Mn of 10,000 g/mol or more (GPC-PS) of the polymer(s) prior to functionalization, provided that, if the polymer(s) prior to functionalization is(are) a copolymer of isoprene and butadiene, then the Mn of the copolymer is greater than 25,000 g/mol (GPC-PS),

where the lubricating oil composition may preferably exhibit:

1) an SAE viscosity grade of 20W-X, 15W-X, 10W-X, 5W-X, or 0W-X (such as 10W-X or 5W-X), where X represents any one of 8, 12, 16, 20, 30, 40, and 50 (such as 30); and
2) optionally, an average piston cleanliness, as determined by Daimler OM471 FE1 (CEC L-118-21), of 70 % or more such as 73 % or more such as 74 % or more, of 75 % or more such as 76 % or more, of 78 % or more such as 80 % or more such as 80.5 % or more, and/or
3) optionally, an average wear on gear train wheels, as determined by Daimler OM471 FE1 (CEC L-118-21), of 75 % or more, of 80 % or more such as 81 % or more, of 82 % or more such as 82.5 % or more such as 83 % or more, and/or
4) optionally, an average liner wear, as determined by Daimler OM471 FE1 (CEC L-118-21), of 8 μm or less, of 5 μm or less, of 3 μm or less such as 2 μm or less such as 1 μm or less, and/or
5) optionally, an oxidation, as determined by Daimler OM471 FE1 (CEC L-118-21), of 65 A/cm or less, of 55 A/cm or less such as 51 A/cm or less such as 49 A/cm or less such as 45 A/cm or less such as 40 A/cm or less.

[0066] The instant disclosure also relates to a lubricant composition of an oil of lubricating viscosity, comprising from 0.1 to 30 mass% (in particular 0.1 to 20 mass%, alternately 0.1 to 12 mass%, alternately 3 to 10 mass%, alternately 6 to 8 mass%), based upon the weight of the lubricating composition, of a **dispersant mixture,** the dispersant mixture comprising

(1) an amide, imide, and/or ester functionalized partially or fully saturated polymer comprising C_{4-5} olefins having:

i) an Mw/Mn of less than 2,
ii) a Functionality Distribution (Fd) value of 3.5 or less, and
iii) an Mn of 10,000 g/mol or more (GPC-PS) of the polymer prior to functionalization; and

(2) one or more poly(alkenyl) succinimide dispersant(s) (such as blends of poly(alkenyl) succinimide dispersants), derived from a polyalkenyl-substituted succinic anhydride prepared using a chlorine-assisted alkylation process and a polyamine ("chloro dispersant(s)"); and
(3) one or more poly(alkenyl) succinimide dispersant(s) (such as blends of poly(alkenyl) succinimide dispersants), derived from a polyalkenyl succinic anhydride prepared using a halogen-free thermal alkylation process and a polyamine ("thermal dispersant(s)"), which is present in an amount such that the weight ratio of the chloro dispersant(s) (2) to said thermal dispersant(s) is at least 4:1 and/or that the weight ratio of the functionalized polymer (1) to said thermal dispersant(s) is at least 0.5:1.

[0067] This disclosure also relates to lubricating oil compositions comprising or resulting from the admixing of:

A) from 1 to 99 mass% (alternately 30 to 95 mass%, alternately 50 to 90 mass%, alternately 60 to 95 mass%, alternately 70 to 85 mass%) based upon the weight of the lubricating oil composition, of one or more **base oil(s)**, or

alternately 50 mass% of more of one or more **base oil(s)**, based upon the weight of the lubricating composition;
B) from 0.1 to 20 mass% (in particular 0.15 to 10 mass%, alternately 0.2 to 5 mass%, alternately 0.25 to 2 mass%, alternately 0.5 to 1 mass%, alternately 0.2 to 1 mass%), based upon the weight of the lubricating oil composition, of one or more **amide, imide, and/or ester functionalized partially or fully saturated polymer(s)** described herein;
C) from 0.01 to 20 mass% (in particular 0.1 to 10 mass%, alternately 0.15 mass% to 5 mass%, alternately 0.2 to 2 mass%, alternately 0.2 to 0.6 mass%), based upon the weight of the lubricating oil composition, of one or more **detergent(s)** (such as blends of detergents);
D) optionally, from 0.001 to 5 mass% (in particular 0.01 to 4 mass%, alternately 0.015 to 3 mass%, alternately 0.02-0.04 mass%), based upon the weight of the lubricating oil composition, of one or more **friction modifier(s)** (such as blends of friction modifiers);
E) from 0.1 to 20 mass% (in particular 0.1 to 12 mass%, alternately 0.25 to 8 mass%, alternately 0.5 to 6 mass%, alternately 0.05 to 5 mass%, alternately 3.5 to 5 mass%), based on total weight of the lubricating oil composition, of one or more **antioxidant(s)** (such as blends of antioxidants);
F) optionally, from 0.01 to 5 mass% (in particular, 0.01 to 3 mass%, alternately 0.02 to 1.5 mass%, alternately 0.025 to 0.2 mass%), based upon the weight of the lubricating oil composition, of one or more **pour point depressant(s)** (such as blends of pour point depressants);
G) optionally, from 0.001 to 5 mass% (in particular, 0.001 to 3 mass%, alternately 0.005 to 1.5 mass%, alternately 0.005 to 0.01 mass%), based upon the weight of the lubricating oil composition, of one or more **anti-foam agent(s)** (such as blends of anti-foam agents);
H) optionally, from 0.001 to 10 mass% (in particular, 0.01 to 6 wt%, alternately 0.01 to 5 mass%, alternately 0.1 to 4 mass%, alternately 0.1 to 2 mass%, alternately 0.1 to 0.22 mass%), based upon the weight of the lubricating oil composition, of one or more **viscosity modifier(s)** (such as blends of viscosity modifiers);
I) from 0.1 to 20 mass% (in particular 0.1 to 12 mass%, alternately 0.1 to 10 mass%, alternately 1 to 8 mass%), based upon the weight of the lubricating composition, of one or more **dispersant(s)** (such as blends of dispersants), comprising, in particular consisting of, one or more poly(alkenyl) succinimide dispersant(s) (such as blends of poly(alkenyl) succinimide dispersants), derived from a polyalkenyl-substituted succinic anhydride prepared using a chlorine-assisted alkylation process and a polyamine ("chloro dispersant(s)"), and one or more poly(alkenyl) succinimide dispersant(s) (such as blends of poly(alkenyl) succinimide dispersants), derived from a polyalkenyl succinic anhydride prepared using a halogen-free thermal alkylation process and a polyamine ("thermal dispersant(s)"), and the thermal dispersant(s) is present in an amount such that the weight ratio of the chloro dispersant(s) to said thermal dispersant(s) is at least 4:1, in particular about 9:2;
J) optionally, from 0.01 to 5 wt% (in particular, 0.01 to 3 mass%, alternately 0.05 to 1.5 mass%, alternately 0.05 to 0.1 mass%), based upon the weight of the lubricating oil composition, of one or more **inhibitor(s) and/or anti-rust agent(s)** (such as blends of inhibitors and /or anti-rust agents);
K) from 0.001 to 10 mass% (in particular, 0.01 to 5 wt%, alternately 0.1 to 3 mass%, alternately 0.15 to 1.5 mass%, alternately 0.2 to 1 mass%, alternately 0.06 to 0.6 mass%), based upon the weight of the lubricating composition, of one or more **anti-wear agent(s)** (such as blends of anti-wear agents, such as ZDDP);
M) optionally, from 0.01 to 5 wt% (in particular, 0.05 to 2 mass%, alternately 0.1 to 1 mass%), based upon the weight of the lubricating oil composition, of one or more seal compatibility agents, such as **seal swell agent(s),** and/or
O) optionally, from 0.01 to 5 mass% (in particular, 0.1 to 3 mass%, alternately 0.1 to 1.5 mass%), based upon the weight of the lubricating oil composition, of one or more unsaturated C_{12}-C_{60} hydrocarbons (such as C_{12}-C_{24} linear alpha-olefins **(LAOs),** oligomers/polymers of polyisobutylenes, and/or blends thereof).

[0068] Alternatively, the lubricating oil compositions of the present invention (including but not limited to those disclosed above) may contain at least 50 mass% based upon the weight of the lubricating oil composition, of one or more base oil(s), such as 50 to 90 mass%, alternately 60 to 95 mass%, alternately 70 to 85 mass%. In particular, the lubricating oil compositions of the present invention (including but not limited to those disclosed above) may contain at least 30 mass% based upon the weight of the lubricating oil composition, of one or more Group III base oil(s), such as 30 to 55 mass%, alternately 35 to 50 mass%, and at least 25 mass% based upon the weight of the lubricating oil composition, of one or more Group II base oil(s), such as 25 to 45 mass%, alternately 30 to 40 mass%.

[0069] For purposes of this disclosure, component B) functionalized polymers are not added in the elements C, D, E, F G, H, I, J, K, M, and/or O above for determining weight percentages, even though they may show similar properties, e.g., element B) functionalized polymers may impact wear positively, but is not added into element K) for determining weight percent of anti-wear agents. Specifically, compositions according to the present disclosure may contain an additive having a different enumerated function that are also aminated (for example, the dispersant component PIBSA-PAM and others described below in the dispersant section). These additives are not included as functionalized polymer for purposes of determining the amount of functionalized polymer in a lubricating oil composition or additive concentrate herein. However, component B) functionalized polymer along with component I) poly(alkenyl) succinimide dispersant(s) constitute a dispersant mixture described herein.

[0070] In embodiments, all of elements D, E, F G, H, I, J, K, M, and O are present in addition to the base oil, detergent, and the one or more functionalized polymers described herein.

[0071] In embodiments, elements D, E, F G, H, I, J, and K are present in addition to the base oil, detergent, and the one or more functionalized polymers described herein.

[0072] In embodiments, elements I, and E are present in addition to the base oil, detergent, and the one or more functionalized polymers described herein.

[0073] In embodiments, element K is present in addition to the base oil, detergent, and the one or more functionalized polymers described herein.

[0074] Suitably, the lubricant composition may have a total base number (TBN) of 4 to 15 mgKOH/g, preferably 5 to 12 mgKOH/g, such as 7 to 12 mgKOH/g, such as 8 to 11 mgKOH/g, as measured by ASTM D2896.

[0075] The lubricating compositions of the present disclosure may contain particularly low levels of phosphorus, namely not greater than 1000, preferably not greater than 800, more preferably not greater than 500, such as 1 to 1000, such as 50 to 800, such as 100 to 500 parts per million (ppm) by mass of phosphorus, expressed as atoms of phosphorus, based on the total mass of the lubricating compositions, as measured by ASTM D5185.

[0076] Suitably, the lubricant composition may have a phosphorus level of 1000 ppm or less, alternately 800 ppm or less, alternately 500 ppm or less, as measured by ASTM D5185.

[0077] The lubricating compositions of the present disclosure may contain a ratio of atoms of Magnesium to atoms of Calcium based on the total mass of the lubricating compositions, as measured by ASTM D5185, of at least to 0.5, preferably at least 0.6, more preferably at least 0.65.

[0078] Typically, the lubricating compositions may contain low levels of sulfur. Preferably, the lubricating composition contains up to 0.4, more preferably up to 0.3, most preferably up to 0.2, such as 0.1 to 0.4 mass% sulfur, based on the total mass of the lubricating oil composition, as measured by ASTM D5185.

[0079] Typically, the lubricating compositions may contain particularly low levels of sulfated ash, such as 1.0 % or less, such as 0.9 mass% or less, preferably 0.6 mass or less %, preferably 0.5 mass% or less, alternately 0.0001 to 0.5 mass% or less sulfated ash, based on the total mass of the lubricating composition, as measured by ASTM D874-13a (2018).

[0080] Generally, the kinematic viscosity at 100° C ("KV100") of the lubricating composition may range from 2 to 30 cSt, such as 2 to 20 cSt, such as 5 to 15 cSt as determined according to ASTM D 445-19a).

[0081] In embodiments, the kinematic viscosity at 100° C ("KV100") of the lubricating composition may range from 6 to 17 cSt, such as 9 to 16.3 cSt, such as 9.3 to less than 12.5 cSt, such as 12.5 to less than 16.3 cSt, as determined according to ASTM D 445-19a).

[0082] Generally, the total base number of the lubricating composition may range from 1 to 30, such as 5 to 15 mgKOH/g, (as determined according to ASTM D2896).

[0083] Preferably, the lubricating composition of the present disclosure may be a multigrade oil identified by the viscometric descriptor SAE 20W-X, SAE 15W-X, SAE 10W-X, SAE 5W-X or SAE 0W-X, where X represents any one of 8, 12, 16, 20, 30, 40, and 50; the characteristics of the different viscometric grades can be found in the SAE J300 classification. Alternately, the lubricating composition may be the form of viscosity grade SAE 15W-X, SAE 10W-X, SAE 5W-X or SAE 0W-X, such as in the form of SAE 5W-X, wherein X represents any one of 8, 12, 16, 20, 30, 40, and 50. Preferably X is 8, 12, 16, 20, or 30. Alternately, the lubricating composition of the present disclosure may be a multigrade oil identified by the viscometric descriptor SAE 10W-30, 15W-40, 5W-30, 5W-40, 10W-40, 5W-50, such as SAE 5W-30. (See standard SAE J300 published January 2015 by SAE International, formerly known as Society of Automotive Engineers).

[0084] Optionally, the lubricating composition may be absent phenate detergent.

[0085] Optionally, the lubricating composition may be absent PIBSA ester dispersant.

[0086] Optionally, the lubricating composition may be absent phenolic antioxidant. Alternatively, the lubricating composition may comprise phenolic antioxidant.

[0087] Optionally, the lubricating composition may be absent sulphurised methyl ester antioxidant.

[0088] In embodiments, the lubricating oil composition may comprise less than 1000 ppm boron, alternately less than 600 ppm boron, alternately from 80 to 350 ppm boron. Alternately, the LOC may be absent boron.

[0089] In embodiments, the lubricating oil composition may comprise less than 20 (such as less than 15, such as less than 10, such as less than 6) mass%, functionalized (such as aminated) polybutene (such as polyisobutylene), such as PIBSA-PAM. In embodiments, the lubricating oil composition comprises more than 0.1 (such as 0.1 to 10, such as 0.5 to 8) mass%, functionalized (such as aminated) polybutene (such as polyisobutylene), such as PIBSA-PAM.

[0090] In embodiments, the lubricating oil composition comprises more than 0.5 (such as 0.5 to 8, such as 2 to 8) mass%, functionalized (such as aminated) polybutene (such as polyisobutylene), such as PIBSA-PAM, derived from a polyisobutylene-substituted succinic anhydride prepared using a chlorine-assisted alkylation process and a polyamine.

[0091] In embodiments, the lubricating oil composition comprises more than 0.5 (such as 0.5 to 8, such as 0.5 to 2) mass%, functionalized (such as aminated) polybutene (such as polyisobutylene), such as PIBSA-PAM, derived from a polyisobutylene-substituted succinic anhydride prepared using a halogen-free thermal alkylation process and a polyamine.

[0092] In embodiments, the lubricating oil composition comprises more than 0.1 (such as 0.1 to 5, such as 0.1 to 3, such as 0.5 to 2) mass%, functionalized (such as aminated) polybutene (such as polyisobutylene) having a high terminal vinylidene content, such as HR-PIBSA-PAM.

[0093] In embodiments, the lubricating oil composition may comprise acylated polymers, such as polyisobutylene succinic acid (PIBSA), optionally having an Mn of 500 to 50,000 g/mol, such as 600 to 5,000 g/mol, such as 700 to 3000 g/mol. In embodiments, the lubricating oil composition may comprise acylated polymers, such as polyisobutylene succinic acid, having an Mn of 500 to 1600 g/mol, such as 700 to 1200 g/mol.

[0094] In embodiments, the lubricating oil composition may comprise 20 (such as 15, such as 10, such as 5, such as 3, such as 1) mass% or less block copolymer, such as block, star, random, and/or tapered block copolymer).

[0095] In embodiments, the lubricating oil composition may be substantially free of or may be absent block copolymer, such as block, star, random, and/or tapered block copolymer.

[0096] In embodiments, the lubricating oil composition may comprise 20 (such as 15, such as 10, such as 5, such as 3, such as 1) mass% or less styrenic copolymer, such as block, star, random, and/or tapered styrenic block copolymer).

[0097] In embodiments, the lubricating oil composition may be substantially free or absent styrenic copolymer, such as block, star, random, and/or tapered styrenic block copolymer.

[0098] In embodiments, the lubricating oil composition may comprise less than 20 (such as less than 15, such as less than 10, such as less than 5, such as less than 3, such as less than 1) mass% of functionalized diluent, such as functionalized oil.

[0099] In embodiments, the lubricating oil composition may comprise, may be substantially free of, or may be absent functionalized diluent, such as functionalized oil.

[0100] In embodiments, the lubricating oil composition may comprise less than 20 (such as less than 15, such as less than 10, such as less than 5, such as less than 3, such as less than 1) mass% of solvent, such as aromatic solvent.

[0101] In embodiments, the lubricating oil composition may be substantially free of or absent solvent, such as functionalized solvent.

[0102] In embodiments, the lubricating oil composition may have a total saponification number (SAP) of 25 (such as 28, such as 30, such as 32) mgKOH/g or more, as determined by ASTM 94.

[0103] In embodiments, the lubricating oil composition may have a total saponification number (SAP) of 25 (such as 28, such as 30, such as 32) mgKOH/g or more, as determined by ASTM 94 and the functionalized polymer has a Functionality Distribution (Fd) value of 3.5 or less (such as 3.4 or less, such as from 1 to 3.3, such as from 1.1 to 3.2, such as from 1.2 to 3.0, such as 1.4 to 2.9, as determined by GPC-PS as described in the Experimental section below).

[0104] In embodiments, the lubricating oil composition may have a total saponification number (SAP) of 25 (such as 28, such as 30, such as 32) mgKOH/g or more, as determined by ASTM 94 and the functionalized polymer has an average functionality of 1.4 to 20 FG grafts/polymer chain, such as 1.4 to 15 FG grafts/polymer chain, such as 3 to 12.5 FG grafts/polymer chain, such as 4 to 10 FG grafts/polymer chain, as determined by GPC-PS as described in the Experimental section below.

[0105] In embodiments, the lubricating oil composition may comprise less than 0.5 (such as less than 0.4, such as less than 0.3, such as less than 0.2, such as less than 0.1, substantially absent, or zero) wt%, based upon the weight of the LOC, of secondary hydrocarbyl amine compounds and tertiary hydrocarbyl amine compounds.

[0106] In embodiments, the lubricating oil composition may be substantially absent, or may comprise no, secondary hydrocarbyl amine compounds and tertiary hydrocarbyl amine compounds.

[0107] In embodiments, the lubricating compositions of the present disclosure may be a heavy-duty diesel oil (*e.g.,* for use in an engine for a heavy-duty diesel vehicle, *i.e.,* a heavy-duty diesel vehicle having a gross vehicle weight rating of 10,000 pounds or more.)

[0108] In embodiments, the lubricating compositions of the present disclosure may be a passenger car motor oil.

[0109] In embodiments, the lubricating compositions of the present disclosure may be a passenger car diesel oil.

[0110] In embodiments, the lubricating composition of the present disclosure may be a diesel engine lubricating composition comprising: an oil of lubricating viscosity having greater than 50 wt% of Group I, II, III, IV, and/or V oil (such as one or more Group II base oil(s), one or more Group III base oil(s), or mixtures thereof); a first and a second PIB succinimide dispersant derived from an 1800 to 2500 Mn PIB; a third and a fourth PIB succinimide dispersant derived from a PIB with an Mn less than 1600, where at least one of the first PIB succinimide dispersant and the second PIB succinimide dispersant has a high terminal vinylidene content, at least one of the third PIB succinimide dispersant and the fourth PIB succinimide dispersant is boron-free (optionally, at least one of the third PIB succinimide dispersant and the fourth PIB succinimide dispersant is borated); a amide, imide, and/or ester functionalized partially or fully saturated polymer comprising C_{4-5} olefins as described herein; one or more alkaline earth metal sulfonate detergent(s); and a phosphorus anti-wear agent present in an amount to deliver 100 to 500 ppm phosphorous to the lubricating composition, the lubricating composition having a total sulfated ash of between 0.1 to 0.5 wt%.

[0111] The lubricating compositions disclosed herein, such as diesel engine lubricating compositions, may have a kinematic viscosity as measured by ASTM D-445 at 100° C of from 2.0 to 12.5, such as from 5.0 to 12.5, such as from 7.5 to 12.0 (such as 9.0 to 12.0, or 9.7 to 11.7, or 9.7 to 11.5) cSt (mm^2/s).

[0112] The lubricating composition disclosed herein, such as diesel engine lubricating compositions, may have a high temperature, high shear viscosity (HTHS) as measured by ASTM D4683 at 150° C of less than 3.6 mPa•s, or less than 3.5 mPa•s, or less than 3.4 mPa•s, or less than 3.3 mPa•s, or less than 3.2 mPa•s, or less than 3.1 mPa•s. In another embodiment, the HTHS of the lubricating composition is from 2.4 to 3.5 mPa•s, or from 2.6 to 3.1 mPa•s, or from 2.8 to 3.1 mPa•s.

[0113] The lubricating composition, such as diesel engine lubricating compositions, may have a SAE viscosity grade of 5W-X, wherein Y may be 8, 12, 16, 20, or 30. In a particular embodiment, the lubricating oil composition has an SAE viscosity grade of 5W-30.

[0114] The lubricating compositions disclosed herein, such as diesel engine lubricating compositions, may have: 1) a kinematic viscosity as measured by ASTM D-445 at 100° C of from 7.5 to 12.0 (such as 9.0 to 12.0, or 9.7 to 11.7, or 9.7 to 11.5) cSt (mm^2/s); 2) a high temperature, high shear viscosity (HTHS) as measured by ASTM D4683 at 150° C of less than 3.6 mPa•s, or less than 3.5 mPa•s, or less than 3.4 mPa•s, or less than 3.3 mPa•s, or less than 3.2 mPa•s, or less than 3.1 mPa•s (alternately from 2.4 to 3.5 mPa•s, or from 2.6 to 3.1 mPa•s, or from 2.8 to 3.1 mPa•s); and 3) a SAE viscosity grade of 5W-30.

Additive Concentrates

[0115] An additive concentrate, also referred to as an additive package, adpak, or addpack, is a (concentrate) composition having less than 50 mass% (such as less than 40 mass%, such as less than 30 mass%, such as less than 25 mass%, such as less than 20 mass%) base oil and lubricant composition additives (such as described herein) which is typically then further blended with additional base oil to form a lubricating oil product.

[0116] This disclosure relates to concentrate compositions comprising or resulting from the admixing of:

(a) from 1 to less than 50 mass% (alternately 5 to 45 mass%, alternately 7 to 40 mass%, alternately 10 to 35 mass%, alternately 10 to 25 mass%) of one or more **base oil(s),** based upon the weight of the concentrate composition;

(b) from 0.1 to 40 mass% (in particular 0.15 to 20 mass%, alternately 0.2 to 10 mass%, alternately 0.25 to 5 mass%, alternately 0.5 to 4 mass%), based upon the weight of the concentrate composition, of a **functionalized polymer** comprising a partially or fully saturated olefin homopolymer or copolymer backbone and at least one functional group (such as a group derived from an amine or a hydroxyl group), having: an Mn of 10,000 g/mol or more (GPC-PS) of the polymer prior to functionalization, and preferably having been functionalized with an acylating agent and subsequently reacted with a compound containing amino and/or hydroxyl groups, (such as one or more amide, imide, and/or ester functionalized partially or fully saturated polymers comprising C_{2-5} olefins) having: i) an Mw/Mn of less than 2, ii) optionally, a Functionality Distribution (Fd) value of 3.5 or less (GPC-PS), and iii) an Mn of 10,000 g/mol or more (GPC-PS) of the polymer(s) prior to functionalization, provided that, if the polymer(s) prior to functionalization is (are) a copolymer of isoprene and butadiene, then the Mn of the copolymer is greater than 25,000 g/mol (GPC-PS));

c) from 0.1 to 60 mass% (alternately 0.1 to 40 mass%, alternately 0.5 to 30 mass%, alternately 1 to 25 mass%, alternately 15 to 25 mass%), based upon the weight of the concentration composition, of one or more poly(alkenyl) succinimide dispersant(s) (such as blends of poly(alkenyl) succinimide dispersants), derived from a polyalkenyl-substituted succinic anhydride prepared using a chlorine-assisted alkylation process and a polyamine (**"chloro dispersant(s)");** and

d) from 0.1 to 20 mass% (alternately 0.1 to 12 mass%, alternately 0.25 to 10 mass%, alternately 0.5 to 8 mass%, alternately 1.5 to 7 mass%, alternately 3 to 6 mass%), based upon the weight of the concentrate composition, of one or more poly(alkenyl) succinimide dispersant(s) (such as blends of poly(alkenyl) succinimide dispersants), derived from a polyalkenyl succinic anhydride prepared using a halogen-free thermal alkylation process and a polyamine **("thermal dispersant(s)"),** which is present in an amount such that the weight ratio of the chloro dispersant(s) (c) to said thermaldispersant(s) is at least 4:1;

e) optionally 0 to 50 mass% (such as absent or substantially absent from the lubricating oil composition, alternately 0.1 to 35 mass%, alternately 0.25 to 25 mass%, alternately 0.5 to 22 mass%, alternately 0.05 to 20 mass%, alternately 14 to 20 mass%), based upon the weight of the concentrate composition, of one or more **antioxidant(s)** (such as blends of antioxidants), where if present, optionally the one or more antioxidant(s) is a mixture of one or more amine antioxidant(s) and one or more phenol antioxidant(s), preferably at a ratio of at least 2:1;

[0117] This disclosure relates to concentrate compositions comprising or resulting from the admixing of:

(i) from 1 to less than 50 mass% (alternately 5 to 45 mass%, alternately 7 to 40 mass%, alternately 10 to 35 mass%, alternately 10 to 25 mass%) of one or more base **oil(s),** based upon the weight of the concentrate composition;

(ii) from 0.1 to 70 mass% (in particular 0.1 to 50 mass%, alternately 0.1 to 40 mass%, alternately 1 to 30 mass%), based upon the weight of the concentrate composition, of one or more **poly(alkenyl) succinimide dispersant(s)** (such as blends of poly(alkenyl) succinimide dispersants), comprising one or more poly(alkenyl) succinimide dispersant(s) (such as blends of poly(alkenyl) succinimide dispersants), derived from a polyalkenyl-substituted succinic anhydride prepared using a chlorine-assisted alkylation process and a polyamine ("chloro dispersant(s)"), and one or more poly(alkenyl) succinimide dispersant(s) (such as blends of poly(alkenyl) succinimide dispersants), derived from a polyalkenyl succinic anhydride prepared using a halogen-free thermal alkylation process and a polyamine ("thermal dispersant(s)"), and the thermal dispersant(s) is present in an amount such that the weight ratio of the chloro dispersant(s) to said thermal dispersant(s) is at least 4:1; and

(iii) from 0.01 to 30 mass% (in particular 0.1 to 20 mass%, alternately 0.5 mass% to 10 mass%, alternately 0.5 to 5 mass%), based upon the weight of the concentrate composition, of one or more **detergent(s)** (such as blends of detergents);

(iv) from 0.001 to 20 mass% (in particular, 0.01 to 10 wt%, alternately 0.1 to 5 mass%, alternately 0.5 to 5 mass%, alternately 1 to 3 mass%), based upon the weight of the concentrate composition, of one or more **anti-wear agent(s)** (such as blends of anti-wear agents, such as zinc dialkyl dithio phosphate);

v) from 0.1 to 50 mass% (in particular 0.1 to 35 mass%, alternately 0.25 to 25 mass%, alternately 0.5 to 22 mass%, alternately 0.05 to 20 mass%, alternately 14 to 20 mass%) based upon the weight of the concentrate composition, of one or more **antioxidant(s)** (such as blends of antioxidants, such as a mixture of one or more amine antioxidant(s) and one or more phenol antioxidant(s), preferably at a ratio of at least 2:1);

(vi) from 0.1 to 40 mass% (in particular 0.15 to 20 mass%, alternately 0.2 to 10 mass%, alternately 0.25 to 5 mass%, alternately 0.5 to 4 mass%), based upon the weight of the composition, of one or more **amide, imide, and/or ester functionalized partially or fully saturated polymers** comprising C_{4-5} olefins having:

i) an Mw/Mn of less than 2,
ii) a Functionality Distribution (Fd) value of 3.5 or less (GPC-PS), and
ii) an Mn of 10,000 g/mol or more (GPC-PS) of the polymer(s) prior to functionalization, provided that, if the polymer(s) prior to functionalization is(are) a copolymer of isoprene and butadiene, then the Mn of the copolymer is greater than 25,000 g/mol (GPC-PS),

(vii) optional additional components, pour point depressants, anti-foam agents, viscosity modifiers, corrosion inhibitors, extreme pressure additives, demulsifiers, seal compatibility agents, additive diluent base oils, friction modifier(s) (such as, organic FM, such as organic ester, such as fatty acid ester), etc.

[0118] The instant disclosure also relates to a concentrate composition, comprising from 0.1 to 50 mass% (in particular 0.1 to 40 mass%, alternately 15 to 40 mass%, alternately 20 to 32 mass%, alternately 25 to 30 mass%), based upon the weight of the concentrate composition, of a **dispersant mixture,** the dispersant mixture comprising:

(1) an amide, imide, and/or ester functionalized partially or fully saturated polymer comprising C_{4-5} olefins having:

i) an Mw/Mn of less than 2,
ii) a Functionality Distribution (Fd) value of 3.5 or less, and
iii) an Mn of 10,000 g/mol or more (GPC-PS) of the polymer prior to functionalization; and

(2) one or more poly(alkenyl) succinimide dispersant(s) (such as blends of poly(alkenyl) succinimide dispersants), derived from a polyalkenyl-substituted succinic anhydride prepared using a chlorine-assisted alkylation process and a polyamine ("chloro dispersant(s)"); and

(3) one or more poly(alkenyl) succinimide dispersant(s) (such as blends of poly(alkenyl) succinimide dispersants), derived from a polyalkenyl succinic anhydride prepared using a halogen-free thermal alkylation process and a polyamine ("thermal dispersant(s)"), which is present in an amount such that the weight ratio of the chloro dispersant(s) (2) to said thermal dispersant(s) is at least 4:1 and/or that the weight ratio of the functionalized polymer (1) to said thermal dispersant(s) is at least 0.5:1.

[0119] In embodiments, the dispersant mixture in the concentrate composition disclosed herein comprises:

(1) 0.01 to 15 mass% (in particular 1 to 12 mass%, alternately 5 to 11 mass%, alternately 7.5 to 10.5 mass%, alternately 8.5 to 10 mass%) based upon the total mass of the dispersant mixture, of an amide, imide, and/or ester functionalized partially or fully saturated polymer comprising C_{4-5} olefins described herein; and

(2) 50 to 90 mass% (in particular 55 to 85 mass%, alternately 62 to 82 mass%, alternately 68 to 80 mass%, alternately

70 to 76 mass%) based upon the total mass of the dispersant mixture, of one or more chloro dispersant(s); and
(3) 10 to 30 mass% (in particular 12 to 25 mass%, alternately 14 to 22 mass%, alternately 15 to 20 mass%, alternately 15.5 to 17.5 mass%) based upon the total mass of the dispersant mixture, of one or more thermal dispersant(s).

[0120] In embodiments, the concentrate composition disclosed herein may optionally comprise one or more antioxidant(s).

[0121] In embodiments, the concentrate composition disclosed herein may further comprise one or more additional additive(s) selected from the group consisting of detergents, friction modifiers, anti-foam agents, corrosion inhibitors/anti-rust agents, and anti-wear agents.

[0122] This disclosure also relates to concentrate compositions comprising or resulting from the admixing of:

A) from 1 to less than 50 mass% (alternately 5 to 45 mass%, alternately 7 to 40 mass%, alternately 10 to 35 mass%, alternately 10 to 25 mass%), based upon the weight of the concentrate composition, of one or more **base oil(s);**

B) from 0.1 to 40 mass% (in particular 0.15 to 20 mass%, alternately 0.2 to 10 mass%, alternately 0.25 to 5 mass%, alternately 0.5 to 4 mass%), based upon the weight of the concentrate composition, of one or more **amide, imide, and/or ester functionalized partially or fully saturated polymer(s)** described herein;

C) from 0.01 to 30 mass% (in particular 0.1 to 20 mass%, alternately 0.5 mass% to 10 mass%, alternately 0.5 to 5 mass%), based upon the weight of the concentrate composition, of one or more **detergent(s)** (such as blends of detergents);

D) optionally, from 0.001 to 10 mass% (in particular 0.01 to 8 mass%, alternately 0.05 to 5 mass%, alternately 0.05-0.2 mass%), based upon the weight of the concentrate composition, of one or more **friction modifier(s)** (such as blends of friction modifiers);

E) from 0.1 to 50 mass% (in particular 0.1 to 35 mass%, alternately 0.25 to 25 mass%, alternately 0.5 to 22 mass%, alternately 0.05 to 20 mass%, alternately 14 to 20 mass%), based on total weight of the concentrate composition, of one or more **antioxidant(s)** (such as blends of antioxidants);

G) optionally, from 0.001 to 8 mass% (in particular, 0.001 to 5 mass%, alternately 0.005 to 2 mass%, alternately 0.01 to 0.1 mass%), based upon the weight of the concentrate composition, of one or more **anti-foam agent(s)** (such as blends of anti-foam agents);

I) from 0.1 to 70 mass% (in particular 0.1 to 50 mass%, alternately 0.1 to 40 mass%, alternately 1 to 30 mass%), based upon the weight of the concentrate composition, of one or more **dispersant(s)** (such as blends of dispersants), comprising one or more poly(alkenyl) succinimide dispersant(s) (such as blends of poly(alkenyl) succinimide dispersants), derived from a polyalkenyl-substituted succinic anhydride prepared using a chlorine-assisted alkylation process and a polyamine ("chloro dispersant(s)"), and one or more poly(alkenyl) succinimide dispersant(s) (such as blends of poly(alkenyl) succinimide dispersants), derived from a polyalkenyl succinic anhydride prepared using a halogen-free thermal alkylation process and a polyamine ("thermal dispersant(s)"), and the thermal dispersant(s) is present in an amount such that the weight ratio of the chloro dispersant(s) to said thermal dispersant(s) is at least 4:1, in particular about 9:2;

J) optionally, from 0.01 to 10 wt% (in particular, 0.01 to 5 mass%, alternately 0.05 to 3 mass%, alternately 0.1 to 0.5 mass%), based upon the weight of the lubricating oil composition, of one or more **inhibitor(s) and/or anti-rust agent(s)** (such as blends of inhibitors and /or anti-rust agents);

K) from 0.001 to 20 mass% (in particular, 0.01 to 10 wt%, alternately 0.1 to 5 mass%, alternately 0.5 to 5 mass%, alternately 1 to 3 mass%), based upon the weight of the lubricating composition, of one or more **anti-wear agent(s)** (such as blends of anti-wear agents, such as ZDDP).

[0123] Concentrate compositions may be present in the lubricating oil composition at from of 0.5 mass% to 35 mass%, such as 5 mass% to 30 mass%, such as 7.5 mass% to 25 mass%, such as 10 to 22.5 mass%, such as 15 to 20 mass%, based upon the mass of the lubricating oil composition.

[0124] Optionally, the concentrate composition may be absent functionalized oil.

[0125] In embodiments, the concentrate composition may optionally be absent solvent (such as aliphatic or aromatic solvent) and/or absent functionalized base oil.

[0126] Optionally, the concentrate composition may be absent phenate detergent.

[0127] Optionally, the concentrate composition may be absent PIBSA ester dispersant.

[0128] Optionally, the concentrate composition may be absent phenolic antioxidant. Alternatively, the concentrate composition may comprise phenolic antioxidant.

[0129] Optionally, the concentrate composition may be absent sulphurised methyl ester antioxidant.

[0130] In embodiments, the concentrate composition may comprise less than 1000 ppm boron, alternately less than 600 ppm boron, alternately from 80 to 350 ppm boron. Alternately, the concentrate may be absent boron.

[0131] In embodiments, the concentrate composition may comprise less than 40 (such as less than 35, such as less than

30, such as less than 26) mass%, functionalized (such as aminated) polybutene (such as polyisobutylene), such as PIBSA-PAM. In embodiments, the lubricating oil composition comprises more than 0.1 (such as 0.1 to 30, such as 0.5 to 26) mass%, functionalized (such as aminated) polybutene (such as polyisobutylene), such as PIBSA-PAM.

[0132] In embodiments, the concentrate composition comprises more than 0.5 (such as 0.5 to 25, such as 10 to 25) mass%, functionalized (such as aminated) polybutene (such as polyisobutylene), such as PIBSA-PAM, derived from a polyisobutylene-substituted succinic anhydride prepared using a chlorine-assisted alkylation process and a polyamine.

[0133] In embodiments, the concentrate composition comprises more than 0.5 (such as 0.5 to 25, such as 0.5 to 10) mass%, functionalized (such as aminated) polybutene (such as polyisobutylene), such as PIBSA-PAM, derived from a polyisobutylene-substituted succinic anhydride prepared using a halogen-free thermal alkylation process and a polyamine.

[0134] In embodiments, the concentrate composition comprises more than 0.1 (such as 0.1 to 10, such as 0.1 to 8, such as 0.5 to 5) mass%, functionalized (such as aminated) polybutene (such as polyisobutylene) having a high terminal vinylidene content, such as HR-PIBSA-PAM.

[0135] In embodiments, the concentrate composition may comprise acylated polymers, such as polyisobutylene succinic acid (PIBSA), optionally having an Mn of 500 to 50,000 g/mol, such as 600 to 5,000 g/mol, such as 700 to 3000 g/mol. In embodiments, the lubricating oil composition may comprise acylated polymers, such as polyisobutylene succinic acid, having an Mn of 500 to 1600 g/mol, such as 700 to 1200 g/mol.

[0136] In embodiments, the concentrate composition may comprise 20 (such as 15, such as 10, such as 5, such as 3, such as 1) mass% or less block copolymer, such as block, star, random, and/or tapered block copolymer.

[0137] In embodiments, the concentrate composition may be substantially free of or absent block copolymer, such as block, star, random, and/or tapered block copolymer.

[0138] In embodiments, the concentrate composition may comprise 20 mass% or less (such as 15 mass% or less, such as 10 mass% or less, such as 5 mass% or less, such as 3 mass% or less, such as 1) mass% or less styrenic copolymer, such as block, star, random, and/or tapered styrenic block copolymer).

[0139] In embodiments, the concentrate composition may be substantially free of or absent styrenic copolymer, such as block, star, random, and/or tapered styrenic block copolymer).

[0140] In embodiments, the concentrate composition may comprise less than 20 (such as less than 15, such as 10, such as less than 5, such as less than 3, such as 1) mass% of functionalized diluent, such as functionalized oil.

[0141] In embodiments, the concentrate composition may substantially free of or absent functionalized diluent, such as functionalized oil.

[0142] In embodiments, the concentrate composition may comprise less than 0.5 (such as less than 0.4, such as less than 0.3, such as less than 0.2, such as 0.1, substantially absent, no) wt%, based upon the weight of the concentrate composition, of secondary hydrocarbyl amine compounds and tertiary hydrocarbyl amine compounds.

[0143] In embodiments, the concentrate composition may be substantially absent, or may comprise no, secondary hydrocarbyl amine compounds and tertiary hydrocarbyl amine compounds.

[0144] In embodiments, the concentrate composition may have a kinematic viscosity at 100° C of less than 1000 cSt, such as less than 500 cSt, such as less than 200 cSt.

A. Base Oil

[0145] The base oil (also referred to as "base stock," "lubricating oil basestock," or "oil of lubricating viscosity") useful herein may be a single oil or a blend of oils, and is typically a large liquid constituent of a lubricating composition, also referred to as a lubricant, into which additives and optional additional oils are blended, for example, to produce a lubricating composition, such as a final lubricant composition, a concentrate, or other lubricating composition.

[0146] A base oil may be selected from vegetable, animal, mineral, and synthetic lubricating oils, and mixtures thereof. It may range in viscosity from light distillate mineral oils to heavy lubricating oils, such as those for gas engine oil, mineral lubricating oil, motor vehicle oil, and heavy-duty diesel oil. Generally, the kinematic viscosity at 100° C ("KV100") of the base oil ranges from 1 to 30, such as 2 to 25 cSt, such as 5 to 20 cSt, as determined according to ASTM D445-19a, in particular, from 1.0 cSt to 10 cSt, from 1.5 cSt to 3.3 cSt, from 2.7 cSt to 8.1 cSt, from 3.0 cSt to 7.2 cSt, or from 2.5 cSt to 6.5 cSt. Generally, the high temperature high shear (HTHS) viscosity at 150° C of the base oil ranges from 0.5 to 20 cP such as 1 to 10 cP, such as 2 to 5 cP as determined according to ASTM D4683-20.

[0147] Typically, when lubricating oil basestock(s) is used to make a concentrate, it may advantageously be present in a concentrate-forming amount to give a concentrate containing, from 5 wt% to 80 wt%, from 10 wt% to 70 wt%, or from 5wt% to 50wt% of active ingredient, based upon the weight of the concentrate.

[0148] Common oils useful as base oils include animal and vegetable oils (e.g., castor and lard oil), liquid petroleum oils, and hydrorefined and/or solvent-treated mineral lubricating oils of the paraffinic, naphthenic, and mixed paraffinic-naphthenic types. Oils derived from coal or shale are also useful base oils. Base stocks may be manufactured using a variety of different processes including, but not limited to, distillation, solvent refining, hydrogen processing, oligomerization, esterification, and re-refining.

[0149] Synthetic lubricating oils useful herein as base oils include hydrocarbon oils such as homopolymerized and copolymerized olefins, referred to as polyalphaolefins or PAO's or group IV base oils [according to the API EOLCS 1509 definition (American Petroleum Institute Publication 1509, see section E.1.3, 19th edition, January 2021, www.API.org)]. Examples of PAO's useful as base oils include: poly(ethylenes), copolymers of ethylene and propylene, polybutylenes, polypropylenes, propylene-isobutylene copolymers, chlorinated polybutylenes, poly(1-hexenes), poly(1-octenes), poly(1-decenes), homo- or co-polymers of C_8 to C_{20} alkenes, homo- or co-polymers of C_8, and/or C_{10}, and/or C_{12} alkenes, C_8/C_{10} copolymers, $C_8/C_{10}/C_{12}$ copolymers, and C_{10}/C_{12} copolymers, and the derivatives, analogues and homologues thereof.

[0150] In another embodiment, the base oil may comprise polyalphaolefins comprising oligomers of linear olefins having 6 to 14 carbon atoms, more preferably 8 to 12 carbon atoms, more preferably 10 carbon atoms having a Kinematic viscosity at 100° C of 10 or more (as measured by ASTM D445); and preferably having a viscosity index ("VI"), as determined by ASTM D2270, of 100 or more, preferably 110 or more, more preferably 120 or more, more preferably 130 or more, more preferably 140 or more; and/or having a pour point of -5° C or less (as determined by ASTM D97), more preferably -10° C or less, more preferably - 20° C or less.

[0151] In another embodiment polyalphaolefin oligomers useful in the present disclosure may comprise C_{20} to C_{1500} paraffins, preferably C_{40} to C_{1000} paraffins, preferably C_{50} to C_{750} paraffins, preferably C_{50} to C_{500} paraffins. The PAO oligomers are dimers, trimers, tetramers, pentamers, *etc.,* of C_5 to C_{14} alpha-olefins in one embodiment, and C_6 to C_{12} alpha-olefins in another embodiment, and C_8 to C_{12} alpha-olefins in another embodiment. Suitable olefins include 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-undecene, and 1-dodecene. In one embodiment, the olefin is a combination of 1-octene, 1-decene, and 1-dodecene, or alternately may be substantially 1-decene, and the PAO is a mixture of dimers, trimers, tetramers, and pentamers (and higher) thereof. Useful PAO's are described more particularly in, for example, US Patent Nos. 5,171,908 and 5,783,531, and in Synthetic Lubricants and High-Performance Functional Fluids 1-52 (Leslie R. Rudnick & Ronald L. Shubkin, ed. Marcel Dekker, Inc. 1999).

[0152] PAO's useful in the present disclosure typically possess a number average molecular weight of from 100 to 21,000 g/mol in one embodiment, and from 200 to 10,000 g/mol in another embodiment, and from 200 to 7,000 g/mol in yet another embodiment, and from 200 to 2,000 g/mol in yet another embodiment, and from 200 to 500 g/mol in yet another embodiment. Desirable PAO's are commercially available as SpectraSyn™ Hi-Vis, SpectraSyn™ Low-Vis, SpectraSyn™ plus, SpectraSyn™ Elite PAO's (ExxonMobil Chemical Company, Houston Texas) and Durasyn PAO's from Ineos Oligomers USA LLC.

[0153] Synthetic lubricating oils useful as base oils also include hydrocarbon oils such as homopolymerized and copolymerized: 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.

[0154] Another suitable class of synthetic lubricating oils useful as base oils comprises the esters of dicarboxylic acids (*e.g.*, phthalic acid, succinic acid, alkyl succinic acids and alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, sebasic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkylmalonic acids, alkenyl malonic acids) reacted 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.

[0155] Esters useful as synthetic oils herein also include those made from C_5 to C_{12} monocarboxylic acids and polyols, and polyol ethers such as neopentyl glycol, trimethylolpropane, pentaerythritol, dipentaerythritol, and tripentaerythritol.

[0156] Desirable ester base oils are commercially available as Esterex™ Esters (ExxonMobil Chemical Company, Houston, Texas).

[0157] Silicon-based oils such as the polyalkyl-, polyaryl-, polyalkoxy- or polyaryloxysilicone oils and silicate oils comprise another useful class of synthetic lubricants useful herein; such oils include tetraethyl silicate, tetraisopropyl silicate, tetra-(2-ethylhexyl) silicate, tetra-(4-methyl-2-ethylhexyl)silicate, tetra-(p-tert-butyl-phenyl) silicate, hexa-(4-methyl-2-ethylhexyl)disiloxane, poly(methyl)siloxanes, and poly(methylphenyl)-siloxanes.

[0158] Other synthetic lubricating oils useful herein include liquid esters of phosphorous-containing acids (*e.g.*, tricresyl phosphate, trioctyl phosphate, diethyl ester of decylphosphonic acid) and polymeric tetrahydrofurans.

[0159] Unrefined, refined, and re-refined oils can be used in the lubricating compositions of the present disclosure. 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 an ester oil obtained directly from an esterification process and used without further treatment is considered an 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 used by those in the art. Re-refined oils are oils obtained by processes similar to those used to obtain refined oils where the refining processes are applied to previously refined oils which have been previously used in service. Such re-refined oils are also referred to as reclaimed or reprocessed oils and often are additionally processed for removal of spent additive and oil breakdown products. A re-refined base oil is preferably substantially free from materials introduced through manufacturing, contamination, or previous use.

[0160] Other examples of useful base oils are gas-to-liquid ("GTL") base oils, *i.e.,* the base oil is an oil derived from hydrocarbons made from synthesis gas ("syn gas") containing H2 and CO using a Fischer-Tropsch catalyst. These hydrocarbons typically require further processing in order to be useful as a base oil. For example, they may, by methods known in the art, be hydroisomerized; hydrocracked and hydroisomerized; dewaxed; or hydroisomerized and dewaxed. For further information on useful GTL base oils and blends thereof, please see US Patent No. 10,913,916 (col 4, ln 62 to col 5, ln 60) and US Patent No. 10,781,397 (col 14, ln 54 to col 15, ln 5, and col 16, ln 44 to col 17, ln 55).

[0161] In particular, oils from renewable sources, *i.e.,* based in part on carbon and energy captured from the environment, such as biological sources, are useful herein.

[0162] The various base oils are often categorized as Group I, II, III, IV, or V according to the API EOLCS 1509 definition (American Petroleum Institute Publication 1509, see section E.1.3, 19th edition, January 2021, www.API.org). Generally speaking, Group I base stocks have a viscosity index of between about 80 to 120 and contain greater than about 0.03 % sulfur and/or less than about 90 % saturates. Group II base stocks have a viscosity index of between about 80 to 120 and contain less than or equal to about 0.03 % sulfur and greater than or equal to about 90 % saturates. Group III base stocks have a viscosity index greater than about 120 and contain less than or equal to about 0.03 % sulfur and greater than about 90 % saturates. Group IV base stocks includes polyalphaolefins (PAO). Group V base stocks include base stocks not included in Groups I-IV. (Viscosity index measured by ASTM D 2270, saturates is measured by ASTM D2007, and sulfur is measured by ASTM D5185, D2622, ASTM D4294, ASTM D4927, and ASTM D3120).

[0163] Base oils for use in the formulated lubricating compositions useful in the present disclosure are any one, two, three, or more of the variety of oils described herein. In desirable embodiments, base oils for use in the formulated lubricating compositions useful in the present disclosure are those described as API Group I(including Group I+), Group II (including Group II+), Group III (including Group III+), Group IV, and Group V oils and mixtures thereof, preferably API Group II, Group III, Group IV, and Group V oils and mixtures thereof. The base oil may be a Group III, Group III+, IV, and Group V base oils due to their exceptional volatility, stability, viscometric, and cleanliness features. Minor quantities of Group I basestock, such as the amount used to dilute additives for blending into formulated lube oil products, can be tolerated but are typically kept to a minimum, *e.g.*, amounts only associated with their use as diluent/carrier oil for additives used on an "as-received" basis. In regard to the Group II stocks, it is often more useful that the Group II base stock be in the higher quality range associated with that stock, *i.e.,* a Group II stock having a viscosity index in the range from 100 to 120.

[0164] The base oil useful herein may be selected from any of the synthetic, natural, or re-refined oils (such as those typically used as crankcase lubricating oils for spark-ignited and compression-ignited engines). Mixtures of synthetic and/or natural and/or re-refined base oils may be used if desired. Multi-modal mixtures (such as bi- or tri-modal mixtures) of Group I, II, III, IV, and/or V base stocks may be used if desired.

[0165] The base oil or base oil blend used herein conveniently has a kinematic viscosity at 100° C (KV100, as measured according to ASTM D445-19a, and reported in units of centistoke (cSt) or it its equivalent, mm2/s), of about 2 to about 40 cSt, alternately of 3 to 30 cSt, alternately 4 to 20 cSt at 100° C, alternately 5 to 10 cSt, alternately the base oil or base oil blend may have a kinematic viscosity at 100° C of 2 to 20 cSt, of 2.5 to 2 cSt, and preferably of about 2.5 cSt to about 9 cSt.

[0166] The base oil or base oil blend preferably has a saturate content of at least 65 mass%, more preferably at least 75 mass%, such as at least 85 mass%, such as at least than 90 mass% as determined by ASTM D2007.

[0167] Preferably, the base oil or base oil blend will have a sulfur content of less than 1 mass%, preferably less than 0.6 mass%, most preferably less than 0.4 mass%, such as less than 0.3 mass%, based on the total mass of the lubricating composition, as measured by ASTM D5185.

[0168] In embodiments, the volatility of the base oil or base oil blend, as measured by the Noack test (ASTM D5800, procedure B), is less than or equal to 30 mass%, such as less than or equal to 25 mass%, such as less than or equal to 20 mass%, such as less than or equal to 16 mass%, such as less than or equal to 12 mass%, such as less than or equal to 10 mass%, based on the total mass of the lubricating composition.

[0169] In embodiments, the viscosity index (VI) of the base oil is at least 95, preferably at least 110, more preferably at least 120, even more preferably at least 125, most preferably from about 130 to 240, in particular from about 105 to 140 (as determined by ASTM D2270).

[0170] The base oil may be provided in a major amount, in combination with a minor amount of one or more additive components as described hereinafter, constituting a lubricant. This preparation may be accomplished by adding the additives directly to the oil or by adding the one or more additives in the form of a concentrate thereof to disperse or dissolve the additive(s). Additives may be added to the oil by any method known to those skilled in the art, either before, at the same time as, or after addition of other additives.

[0171] The base oil may be provided in a minor amount, in combination with minor amounts of one or more additive components as described hereinafter, constituting an additive concentrate. This preparation may be accomplished by adding the additives directly to the oil or by adding the one or more additives in the form of a solution, slurry or suspension thereof to disperse or dissolve the additive(s) in the oil. Additives may be added to the oil by any method known to those skilled in the art, either before, at the same time as, or after addition of other additives.

[0172] The base oil typically constitutes the major component of an engine oil lubricant composition of the present disclosure and typically is present in an amount ranging from at least about 50 wt%, such as about 50 to about 99 wt%, preferably from about 70 to about 95 wt%, and more preferably from about 80 to about 95 wt%, based on the total weight of the composition.

[0173] Typically, one or more base oils are present in the lubricating composition in an amount of 32 wt% or more, alternately 55 wt% or more, alternately 60 wt% or more, alternately 65 wt% or more, based on the total weight of the lubricating composition. Typically, one or more base oils are present in the lubricating composition at an amount of 98 wt% or less, more preferably 95 wt% or less, even more preferably 90 wt% or less. Alternately, one or more base oils are present in the lubricating composition at from 1 to 99 mass%, alternately 50 to 97 mass%, alternately to 60 to 95 mass%, alternately 70 to 95 mass%, based upon the weight of the lubricating composition.

[0174] The base oils and blends thereof described above are also useful for making concentrates as well as for making lubricants therefrom.

[0175] Concentrates constitute a convenient means of handling additives before their use, as well as facilitating solution or dispersion of additives in lubricants. When preparing a lubricant that contains more than one type of additive (sometime referred to as "additive components"), each additive may be incorporated separately, each in the form of a concentrate. In many instances, however, it is convenient to provide a so-called additive "package" (also referred to as an "addpack") comprising one or more additives/co-additives, such as described hereinafter, in a single concentrate.

[0176] Typically, one or more base oils are present in the concentrate composition in an amount of 50 wt% or less, alternately 40wt% or less, alternately 30wt% or less, alternately 20 wt% or less, based on the total weight of the concentrate composition. Typically, one or more base oils are present in the concentrate composition at an amount of 0.1 to 49 mass%, alternately 5 to 40 mass%, alternately to 10 to 30 mass%, alternately 15 to 25 mass%, based upon the weight of the concentrate composition.

[0177] In embodiments, the acylation/functionalization reactions described herein may take place in the presence of base oil diluent. As a side product, functionalized base oil can be produced. The oil may become acylated and/or functionalized itself. For example, maleated base oil or aminated base oil may be present after the functionalization reactions described herein.

[0178] It is contemplated that the functionalized base oil may comprise the acylated oil.

[0179] It is contemplated that the functionalized base oil may comprise the reaction product of the acylated oil with an amine to form an amide, imide or combination thereof.

[0180] It is contemplated that the functionalized base oil may comprise both acylated oil and reaction product of the acylated oil with an amine to form an amide, imide or combination thereof.

[0181] In embodiments the lubricating oil composition and/or additive concentrate may comprise functionalized base oil, such as acylated oil and/or reaction product of the acylated oil with an amine or alcohol to form an amide, imide, ester, or combination thereof, in an amount of 40 wt% or less, alternately 20 wt% or less, alternately 10 wt% or less, alternately 5 wt% or less, based on the total weight of the concentrate composition. Typically, one or more functionalized base oil, such as acylated oil and/or reaction product of the acylated oil with an amine or alcohol to form an amide, imide, ester, or combination thereof, are present in the concentrate at an amount of 0.01 to 40 mass%, alternately 0.1 to 20 mass%, alternately to 1 to 10 mass%, alternately 1.5 to 5 mass%, based upon the weight of the concentrate composition.

[0182] Typically, one or more functionalized base oil, such as acylated oil and/or reaction product of the acylated oil with an amine or alcohol to form an amide, imide, ester, or combination thereof, are present in the lubricating oil composition at an amount of 0.01 to 40 mass%, alternately 0.1 to 20 mass%, alternately to 1 to 10 mass%, alternately 1.5 to 5 mass%, based upon the weight of the lubricating oil composition.

[0183] In embodiments, functionalized oil may be present in a lubricating oil composition at 3 mass% or less, preferably 2 mass% or less, preferably 1 mass% or less, preferably at 0.1 mass% or less, preferably at 0 mass%, based upon the weight of the lubricating oil composition.

[0184] In embodiments, functionalized oil may be present in an additive concentrate at 3 mass% or less, preferably 2 mass% or less, preferably 1 mass% or less, preferably at 0.1 mass% or less, preferably at 0 mass%, based upon the weight of the concentrate composition.

[0185] In embodiments, the acylation/functionalization reactions described herein may take place in solvent-containing media. As a side product, functionalized solvent can be produced. The solvent may become acylated and/or functionalized itself. In embodiments, acylated and/or functionalized solvent may be present in a concentrate composition at 3 mass% or less, preferably 2 mass% or less, preferably 1 mass% or less, preferably at 0.1 mass% or less, preferably at 0 mass%, based upon the weight of the concentrate composition. In embodiments, functionalized solvent may be present in a lubricating oil composition at 3 mass% or less, preferably 2 mass% or less, preferably 1 mass% or less, preferably at 0.1

mass% or less, preferably at 0 mass%, based upon the weight of the lubricating oil composition.

[0186] In the lubricating oil compositions and the additive concentrates of the present invention, the base oil may be comprised entirely of one or more Group II base oil(s), of one or more Group III base oil(s), or of a mixture of one or more Group II and one or more Group III base oil(s). In particular embodiments, the base oil comprised in the lubricating oil composition and the additive concentrate of the invention is solely one or more Group III base oils. Alternatively, in particular embodiments, the base oils comprised in the lubricating oil composition and the additive concentrate of the invention are a mixture of one or more group II and one or more Group III base oils(s). In certain embodiments, where the base oil is a mixture of one or more Group II and one or more Group III base oil(s), the base oil comprises at least 20 mass%, such as at least 30 mass%, such as at least 50 mass% of one or more Group II base oil(s) (based on the total mass of base oil present in the lubricating oil composition). In particular embodiments, the lubricating oil compositions of the present invention comprise 25 to 65 mass%, such as 30 to 55 mass%, such as 34 to 48 mass% of one or more group III base oil(s) based upon the total mass of the lubricating oil composition; and 20to 60 mass%, such as 28 to 48 mass%, such as 30 to 38 mass% of one or more group II base oil(s) based upon the total mass of the lubricating oil composition

[0187] In certain embodiments, the Group III base oil(s), irrespective whether used solely or in a mixture with Group II base oil(s), comprises at least 25 %, such as at least 50 %, such as at least 75 %, such as at least 80 %, up to 100% of a Group III base oil having a viscosity of 6 cSt or less and/or a Group III base oil of 4 cSt or less (based on the total mass of Group III base oil(s) present in the lubricating oil composition).

[0188] In particular embodiments, the base oil(s) used in the lubricating oil compositions and additive concentrates of the present invention is a mixture of one or more Group II and one or more Group III base oil(s), and the one or more group III base oil(s) and the one or more group II base oil(s) are present at a ratio of about 70:30 to about 30:70, such as about 65:35 to about 40:60, such as about 60:40 to about 45:55, such as about 55:45 to about 50:50.

[0189] In the present disclosure, for the sake of clarity, any additive package diluent (used to dilute an active ingredient in a component of a lubricating oil composition or an additive concentrate of the present invention) is not considered to be referred to as a "base oil" in the sense of a separate component as described herein.

B. Functionalized Polymer

[0190] This disclosure relates to a functionalized polymer comprising a polymer that prior to functionalization has an Mn of about 10,000 g/mol or more, such as 20,000 g/mol or more, such as 25,000 g/mol or more, such as 30,000 g/mol or more, such as 35,000 g/mol or more (GPC-PS). Alternately, functionalized polymer comprises a polymer that prior to functionalization has an Mn of 10,000 to 300,000 g/mol, such as 20,000 to about 150,000 g/mol, such as 30,000 to about 125,000 g/mol, such as 35,000 to about 100,000 g/mol, such as 40,000 to 80,000 g/mol (GPC-PS). The polymer prior to functionalization may have an Mw/Mn of less than 2 (such as less than 1.6, such as less than 1.5, such as 1.4 or less, such as from 1 to 1.3, such as from 1.0 to 1.25, such as from 1.0 to 1.2, such as 1.0 to 1.15, such as from 1.0 to 1.1 as determined by GPC-PS). The polymer prior to functionalization may comprise repeat units of one or more olefins having 4 to 5 carbon atoms (preferably conjugated dienes having 4 to 5 carbon atoms). Prior to functionalization the polymer (such as a C_{4-5} polymer) is preferably fully or partially saturated (such as fully or partially hydrogenated). The functionalized polymer may be obtained by reacting the polymer with an acylating agent to form acylated polymer and then reacting acylated polymer with an amine or alcohol to form an amide, imide, ester, or combination thereof. The functionalized polymer may also be obtained by reacting an acylated polymer (such as a commercially available maleated fully or partially hydrogenated C_{4-5} polymer) with an amine to form an amide, imide or combination thereof.

[0191] This disclosure further relates to amide, imide, and/or ester functionalized saturated (such as hydrogenated) polymers of C_{4-5} conjugated dienes described herein obtained by reacting fully or partially saturated (such as fully or partially hydrogenated) polymers of C_{4-5} conjugated dienes having an Mw/Mn of less than 2, with an acylating agent, such as maleic acid or maleic anhydride and thereafter reacting the acylated polymer with an amine (such as a polyamine) to form an imide, amide or combination thereof.

[0192] This disclosure relates to polymers containing one or more pendant amine groups and comprising or resulting from the admixing of: at least partially (preferably completely) hydrogenated C_{4-5} olefin polymers with an acylating agent, such as maleic acid or maleic anhydride, and thereafter reacting the acylated polymer with a polyamine to form an imide, amide or combination thereof.

[0193] In embodiments, the functionalized polymer is not prepared in aromatic solvent (such as benzene or toluene), or aromatic solvent is present at 2 wt% or less (such as 1 wt% or less, such as 0.5 wt% or less), based upon the weight of solvent, diluent, and polymer.

[0194] In embodiments, the functionalized polymer is not prepared in an alkylated naphthylenic solvent, or alkylated naphthylenic solvent is present at 5 wt% or less (such as 3 wt% or less, such as 1 wt% or less), based upon the weight of solvent, diluent, and polymer.

[0195] The polymer useful herein to prepare the functionalized polymer may be a homopolymer of butadiene, isoprene, or the like.

[0196] In embodiments, the polymer useful herein to prepare the functionalized polymer may be a homopolymer of isoprene, or a copolymer of isoprene and less than 5 mol% (such as less than 3 mol%, such as less than 1 mol%, such as less than 0.1 mol%) comonomer. In some embodiments, the polymer backbone prior to functionalization comprises at least 90% isoprene repeat units. In particular embodiments, the functionalized polymer has a backbone of homo-polyisoprene or essentially homo-polyisoprene.

[0197] The polymer useful herein to prepare the functionalized polymer may be copolymer of isoprene and one or more of styrene, methyl-styrene, 2,3-dimethyl-butadiene, 2-methyl-1,3-pentadiene, myrcene, 3-methyl-1,3-pentadiene, 4-methyl-1,3-pentadiene, 2-phenyl-1,3-butadiene, 2-phenyl-1,3-pentadiene, 3-phenyl-1,3 pentadiene, 2,3-dimethyl-1,3-pentadiene, 2-hexyl-1,3-butadiene, 3-methyl-1,3-hexadiene, 2-benzyl-1,3-butadiene, 2-p-tolyl-1,3-butadiene 1,3-butadiene, 1,3-pentadiene, 1,3-hexadiene, 1,3-heptadiene, 2,4-heptadiene, 1,3-octadiene, 2,4-octadiene, 3,5-octadiene, 1,3-nonadiene, 2,4-nonadiene, 3,5-nonadiene, 1,3-decadiene, 2,4-decadiene, and 3,5-decadiene, (optionally the comonomer(s) are present at less than 20 mol%, less than 5 mol%, such as less than 3 mol%, such as less than 1 mol%, such as less than 0.1 mol%).

[0198] Generally, the polymerized conjugated diene polymer useful herein to prepare the functionalized polymer includes a mixture of 1,4- and 1,2-insertions (*a.k.a.* 2,1-insertions; for butadiene, 1,2-insertions are the same as 3,4-insertions). As measured by 1H NMR, the polymerized conjugated diene polymer useful herein to prepare the functionalized polymer contains at least about 50 % of 1,4-insertions, such as at least about 75 % of 1,4 insertions, such as at least about 80 % of 1,4 insertions, such as at least about 90 % of 1,4 insertions, such as at least about 95 % of 1,4 insertions, such as at least 98 % of 1,4 insertions, based upon the total of the 2,1 insertions, 1,4 insertions, and 3,4 insertions of isoprene. For purposes of this disclosure: 1) the phrase "1,4 insertion" includes 1,4 and 4,1 insertions, 2) the phrase "2,1 insertion" includes 2,1 and 1,2 insertions, and 3) the phrase "3,4 insertion" includes 3,4 and 4,3 insertions.

[0199] Optionally, the polymer backbone comprises repeat units of one or more polar monomers, such as (but not limited to) those selected from the group consisting of fumarates, acrylates and combinations thereof.

[0200] Optionally, styrene repeat units may be absent in the polymer useful herein to prepare the functionalized polymer. Optionally, styrene repeat units may be absent in the functionalized hydrogenated/saturated polymers.

[0201] Optionally, butadiene repeat units may be absent in the polymer useful herein to prepare the functionalized polymer. Optionally, butadiene repeat units may be absent in the functionalized hydrogenated/saturated polymers.

[0202] Optionally, the polymer useful herein to prepare the functionalized polymer may be not homopolybutylene. Optionally, the functionalized hydrogenated/saturated polymer may be not homopolybutylene.

[0203] Optionally, the polymer useful herein to prepare the functionalized polymer may be not homopolyisobutylene. Optionally, the functionalized hydrogenated/saturated polymer may be not homopolyisobutylene.

[0204] Optionally, the polymer useful herein to prepare the functionalized polymer may not be a copolymer of isoprene and butadiene. Optionally, the functionalized hydrogenated/saturated polymer may not be a copolymer of isoprene and butadiene.

[0205] The polymer useful herein to prepare the functionalized polymer and/or the functionalized polymer may be homopolymer or copolymer. The copolymer may be a random copolymer, a tapered block copolymer, a star copolymer, or a block copolymer. Block copolymers are formed from a monomer mixture comprising one or more first monomers (such as isobutylene), wherein, for example, a first monomer forms a discrete block of the polymer joined to a second discrete block of the polymer formed from a second monomer (such as butadiene). While block copolymers have substantially discrete blocks formed from the monomers, a tapered block copolymer may be composed of, at one end, a relatively pure first monomer and, at the other end, a relatively pure second monomer. The middle of the tapered block copolymer may be more of a gradient composition of the two monomers.

[0206] The polymer useful herein to prepare the functionalized polymer may typically have an Mn (i.e., prior to functionalization) of 10,000 to 150,000 g/mol, alternately about 10,000 to about 100,000 g/mol, or 20,000 to about 150,000 g/mol, alternately 30,000 to about 125,000 g/mol, such as about 30,000 to about 50,000 g/mol, such as about 30,000 to about 40,000 g/mol, alternately 35,000 to about 100,000 g/mol, alternately 40,000 to 80,000 g/mol (GPC-PS). Alternatively, the polymer prior to functionalization may have an Mn of at least 25,000 g/mol, such as at least 30,000 g/mol (GPC-PS).

[0207] Polymers useful herein to prepare the functionalized polymers may typically have an Mw/Mn (as determined by GPC-PS) of 1 to 2, alternately greater than 1 to less than 2, alternately 1.1 to 1.8, alternately 1.2 to 1.5. Alternately, the polymers useful herein to prepare the functionalized polymers may typically have an Mw/Mn of 1 or greater than 1 to less than 2 (such as less than 1.8, such as less than 1.7, such as less than 1.6, such as less than 1.5, such as less than 1.4, such as less than 1.3, such as 1.25 or less, such as less than 1.2, such as less than 1.15, such as less than 1.12, such as less than 1.10).

[0208] The polymers used to prepare the functionalized polymers may have an Mz (as determined by GPC-PS) of 20,000 to 150,000 g/mol, alternately 30,000 to about 125,000 g/mol, alternately 35,000 to about 100,000 g/mol, alternately 40,000 to 80,000 g/mol, such as about 50,000 to about 60,000 g/mol, alternately 40,000 to 60,000 g/mol (GPC-PS).

[0209] Polymers useful herein to prepare the functionalized polymers may have a glass transition temperature (Tg) of

-25° C or less, such as -40° C or less, such as -50° C or less, as determined by Differential Scanning calorimetry (DSC) using a Perkin Elmer or TA Instrument Thermal Analysis System (sample is heated from ambient to 210° C at 10° C/minute and held at 210° C for 5 minutes, then cooled down to -40° C at 10° C/minute and held for 5 minutes.)

[0210] Polymers useful herein to prepare the functionalized polymers typically have a residual unsaturation of less than 3 %, such less than 2 %, such less than 1 %, such as less than 0.5 %, such as less than 0.25 % based upon number of double bonds in the non-hydrogenated polymer.

[0211] Polymers useful herein to prepare the functionalized polymers typically have a residual metal (such as Li, Co, and Al) content of less than 100 ppm, such less than 50 ppm, such as less than 25 ppm, such as less than 10 ppm, such as less than 5 ppm.

Hydrogenation

[0212] The C_{4-5} polymers useful herein to prepare the functionalized polymer can be hydrogenated partially or completely by any hydrogenating agent known to one of ordinary skill in the art. For example, a saturated or partially saturated polymer can be prepared by (a) providing a C_{4-5} polymer containing unsaturations (such as double or triple bonds); and (b) hydrogenating at least a portion or all of the unsaturations (such as double or triple bonds) in the polymer in the presence of a hydrogenation reagent. In some embodiments, the polymer is fully hydrogenated. In some embodiments, the polymer is partially hydrogenated. In some embodiments, the polymer is saturated (hydrogenated) at 50 % or more, such as 60 % or more, such as 70 % or more, such as 80 % or more, such as 90 % or more, such as 95 % or more, such as 98 % or more, such as 99 % or more, such as from 50 to 100 % saturated (hydrogenated), as determined by ozone adsorption method described in Martino N. Smits and Dirkman Hoefman, Quantative Determination of Olefinic Unsaturation by Measurement of Ozone Absorption Analytical Chemistry Vol 44, No. 9, pg. 1688, 1972, Martino N. Smits.

[0213] In embodiments, the hydrogenation reagent can be hydrogen in the presence of a hydrogenation catalyst. In some embodiments, the hydrogenation catalyst is Pd, Pd/C, Pt, PtO_2, $Ru(PPh_3)_2Cl_2$, Raney nickel, or a combination thereof. In embodiments, the catalyst is a Pd catalyst. In another embodiment, the catalyst is 5 % Pd/C. In a further embodiment, the catalyst may comprise or be 10 % Pd/C in a high-pressure reaction vessel and the hydrogenation reaction is allowed to proceed until completion. Generally, after completion, the reaction mixture can be washed, concentrated, and dried to yield the corresponding hydrogenated product. Alternatively, any reducing agent that can reduce a C=C double bond to a C-C single bond can also be used. For example, the olefin polymer can be hydrogenated by treatment with hydrazine in the presence of a catalyst, such as 5-ethyl-3-methyllumiflavinium perchlorate, under an oxygen atmosphere to give the corresponding hydrogenated products. The reduction reaction with hydrazine is disclosed in Imada et al., J Am. Chem. Soc., 127, pp. 14544-14545, (2005), which is incorporated herein by reference.

Acylation

[0214] The fully or partially saturated (hydrogenated) polymer may be chemically modified (functionalized) to provide a polymer having at least one polar functional group, such as, but not limited to, halogen, epoxy, hydroxy, amino, nitrilo, mercapto, imido, carboxy, and sulfonic acid groups of combinations thereof. The functionalized polymers can be further modified to give a more desired type of functionality. In a preferred case, the fully or partially hydrogenated polymer is functionalized by a method, which includes reacting the fully or partially hydrogenated polymer with an unsaturated carboxylic acid (or derivative thereof, such as maleic anhydride) to provide an acylated polymer (which may then be further functionalized as described below).

[0215] In some embodiments, a carboxylic acid functionality or a reactive equivalent thereof is grafted onto the polymer to form an acylated polymer. An ethylenically unsaturated carboxylic acid material is typically grafted onto the polymer backbone. These materials which are attached to the polymer typically contain at least one ethylenic bond (prior to reaction) and at least one, such as two, carboxylic acid (or its anhydride) groups or a polar group which is convertible into said carboxyl groups by oxidation or hydrolysis. Maleic anhydride or a derivative thereof is suitable. It grafts onto the polymer, to give two carboxylic acid functionalities. Examples of additional unsaturated carboxylic materials include itaconic anhydride, or the corresponding dicarboxylic acids, such as maleic acid, fumaric acid and their esters, as well as cinnamic acid and esters thereof. In certain embodiments, the acylating agent is maleic anhydride.

[0216] The ethylenically unsaturated carboxylic acid material may be grafted onto the polymer in a number of ways. It may be grafted onto the polymer in solution or in essentially pure (molten) form with or without using a radical initiator. Free-radical induced grafting of ethylenically unsaturated carboxylic acid materials may also be conducted in solvents, such as hexane or mineral oil. It may be carried out at an elevated temperature in the range of 100° C to 250° C, *e.g.,* 120° C to 190° C, or 150° C to 180° C, *e.g.,* above 160° C.

[0217] The free-radical initiators which may be used include peroxides, hydroperoxides, and azo compounds, typically those which have a boiling point greater than about 100° C and which decompose thermally within the grafting temperature range to provide free radicals. Representative of these free-radical initiators include azobisisobutyronitrile and 2,5-

dimethyl-hex-3-yne-2,5-bis-tertiary-butyl peroxide. The initiator may be used in an amount of 0.005 % to 1 % by weight based on the weight of the reaction mixture solution. The grafting may be carried out in an inert atmosphere, such as under nitrogen blanketing. The resulting acylated polymer intermediate is characterized by having carboxylic acid acylating functions as a part of its structure.

[0218] In embodiments, the acylated polymer may have 2 or more anhydride groups per polymer molecule and may exhibit less than 10 % gel. Alternately, the acylated polymer may have less than 2 anhydride groups per polymer molecule and may exhibit less than 10 % gel. (See also col 17, ln 14 -col 18, ln 11 of US Patent No. 5,429,758).

[0219] Alternately, in some embodiments, the acylated polymer may have a gel content of less than about 5 wt%, less than 3 wt%, less than 2 wt%, less than 1 wt%, less than 0.5 wt%, less than 0.1 wt%, or 0 wt%, where the gel content is measured by determining the amount of material that is extractable from the polymer by using boiling xylene (or cyclohexane) as an extractant. The percent of soluble and insoluble (gel) material in a polymer composition is determined by soaking a nominally 0.5 mm thick thin film specimen of polymer for 48 hours in cyclohexane at 23° C or refluxing the thin film specimen in boiling xylene for one half hour, removing the solvent, weighing the dried residue and calculating the amount of soluble and insoluble (gel) material. This method is generally described in US Patent No. 4,311,628, which is incorporated herein by reference. For purposes of this disclosure, gel content is measured using boiling xylene, unless the sample is not soluble in xylene, then the cyclohexane method is used.

[0220] In embodiments, the acylated polymer may have a Saponification Number (SAP) of 5 g/KOH or more, such as 10 g/KOH or more, such as 20 g/KOH or more, such as 30 g/KOH or more, such as 50 g/KOH or more, such as 10 to 60 g/KOH, such as 20 to 40 g/KOH as determined by ASTM D94.

[0221] In embodiments, the acylated polymer composition may have less than 5 wt% unreacted acylating agent (such as maleic anhydride), such as less than 4 wt%, such as less than 3 wt%, such as less than 1 wt%, such as less than 0.5 wt%, such as less than 0.25 wt%, such as less than 0.1 wt%, based upon the weight of the acylated polymer composition (*i.e.*, polymer, acylating agent, and diluent).

[0222] In embodiments, the acylation reactions described herein may take place in base oil diluent. As a side product, functionalized base oil can be produced. The oil may become acylated itself. For example, maleated base oil may be present after the acylation reactions described herein.

[0223] It is contemplated that the functionalized base oil may comprise the acylated oil and/or the reaction product of the acylated oil with an amine to form an amide, imide or combination thereof.

[0224] Preferably, the acylated oil and/or reaction product of the acylated oil with an amine or alcohol to form an amide, imide, ester, or combination thereof, may be present in a concentrate in an amount of 40 wt% or less, alternately 20 wt% or less, alternately 10 wt% or less, alternately 5 wt% or less, alternately 3 mass% or less, preferably 2 mass% or less, preferably 1 mass% or less, preferably at 0.1 mass% or less, preferably at 0 mass% (such as 0 to 40 mass%, alternately 0.01 to 40 mass%, alternately 0.1 to 20 mass%, alternately to 1 to 10 mass%, alternately 1.5 to 5 mass%), based upon the weight of the concentrate composition.

[0225] Preferably one or more functionalized base oils, such as acylated oil and/or reaction product of the acylated oil with an amine or alcohol to form an amide, imide, ester, or combination thereof, may be present in the lubricating oil composition at an amount of 0.01 to 40 mass%, alternately 0.1 to 20 mass%, alternately to 1 to 10 mass%, alternately 1.5 to 5 mass%, (such as at 3 mass% or less, preferably 2 mass% or less, preferably 1 mass% or less, preferably at 0.1 mass% or less, preferably at 0 mass%), based upon the weight of the lubricating oil composition.

[0226] In embodiments, the acylation reactions described herein take place in solvent containing media. As a side product, acylated/functionalized solvent can be produced. In embodiments, acylated and/or functionalized solvent may be present in a concentrate composition at 3 mass% or less, preferably 2 mass% or less, preferably 1 mass% or less, preferably at 0.1 mass% or less, preferably at 0 mass%, based upon the weight of the concentrate composition. In embodiments, functionalized solvent may be present in a lubricating oil composition at 3 mass% or less, preferably 2 mass% or less, preferably 1 mass% or less, preferably at 0.1 mass% or less, preferably at 0 mass%, based upon the weight of the lubricating oil composition.

[0227] In embodiments, the acylating agent may be added in such a way as to minimize side reactions (such as reaction with base oil or other diluent present in the reaction vessel).

[0228] In embodiments, the acylating reaction may occur where the acylating agent (such as maleic acid or maleic anhydride) is added in a continuous or semi-continuous (such as intermittent) stream (such as, for example, in controlled relatively equal portions over the reaction time, or larger and/or smaller portions at different points in the reaction) to minimize functionalized base oil and other side reactions. As an example, the acylating agent may be added in a continuous fashion where the amounts of polymer and acylating agents are added in controlled stoichiometric amounts. As another example, the polymer may be added to a reaction vessel in batch fashion and the acylating agent added slowly or in a semi-continuous fashion (such as adding the acylating agent in 2 or more, such as 5 or more, such as 10 or more, such as 20 or more, such as 30 or more, such as 40 or more, such as 50 or more, such as 60 or more discrete amounts or portions). Alternately, the polymer can be added to the reaction vessel in X number of portions and the acylating agent added in 1.5X or more (such as 2X or more, such as 5X or more, such as 10X or more, such as 20X or more, such as 30X or more, such as 40X or more, such as 50X or more, such as 60X or more) number of portions. This same effect may also be achieved by diluting or concentrating a polymer solution and/or the acylating agent solution to the same or different extents.

[0229] Preferably, the acylating agent may be added in such a way as to minimize side reactions, such as in a continuous or semi-continuous fashion.

[0230] The reaction may also be run so as to minimize side reactions by using high concentrations of the polymer in diluent, such as 45 wt% or more, or 50 wt% or more, or 55 wt% or more, or 60 wt% or more in batch, semi-continuous, or continuous reactor operations. For example, the polymer (such as a hydrogenated isoprene polymer, such as hydrogenated homo-polyisoprene) may be introduced into batch, semi-continuous, or continuous reactor operations as solution or suspension (such as a slurry) in diluent (such as oil (e.g., base oil, such as a Group I, II, III, IV, and/or V base oil, such as a Group II and/or Group III base oil) or alkane solvent or diluent or a combination thereof), where the polymer may be present in the solution or suspension at 45 wt% or more (or 50 wt% or more, or 55 wt% or more, or 60 wt% or more), based upon the weight of the polymer and diluent.

[0231] In embodiments, the side reactions may be minimized by: 1) adding the acylating agent in a continuous or semi-continuous fashion, and/or 2) the polymer is introduced into batch, semi-continuous or continuous reactor operations as solution or suspension in diluent where the polymer is present at 45 wt% or more, based upon the weight of the polymer and diluent.

[0232] In embodiments, side reactions are minimized, optionally by adding the acylating agent in a continuous or semi-continuous fashion, and/or by introducing the fully or partially hydrogenated polymer (such as isoprene polymer) into batch, semi-continuous, or continuous reactor operations as solution or suspension in diluent, said solution or suspension comprising 45 wt% or more (or 50 wt% or more, or 55 wt% or more, or 60 wt% or more), of the fully or partially hydrogenated polymer, based upon the weight of the fully or partially hydrogenated polymer and diluent.

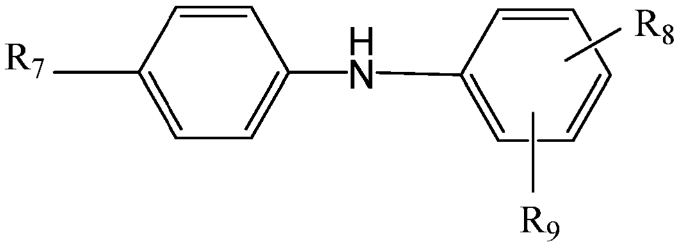
[0233] In embodiments, side reactions are minimized, optionally by adding the acylating agent in a continuous or semi-continuous fashion, and by introducing the fully or partially hydrogenated polymer (such as isoprene polymer) into batch, semi-continuous, or continuous reactor operations as solution or suspension in diluent, said solution or suspension comprising 45 wt% or more (or 50 wt% or more, or 55 wt% or more, or 60 wt% or more), of the fully or partially hydrogenated polymer, based upon the weight of the fully or partially hydrogenated polymer and diluent.

Functionalization

[0234] In embodiments, the acylated polymer may be reacted with an alcohol or an amine to form an amide, imide, ester or combinations thereof. The reaction may consist of condensation to form an imide, an amide, a half-amide, amide-ester, diester, or an amine salt. A primary amino group will typically condense to form an amide or, in the case of maleic anhydride, an imide. It is noted the amine may have a single primary amino group or multiple primary amino groups.

[0235] Suitable amines may include one or more aromatic amines, such as amines wherein a carbon atom of the aromatic ring structure is attached directly to the amino nitrogen. The amine may also be aliphatic. The amine may be a monoamine or a polyamine. In embodiments aliphatic amines can be used alone or in combination with each other or in combination with aromatic amines. The amount of aromatic amine may, in some embodiments, be a major or minor amount compared with the amount of the non-aromatic amines, or in some instances, the composition may be substantially free of aromatic amine. Alternately, the composition may be substantially free of aliphatic amine.

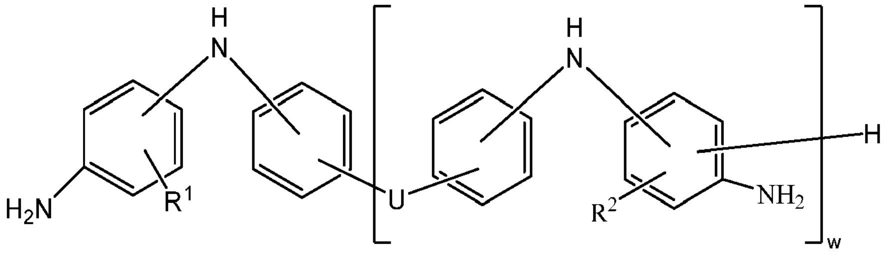
[0236] Examples of aromatic amines which may be used herein include one or more N-arylphenylenediamine(s) represented by the formula:



wherein R_7 is H, - NHaryl, - NHalkaryl, or a branched or straight chain hydrocarbyl radical having from about 4 to about 24 carbon atoms selected from alkyl, alkenyl, alkoxyl, aralkyl or alkaryl; R_9 is - NH_2, - $(NH(CH2)_n)_m$NH2, - NHalkyl, - NHaralkyl, or - CH2-aryl-NH2, in which n and m each have a value from about 1 to about 10; and R_8 is hydrogen, or alkyl, alkenyl, alkoxyl, aralkyl, or alkaryl, having from about 4 to about 24 carbon atoms.

[0237] Suitable N-arylphenylenediamines include N-phenylphenylenediamines (NPPDA), for example, N-phenyl-4,4-phenylenediamine, N-phenyl-1,3-phenylenediamine, and N-phenyl-1,2-phenylenediamine and N-naphthyl-1,4-phenylenediamine. Other derivatives of NPPDA may also be included, such as N-propyl-N'-phenylphenylenediamine.

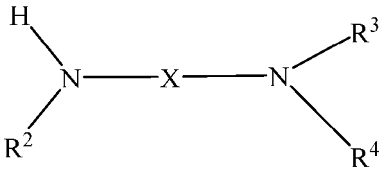
[0238] In embodiments, the amine reacted with the acylated polymer is an amine having at least 3 or 4 aromatic groups and may be represented by the following formula:



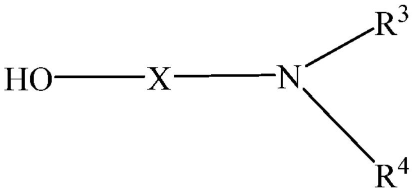
wherein independently each variable, R^1 may be hydrogen or a C_1 to C_5 alkyl group (typically hydrogen); R^2 may be hydrogen or a C_1 to C_5 alkyl group (typically hydrogen); U may be an aliphatic, alicyclic or aromatic group, with the proviso that when U is aliphatic, the aliphatic group may be linear or branched alkylene group containing 1 to 5, or 1 to 2 carbon atoms; and w may be 1 to 10, or 1 to 4, or 1 to 2 (typically 1).

[0239] Other examples of aromatic amines include aniline, N-alkylanilines such as N-methyl aniline, and N-butylaniline, di-(para-methylphenyl)amine, naphthylamine, 4-aminodiphenylamine, N,N-dimethylphenylenediamine, 4-(4-nitro- phenylazo)aniline (disperse orange 3), sulfamethazine, 4-phenoxyaniline, 3-nitroaniline, 4-aminoacetanilide, 4-amino-2-hydroxy-benzoic acid phenyl ester (phenyl amino salicylate), N-(4-amino-5-methoxy-2-methyl-phenyl)-benzamide (fast violet B), N-(4-amino- 2,5-dimethoxy-phenyl)-benzamide (fast blue RR), N-(4-amino-2,5-diethoxy-phenyl)-benzamide (fast blue BB), N-(4-amino-phenyl)-benzamide and 4-phenylazoaniline. Suitable amines are referenced in US Patent No. 7,790,661 and are hereby incorporated by reference.

[0240] In embodiments, the compound condensing with the acylated polymer can be represented by the following formulas:

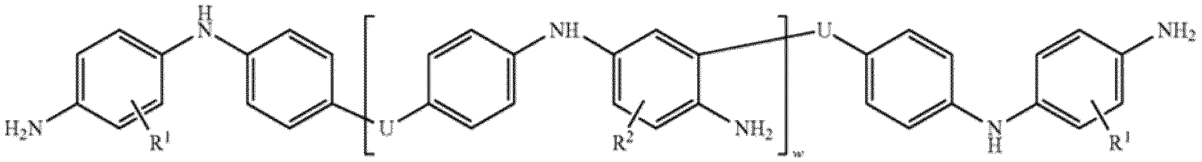


wherein X is an alkylene group containing about 1 to about 4 carbon atoms; R^2, R^3 and R^4 are hydrogen hydrocarbyl groups.



wherein X is an alkylene group containing about 1 to about 4 carbon atoms; R^3 and R^4 are hydrocarbyl groups.

[0241] Alternately, the amine may be an amine having at least 4 aromatic groups and an aldehyde (such as formaldehyde). The aromatic amine may be represented by formula:

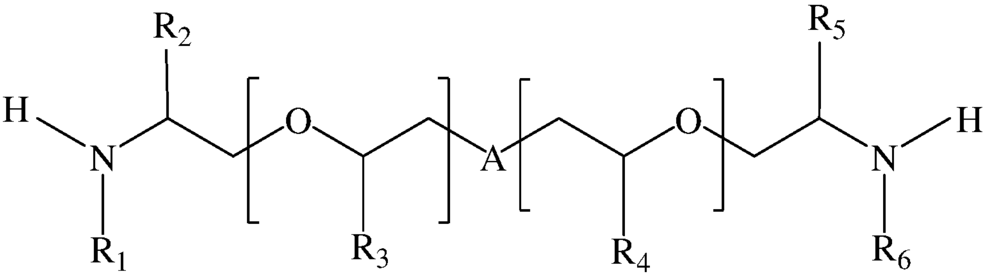


wherein, R^1 is hydrogen or a C_{1-5} alkyl group (typically hydrogen); R^2 is hydrogen or a C_{1-5} alkyl group (typically hydrogen); U is an aliphatic, alicyclic or aromatic group, optionally with the proviso that when U is aliphatic, the aliphatic group may be linear or branched alkylene group containing 1, 2, 3, 4, or 5, or 1 to 2 carbon atoms; and w is 0, 1, 2, 3, 4, 5, 6, 7, 8, or 9, such as 0, 1, 2, or 3 or 0 or 1 (typically 0). For further information on such amines see, *e.g.,* US 2017/0073606, page 5 paragraph [0064]-[0070] and European Patent No. 2 401 348.

[0242] Examples of compounds capable of condensing with the acylating agent and further having a tertiary amino group can include but are not limited to: dimethylaminopropylamine, N,N-dimethyl-aminopropy-lamine, N,N-diethyl-aminopropylamine, N,N-dimethyl-ami-noethylamine ethylenediamine, 1,2-propylenediamine, 1,3-propylenediamine, the isomeric butylenediamines, pentanediamines, hexanediamines, heptanediamines, diethylenetriamine, dipropylenetriamine, dibutylenetriamine, triethylenetetraamine, tetraethylene pentaamine, pentaethylenehexaamine, hexamethylenetetramine, and bis (hexamethylene) triamine, the diaminobenzenes, the diaminopyridines or mixtures thereof. The compounds capable of condensing with the acylating agent and further having a tertiary amino group can further include aminoalkyl substituted heterocyclic compounds such as 1-(3-aminopropyl)imidazole and 4-(3-aminopropyl)morpholine, 1-(2-aminoethyl)piperidine, 3,3-di-amino-N-methyldipropylamine, 3',3-aminobis(N,N-dimethylpropylamine). Another example of compounds capable of condensing with the acylating agent and having a tertiary amino group include alkanolamines including, but not limited to, triethanolamine, trimethanolamine, N,N-dimethylaminopropanol, N,N-diethylaminopropanol, N,N-diethylaminobutanol, N,N,N-tris (hydroxyethyl)amine, N,N,N-tris(hydroxymethyl)amine.

[0243] In embodiments, the polymer may be reacted with a polyether aromatic compound. Typically, the polyether aromatic compound will have at least two functional groups, each capable of reacting with a monocarboxylic acid or ester thereof, or dicarboxylic acid, anhydride or ester thereof, or mixtures thereof. In embodiments, the polyether aromatic compound is derived from an aromatic compound containing at least one amine group and wherein the poly ether is capable of reacting with a monocarboxylic acid or ester thereof, or dicarboxylic acid, anhydride or ester thereof.

[0244] Examples of suitable polyether aromatic amines include compounds having the following structure:



in which A represents an aromatic aminic moiety wherein the ether groups are linked through at least one amine group on the aromatic moiety; R_1 and R_6 are independently hydrogen, alkyl, alkaryl, aralkyl, or aryl or mixtures thereof; R_2, R_3, R_4, and R_5 are independently hydrogen or alkyl containing from about 1 to about 6 carbon atoms of mixtures thereof; and a and x are independently integers from about 1 to about 50.

[0245] The acylated polymer may be reacted with a polyether amine or polyether polyamine. Typical polyether amine compounds contain at least one ether unit and are chain terminated with at least one amine moiety. The polyether polyamines can be based on polymers derived from C_2-C_6 epoxides such as ethylene oxide, propylene oxide, and butylene oxide. Examples of polyether polyamines are sold under the Jeffamine™ brand and are commercially available from Hunstman Corporation.

[0246] Amines useful herein for combination with the acylated polymer include one or more of: N-phenyldiamines (such as N-phenyl-1,4-phenylenediamine, N-phenyl-p-phenylenediamine (a.k.a. 4-amino-diphenylamine, ADPA), N-phenyl-1,3-phenylenediamine, N-phenyl-1,2-phenylenediamine), nitroaniline (such as 3-nitroaniline), N-phenylethane-diamine (such as N1-phenylethane-1,2-diamine), N-aminophenylacetamide (such as N-(4-aminophenyl)acetamide), morpholinopropanamine (such as 3-morpholinopropan-1-amine), and aminoethylpiperazine (such as 1-(2-aminoethyl)piperazine). In particular embodiments of the present invention, the amine is 4-amino-diphenylamine, ADPA.

[0247] In embodiments, the functionalization (such as amination) reactions described herein may take place in diluent (such as base oil or alkane solvent). As a side product, functionalized diluent (such as functionalized base oil) can be produced. It is contemplated that the functionalized diluent (such as functionalized base oil) may comprise reaction product of the acylated diluent (such as acylated base oil) with an amine to form an amide, imide or combination thereof.

[0248] Preferably, the reaction product of the acylated diluent (such as acylated oil) with an amine or alcohol to form an amide, imide, ester, or combination thereof, may be present in a concentrate in an amount of 40 wt% or less, alternately 20 wt% or less, alternately 10 wt% or less, alternately 5 wt% or less, alternately 3 mass% or less, preferably 2 mass% or less, preferably 1 mass% or less, preferably at 0.1 mass% or less, preferably at 0 mass% (such as 0 to 40 mass%, alternately 0.01 to 40 mass%, alternately 0.1 to 20 mass%, alternately to 1 to 10 mass%, alternately 1.5 to 5 mass%), based upon the weight of the concentrate composition.

[0249] Preferably one or more functionalized base oils, such as the reaction product of the acylated diluent (such as acylated base oil) with an amine or alcohol to form an amide, imide, ester, or combination thereof, may be present in the lubricating oil composition at an amount of 0.01 to 40 mass%, alternately 0.1 to 20 mass%, alternately to 1 to 10 mass%, alternately 1.5 to 5 mass%, (such as at 3 mass% or less, preferably 2 mass% or less, preferably 1 mass% or less, preferably at 0.1 mass% or less, preferably at 0 mass%), based upon the weight of the lubricating oil composition.

[0250] In embodiments, the functionalization (such as amination) reactions described herein may take place in solvent-containing media. As a side product, functionalized solvent can be produced. In embodiments, the functionalized solvent may be present in a concentrate composition at 3 mass% or less, preferably 2 mass% or less, preferably 1 mass% or less, preferably at 0.1 mass% or less, preferably at 0 mass%, based upon the weight of the concentrate composition. In embodiments, functionalized solvent may be present in a lubricating oil composition at 3 mass% or less, preferably 2 mass% or less, preferably 1 mass% or less, preferably at 0.1 mass% or less, preferably at 0 mass%, based upon the weight of the lubricating oil composition.

[0251] In embodiments, the acylated base oil/solvent may be removed prior to functionalization.

Conjugated Diene Functionalized Polymer

[0252] The functionalized polymer may be a homopolymer of C_4 or C_5 olefins, such as a homopolymer of butadiene or a homopolymer of isoprene.

[0253] In embodiments, the functionalized polymer may be a homopolymer of isoprene, or a copolymer of isoprene and less than 5 mol% (such as less than 3 mol%, such as less than 1 mol%, such as less than 0.1 mol%) comonomer.

[0254] The functionalized polymer may comprise or be a copolymer of isoprene and one or more of styrene, methylstyrene, 2,3-dimethyl-butadiene, 2-methyl-1,3-pentadiene, myrcene, 3-methyl-1,3-pentadiene, 4-methyl-1,3-pentadiene, 2-phenyl-1,3-butadiene, 2-phenyl-1,3-pentadiene, 3-phenyl-1,3 pentadiene, 2,3-dimethyl-1,3-pentadiene, 2-hexyl-1,3-butadiene, 3-methyl-1,3-hexadiene, 2-benzyl-1,3-butadiene, 2-p-tolyl-1,3-butadiene 1,3-butadiene, 1,3-pentadiene, 1,3-hexadiene, 1,3-heptadiene, 2,4-heptadiene, 1,3-octadiene, 2,4-octadiene, 3,5-octadiene, 1,3-nonadiene, 2,4-nonadiene, 3,5-nonadiene, 1,3-decadiene, 2,4-decadiene, and 3,5-decadiene, (optionally the comonomer(s) are present at less than 20 mol%, less than 5 mol%, such as less than 3 mol%, such as less than 1 mol%, such as less than 0.1 mol%)

[0255] In embodiments, the functionalized polymer comprises 10 (such as 9, such as 8, such as 7, such as 6, such as 5, such as 4, such as 3, such as 2, such as 1) wt%, or less, based upon the weight of the functionalized polymer, of styrene monomer.

[0256] In embodiments, styrene repeat units may be absent in the functionalized polymer.

[0257] In embodiments, the functionalized polymer may be a block or taperered block copolymer that does not comprise a styrene block.

[0258] In embodiments, the functionalized polymer may be a block or taperered block copolymer comprising (or consisting of or consisting essentially of) isoprene.

[0259] In embodiments, the functionalized polymer may be a block or taperered block copolymer comprising 50 wt% or more isoprene, based upon the weight of the copolymer.

[0260] In embodiments, the functionalized polymer may be a block or taperered block copolymer comprising (or consisting of or consisting essentially of) C_{4-5} conjugated diene, preferably comprising 50 (such as 60, such as 70, such as 80, such as 90, such as 95, such as 98) wt% or more C_{4-5} conjugated diene, based upon the weight of the copolymer.

[0261] In embodiments, the functionalized polymer may be a copolymer comprising 50 (such as 60, such as 70, such as 80, such as 90, such as 95, such as 98) wt% or more isoprene, based upon the weight of the copolymer.

[0262] In embodiments, the functionalized polymer may be a copolymer comprising 50 (such as 60, such as 70, such as 80, such as 90, such as 95, such as 98) wt% or more butadiene, based upon the weight of the copolymer.

[0263] In embodiments, the functionalized polymer may be a copolymer comprising 50 (such as 60, such as 70, such as 80, such as 90, such as 95, such as 98) wt% or more butadiene and isoprene, based upon the weight of the copolymer.

[0264] In embodiments, the functionalized polymer may be a di-block copolymer comprising at least one block of isoprene homo-or co- polymer.

[0265] Optionally, butadiene repeat units may be absent in the functionalized polymer.

[0266] Optionally, the functionalized polymer may be not homopolyisobutylene.

[0267] Optionally, the functionalized polymer may be not a copolymer of isoprene and butadiene.

[0268] Generally, the polymerized conjugated diene in the functionalized polymer includes monomer units that have been inserted in the growing polymer chain by conjugated addition and non-conjugated addition. In embodiments the functionalized polymer contains at least about 50 % of by conjugated addition insertions, such as at least about 75 % of by conjugated addition insertions, such as about 80 % of by conjugated addition insertions, such as from about 85 % to about 100 % of by conjugated addition insertions, based upon the total number of by conjugated addition and non-conjugated insertions, as measured by ^{13}C NMR.

[0269] The insertion of isoprene most often occurs by 2,1 insertions, 1,4 insertions (trans and cis), and 3,4 insertions of isoprene. (Measurements of the insertion geometry are determined by ^{1}H NMR.). As measured by ^{1}H NMR, the functionalized isoprene polymer contains at least about 50 % of 1,4-insertions, such as at least about 75 % of 1,4 insertions, such as at least about 80 % of 1,4 insertions, such as at least about 90 % of 1,4 insertions, such as at least about

95 % of 1,4 insertions, such as at least 98 % of 1,4 insertions, based upon the total of the 2,1 insertions, 1,4 insertions, and 3,4 insertions of isoprene. For purposes of this disclosure: 1) the phrase "1,4 insertion" includes 1,4 and 4,1 insertions, 2) the phrase "2,1 insertion" includes 2,1 and 1,2 insertions, and 3) the phrase "3,4 insertion" includes 3,4 and 4,3 insertions.

[0270] The functionalized polymer may be homopolymer or copolymer. Optionally, the functionalized polymer comprises a homopolymer or copolymer of isoprene. The copolymer may be a random copolymer, a tapered block copolymer, a star copolymer, or a block copolymer.

[0271] The functionalized polymer may typically have an Mn of 20,000 to 150,000 g/mol, alternately 20,000 to about 150,000 g/mol, alternately 30,000 to about 125,000 g/mol, alternately 35,000 to about 100,000 g/mol, alternately 40,000 to 80,000 g/mol (GPC-PS).

[0272] The polymer prior to functionalization may typically have an Mn/Mw (GPC-PS) of 1.0 to 2, such as 1.1 to 1.5, such as 1.1 to 1.3, such as 1.1 to 1.2. As functionalization occurs, Mw/Mn broadening may occur.

[0273] The functionalized polymer may typically have an Mw/Mn (GPC-PS) of 1 to 3, alternately 1 to 2, alternately greater than 1 to less than 2, alternately 1.05 to 1.9, alternately 1.10 to 1.8, alternately 1.10 to 1.7, alternately 1.12 to 1.6, alternately 1.13 to 1.5, alternately 1.15 to 1.4, alternately 1.15 to 1.3. Alternately, the functionalized polymer may typically have an Mw/Mn of 1 or greater than 1 to less than 2 (such as less than 1.8, such as less than 1.7, such as less than 1.6, such as less than 1.4, such as less than 1.2, such as less than 1.15, such as less than 1.12, such as less than 1.10).

[0274] In embodiments, the functionalized polymer may have a Saponification Number (SAP) of 25 (such as 28, such as 30, such as 32, such as 34) mgKOH/g or more, as determined by ASTM D94.

[0275] In embodiments, the functionalized polymer may contribute 17% or more (such as 20 % or more, such as 17 to 40 %, such as 20 to 30 %) to the Saponification Number of the lubricating oil composition.

[0276] In embodiments, the functionalized polymer may have an average functionality of 1.4 to 20 FG grafts/polymer chain, such as 1.4 to 15 FG grafts/polymer chain, such as 3 to 12.5 FG grafts/polymer chain, such as 4 to 10 FG grafts/polymer chain, as determined by GPC-PS, for example 7, 8 or 9 FG grafts/polymer chain.

[0277] The functionalized polymer may have an average functionality of 15 (such as 14, 13, 12 ,11, 10, 9, 8, 7, or 6) or less FG grafts/polymer chain, as determined by GPC-PS.

[0278] The functionalized polymer may have an average functionality of 1 (such as 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, 2.0, 2.1, 2.2, 2.3, 2.4, 2.5, 2.6, 2.7, 2.8, 2.9, 3.0, 3.1, 3.2, 3.3, 3.4, 3.5, 3.6, 3.7, 3.8, 3.9, or 4.0) or more FG grafts/polymer chain, as determined by GPC-PS.

[0279] The functionalized polymer may have an average functionality from 1 (such as 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, 2.0, 2.1, 2.2, 2.3, 2.4, 2.5, 2.6, 2.7, 2.8, 2.9, 3.0, 3.1, 3.2, 3.3, 3.4, 3.5, 3.6, 3.7, 3.8, 3.9, or 4.0) to 15 (such as 14, 13, 12,11, 10, 9, 8, 7, or 6) FG grafts/polymer chain, as determined by GPC-PS.

[0280] In embodiments, the functionalized polymer may have an aromatic content of 5 % or less, such as 3 % or less, such as 1 % or less, such as 0 %, based upon the weight of the polymer.

[0281] In embodiments, the functionalized polymer may comprise acylated polymers of branched C_{4-5} monomers having an Mn of 20,000 to 500,000 g/mol having an Mw/Mn of 2 or less, such as from 1 to 2.0, as determined by GPC-PS.

[0282] In embodiments, the functionalized polymer may have a number average molecular weight (Mn) of 15,000 (such as 20,000, such as 25,000, such as 30,000, such as 35,000 such as 40,000) g/mol or more, as determined by GPC-PS. In certain embodiments, the functionalized polymer may have a number average molecular weight (Mn) of 20,000 to 60,000, and particularly of 30,000 to 40,000 g/mol (GPC-PS).

[0283] In embodiments, the functionalized polymer may have a weight average molecular weight (Mw) of 50,000 (such as 40,000, such as 35,000) g/mol or less, as determined by GPC-PS. In embodiments, the functionalized polymer may have a weight average molecular weight (Mw) of 1000 to 50,000 g/mol, such as 5000 to 40,000 g/mol as determined by GPC-PS.

[0284] In embodiments, the functionalized polymer may have a z average molecular weight (Mz) of 5000 to 150,000 g/mol, such as 10,000 to 150,000 g/mol, such as 15,000 to 70,000 g/mol, such as 20,000 to 150,000 g/mol, alternately 20,000 to about 150,000 g/mol, alternately 30,000 to about 125,000 g/mol, alternately 35,000 to about 100,000 g/mol, alternately 40,000 to 80,000 g/mol, alternately 40,000 to 60,000 g/mol (GPC-PS).

[0285] In embodiments, the functionalized polymer may have a gel content of less than about 5 wt%, less than 3 wt%, less than 2 wt%, less than 1 wt%, less than 0.5 wt%, less than 0.1 wt%, or 0 wt%, where the gel content is measured by determining the amount of material that is extractable from the polymer by using boiling xylene (or cyclohexane) as an extractant. The percent of soluble and insoluble (gel) material in a polymer composition is determined as described herein.

[0286] In embodiments, the functionalized polymer may have a Functionality Distribution (Fd) value of 3.5 or less (such as 3.4 or less, such as from 1 to 3.3, such as from 1.1 to 3.2, such as from 1.2 to 3.0, such as 1.4 to 2.9, such as 1.7 to 1.9, as determined by GPC-PS) (Functionality Distribution (Fd) value is determined as set out in the Example section below) and an average functionality of 1.4 to 20 FG grafts/polymer chain, such as 1.4 to 15 FG grafts/polymer chain, such as 3 to 12.5 FG grafts/polymer chain, such as 4 to 10 FG grafts/polymer chain, such as 7, 8 or 9 FG grafts/polymer chain, as determined by GPC-PS.

[0287] This disclosure relates to amide, imide, and/or ester functionalized hydrogenated/saturated polymers comprising (consisting essentially of or consisting of) C_{4-5} olefins having an Mw/Mn of less than 2, a Functionality Distribution (Fd) value of 3.5 or less (such as 3.4 or less, such as from 1 to 3.3, such as from 1.1 to 3.2, such as from 1.2 to 3.0, such as 1.4 to 2.9, as determined by GPC-PS, and wherein, if the polymer prior to functionalization is a C_4 olefin polymer such as polyisobutylene, polybutadiene, or a copolymer thereof (preferably a polyisobutylene or a copolymer of isobutylene and butadiene), then the C_4 olefin polymer has an Mn of 10,000 g/mol or more (GPC-PS), and if the polymer prior to functionalization is a C_4/C_5 copolymer of isoprene and butadiene, then the Mn of the copolymer is greater than 25,000 Mn (GPC-PS).

[0288] This disclosure also relates to amide, imide, and/or ester functionalized hydrogenated/saturated polymers comprising 90 mol% or more isoprene repeat units, having an Mw/Mn of less than 2, a Functionality Distribution (Fd) value of 3.5 or less (such as 3.4 or less, such as from 1 to 3.3, such as from 1.1 to 3.2, such as from 1.2 to 3.0, such as 1.4 to 2.9, as determined by GPC-PS), and wherein the polymer prior to functionalization has an Mn of 10,000 g/mol or more, such as 30,000 g/mol or more (GPC-PS).

[0289] This disclosure also relates to amide, imide, and/or ester functionalized hydrogenated/saturated homopolymers of isoprene having an Mw/Mn of less than 2, such as less than 1.8, a Functionality Distribution (Fd) value of 3.5 or less (such as 3.4 or less, such as 2.5 or less, or from 1 to 3.3, such as from 1.1 to 3.2, such as from 1.2 to 3.0, such as 1.4 to 2.9, as determined by GPC-PS), an average functionality (Fv) of 4 to 10 functional group grafts/polymer chain, and wherein the polymer prior to functionalization has an Mn of 20,000 g/mol or more, such as 20,000 to 50,000 g/mol (as determined by GPC-PS).

[0290] In particular embodiments, the functionalized polymer used in the lubricating oil compositions and additive concentrates of the present invention has an Mw/Mn of from 1.0 to 2, such as from 1.1 to 1.8, such as from 1.2 to 1.5; a Functionality Distribution (Fd) value of from 1.0 to 3.5. such as from 1.5 to 2.5, such as from 1.9 to 2.1, as determined by GPC-PS as disclosed herein; an average functionality (Fv) of 4 to 10, such as from 6 to 8 (determined as disclosed herein); an Mn of 20,000 to 50,000 g/mol, such as 30,000 to 40,000 g/mol (GPC-PS); and/or an Mz of 40,000 to 70,000 g/mol, such as 50,000 to 60,000 g/mol (GPC-PS); and/or has a backbone of homo-polyisoprene that has been functionalized with maleic anhydride and further reacted with a polyamine, such as an N-phenylphenylene diamine (NPPDA), such as 4-amino-diphenylamine (ADPA).

[0291] In the compositions according to the present disclosure, component B) is considered as constituting a dispersant mixture as disclosed herein, along with (poly)alkenyl succinic dispersants of component I). Thus, component B) and (poly) alkenyl succinic dispersants of component I) are taken together for purposes of determining the amount of dispersant mixture in a lubricating oil composition or additive concentrate disclosed herein. In certain embodiments, the dispersant mixture comprises the functionalized polymer at 0.01 to 15 mass%, such as 1 to 12 mass%, such as 5 to 11 mass%, such as 7.5 to 10.5 mass%, such as 8.5 to 10 mass% based upon the total mass of the dispersant mixture.

[0292] The lubricating oil composition and additive concentrate according to the present disclosure may further comprise one or more additives such as detergents, friction modifiers, antioxidants, pour point depressants, anti-foam agents, viscosity modifiers, dispersants corrosion inhibitors, anti-wear agents, extreme pressure additives, demulsifiers, seal compatibility agents, additive diluent base oils, etc. Specific examples of such additives are described in, for example, Kirk-Othmer Encyclopedia of Chemical Technology, third edition, volume 14, pp. 477-526, and several are discussed in further detail below.

C. Detergents

[0293] The lubricating composition may comprise one or more metal detergents (such as blends of metal detergents) also referred to as a "detergent additive." Metal detergents typically function both as detergents to reduce or remove deposits and as acid neutralizers or rust inhibitors, thereby reducing wear and corrosion and extending engine life.

[0294] Detergents generally comprise a polar head with a long hydrophobic tail, with the polar head comprising a metal salt of an acidic organic compound. The salts may contain a substantially stoichiometric amount of the metal in which case they are usually described as normal or neutral salts, and would typically have a total base number ("TBN" as measured by ASTM D2896) of up to 150 mgKOH/g, such as from 0 to 80 (or 5-30) mgKOH/g. A large amount of a metal base may be incorporated by reacting excess metal compound (*e.g.,* an oxide or hydroxide) with an acidic gas (*e.g.,* carbon dioxide). Such detergents, sometimes referred to as overbased, may have a TBN of 100 mgKOH/g or more (such as 200 mgKOH/g or more), and typically will have a TBN of 250 mgKOH/g or more, such as 300 mgKOH/g or more, such as from 200 to 800 mgKOH/g, 225 to 700 mgKOH/g, 250 to 650 mgKOH/g, or 300 to 600 mgKOH/g, such as 150 to 650 mgKOH/g.

[0295] Suitable detergents include, oil-soluble neutral and overbased sulfonates, phenates, sulfurized phenates, thiophosphonates, salicylates, naphthenates and other oil-soluble carboxylates of a metal, particularly the alkali metals (Group 1 metals, *e.g.*, Li, Na, K, Rb) or alkaline earth metals (Group 2 metals, *e.g.,* Be, Mg, Ca, Sr, Ba), particularly, sodium, potassium, lithium, calcium, and magnesium, such as Ca and/or Mg. Furthermore, the detergent may comprise a hybrid detergent comprising any combination of sodium, potassium, lithium, calcium, or magnesium salts of sulfonates, phenates, sulfurized phenates, thiophosphonates, salicylates, and naphthenates or other oil-soluble carboxylates of a

Group 1 and/or 2 metal.

[0296] Preferably, the detergent additive(s) useful in the present disclosure comprises calcium and/or magnesium metal salts. The detergent may be a calcium and/or magnesium carboxylate (*e.g.*, salicylates), sulfonate, or phenate detergent. More preferably, the detergent additives are selected from magnesium salicylate, calcium salicylate, magnesium sulfonate, calcium sulfonate, magnesium phenate, calcium phenate, and hybrid detergents comprising two, three, four, or more of more of these detergents and/or combinations thereof.

[0297] The metal-containing detergent may also include "hybrid" detergents formed with mixed surfactant systems including phenate and/or sulfonate components, *e.g.*, phenate/salicylates, sulfonate/phenates, sulfonate/salicylates, sulfonates/phenates/salicylates, as described, for example, in US Patent Nos. 6,429,178; 6,429,179; 6,153,565; and 6,281,179. Where, for example, a hybrid sulfonate/phenate detergent is employed, the hybrid detergent would be considered equivalent to amounts of distinct phenate and sulfonate detergents introducing like amounts of phenate and sulfonate soaps, respectively.

[0298] The overbased metal-containing detergent may be sodium salts, calcium salts, magnesium salts, or mixtures thereof of the phenates, sulfur-containing phenates, sulfonates, salixarates, and salicylates. Overbased phenates and salicylates typically have a total base number of 180 to 650 mgKOH/g, such as 200 to 450 TBN mgKOH/g. Overbased sulfonates typically have a total base number of 250 to 600 mgKOH/g, or 300 to 500 mgKOH/g. In embodiments, the sulfonate detergent may be predominantly a linear alkylbenzene sulfonate detergent having a metal ratio of at least 8 as is described in paragraphs [0026] to [0037] of US Patent Application Publication No. 2005/065045 (and granted as US Patent No. 7,407,919). The overbased detergent may be present at 0 wt% to 15 wt%, or 0.1 wt% to 10 wt%, or 0.2 wt% to 8wt%, or 0.2 wt% to 3 wt%, based upon of the lubricating composition. For example, in a heavy-duty diesel engine, the detergent may be present at 2 wt% to 3 wt% of the lubricating composition. For a passenger car engine, the detergent may be present at 0.2 wt% to 1 wt% of the lubricating composition.

[0299] The detergent additive(s) may comprise one or more magnesium sulfonate detergents. The magnesium detergent may be a neutral salt or an overbased salt. Suitably the magnesium detergent is an overbased magnesium sulfonate having a TBN of from 80 to 650 mgKOH/g (ASTM D2896), such as 200 to 500 mgKOH/g, such as 240 to 450 mgKOH/g.

[0300] Alternately, the detergent additive(s) is a magnesium salicylate. Suitably the magnesium detergent is a magnesium salicylate having TBN of from 30 to 650 mgKOH/g (ASTM D2896), such as 50 to 500 mgKOH/g, such as 200 to 500 mgKOH/g, such as 240 to 450 mgKOH/g or alternately of 150 mgKOH/g or less, such as 100 mgKOH/g or less.

[0301] Alternately, the detergent additive(s) is a combination of magnesium salicylate and magnesium sulfonate.

[0302] The magnesium detergent provides the lubricating composition thereof with from 200-4000 ppm of magnesium atoms, suitably from 200-2000 ppm, from 300 to 1500 or from 450-1200 ppm of magnesium atoms (ASTM D5185).

[0303] The detergent composition may comprise (or consist of) a combination of one or more magnesium sulfonate detergents and one or more calcium salicylate detergents.

[0304] The combination of one or more magnesium sulfonate detergents and one or more calcium salicylate detergents provides the lubricating composition thereof with: 1) from 200-4000 ppm of magnesium atoms, suitably from 200-2000 ppm, from 300 to 1500 ppm or from 450-1200 ppm of magnesium atoms (ASTM D5185), and 2) at least 500 ppm, preferably at least 750 ppm, more preferably at least 900 ppm of atomic calcium, such as from 500-4000 ppm, preferably from 750-3000 ppm, more preferably from 900-2000 ppm atomic calcium (ASTM D5185).

[0305] The detergent may comprise one or more calcium detergents such as calcium carboxylate (*e.g.,* salicylate), sulfonate, or phenate detergent.

[0306] Suitably the calcium detergent has a TBN of from 30 to 700 mgKOH/g (ASTM D2896), such as 50 to 650 mgKOH/g, such as 200 to 500 mgKOH/g, such as 240 to 450 mgKOH/g or alternately of 150 mgKOH/g or less, such as 100 mgKOH/g or less, or 200 mgKOH/g or more, or 300 mgKOH/g or more, or 350 mgKOH/g or more.

[0307] Suitably, the calcium detergent is a calcium salicylate, sulfonate, or phenate having a TBN of from 30 to 700 mgKOH/g, 30 to 650 mgKOH/g (ASTM D2896), such as 50 to 650 mgKOH/g, such as 200 to 500 mgKOH/g, such as 240 to 450 mgKOH/g or alternately of 150 mgKOH/g or less, such as 100 mgKOH/g or less, or 200 mgKOH/g or more, or 300 mgKOH/g or more, or 350 mgKOH/g or more.

[0308] Calcium detergent is typically present in amount sufficient to provide at least 500 ppm, preferably at least 750 more preferably at least 900 ppm atomic calcium to the lubricating oil composition (ASTM D5185). If present, any calcium detergent is suitably present in amount sufficient to provide no more than 4000 ppm, preferably no more than 3000 ppm, more preferably no more than 2000 ppm atomic calcium to the lubricating oil composition (ASTM D5185). If present, any calcium detergent is suitably present in amount sufficient to provide at from 500-4000 ppm, preferably from 750-3000 ppm more preferably from 900-2000 ppm atomic calcium to the lubricating oil composition (ASTM D5185).

[0309] Suitably the total atomic amount of metal from detergent in the lubrication composition according to all aspects of the disclosure is no more than 5000 ppm, preferably no more than 4000 pm and more preferably no more than 2000 ppm (ASTM D5185). The total amount of atomic metal from detergent in the lubrication oil composition according to all aspects of the disclosure is suitably at least 500 ppm, preferably at least 800 ppm and more preferably at least 1000 ppm (ASTM

D5185). The total amount of atomic metal from detergent in the lubrication oil composition according to all aspects of the disclosure is suitably from 500 to 5000 ppm, preferably from 500 to 3000 ppm and more preferably from 500 to 2000 ppm (ASTM D5185).

[0310] Sulfonate detergents 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 includ those obtained by alkylating benzene, toluene, xylene, naphthalene, diphenyl, or their halogen derivatives such as chlorobenzene, chlorotoluene, and chloronaphthalene. 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 about 80 or more carbon atoms, preferably from about 16 to about 60 carbon atoms per alkyl substituted aromatic moiety. The oil soluble sulfonates or alkaryl sulfonic acids may be neutralized with oxides, hydroxides, alkoxides, carbonates, carboxylate, sulfides, hydrosulfides, nitrates, borates and ethers of the metal. The amount of metal compound is chosen having regard to the desired TBN of the final product, but typically ranges from about 100 to 220 mass% (preferably at least 125 mass%) of that stoichiometrically required.

[0311] Metal salts of phenols and sulfurized phenols are prepared by reaction with an appropriate metal compound such as an oxide or hydroxide and neutral or overbased products may be obtained by methods well known in the art. Sulfurized phenols may be prepared by reacting a phenol with sulfur or a sulfur-containing compound such as hydrogen sulfide, sulfur monohalide, or sulfur dihalide, to form products which are generally mixtures of compounds in which 2 or more phenols are bridged by sulfur-containing bridges.

[0312] Carboxylate detergents, *e.g.*, salicylates, can be prepared by reacting an aromatic carboxylic acid (such as a C_{5}-$_{100}$, C_{9}-$_{30}$, C_{14}-$_{24}$ alkyl-substituted hydroxy-benzoic acid) with an appropriate metal compound such as an oxide or hydroxide and neutral or overbased products may be obtained by methods well known in the art. The aromatic moiety of the aromatic carboxylic acid can contain heteroatoms, such as nitrogen and oxygen. Preferably, the moiety contains only carbon atoms; more preferably the moiety contains six or more carbon atoms; for example, benzene is a preferred moiety. The aromatic carboxylic acid may contain one or more aromatic moieties, such as one or more benzene rings, either fused or connected via alkylene bridges.

[0313] Preferred substituents in oil-soluble salicylic acids are alkyl substituents. In alkyl - substituted salicylic acids, the alkyl groups advantageously contain 5 to 100, preferably 9 to 30, especially 14 to 20, carbon atoms. Where there is more than one alkyl group, the average number of carbon atoms in all of the alkyl groups is preferably at least 9 to ensure adequate oil solubility.

[0314] In embodiments, the ratio of atomic detergent metal to atomic molybdenum in the lubricating oil composition may be less than 3:1, such as less than 2:1.

[0315] Further, as metal organic and inorganic base salts, which are used as detergents can contribute to the sulfated ash content of a lubricating oil composition, in embodiments of the present disclosure, the amounts of such additives are minimized. In order to maintain a low sulfur level, salicylate detergents can be used and the lubricating composition herein may comprise one or more salicylate detergents (said detergents are preferably used in amounts in the range of 0.05 to 20.0 wt%, more preferably from 1.0 to 10.0 wt% and most preferably in the range of from 2.0 to 5.0 wt%, based on the total weight of the lubricating composition).

[0316] The total sulfated ash content of the lubricating composition herein is typically not greater than 2.0 wt%, alternately at a level of not greater than 1.0 wt%, alternately at a level of not greater than 0.8 wt%, and alternately at a level not greater than 0.5 wt%, based on the total weight of the lubricating composition as determined by ASTM D874.

[0317] Furthermore, it is useful that each of the detergents, independently, have a TBN (total base number) value in the range of from 10 to 700 mgKOH/g, 10 to 500 mgKOH/g, alternately in the range of from 100 to 650, alternately in the range of from 10 to 500 mgKOH/g, alternately in the range of from 30 to 350 mgKOH/g, and alternately in the range of from 50 to 300 mgKOH/g, as measured by ISO 3771.

[0318] The sulfonate detergents (such as Ca and/or Mg sulfonate detergents) may be present in an amount to deliver 0.1 wt% to 1.5 wt%, or 0.15 to 1.2 wt%, or 0.2 wt% to 0.9 wt% sulfonate soap to the lubricant composition.

[0319] The salicylate detergents (such as Ca and/or Mg salicylate detergents) are present in an amount to deliver 0.3 wt% to 1.4 wt%, or 0.35 wt% to 1.2 wt%, or 0.4 wt% to 1.0 wt% salicylate soap to the lubricant composition.

[0320] The sulfonate soap may be present in an amount 0.2 wt% to 0.8 wt% of the lubricant composition, and the salicylate soap may be present in an amount 0.3 wt% to 1.0 wt% of the lubricant composition.

[0321] The total of all alkaline earth metal detergent soap may be present in an amount 0.6 wt% to 2.1 wt%, or 0.7 wt% to 1.4 wt% of the lubricant composition.

[0322] Typically, lubricating compositions formulated for use in heavy-duty diesel engines comprise detergents at from about 0.1 to about 10 mass%, alternately from about 0.5 to about 7.5 mass%, alternately from about 1 to about 6.5 mass%, based on the lubricating composition.

[0323] Typically, lubricating compositions formulated for use in a passenger-car engines comprise detergents at from about 0.1 to about 10 mass%, alternately from about 0.5 to about 7.5 mass%, alternately from about 1 to about 6.5 mass%, based on the lubricating composition.

[0324] Typically, lubricating compositions formulated for use in a drive train (e.g., transmissions) comprise detergents at from about 0.1 to about 10 mass%, alternately from about 0.5 to about 7.5 mass%, alternately from about 2 to about 6.5 mass%, based on the lubricating composition.

[0325] In embodiments, the one or more detergent(s) used in the lubricating oil compositions and additive concentrates of the present invention is present at 0.01 to 3 mass%, such as 0.1 to 1 mass%, such as 0.2 to 0.6 mass% based upon the total mass of the lubricating oil composition, and/or at 0.1 to 5 mass%, such as 0.5 to 4 mass%, such as 1 to 3 mass% based upon the total mass of the additive concentrate.

[0326] In embodiments, the detergent(s) used in the lubricating oil compositions and additive concentrates of the present invention is selected from the group consisting of oil-soluble neutral or overbased sulfonates and phenates of an alkali or alkaline earth metal, in particular from the group consisting of oil-soluble neutral or overbased sulfonates of calcium or magnesium (such as calcium sulfonate and/or magnesium sulfonate).

[0327] In particular embodiments, the lubricating oil compositions and additive concentrates of the present invention are absent phenate detergent and/or absent salicylate detergent. Preferably, the lubricating oil compositions and additive concentrates of the present invention comprise no or substantially no phenate detergent, such as less than 1.2 mass%, such as less than 1.0 mass%, such as less than 0.5 mass% based on the total mass of the lubricating oil composition or additive concentrate, and/or no or substantially no salicylate detergent, such as less than 1.2 mass%, such as less than 1.0 mass%, such as less than 0.5 mass% based on the total mass of the lubricating oil composition or additive concentrate. More preferably, the detergent(s) used in the lubricating oil compositions and additive concentrates of the present invention is, in particular consists of, a mixture of calcium sulfonate and magnesium sulfonate.

D. Friction Modifiers

[0328] A friction modifier is any material or materials that can alter the coefficient of friction of a surface lubricated by any lubricant or fluid-containing such material(s). Friction modifiers, also known as friction reducers, or lubricity agents or oiliness agents, and other such agents that change the ability of base oils, formulated lubricating compositions, or functional fluids, to modify the coefficient of friction of a lubricated surface may be effectively used in combination with the base oils or lubricating compositions of the present disclosure if desired. Friction modifiers that lower the coefficient of friction are particularly advantageous in combination with the base oils and lubricating compositions of this disclosure.

[0329] Illustrative friction modifiers may include, for example, organometallic compounds or materials, or mixtures thereof. Illustrative organometallic friction modifiers useful in the lubricating oil formulations of this disclosure include, for example, tungsten and/or molybdenum compounds, such as molybdenum amine, molybdenum diamine, an organotungstenate, a molybdenum dithiocarbamate, molybdenum dithiophosphates, molybdenum amine complexes, molybdenum carboxylates, and the like, and mixtures thereof. Examples of useful molybdenum-containing compounds may conveniently include molybdenum dithiocarbamates, trinuclear molybdenum compounds, for example, as described in PCT Publication No. WO 98/26030, sulfides of molybdenum and molybdenum dithiophosphate.

[0330] Other known friction modifiers comprise oil-soluble organo-molybdenum compounds. Such organo-molybdenum friction modifiers may also provide antioxidant and anti-wear credits to a lubricating oil composition. Examples of such oil-soluble organo-molybdenum compounds include dithiocarbamates, dithiophosphates, dithiophosphinates, xanthates, thioxanthates, sulfides, and the like, and mixtures thereof. Particularly preferred are molybdenum dithiocarbamates, dialkyldithiophosphates, alkyl xanthates and alkylthioxanthates.

[0331] Additionally, the molybdenum compound may be an acidic molybdenum compound. These compounds will react with a basic nitrogen compound as measured by ASTM test D664 or D2896 titration procedure and are typically hexavalent. Included are molybdic acid, ammonium molybdate, sodium molybdate, potassium molybdate, and other alkali metal molybdates and other molybdenum salts, *e.g.,* hydrogen sodium molybdate, $MoOC_{14}$, MoO_2Br_2, MO2O3C16, molybdenum trioxide or similar acidic molybdenum compounds.

[0332] Among the molybdenum compounds useful in the compositions of this disclosure are organo-molybdenum compounds of the formula $Mo(R''OCS_2)_4$ and $Mo(R''SCS_2)_4$, wherein R" is an organo group selected from the group consisting of alkyl, aryl, aralkyl and alkoxyalkyl, generally of from 1 to 30 carbon atoms, and preferably 2 to 12 carbon atoms and most preferably alkyl of 2 to 12 carbon atoms. Especially preferred are the dialkyldithiocarbamates of molybdenum.

[0333] Another group of organo-molybdenum compounds useful in the lubricating compositions of this disclosure are trinuclear molybdenum compounds, especially those of the formula Mo3SkLnQz and mixtures thereof wherein the L are independently selected ligands having organo groups with a sufficient number of carbon atoms to render the compound soluble or dispersible in the oil, n is from 1 to 4, k varies from 4 to 7, Q is selected from the group of neutral electron-donating compounds such as water, amines, alcohols, phosphines, and ethers, and z ranges from 0 to 5 and includes non-stoichiometric values. At least 21 carbon atoms should be present among all the ligand/organo groups, such as at least 25, at least 30, or at least 35, carbon atoms.

[0334] Lubricating oil compositions useful in all aspects of the present disclosure preferably contain at least 10 ppm, at least 30 ppm, at least 40 ppm and more preferably at least 50 ppm molybdenum. Suitably, lubricating oil compositions useful in all aspects of the present disclosure contain no more than 1000 ppm, no more than 750 ppm, or no more than 500 ppm of molybdenum. Lubricating oil compositions useful in all aspects of the present disclosure preferably contain from 10 to 1000, such as 30 to 750 or 40 to 500, ppm of molybdenum (measured as atoms of molybdenum).

[0335] For more information or useful friction modifiers containing Mo, please see US Patent No. 10,829,712 (col 8, ln 58 to col 11, ln 31).

[0336] Ashless friction modifiers may be present in the lubricating oil compositions of the present disclosure and are known generally and include esters formed by reacting carboxylic acids and anhydrides with alkanols and amine-based friction modifiers. Other useful friction modifiers generally include a polar terminal group (e.g., carboxyl or hydroxyl) covalently bonded to an oleophilic hydrocarbon chain. Esters of carboxylic acids and anhydrides with alkanols are described in US Patent No. 4,702,850. Examples of other conventional organic friction modifiers are described by M. Belzer in the "Journal of Tribology" (1992), Vol. 114, pp. 675-682 and M. Belzer and S. Jahanmir in "Lubrication Science" (1988), Vol. 1, pp. 3-26. Typically, the total amount of organic ashless friction modifier in a lubricant according to the present disclosure does not exceed 5 mass%, based on the total mass of the lubricating oil composition and preferably does not exceed 2 mass% and more preferably does not exceed 0.5 mass%.

[0337] Illustrative friction modifiers useful in the lubricating compositions described herein include, for example, alkoxylated fatty acid esters, alkanolamides, polyol fatty acid esters, borated glycerol fatty acid esters, fatty alcohol ethers, and mixtures thereof.

[0338] Illustrative alkoxylated fatty acid esters include, for example, polyoxyethylene stearate, fatty acid polyglycol ester, and the like. These can include polyoxypropylene stearate, polyoxybutylene stearate, polyoxyethylene isosterate, polyoxypropylene isostearate, polyoxyethylene palmitate, and the like.

[0339] Illustrative alkanolamides include, for example, lauric acid diethylalkanolamide, palmic acid diethylalkanolamide, and the like. These can include oleic acid diethyalkanolamide, stearic acid diethylalkanolamide, oleic acid diethylalkanolamide, polyethoxylated hydrocarbylamides, polypropoxylated hydrocarbylamides, and the like.

[0340] Illustrative polyol fatty acid esters include, for example, glycerol monooleate, saturated mono-, di-, and triglyceride esters, glycerol monostearate, and the like. These can include polyol esters, hydroxyl-containing polyol esters, and the like.

[0341] Illustrative borated glycerol fatty acid esters include, for example, borated glycerol monooleate, borated saturated mono-, di-, and tri-glyceride esters, borated glycerol monosterate, and the like. In addition to glycerol polyols, these can include trimethylolpropane, pentaerythritol, sorbitan, and the like. These esters can be polyol monocarboxylate esters, polyol dicarboxylate esters, and on occasion polyoltricarboxylate esters. Preferred can be the glycerol monooleates, glycerol di-oleates, glycerol tri-oleates, glycerol monooleates, glycerol di-stearates, and glycerol tri-stearates and the corresponding glycerol mono-palmitates, glycerol di-palmitates, and glycerol tri-palmitates, and the respective isostearates, linoleates, and the like. Ethoxylated, propoxylated, and/or butoxylated fatty acid esters of polyols, especially using glycerol as underlying polyol are useful herein.

[0342] Illustrative fatty alcohol ethers include, for example, stearyl ether, myristyl ether, and the like. Alcohols, including those that have carbon numbers from C_3 to C_{50}, can be ethoxylated, propoxylated, or butoxylated to form the corresponding fatty alkyl ethers. The underlying alcohol portion can preferably be stearyl, myristyl, C_{11}-C_{13} hydrocarbon, oleyl, isosteryl, and the like.

[0343] Useful concentrations of friction modifiers may range from 0.01 wt% to 5 wt%, or about 0.001 wt% to about 2.5 wt%, or about 0.05 wt% to about 1.5 wt%, or about 0.051 wt% to about 1 wt%. Concentrations of molybdenum-containing materials are often described in terms of Mo metal concentration. Advantageous concentrations of Mo may range from 25 ppm to 700 ppm or more, and often with a preferred range of 50-200 ppm. Friction modifiers of all types may be used alone or in mixtures with the materials of this disclosure. Often mixtures of two or more friction modifiers, or mixtures of friction modifier(s) with alternate surface-active material(s), are also desirable. For example, combinations of Mo-containing compounds with polyol fatty acid esters, such as glycerol mono-oleate are useful herein.

[0344] In embodiments, the one or friction modifier(s) used in the lubricating oil compositions and additive concentrates of the present invention is present at 0.001 to 0.2 mass%, such as 0.01 to 0.06 mass%, such as 0.02 to 0.04 mass% based upon the total mass of the lubricating oil composition, and/or at 0.01 to 1 mass%, such as 0.02 to 0.5 mass%, such as 0.05 to 0.2 mass% based upon the total mass of the additive concentrate.

[0345] In particular embodiments, the lubricating oil compositions and additive concentrates of the present invention are absent alkoxylated fatty acid esters, alkanolamides, polyol fatty acid esters, borated glycerol fatty acid esters and/or fatty alcohol ethers. Preferably, the friction modifier(s) used in the lubricating oil compositions and additive concentrates of the present invention comprises, in particular is, at least one oil-soluble organo-molybdenum compound, such as at least one molybdenum dithiocarbamate compound, such as trimeric molybdenum dithiocarbamate compound.

E. Antioxidants

[0346] Antioxidants retard the oxidative degradation of base oils during service. Such degradation may result in deposits on metal surfaces, the presence of sludge, a viscosity increase in a lubricant, and the like. A wide variety of oxidation inhibitors that are useful in lubricating oil compositions. See Lubricants and Related Products, Klamann, Wiley VCH, 1984; US Patent Nos. 4,798,684 and 5,084,197, for example.

[0347] Useful antioxidants include hindered phenols. These phenolic antioxidants may be ashless (metal-free) phenolic compounds or neutral or basic metal salts of certain phenolic compounds. Typical phenolic antioxidant compounds are the hindered phenolics, which contain a sterically hindered hydroxyl group, and these include those derivatives of dihydroxy aryl compounds in which the hydroxyl groups are in the o- or p-position to each other. Typical phenolic antioxidants include the hindered phenols substituted with C_{6+} alkyl groups and the alkylene coupled derivatives of these hindered phenols. Examples of phenolic materials of this type 2-t-butyl-4-heptyl phenol; 2-t-butyl-4-octyl phenol; 2-t-butyl-4-dodecyl phenol; 2,6-dit-butyl-4-heptyl phenol; 2,6-di-t-butyl-4-dodecyl phenol; 2-methyl-6-t-butyl-4-heptyl phenol; and 2-methyl-6-t-butyl-4-dodecyl phenol. Other useful hindered mono-phenolic antioxidants may include, for example, hindered 2,6-di-alkyl-phenolic proprionic ester derivatives. Bis-phenolic antioxidants may also be advantageously used herein. Examples of ortho-coupled phenols include: 2,2'-bis(4-heptyl-6-t-butyl-phenol); 2,2'-bis(4-octyl-6-t-butyl-phenol); and 2,2'-bis(4-dodecyl-6-t-butyl-phenol). Para-coupled bisphenols include, for example, 4,4'-bis(2,6-di-t-butyl-phenol) and 4,4'-methylene-bis(2,6-di-t-butyl-phenol).

[0348] Effective amounts of one or more catalytic antioxidants may also be used. The catalytic antioxidants comprise an effective amount of a) one or more oil soluble polymetal organic compounds; and, effective amounts of b) one or more substituted N,N'-diaryl-o-phenylenediamine compounds or c) one or more hindered phenol compounds; or a combination of both b) and c). Catalytic antioxidants useful herein are more fully described in US Patent No. 8,048,833.

[0349] Non-phenolic oxidation inhibitors, which may be used include aromatic amine antioxidants and these may be used either as such or in combination with phenolics. Typical examples of non-phenolic antioxidants include: alkylated and non-alkylated aromatic amines such as aromatic monoamines of the formula $R_8R_9R_{10}N$, where R_8 is an aliphatic, aromatic or substituted aromatic group, R_9 is an aromatic or a substituted aromatic group, and R_{10} is H, alkyl, aryl or $R_{11}S(O)XR_{12}$ where R_{11} is an alkylene, alkenylene, or aralkylene group, R_{12} is an alkyl group, or an alkenyl, aryl, or alkaryl group, and x is 0, 1, or 2. The aliphatic group R_8 may contain from 1 to about 20 carbon atoms, and preferably contains from about 6 to 12 carbon atoms. The aliphatic group is typically a saturated aliphatic group. Preferably, both R_8 and R_9 are aromatic or substituted aromatic groups, and the aromatic group may be a fused ring aromatic group such as naphthyl. Aromatic groups R_8 and R_9 may be joined together with other groups such as S.

[0350] Typical aromatic amines antioxidants have alkyl substituent groups of at least about 6 carbon atoms. Examples of aliphatic groups include hexyl, heptyl, octyl, nonyl, and decyl. Generally, the aliphatic groups will not contain more than about 14 carbon atoms. The general types of amine antioxidants useful in the present compositions include diphenylamines, phenyl naphthylamines, phenothiazines, imidodibenzyls and diphenyl phenylene diamines. Mixtures of two or more aromatic amines are also useful. Polymeric amine antioxidants can also be used. Particular examples of aromatic amine antioxidants useful in the present disclosure include: p,p'-dioctyldiphenylamine; t-octylphenyl-alpha-naphthylamine; phenyl-alpha-naphthylamine; and p-octylphenyl-alpha-naphthylamine.

[0351] Sulfur-containing antioxidants are also useful herein. In particular, one or more oil-soluble or oil-dispersible sulfur-containing antioxidant(s) can be used as an antioxidant additive. For example, sulfurized alkyl phenols and alkali or alkaline earth metal salts thereof also are useful antioxidants herein. Suitably, the lubricating oil composition(s) of the present disclosure may include the one or more sulfur-containing antioxidant(s) in an amount to provide the lubricating oil composition with from 0.02 to 0.2, preferably from 0.02 to 0.15, even more preferably 0.02 to 0.1, even more preferably 0.04 to 0.1, mass% sulfur based on the total mass of the lubricating oil composition. Optionally the oil-soluble or oil-dispersible sulfur-containing antioxidant(s) are selected from sulfurized C_4 to C_{25} olefin(s), sulfurized aliphatic (C_7 to C_{29}) hydrocarbyl fatty acid ester(s), ashless sulfurized phenolic antioxidant(s), sulfur-containing organo-molybdenum compound(s), and combinations thereof. For further information, on sulfurized materials useful as antioxidants herein, please see US Patent No. 10,731,101 (col 15, ln 55 to col 22, ln 12).

[0352] Antioxidants useful herein include hindered phenols and/or arylamines. These antioxidants may be used individually by type or in combination with one another.

[0353] Typical antioxidants include: Irganox™ L67, Irganox™ L135, Ethanox™ 4702, Lanxess Additin™ RC 7110; Ethanox™ 4782J; Irganox™ 1135, Irganox™ 5057, sulfurized lard oil and palm oil fatty acid methyl ester.

[0354] Antioxidant additives may be used in an amount of about 0.01 to 10 (alternately 0.01 to 5, alternately 0.01 to 3 wt%, alternately about 0.03 to 5 wt%, alternately 0.05 to less than 3 wt%, based upon the weight of the lubricating composition.

[0355] In embodiments, the antioxidants(s) used in the lubricating oil compositions and additive concentrates of the present invention is present at 0.1 to 10 mass%, such as 3 to 8 mass%, such as 3.5 to 5 mass% based upon the total mass of the lubricating oil composition, and/or at 5 to 25 mass%, such as 10 to 22 mass%, such as 14 to 20 mass% based upon the total mass of the additive concentrate.

[0356] In embodiments, the antioxidant(s) used in the lubricating oil compositions and additive concentrates of the present invention is at least one or more amine antioxidant(s) and/or at least one or more phenol antioxidant(s). Preferably, the antioxidant(s) used in the lubricating oil compositions and additive concentrates of the present invention is a mixture of one or more amine antioxidant(s) and one or more phenol antioxidant(s), more preferably at a ratio of about 5:2 to about 9:5, such as about 2:1.

[0357] In particular embodiments, the lubricating oil compositions and additive concentrates of the present invention are absent sulfur-containing antioxidants. Preferably, the lubricating oil compositions and additive concentrates of the present invention comprise no or substantially no sulphurised methyl ester antioxidants, such as less than 2.5 mass%, such as less than 2.2 mass%, such as less than 1.5 mass%, such as less than 0.5 mass% based on the total mass of the additive concentrate. More preferably, the antioxidant(s) used in the lubricating oil compositions and additive concentrates of the present invention is, in particular consists of, a mixture of alkylated diphenylamine antioxidant and hindered phenol antioxidant.

[0358] Compositions according to the present disclosure may contain an additive having a different enumerated function that also has secondary effects as an antioxidant (for example, phosphorus-containing anti-wear agents (such as ZDDP) may also have antioxidant effects). These additives are not included as antioxidants for purposes of determining the amount of antioxidant in a lubricating oil composition or additive concentrate herein.

F. Pour Point Depressants

[0359] Conventional pour point depressants (also known as lube oil flow improvers) may be added to the compositions of the present disclosure if desired. These pour point depressants may be added to lubricating compositions of the present disclosure to lower the minimum temperature at which the fluid will flow or can be poured. Examples of suitable pour point depressants include polymethacrylates, polyacrylates, polyarylamides, condensation products of haloparaffin waxes and aromatic compounds, vinyl carboxylate polymers, and terpolymers of dialkylfumarates, vinyl esters of fatty acids and allyl vinyl ethers. US Patent Nos. 1,815,022; 2,015,748; 2,191,498; 2,387,501; 2,655,479; 2,666,746; 2,721,877; 2,721,878; and 3,250,715 describe useful pour point depressants and/or the preparation thereof. Such additives may be used in an amount of about 0.01 to 5 wt%, preferably about 0.01 to 1.5 wt%, based upon the weight of the lubricating composition.

[0360] In embodiments, the pour point depressant(s) used in the lubricating oil compositions and additive concentrates of the present invention is present at 0.001 to 1 mass%, such as 0.01 to 0.5 mass%, such as 0.05 to 0.2 mass% based upon the total mass of the lubricating oil composition.

[0361] In particular embodiments, the pour point depressant(s) used in the lubricating oil compositions of the present invention is a C_{12-18} dialkylfumarate/vinyl acetate copolymer (which is commercially available as Infineum V387™).

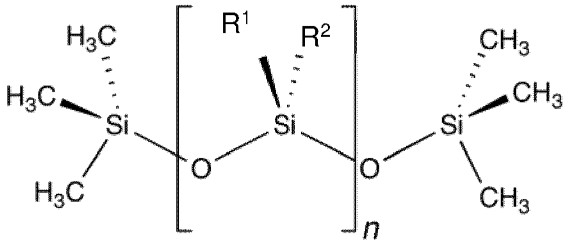
G. Anti-Foam Agents

[0362] Anti-foam agents may advantageously be added to lubricant compositions described herein. These agents prevent or retard the formation of stable foams. Silicones and/organic polymers are typical anti-foam agents. For example, polysiloxanes, such as silicon oil or polydimethyl siloxane, provide anti-foam properties.

[0363] Anti-foam agents are commercially available and may be used in minor amounts such as 5 wt% or less, 3 wt% or less, 1 wt% or less, 0.1 wt% or less, such as from 5 to wt% to 0.1 ppm such as from 3 wt% to 0.5 ppm, such as from 1 wt% to 10 ppm.

[0364] For example, it may be that the lubricating oil composition comprises an anti-foam agent comprising polyalkyl siloxane, such as a polydialkyl siloxane, for example, wherein the alkyl is a C_1-C_{10} alkyl group, *e.g.,* a polydimethylsiloxane (PDMS), also known as a silicone oil. Alternately, the siloxane is a poly(R^3)siloxane, wherein R^3 is one or more same or different linear branched or cyclic hydrocarbyls, such as alkyls or aryls, typically having 1 to 20 carbon atoms. It may be that, for example, the lubricating oil composition comprises a polymeric siloxane compound according to Formula 1 below wherein R^1 and R^2 are independently methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl or decyl, phenyl, naphthyl, alkyl substituted phenyl, or isomers thereof (such as methyl, phenyl) and n is from 2 to 1000, such as 50 to 450, alternately such as 40 to 100.

[0365] Additionally, or alternatively, it may be that the lubricating oil composition comprises an organo-modified siloxane (OMS), such as a siloxane modified with an organo group such as a polyether (e.g., ethylene-propyleneoxide copolymer), long chain hydrocarbyl (*e.g.,* C_{11}-C_{100} alkyl), or aryl (*e.g.,* C_6-C_{14} aryl). It may be that, for example, the lubricating oil composition comprises an organo-modified siloxane compound according to Formula 1, wherein n is from 2 to 2000, such as 50 to 450 (alternately such as 40 to 100), and wherein R^1 and R^2 are the same or different, optionally wherein each of R^1 and R^2 is, independently an organo group, such as an organo group selected from polyether (e.g., ethylene-propyleneoxide copolymer), long chain hydrocarbyl (*e.g.,* C_{11}-C_{100} alkyl), or aryl (*e.g.,* C_6-C_{14} aryl). Preferably, one of R^1 and R^2 is CH_3.



Formula 1

[0366] Based on the total weight of the lubricant composition, the siloxane according to Formula 1 is incorporated so as to provide about 0.1 to less than about 30 ppm Si, or about 0.1 to about 25 ppm Si, or about 0.1 to about 20 ppm Si, or about 0.1 to about 15 ppm Si, or about 0.1 to about 10 ppm Si. More preferably, it is in the range of about 3-10 ppm Si.

[0367] In embodiments, silicone anti-foam agents useful herein are available from Dow Corning Corporation and Union Carbide Corporation, such as Dow Corning FS-1265 (1000 centistokes), Dow Corning DC-200, and Union Carbide UC-L45. Silicone anti-foamants useful herein include polydimethylsiloxane, phenyl-methyl polysiloxane, linear, cyclic or branched siloxanes, silicone polymers and copolymers, and/organo-silicone copolymers. Also, a siloxane polyether copolymer Anti-foamant available from OSI Specialties, Inc. of Farmington Hills, Michigan and may be substituted or included. One such material is sold as SILWET-L-7220.

[0368] Acrylate polymer anti-foam agent can also be used herein. Typical acrylate anti-foamants include polyacrylate anti-foamant available from Monsanto Polymer Products Co. known as PC-1244. A preferred acrylate polymer anti-foam agent useful herein is PX™3841 (*i.e.,* an alkyl acrylate polymer), commercially available from Dorf Ketl, also referred to as Mobilad™C402.

[0369] In embodiments, a combination of silicone anti-foamant and acrylate anti-foamant can be used, such as at a weight ratio of the silicone anti-foamant to the acrylate anti-foamant of from about 5:1 to about 1:5, see, for example, US Patent Application Publication No. 2021/0189283.

[0370] In embodiments, the anti-foam agent(s) used in the lubricating oil compositions and additive concentrates of the present invention is present at 0.001 to 0.1 mass%, such as 0.003 to 0.03 mass%, such as 0.005 to 0.01 mass% based upon the total mass of the lubricating oil composition, and/or at 0.001 to 0.5 mass%, such as 0.01 to 0.1 mass%, such as 0.02 to 0.04 mass% based upon the total mass of the additive concentrate.

[0371] In particular embodiments, the anti-foam agent(s) used in the lubricating oil compositions and additive concentrates of the present invention is absent acrylate anti-foam agent. In particular embodiments, the anti-foam agent(s) used in the lubricating oil compositions and additive concentrates of the present invention is, in particular consists of, a silicone anti-foamant, such as polydimethylsiloxane.

H. Viscosity Modifiers

[0372] Viscosity modifiers (also referred to as viscosity index improvers or viscosity improvers) can be included in the lubricating compositions described herein. Viscosity modifiers provide lubricants with high and low temperature operability. These additives impart shear stability at elevated temperatures and acceptable viscosity at low temperatures. Suitable viscosity modifiers include high molecular weight hydrocarbons, polyesters, and viscosity modifier dispersants that can function as both a viscosity modifier and a dispersant. Typical molecular weights of these polymers are between about 10,000 to 1,500,000 g/mol, more typically about 20,000 to 1,200,000 g/mol, and even more typically between about 50,000 and 1,000,000 g/mol.

[0373] Examples of suitable viscosity modifiers are linear or star-shaped polymers and copolymers of methacrylate, butadiene, olefins, or alkylated styrenes. Polyisobutylene is a commonly used viscosity modifier. Another suitable viscosity modifier is polymethacrylate (copolymers of various chain length alkyl methacrylates, for example), some formulations of which also serve as pour point depressants. Other suitable viscosity modifiers include copolymers of ethylene and propylene, hydrogenated block copolymers of styrene and isoprene, and polyacrylates (copolymers of various chain length acrylates, for example). Specific examples include styrene-isoprene or styrene-butadiene based polymers of 50,000 to 200,000 g/mol molecular weight.

[0374] Copolymers useful as viscosity modifiers include those commercially available from Chevron Oronite Company LLC under the trade designation "PARATONE™" (such as "PARATONE™ 8921," "PARATONE™ 68231," and "PARATONE™ 8941"); from Afton Chemical Corporation under the trade designation "HiTEC™" (such as HiTEC™ 5850B, and HiTEC™5777); and from The Lubrizol Corporation under the trade designation "Lubrizol™ 7067C". Hydrogenated polyisoprene star polymers useful as viscosity modifiers herein include those commercially available from Infineum International Limited, e.g., under the trade designation "SV200™" and "SV600™". Hydrogenated diene-styrene block copolymers useful as viscosity modifiers herein are commercially available from Infineum International Limited, e.g., under the trade designation "SV 50™".

[0375] Polymers useful as viscosity modifiers herein include polymethacrylate or polyacrylate polymers, such as linear polymethacrylate or polyacrylate polymers, such as those available from Evnoik Industries under the trade designation "Viscoplex™" (*e.g.*, Viscoplex™ 6-954) or star polymers which are available from Lubrizol Corporation under the trade designation Asteric™ (*e.g.*, Lubrizol™ 87708 and Lubrizol™ 87725).

[0376] Vinyl aromatic-containing polymers useful as viscosity modifiers herein may be derived from vinyl aromatic hydrocarbon monomers, such as styrenic monomers, such as styrene. Illustrative vinyl aromatic-containing copolymers useful herein may be represented by the following general formula: A-B wherein A is a polymeric block derived predominantly from vinyl aromatic hydrocarbon monomer (such as styrene), and B is a polymeric block derived predominantly from conjugated diene monomer (such as isoprene).

[0377] Vinyl aromatic-containing polymers useful as viscosity modifiers may have a Kinematic viscosity at 100° C of 20 cSt or less, such as 15 cSt or less, such as 12 cSt or less, but may be diluted (such as in Group I, II, and/or III basestock) to higher Kinematic viscosities at 100° C, such as to 40 cSt or more, such as 100 cSt or more, such as 1000 cSt or more, such as 1000 to 2000 cSt.).

[0378] Typically, the viscosity modifiers may be used in an amount of about 0.01 to about 10 wt%, such as about 0.1 to about 7 wt%, such as 0.1 to about 4 wt%, such as about 0.2 to about 2 wt%, such as about 0.2 to about 1 wt%, and such as about 0.2 to about 0.5 wt%, based on the total weight of the formulated lubricant composition.

[0379] In embodiments, the viscosity modifier(s) used in the lubricating oil compositions of the present invention is present at 0.001 to 0.5 mass%, such as 0.05 to 0.3 mass%, such as 0.1 to 0.22 mass% of one or more viscosity modifier(s) based upon the total mass of the lubricating oil composition.

[0380] Viscosity modifiers are typically added as concentrates, in large amounts of diluent oil. The "as delivered" viscosity modifier typically contains from 20 wt% to 75 wt% of an active polymer for polymethacrylate or polyacrylate polymers, or from 8 wt% to 20 wt% of an active polymer for olefin copolymers, hydrogenated polyisoprene star polymers, or hydrogenated diene-styrene block copolymers, in the "as delivered" polymer concentrate.

[0381] In particular embodiments, the "as delivered" viscosity modifier(s) used in the lubricating oil compositions of the present invention is an olefin copolymer viscosity modifier (which is commercially available as Oronite Paratone® 24EX).

I. Dispersants

[0382] During engine operation, oil-insoluble oxidation byproducts are produced. Dispersants help keep these byproducts in solution, thus diminishing their deposition on metal surfaces. Dispersants used in the formulation of the lubricating compositions herein may be ashless or ash-forming in nature. Preferably, the dispersant is ashless. So called ashless dispersants are organic materials that form substantially no ash upon combustion. For example, non-metal-containing or borated metal-free dispersants are considered ashless. In contrast, metal-containing detergents tend to form ash upon combustion.

[0383] Dispersants useful herein typically contain a polar group attached to a relatively high molecular weight hydrocarbon chain. The polar group typically contains at least one element of nitrogen, oxygen, or phosphorus. Typical hydrocarbon chains contain 40 to 500, such as 50 to 400 carbon atoms.

Dispersants of (Poly)alkenylsuccinic derivatives

[0384] A particularly useful class of dispersants includes the (poly)alkenylsuccinic derivatives, typically produced by the reaction of a long chain hydrocarbyl-substituted succinic compound, usually a hydrocarbyl-substituted succinic anhydride, with a polyhydroxy or polyamino compound. The long chain hydrocarbyl group constituting the oleophilic portion of the molecule which confers solubility in the oil, is often a polyisobutylene group (typically the long chain hydrocarbyl group, such as a polyisobutylene group, has an Mn of 400 to 3000 g/mol, such as 450 to 2500 g/mol). Many examples of this type of dispersant are well known commercially and in the literature. Exemplary US Patents describing such dispersants include US Patent Nos. 3,172,892; 3,2145,707; 3,219,666; 3,316,177; 3,341,542; 3,444,170; 3,454,607; 3,541,012; 3,630,904; 3,632,511; 3,787,374 and 4,234,435. Other types of dispersants are described in US Patent Nos. 3,036,003; 3,200,107; 3,254,025; 3,275,554; 3,438,757; 3,454,555; 3,565,804; 3,413,347; 3,697,574; 3,725,277; 3,725,480; 3,726,882; 4,454,059; 3,329,658; 3,449,250; 3,519,565; 3,666,730; 3,687,849; 3,702,300; 4,100,082; 5,705,458. A further description of dispersants useful herein may be found, for example, in European Patent Applications Nos. 0 471 071 and 0 451 380, to which reference is made for this purpose.

[0385] Hydrocarbyl-substituted succinic acid and hydrocarbyl-substituted succinic anhydride derivatives are useful dispersants. In particular, succinimide, succinate esters, or succinate ester amides prepared by the reaction of a hydrocarbon-substituted succinic acid or anhydride compound (typically having at least 25 carbon atoms, such as 28 to 400 carbon atoms, in the hydrocarbon substituent), with at least one equivalent of a polyhydroxy or polyamino compound (such as an alkylene amine) are particularly useful herein. Hydrocarbyl-substituted succinic acid and hydrocarbyl-substituted succinic anhydride derivatives may have a number average molecular weight of at least 400 g/mol, such as at least 900 g/mol, such as at least 1500 g/mol, such as from 400 to 4000 g/mol, such as from 800 to 3000, such as from 2000 to 2800 g/mol, such from about 2100 to 2500 g/mol, and such as from about 2200 to about 2400 g/mol.

[0386] Succinimides, which are particularly useful herein, are formed by the condensation reaction between: 1) hydrocarbyl-substituted succinic anhydrides, such as polyisobutylene succinic anhydride (PIBSA); and 2) polyamine (PAM). Examples of suitable polyamines include: polyhydrocarbyl polyamines, polyalkylene polyamines, hydroxy-substituted polyamines, polyoxyalkylene polyamines, and combinations thereof. Examples of polyamines include tetraethylene pentamine, pentaethylene hexamine, tetraethylenepentamine (TEPA), pentaethylenehaxamine (PEHA), N-phenyl-p-phenylenediamine (ADPA), and other polyamines having an average of 5, 6, 7, 8, or 9 nitrogen atoms per molecule. Mixtures where the average number of nitrogen atoms per polyamine molecule is greater than 7 are commonly called heavy polyamines or H-PAMs and may be commercially available under trade names such as HPA™ and HPA-X™ from DowChemical, E-100™ from Huntsman Chemical, et al. Examples of hydroxy-substituted polyamines include N-hydroxyalkyl-alkylene polyamines such as N-(2-hydroxyethyl)ethylene diamine, N-(2-hydroxyethyl)piperazine, and/or N-hydroxyalkylated alkylene diamines of the type described, for example, in US Patent No. 4,873,009. Examples of polyoxyalkylene polyamines include polyoxyethylene and/or polyoxypropylene diamines and triamines (as well as co-oligomers thereof) having an average Mn from about 200 to about 5000 g/mol. Products of this type are commercially available under the tradename Jeffamine™. Representative examples of useful succinimides are shown in US Patent Nos. 3,087,936; 3,172,892; 3,219,666; 3,272,746; 3,322,670; 3,652,616; 3,948,800; and 6,821,307; and CA Patent No. 1,094,044.

[0387] The polyalkenyl-substituted mono- or dicarboxylic acid, anhydride or ester from which succinimide dispersants are derived can be prepared using either a halogen (e.g., chlorine) assisted alkylation process ("chloro dispersant"), and those prepared using a halogen-free thermal, or "ene" reaction process ("thermal dispersant"). When using "conventional" Lewis acid catalyzed polyalkenes, high functionality carboxylic acid acylating agents, particularly polyisobutylene succinic anhydride ("PIBSA") cannot be provided via the halogen-free thermal reaction process. However, PIBSA having a higher functionality (e.g., a functionality of greater than 1.3) may be prepared via the thermal process using a polyalkene (particularly polyisobutylene) having a high terminal vinylidene content (greater than 65%, such as greater than 70%, 80% or 85%). Processes for producing high terminal vinylidene content polyisobutylene products (referred to as highly reactive polyisobutylene or "HR-PIB") are described, for example, in U.S. Pat. No. 4,152,499, and HR-PIB products are commercially available from TPC, or from BASF under the trade name Glissopal™. PIBSA having a functionality of greater than 1.3 prepared via the thermal process using polyisobutylene having a high terminal vinylidene content are described, together with succinimide dispersants derived therefrom, are described in EP 0 355 895.

[0388] The chloro or thermal dispersants may comprise one or more, optionally borated, higher molecular weight (Mn 1600 g/mol or more, such as 1800 to 3000 g/mol) succinimides and one or more, optionally borated, lower molecular weight (Mn less than 1600 g/mol) succinimides, where the higher molecular weight may be 1600 to 3000 g/mol, such as 1700 to 2800 g/mol, such as 1800 to 2500 g/mol, such as 1850 to 2300 g/mol; and the lower molecular weight may be 600 to less than 1600 g/mol, such as 650 to 1500 g/mol, such as 700 to 1400 g/mol, such as 800 to 1300 g/mol, such as 850 to 1200 g/mol such as 900 to 1150 g/mol, such as 900 to 1000 g/mol. The higher molecular weight succinimide dispersant may be present in the lubricating composition in an amount of from 0.5 to 10 wt%, or from 0.8 to 6 wt%, or from 1.0 to 5 wt%, or from 1.5 to 5 wt%, or from 1.5 to 4.0 wt%; and the lower molecular weight succinimides dispersant may be present in the lubricating composition in an amount of from 1 to 5 wt%, or from 1.5 to 4.8 wt%, or from 1.8 to 4.6 wt%, or from 1.9 to 4.6 wt%, or at 2 wt% or more, such as 2 to 5 wt%. The lower molecular weight succinimides may differ from the higher molecular weight succinimides, by 500 g/mol or more, such as by 750 g/mol or more, such as by 1000 g/mol or more, such as by 1200 g/mol or more, such as by 500 to 3000 g/mol, such as by 750 to 2000 g/mol, such as by 1000 to 1500 g/mol.

[0389] Succinate esters useful as dispersants include those formed by the condensation reaction between hydrocarbyl-substituted succinic anhydrides and alcohols or polyols. For example, the condensation product of a hydrocarbyl-substituted succinic anhydride and pentaerythritol is a useful dispersant.

[0390] Succinate ester amides useful herein are formed by a condensation reaction between hydrocarbyl-substituted succinic anhydrides and alkanol amines. Suitable alkanol amines include ethoxylated polyalkylpolyamines, propoxylated polyalkylpolyamines, and polyalkenylpolyamines such as polyethylene polyamines and/or propoxylated hexamethylenediamine. Representative examples are shown in US Patent No. 4,426,305.

[0391] Hydrocarbyl-substituted succinic anhydrides (such as PIBSA) esters of hydrocarbyl bridged aryloxy alcohols are also useful as dispersants herein. For information on such dispersants, please see US Patent No. 7,485,603, particularly, col 2, ln 65 to col 6, ln 22 and col 23, ln 40 to col 26, ln 46. In particular, PIBSA esters of methylene-bridged naphthyloxy ethanol (*i.e.,* 2-hydroxyethyl-1-naphthol ether (or hydroxy-terminated ethylene oxide oligomer ether of naphthol) are useful herein.

[0392] The molecular weight of the hydrocarbyl-substituted succinic anhydrides used in the preceding paragraphs will typically range from 350 to 4000 g/mol, such as 400 to 3000 g/mol, such as 450 to 2800 g/mol, such as 800 to 2500 g/mol.

The above (poly)alkenylsuccinic derivatives can be post-reacted with various reagents such as sulfur, oxygen, formaldehyde, carboxylic acids such as oleic acid.

[0393] The chloro or thermal dispersants may be present in the lubricant in an amount of 0.1 mass% to 20 mass% of the composition, such as 0.2 to 15 mass%, such as 0.25 to 10 mass%, such as 0.3 to 5 mass%, such as 1.0 mass% to 3.0 mass%, of the lubricating oil composition.

[0394] The above (poly)alkenylsuccinic derivatives, can also be post reacted with boron compounds such as boric acid, borate esters or highly borated dispersants, to form borated dispersants generally having from about 0.1 to about 5 moles of boron per mole of dispersant reaction product.

[0395] Dispersants useful herein include borated succinimides, including those derivatives from mono-succinimides, bis-succinimides, and/or mixtures of mono- and bis-succinimides, wherein the hydrocarbyl succinimide is derived from a hydrocarbylene group such as polyisobutylene having an Mn of from about 300 to about 5000 g/mol, or from about 500 to about 3000 g/mol, or about 1000 to about 2000 g/mol, or a mixture of such hydrocarbylene groups, often with high terminal vinylic groups.

[0396] The boron-containing 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 0.5 wt% to 8 wt%, or 1.0 wt% to 6.5 wt%, or 0.5 wt% to 2.2 wt% of the lubricating composition.

[0397] The boron-containing dispersant may be present in an amount to deliver boron to the composition at 15 ppm to 2000 ppm, or 25 ppm to 1000 ppm, or 40 ppm to 600 ppm, or 80 ppm to 350 ppm.

[0398] The borated dispersant may be used in combination with non-borated dispersant and may be the same or different compound as the non-borated dispersant. In one embodiment, the lubricating composition may include one or more boron-containing dispersants and one or more non-borated dispersants, wherein the total amount of dispersant may be 0.01 wt% to 20 wt%, or 0.1 wt% to 15 wt%, or 0.1 wt% to 10 wt%, or 0.5 wt% to 8 wt%, or 1.0 wt% to 6.5 wt%, or 0.5 wt% to 2.2 wt% of the lubricating composition and wherein the ratio of borated dispersant to non-boroated dispersant may be 1:10 to 10:1 (weight:weight) or 1:5 to 3:1 or 1:3 to 2:1.

[0399] The dispersant may comprise one or more borated or unborated poly(alkenyl)succinimides, where the polyalkyenyl is derived from polyisobutylene and the imide is derived from a polyamine ("PIBSA-PAM").

[0400] The dispersant may comprise one or more PIBSA-PAMs, where the PIB is derived from polyisobutylene having an Mn of from 600 to 5000, such as from 700 to 4000, such as from 800 to 3000, such as from 900 to 2500 g/mol and the polyamine is derived from hydrocarbyl-substituted polyamines, such as tetraethylene pentamine, pentaethylene hexamine, tetraethylenepentamine (TEPA), pentaethylenehaxamine (PEHA), N-phenyl-p-phenylenediamine (ADPA), and other polyamines having an average of 5, 6, 7, 8, or 9 nitrogen atoms per molecule). The dispersant may be borated, typically at levels of up to 4 mass% such as from 1 to 3 mass%. The dispersant may comprise one or more borated and one or more non-borated PIBSA-PAM's. The dispersant may comprise one or more borated PIBSA-PAM's derived from a PIB having an Mn of 700 to 1800 g/mol (such as 800 to 1500 g/mol) and one or more non-borated PIBSA-PAM's derived from a PIB having an Mn of more than 1800 to 5000 g/mol (such as 2000 to 3000 g/mol). The dispersant may comprise one or more non-borated PIBSA-PAM's derived from a PIB having an Mn of 700 to 1800 g/mol (such as 800 to 1500 g/mol) and one or more borated PIBSA-PAM's derived from a PIB having an Mn of more than 1800 to 5000 g/mol (such as 2000 to 3000 g/mol).

[0401] The dispersant may comprise PIBSA derived from a PIB having an Mn of 700 to 5000 g/mol (such as 800 to 3000 g/mol) and one or more borated or non-borated PIBSA-PAM's derived from a PIB having an Mn of 700 to 5000 g/mol.

[0402] The dispersant may comprise PIBSA derived from a PIB having an Mn of 700 to 5000 g/mol (such as 800 to 3000 g/mol) and one or more borated PIBSA-PAM's derived from a PIB having an Mn of 700 to 1800 g/mol (such as 800 to 1500 g/mol) and one or more non-borated PIBSA-PAM's derived from a PIB having an Mn of more than 1800 to 5000 g/mol (such as 2000 to 3000 g/mol). The dispersant may comprise PIBSA derived from a PIB having an Mn of 700 to 5000 g/mol (such as 800 to 3000 g/mol) one or more non-borated PIBSA-PAM's derived from a PIB having an Mn of 700 to 1800 g/mol (such as 800 to 1500 g/mol) and one or more borated PIBSA-PAM's derived from a PIB having an Mn of more than 1800 to 5000 g/mol (such as 2000 to 3000 g/mol).

[0403] The dispersant may comprise one or more borated or non-borated PIBSA-PAM's and one or more PIBSA-esters of hydrocarbyl bridged aryloxy alcohols.

[0404] The dispersant may comprise one or more borated and one or more non-borated PIBSA-PAM's.

[0405] The dispersant may comprise one or more, optionally borated, higher molecular weight (Mn 1600 g/mol or more, such as 1800 to 3000 g/mol) PIBSA-PAM's and one or more, optionally borated, lower molecular weight (Mn less than 1600 g/mol) PIBSA-PAM's, where the higher molecular weight may be 1600 to 3000 g/mol, such as 1700 to 2800 g/mol, such as 1800 to 2500 g/mol, such as 1850 to 2300 g/mol; and the lower molecular weight may be 600 to less than 1600 g/mol, such as 650 to 1500 g/mol, such as 700 to 1400 g/mol, such as 800 to 1300 g/mol, such as 850 to 1200 g/mol, such as 900 to 11500 g/mol, such as 900 to 100 g/mol. The higher molecular weight PIBSA-PAM dispersant may be present in the lubricating composition in an amount of from 0.5 to 10 wt%, or from 0.8 to 6 wt%, or from 1.0 to 5 wt%, or from 1.5 to 5 wt% or from 1.5 to 4.0 wt%; and the lower molecular weight PIBSA-PAM dispersant may be present in the lubricating composition in an amount of from 1 to 5 wt%, or from 1.5 to 4.8 wt%, or from 1.8 to 4.6 wt%, or from 1.9 to 4.6 wt%, or at 2 wt% or more, such as 2 to 5 wt%.

[0406] According to the invention, the dispersant(s) (other than component B)) used in the lubricating oil compositions and additive concentrates of the present invention comprises, in particular consists of, a mixture of one or more chloro dispersant(s) and one or more thermal dispersant(s). In embodiments, the one or more chloro dispersant(s) and one or more thermal dispersant(s) are present at a ratio of about 9:1 to about 3:2, such as about 6:1 to about 3:1, such as about 5:1 to about 4:1, in particular at a ratio of about 9:2.

[0407] In certain embodiments, the one or more chloro dispersant(s) used in the lubricating oil compositions and additive concentrates of the present invention comprises, in particular consists of, one or more borated or unborated poly(alkenyl) succinimide(s), where the polyalkyenyl is derived from polyisobutylene and the imide is derived from a polyamine ("PIBSA-PAM"), in particular one or more borated and one or more non-borated PIBSA-PAM's. In particular embodiments, the one or more chloro dispersant(s) used in the lubricating oil compositions and additive concentrates of the present invention comprises, in particular consists of, one or more higher molecular weight (Mn 1600 g/mol or more, such as 1800 to 3000 g/mol) PIBSA-PAM's and one or more, optionally borated, lower molecular weight (Mn less than 1600 g/mol) PIBSA-PAM's, in particular a first higher molecular weight PIBSA-PAM; and a second and third lower molecular weight PIBSA-PAM (optionally, one of which is borated), where preferably the ratio of the higher molecular weight PIBSA PAM to the lower molecular weight PIBSA-PAM's is about 1:1 to about 2:3.

[0408] In certain embodiments, the one or more thermal dispersant(s) used in the lubricating oil compositions and additive concentrates of the present invention comprises, in particular consists of, one or more poly(alkenyl) succinimide(s), where the polyalkyenyl is derived from polyisobutylene and the imide is derived from a polyamine ("PIBSA-PAM"), in particular where the polyalkyenyl is derived from high terminal vinylidene content polyisobutylene and the imide is derived from a polyamine ("HR-PIBSA-PAM"). In particular embodiments, the one or more thermal dispersant(s) used in the lubricating oil compositions and additive concentrates of the present invention comprises, in particular consists of, one or more higher molecular weight (Mn 1000 g/mol or more, such as 1200 to 3000 g/mol, such as 1500 to 2800 g/mol, such as 1800 to 2500 g/mol, such as 2200 to 2300 g/mol) PIBSA-PAM's, in particular having a Mn of at least 1200 g/mol, such as at least 1500 g/mol, such as at least 1800 g/mol, such as at least 2200 g/mol or at least 2300 g/mol.

Dispersants of Mannich Bases

[0409] Mannich base dispersants useful herein are typically made from the reaction of an amine component, a hydroxy aromatic compound (substituted or unsubstituted, such as alkyl substituted), such as alkylphenols, and an aldehyde, such as formaldehyde. See US Patent Nos. 4,767,551 and 10,899,986. Process aids and catalysts, such as oleic acid and sulfonic acids, can also be part of the reaction mixture. Representative examples are shown in US Patent Nos. 3,697,574; 3,703,536; 3,704,308; 3,751,365; 3,756,953; 3,798,165; 3,803,039; 4,231,759; 9,938,479; 7,491,248; and 10,899,986, and PCT Publication No. WO 01/42399.

Dispersants of Polymethacrylate or Polyacrylate Derivatives

[0410] Polymethacrylate or polyacrylate derivatives are another class of dispersants useful herein. These dispersants are typically prepared by reacting a nitrogen-containing monomer and a methacrylic or acrylic acid esters containing 5-25 carbon atoms in the ester group. Representative examples are shown in US Patent Nos. 2,100,993, and 6,323,164. Polymethacrylate and polyacrylate dispersants are typically lower molecular weights.

[0411] The lubricating composition of the disclosure typically comprises dispersant at 0.1 mass% to 20 mass% of the composition, such as 0.2 to 15 mass%, such as 0.25 to 10 mass%, such as 0.3 to 5 mass%, such as 2.0 mass% to 4.0 mass% of the lubricating oil composition. Alternately the dispersant may be present at 0.1 wt% to 5 wt%, or 0.01 wt% to 4 wt% of the lubricating composition.

[0412] In embodiments, the dispersant(s) used in the lubricating oil compositions and additive concentrates of the present invention is present at 1 to 12 mass%, such as 3 to 10 mass%, such as 6 to 8 mass% of based upon the total mass of the lubricating oil composition, and at 15 to 40 mass%, such as 20 to 32 mass%, such as 25 to 30 mass% based upon the total mass of the additive concentrate.

[0413] In particular embodiments, the dispersant(s) used in the lubricant oil compositions and additive concentrates of the present invention is absent Mannich base dispersants and/or poly(meth)acrylate dispersants. In particular embodiments, the dispersant(s) used in the lubricant oil compositions and additive concentrates of the present invention is absent hydrocarbyl-substituted succinic anhydrides, such as esters of hydrocarbyl bridged aryloxy alcohols. Preferably, the dispersant(s) the dispersant(s) used in the lubricant oil compositions and additive concentrates of the present invention comprise, in particular consists of, poly(alkylene) succinimide dispersants, in particular PIBSA-PAM dispersants. More preferably, the dispersant(s) used in the lubricant oil compositions and additive concentrates of the present invention comprise, in particular consists of, a first and a second PIBSA-PAM dispersant derived from an 1800 to 2500 Mn PIB; a third and a fourth PIBSA-PAM dispersant derived from a PIB with an Mn less than 1600, where at least one of the first PIBSA-

PAM dispersant and the second PIBSA-PAM dispersant has a high terminal vinylidene content, at least one of the third PIBSA-PAM dispersant and the fourth PIBSA-PAM dispersant is boron-free (optionally, at least one of the third PIBSA-PAM dispersant and the fourth PIBSA-PAM dispersant is borated). Particularly preferably, the dispersant(s) used in the lubricant oil compositions and additive concentrates of the present invention comprise, in particular consists of, a first boron-free PIBSA-PAM dispersant derived from an 2200 Mn PIB; a second boron-free PIBSA-PAM dispersant derived from an 2300 Mn high terminal vinylidene content PIB; a third boron-free PIBSA-PAM dispersant derived from a 950 Mn PIB; and a fourth borated PIBSA-PAM dispersant derived from a 950 Mn PIB.

[0414] For further information on dispersants useful herein, please see US Patent No. 10,829,712, col 13, ln 36 to col 16, ln 67 and US Patent No. 7,485,603, col 2, ln 65 to col 6, ln 22, col 8, ln 25 to col 14, ln 53, and col 23, ln 40 to col 26, ln 46.

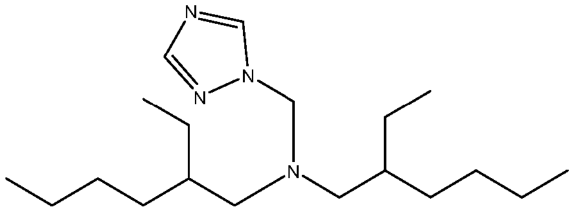
[0415] Compositions according to the present disclosure may contain an additive having a different enumerated function that also has secondary effects as a dispersant (for example, Component B Functionalized Polymer described above, may also have dispersant effects). These additives are not included as dispersants for purposes of determining the amount of dispersant in a lubricating oil composition or concentrate herein. However, (poly)alkenyl succinic dispersants of component I) are considered as constituting a dispersant mixture as disclosed herein, along with component B). Thus, (poly)alkenyl succinic dispersants of component I) and component B) are taken together for purposes of determining the amount of dispersant mixture in a lubricating oil composition or additive concentrate disclosed herein.

[0416] In particular embodiments, the detergent mixture comprises the one or more chloro dispersant(s) at 50 to 90 mass%, such as 55 to 85 mass%, such as 62 to 82 mass%, such as 68 to 80 mass%, such as 70 to 76 mass% based upon the total mass of the dispersant mixture and/or the one or more thermal dispersant(s) at 10 to 30 mass%, such as 12 to 25 mass%, such as 14 to 22 mass%, such as 15 to 20 mass%, such as 15.5 to 17.5 mass% based upon the total mass of the dispersant mixture. Preferably, the dispersant mixture comprises the one or more chloro dispersant(s) and the one or more thermal dispersant(s) at a ratio of about 9:1 to about 3:2, such as about 6:1 to about 3:1, such as about 5:1 to about 4:1. More preferably, the dispersant mixture comprises the one or more chloro dispersant(s) and the one or more thermal dispersant(s) at a ratio of about 9:2.

J. Corrosion Inhibitors/Anti-rust Agents

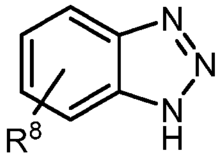
[0417] Corrosion inhibitors may be used to reduce the corrosion of metals and are often alternatively referred to as metal deactivators or metal passivators. Some corrosion inhibitors may alternatively be characterized as antioxidants.

[0418] Suitable corrosion inhibitors may include nitrogen and/or sulfur-containing heterocyclic compounds such as triazoles (*e.g.*, benzotriazoles), substituted thiadiazoles, imidazoles, thiazoles, tetrazoles, hydroxyquinolines, oxazolines, imidazolines, thiophenes, indoles, indazoles, quinolines, benzoxazines, dithiols, oxazoles, oxatriazoles, pyridines, piperazines, triazines and derivatives of any one or more thereof. A useful triazole includes 1H-1,2,4-triazole-1-methanamine, N,N-bis(2-ethylhexyl), Irgamet™ 30, which is commercially available from BASF of Ludwigshafen, Germany and represented by the formula:



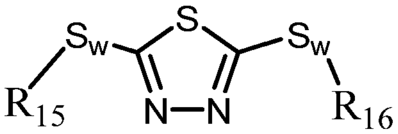
1H-1,2,4-triazole-1-methanamine, N,N-bis(2-ethylhexyl)

[0419] A particular corrosion inhibitor is a benzotriazole represented by the structure:



wherein R^8 is absent (hydrogen) or is a C_1 to C_{20} hydrocarbyl or substituted hydrocarbyl group which may be linear or branched, saturated or unsaturated. It may contain ring structures that are alkyl or aromatic in nature and/or contain heteroatoms such as N, O, or S. Examples of suitable compounds may include benzotriazole, alkyl-substituted benzotriazoles (*e.g.*, tolyltriazole, ethylbenzotriazole, hexylbenzotriazole, octylbenzotriazole, etc.), aryl substituted benzotriazole, alkylaryl- or arylalkyl-substituted benzotriazoles, and the like, as well as combinations thereof. For instance, the triazole may comprise or be a benzotriazole and/or an alkylbenzotriazole in which the alkyl group contains from 1 to about 20 carbon atoms or from 1 to about 8 carbon atoms. Non-limiting examples of such corrosion inhibitors may comprise or be benzotriazole, tolyltriazole, and/or optionally, substituted benzotriazoles such as (n,n-bis(2-ethylhexyl)-4-methyl-1h-benzotriazole-1-methanamine), Irgamet™ 39, which is commercially available from BASF of Ludwigshafen, Germany. A preferred corrosion inhibitor may comprise or be benzotriazole and/or tolyltriazole.

[0420] Additionally, or alternatively, the corrosion inhibitor may include one or more substituted thiadiazoles represented by the structure:



wherein R_{15} and R_{16} are independently hydrogen or a hydrocarbon group, which group may be aliphatic or aromatic, including cyclic, alicyclic, aralkyl, aryl and alkaryl, and wherein each w is independently 1, 2, 3, 4, 5, or 6 (preferably 2, 3, or 4, such as 2). These substituted thiadiazoles are derived from the 2,5-dimercapto-1,3,4-thiadiazole (DMTD) molecule. Many derivatives of DMTD have been described in the art, and any such compounds may be included in the fluid used in the present disclosure. For example, US Patent Nos. 2,719,125; 2,719,126; and 3,087,937; describe the preparation of various 2, 5-bis-(hydrocarbon dithio)-1,3,4-thiadiazoles.

[0421] Further, additionally or alternatively, the corrosion inhibitor may include one or more other derivatives of DMTD, such as a carboxylic ester in which R_{15} and R_{16} may be joined to the sulfide sulfur atom through a carbonyl group. Preparation of these thioester-containing DMTD derivatives is described, for example, in US Patent No. 2,760,933. DMTD derivatives produced by condensation of DMTD with alpha-halogenated aliphatic carboxylic acids having at least 10 carbon atoms are described, for example, in US Patent No. 2,836,564. This process produces DMTD derivatives wherein R_{15} and R_{16} are HOOC-CH(R_{19})-(R_{19} being a hydrocarbyl group). DMTD derivatives further produced by amidation or esterification of these terminal carboxylic acid groups may also be useful.

[0422] The preparation of 2-hydrocarbyldithio-5-mercapto-1,3,4-thiadiazoles is described, for example, in US Patent No. 3,663,561.

[0423] A class of DMTD derivatives may include mixtures of a 2-hydrocarbyldithio-5-mercapto-1,3,4-thiadiazole and a 2,5-bis-hydrocarbyldithio-1,3,4-thiadiazole. Such mixtures may be sold under the tradename HiTEC™ 4313 and are commercially available from Afton Chemical Company.

[0424] The preparation of 2-hydrocarbyldithio-5-mercapto-1,3,4-thiadiazoles is described, for example, in US Patent No. 3,663,561.

[0425] A class of DMTD derivatives may include mixtures of a 2-hydrocarbyldithio-5-mercapto-1,3,4-thiadiazole and a 2,5-bis-hydrocarbyldithio-1,3,4-thiadiazole. Such mixtures may be sold under the tradename HiTEC™ 4313 and are commercially available from Afton Chemical Company.

[0426] Still further, additionally or alternatively, the corrosion inhibitor may include a trifunctional borate having the structure, $B(OR_{46})_3$, in which each R_{46} may be the same or different. As the borate may typically be desirably compatible with the non-aqueous medium of the composition, each R_{46} may, in particular, comprise or be a hydrocarbyl C_1-C_8 moiety. For compositions in which the non-aqueous medium comprises or is a lubricating oil basestock, for example, better compatibility can typically be achieved when the hydrocarbyl moieties are each at least C_4. Non-limiting examples of such corrosion inhibitors thus include, but are not limited to, triethylborate, tripropylborates such as triisopropylborate, tributylborates such as tri-tert-butylborate, tripentylborates, trihexylborates, trioctylborates such as tri-(2-ethylhexyl) borate, monohexyl dibutylborate, and the like, as well as combinations thereof.

[0427] When used, a corrosion inhibitor may comprise a substituted thiadiazole, a substituted benzotriazole, a substituted triazole, a trisubstituted borate, or a combination thereof.

[0428] When desired, corrosion inhibitors can be used in any effective amount, but, when used, may typically be used in amounts from about 0.001 wt% to 5.0 wt%, based on the weight of the composition, e.g., from 0.005 wt% to 3.0 wt% or from 0.01 wt% to 1.0 wt%. Alternately, such additives may be used in an amount of about 0.01 to 5 wt%, preferably about 0.01 to 1.5 wt%, based upon the weight of the lubricating composition.

[0429] In embodiments, the corrosion inhibitor(s)/anti-rust agent(s) used in the lubricating oil compositions and additive concentrates of the present invention is present at 0.001 to 1 mass%, such as 0.01 to 0.5 mass%, such as 0.05 to 0.1 mass% based upon the total mass of the lubricating oil composition, and/or at 0.01 to 2 mass%, such as 0.05 to 1.5 mass% such as 0.1 to 0.5 mass% based upon the total mass of the additive concentrate.

[0430] In particular embodiments, the corrosion inhibitor(s)/anti-rust agent(s) used in the lubricating oil compositions and additive concentrates of the present invention is selected from the group consisting of liquid triazole derivatives, such as liquid triazole amines. Preferably, the corrosion inhibitor(s)/anti-rust agent(s) used in the lubricating oil compositions and additive concentrates of the present invention comprises, in particular consists of, N,N-bis(2-ethylhexyl)-((1,2,4)-triazol-1-yl)methyl)amine (which is commercially available as Irgamet™ 30).

[0431] In alternative embodiments, 3,4-oxypyridinone-containing compositions may contain substantially no *(e.g.,* 0, or less than 0.001 wt%, 0.0005 wt% or less, not intentionally added, and/or absolutely no) triazoles, benzotriazoles, substituted thiadiazoles, imidazoles, thiazoles, tetrazoles, hydroxyquinolines, oxazolines, imidazolines, thiophenes, indoles, indazoles, quinolines, benzoxazines, dithiols, oxazoles, oxatriazoles, pyridines, piperazines, triazines, derivatives thereof, combinations thereof, or all corrosion inhibitors.

[0432] Compositions according to the present disclosure may contain an additive having a different enumerated function that also has secondary effects as a corrosion inhibitor (for example, Component B Functionalized Polymer described above, may also have corrosion inhibitor effects). These additives are not included as corrosion inhibitor for purposes of determining the amount of corrosion inhibitor in a lubricating oil composition or concentrate herein.

K. Anti-wear Agents

[0433] The lubricating oil composition of the present disclosure 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.

[0434] In embodiments, the anti-wear agent(s) used in the lubricating oil compositions and additive concentrates of the present invention are present at 0.01 to 1.5 mass%, such as 0.05 to 1 mass%, such as 0.06 to 0.6 mass% of one or more anti-wear agent(s) based upon the total mass of the lubricating oil composition, and/or at 0.1 to 5 mass%, such as 1 to 2.4 mass%, such as 1.5 to 2.2 mass% based upon the total mass of the additive concentrate.

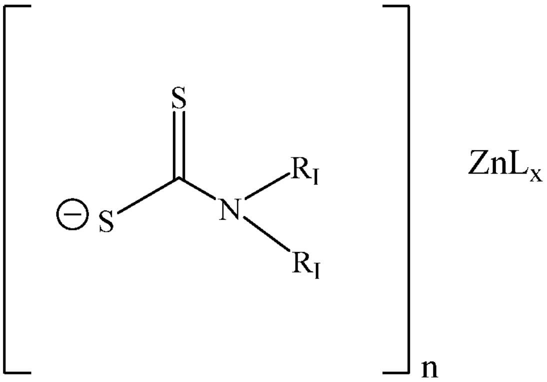
[0435] In particular embodiments, the anti-wear agent(s) used in the lubricating oil compositions and additive concentrates of the present invention is present in an amount to deliver not more than 900 ppm phosphorous, such as not more than 800 ppm phosphorous, such as not more than 700 ppm phosphorous, such as not more than 600 ppm phosphorous, such as not more than 500 ppm phosphorous, such as not more than 490 ppm phosphorous to the lubricating oil composition and/or additive concentrate.

[0436] In 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.

[0437] Useful anti-wear agents also include substituted or unsubstituted thiophosphoric acids, and salts thereof include zinc-containing compounds such as zinc dithiophosphate compounds selected from zinc dialkyl-, diaryl- and/or alkylaryl-dithiophosphates.

[0438] A metal alkylthiophosphate and more particularly a metal dialkyl dithio phosphate in which the metal constituent is zinc, or zinc dialkyl dithio phosphate (ZDDP) can be a useful component of the lubricating compositions of this disclosure. ZDDP can be derived from primary alcohols, secondary alcohols or mixtures thereof. ZDDP compounds generally are of the formula $Zn[SP(S)(OR_1)(OR_2)]_2$ where R_1 and R_2 are C_1-C_{18} alkyl groups, preferably C_2-C_{12} alkyl groups. These alkyl groups may be straight chain or branched. Alcohols used in the ZDDP can be 2-propanol, butanol, secondary butanol, pentanols, hexanols such as 4-methyl-2-pentanol, n-hexanol, n-octanol, 2-ethyl hexanol, alkylated phenols, and the like. Mixtures of secondary alcohols or of primary and secondary alcohol can be used. Alkyl aryl groups may also be used. Useful zinc dithiophosphates include secondary zinc dithiophosphates such as those available from The Lubrizol Corporation under the trade designations "LZ 677A", "LZ 1095" and "LZ 1371", from Chevron Oronite under the trade designation "OLOA 262" and from Afton Chemical under the trade designation "HiTEC™ 7169".

[0439] In embodiments, the zinc compound can be a zinc dithiocarbamate complex, such as the zinc dithiocarbamates represented by the formula:



where each R_I is independently a linear, cyclic, or branched, saturated or unsaturated, aliphatic hydrocarbon moiety having from 1 to about 10 carbon atoms, n is 0, 1, or 2, L is a ligand that saturates the coordination sphere of zinc, and x is 0, 1, 2, 3, or 4. In certain embodiments, the ligand, L, is selected from the group consisting of water, hydroxide, ammonia, amino, amido, alkylthiolate, halide, and combinations thereof.

[0440] The anti-wear additives, such as ZDDP and/or the zinc carbamates, are typically used in amounts of from about 0.4 wt% to about 1.2 wt%, preferably from about 0.5 wt% to about 1.0 wt%, and more preferably from about 0.6 wt% to about 0.8 wt%, based on the total weight of the lubricating composition, although more or less can often be used advantageously. Preferably, the anti-wear additive is ZDDP, preferably a secondary ZDDP, and is present in an amount of from about 0.6 to 1.0 wt% of the total weight of the lubricating composition. In particular embodiments, the anti-wear agent(s) used in the lubricating oil composition and additive concentrates of the present invention comprises, in particular consists of ZDDP.

[0441] Anti-wear additives useful herein also include boron-containing compounds, such as borate esters, borated fatty amines, borated epoxides, alkali metal (or mixed alkali metal or alkaline earth metal) borates and borated overbased metal salts.

[0442] Compositions according to the present disclosure may contain an additive having a different enumerated function that also has secondary effects as an anti-wear agent (for example, Component B Functionalized Polymer described above, may also have anti-wear effects). These additives are not included as anti-wear agents for purposes of determining the amount of anti-wear agents in a lubricating oil composition or concentrate herein.

L. Demulsifiers

[0443] Demulsifiers useful herein include those described in US Patent No. 10,829,712 (col 20, ln 34-40). Typically, a small amount of a demulsifying component may be used herein. A preferred demulsifying component is described in European Patent No. 330 522. It is obtained by reacting an alkylene oxide with an adduct obtained by reacting a bis-epoxide with a polyhydric alcohol. Such additives may be used in an amount of about 0.001 to 5 wt%, preferably about 0.01 to 2 wt%.

M. Seal Compatibility Agents

[0444] Other optional additives include seal compatibility agents such as organic phosphates, aromatic esters, aromatic hydrocarbons, esters (butylbenzyl phthalate, for example), and polybutenyl succinic anhydride. Such additives may be used in an amount of about 0.001 to 5 wt%, preferably about 0.01 to 2 wt%. In embodiments, the seal compatibility agents are sea swell agents, such as PIBSA (polyisobutenyl succinic anhydride). In certain embodiments, PIBSA may be present in the lubricating oil compositions or additive concentrates of the present invention at 0.01 to 5 mass%, such as 0.02 to 3 mass%, such as 0.05 to 1 mass%, such as 0.1 to 0.5 mass% based upon the weight of the lubricating oil composition, and/or at 0.01 to 10 mass%, such as 0.05 to 5 mass%, such as 0.1 to 3 mass%, such as 0.5 to 1.5 mass% based upon the weight of the additive concentrate.

N. Extreme Pressure Agents

[0445] The lubricating oil composition of the present disclosure can contain one or more extreme pressure agents that can prevent sliding metal surfaces from seizing under conditions of extreme pressure. Any extreme pressure agent known by a person of ordinary skill in the art may be used in the lubricating oil composition. Generally, the extreme pressure agent is a compound that can combine chemically with a metal to form a surface film that prevents the welding of asperities in opposing metal surfaces under high loads. Non-limiting examples of suitable extreme pressure agents include sulfurized animal or vegetable fats or oils, sulfurized animal or vegetable fatty acid esters, fully or partially esterified esters of trivalent or pentavalent acids of phosphorus, sulfurized olefins, dihydrocarbyl polysulfides, sulfurized Diels-Alder adducts, sulfurized dicyclopentadiene, sulfurized or co-sulfurized mixtures of fatty acid esters and monounsaturated olefins, co-sulfurized blends of fatty acid, fatty acid ester and alpha-olefin, functionally substituted dihydrocarbyl polysulfides, thia-aldehydes, thia-ketones, epithio compounds, sulfur-containing acetal derivatives, co-sulfurized blends of terpene and acyclic olefins, and poly sulfide olefin products, amine salts of phosphoric acid esters or thiophosphoric acid esters, and combinations thereof. The amount of the extreme pressure 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.

O. Non-basestock Unsaturated Hydrocarbons

[0446] The lubricating oil composition of the present disclosure can contain one or more unsaturated hydrocarbons. These unsaturated hydrocarbons are distinct from any baseoils (lubricating oil basestocks of Group I, II, III, IV and/or V) and/or viscosity modifiers that may be present in the compositions and always have at least one (and typically only one, in the case of linear alpha-olefins, or LAOs) unsaturation per molecule. Without being bound by theory, the unsaturation(s) may provide an antioxidation functionality and/or a sulfur-trapping functionality that may supplement and/or replace one or more antioxidant additives and/or one or more corrosion inhibitor additives, but unsaturated hydrocarbons (LAOs) will typically not provide the only antioxidant nor the only corrosion inhibition functionality in lubrication oil compositions. Non-limiting examples of unsaturated hydrocarbons can include one or more unsaturated C_{12}-C_{60} hydrocarbons (such as C_{12}-C_{48} hydrocarbons, C_{12}-C_{36} hydrocarbons, C_{12}-C_{30} hydrocarbons, or C_{12}-C_{24} hydrocarbons). When only one unsaturation is present, the unsaturated hydrocarbons may be termed linear alpha-olefins (LAOs). Other non-limiting examples of unsaturated hydrocarbons can include oligomers/polymers of polyisobutylenes that have retained (or been post-polymerization modified to exhibit) a (near-) terminal unsaturation, and/or blends thereof. When present, unsaturated hydrocarbons (LAOs) may be present from 0.01 to 5 wt% (in particular, 0.1 to 3 mass%, alternately 0.1 to 1.5 mass%), based on total weight of the lubricating oil composition.

[0447] When lubricating oil compositions contain one or more of the additives discussed above, the additive(s) are typically blended into the composition in an amount sufficient for it to perform its intended function. Typical amounts of such additives useful in the present disclosure, especially for use in crankcase lubricants, are shown in the Table below.

[0448] It is noted that many of the additives are shipped from the additive manufacturer as a concentrate, containing one or more additives together, with a certain amount of base oil or other diluents. Accordingly, the weight amounts in the table below, as well as other amounts mentioned herein, are directed to the amount of active ingredient (that is the non-diluent portion of the ingredient). The weight percent (mass%) indicated below is based on the total weight of the lubricating oil composition.

Typical Amounts of Optional Lubricating Oil Components

[0449]

Additive Formulations	A (mass% a.i.)	B (mass% a.i.)	C (mass% a.i.)	D (mass% a.i.)
borated and or non-borated dispersant different from functionalized copolymer, such as PIBSA-PAM	0 -10	0 - 5	0 - 4	0.5 to 3
Detergents	0.1 - 20	0.1 - 10	0.2 - 9	0.5 to 2
Corrosion Inhibitor Anti-rust /	0 - 7	0.05 - 5	0.1 - 1.5	0 - 1
Antioxidant	0.01 - 10	0.1 - 5	0.1 - 4	0.5 to 3
Pour Point Depressant	optional	0 - 5	0.01 - 1.5	0.05 to 2
Anti-foaming Agent	optional	0 - 5	0.001 - 0.15	0.001 to 0.05
Functionalized Polymer	0.01 - 10	0.1 - 6	0.1 - 4	0.2 to 2
Friction Modifier	optional	0.1 to 10	0.2 to 0.5	0.05 - 0.4
Anti-wear Agent	0.01 - 10	0.1 - 5	0.1 - 3	0.1 to 1
Viscosity Modifier	optional	0 - 10	0.01 - 3	0.01 to 1
Seal Swell Agents	optional	0 - 5	0 - 2	0.01 to 1

(continued)

Additive Formulations	A (mass% a.i.)	B (mass% a.i.)	C (mass% a.i.)	D (mass% a.i.)
Unsaturated Hydrocarbons (LAOs)	optional	0 - 5	0 - 3	0 - 3
Basestock	Balance (such as 50 to 95 %)	Balance	Balance	Balance

[0450] The foregoing additives are typically commercially available materials. These additives may be added independently, but are usually pre-combined in packages, which can be obtained from suppliers of lubricant oil additives. Additive packages with a variety of ingredients, proportions and characteristics are available and selection of the appropriate package will take the use of the ultimate composition into account.

Fuels

[0451] This disclosure also relates to a method of lubricating an automotive internal combustion engine during operation of the engine comprising:

(i) providing to a crankcase of the automotive internal combustion engine the lubricating composition of described herein;
(ii) providing a hydrocarbon fuel in the automotive internal combustion engine; and
(iii) combusting the fuel in the automotive internal combustion engine, such as a spark-ignited or compression-ignited two- or four-stroke reciprocating engines such as a diesel engine or passenger car engine (such as a spark-ignited combustion engine).

[0452] This disclosure also relates to a fuel composition comprising the lubricating oil compositions described herein and a hydrocarbon fuel, wherein the fuel may be derived from petroleum and/or biological sources ("biofuel" or "renewable fuel"). In embodiments, the fuel comprises from 0.1 to 100 mass% renewable fuel, alternately from 1 to 75 mass% renewable fuel, alternately from 5 to 50 mass% renewable fuel, based upon the total mass of the from 1 to 50 mass% renewable fuel and the petroleum derived fuel.

[0453] The renewable fuel component is typically produced from vegetable oil (such as palm oil, rapeseed oil, soybean oil, jatropha oil), microbial oil (such as algae oil), animal fats (such as cooking oil, animal fat, and/or fish fat) and/or biogas. Renewable fuel refers to biofuel produced from biological resources formed through contemporary biological processes. In an embodiment, the renewable fuel component is produced by means of a hydrotreatment process. Hydrotreatment involves various reactions where molecular hydrogen reacts with other components, or the components undergo molecular conversions in the presence of molecular hydrogen and a solid catalyst. The reactions include, but are not limited to, hydrogenation, hydrodeoxygenation, hydrodesulfurization, hydrodenitrification, hydrodemetallization, hydrocracking, and isomerization. The renewable fuel component may have different distillation ranges, which provide the desired properties to the component, depending on the intended use.

Uses

[0454] The lubricating compositions of the disclosure may be used to lubricate mechanical engine components, particularly in internal combustion engines, *e.g.*, spark-ignited or compression-ignited, two- or four-stroke reciprocating engines, by adding the lubricant thereto. Typically, they are crankcase lubricants, such as passenger car motor oils or heavy-duty diesel engine lubricants.

[0455] In particular, the lubricating compositions of the present disclosure are suitably used in the lubrication of the crankcase of a compression-ignited, internal combustion engine, such as a heavy-duty diesel engine.

[0456] In particular, the lubricating compositions of the present disclosure are suitably used in the lubrication of the crankcase of a spark-ignited turbo charged internal combustion engine.

[0457] In embodiments, the lubricating oils of this disclosure are used in spark-assisted high compression internal combustion engines and, when used in high compression spark ignition internal combustion engines the lubricating oil compositions of this disclosure are useful in lubricating high compression spark ignition engines.

[0458] In embodiments, the lubricating compositions of the present disclosure are suitably used in the lubrication of the crankcase of an engine for a heavy-duty diesel vehicle (*i.e.,* a heavy-duty diesel vehicle having a gross vehicle weight rating of 10,000 pounds or more.)

[0459] In embodiments, the lubricating compositions of the present disclosure are suitably used in the lubrication of the crankcase of a passenger car diesel engine.

[0460] In particular, lubricating oil formulations of this disclosure are particularly useful in compression-ignited internal combustion engines, *i.e.,* heavy-duty diesel engines, employing low viscosity oils, such as API FA-4 and future oil categories, in which wear protection of the valve train becomes challenging.

[0461] This disclosure further relates to:

1. An **additive concentrate (or additive package)** comprising a dispersant mixture, the dispersant mixture comprising

    (1) 0.01-15 mass% based upon the total mass of the dispersant mixture, of an amide, imide, and/or ester functionalized partially or fully saturated polymer comprising C_{4-5} olefins having:

        i) an Mw/Mn of less than 2,
        ii) a Functionality Distribution (Fd) value of 3.5 or less, and
        iii) an Mn of 10,000 g/mol or more (GPC-PS) of the polymer prior to functionalization; and

    (2) 50-90 mass% based upon the total mass of the dispersant mixture, of one or more poly(alkenyl) succinimide(s), which is derived from a polyalkenyl-substituted succinic anhydride prepared using a chlorine-assisted alkylation process and a polyamine ("chloro dispersant(s)"); and
    (3) 10-30 mass% based upon the total mass of the dispersant mixture, of one or more poly(alkenyl)succinimide(s), which is derived from a polyalkenyl succinic anhydride prepared using a halogen-free thermal alkylation process and a polyamine ("thermal dispersant(s)").

2. The additive concentrate of paragraph 1, wherein the one or more thermal dispersant(s) is derived from a polyisobutylene succinic anhydride ("PIBSA") and a polyamine ("PAM").
3. The additive concentrate of paragraph 2, wherein the PIBSA is based upon a high terminal vinylidene content polyisobutylene (high reactive polyisobutylene, "HR-PIB").
4. The additive concentrate of paragraph 2 or 3, wherein the PIBSA is based upon a polyisobutylene having a Mn of at least 1200 g/mol, such as at least 1500 g/mol, such as at least 1800 g/mol, such as at least 2200 g/mol or at least 2300 g/mol.
5. The additive concentrate of the preceding paragraphs, wherein the one or more thermal dispersant(s) is PIBSA-PAM based upon a polyisobutylene having a Mn of about 2300 g/mol.
6. The additive concentrate of the preceding paragraphs, wherein the dispersant mixture comprises the functionalized polymer at 1-12 mass%, such as 5-11 mass%, such as 7.5-10.5 mass%, such as 8.5-10 mass% based upon the total mass of the dispersant mixture.
7. The additive concentrate of the preceding paragraphs, wherein the dispersant mixture comprises the one or more chloro dispersant(s) at 55-85 mass%, such as 62-82 mass%, such as 68-80 mass%, such as 70-76 mass% based upon the total mass of the dispersant mixture.
8. The additive concentrate of the preceding paragraphs, wherein the dispersant mixture comprises the one or more thermal dispersant(s) at 12-25 mass%, such as 14-22 mass%, such as 15-20 mass%, such as 15.5-17.5 mass% based upon the total mass of the dispersant mixture.
9. The additive concentrate of the preceding paragraphs, wherein the dispersant mixture comprises the one or more chloro dispersant(s) and the one or more thermal dispersant(s) at a ratio of about 9:1 to about 3:2, such as about 6:1 to about 3:1, such as about 5:1 to about 4:1.
10. The additive concentrate of the preceding paragraphs, wherein the dispersant mixture comprises the one or more chloro dispersant(s) and the one or more thermal dispersant(s) at a ratio of about 9:2.
11. The additive concentrate of the preceding paragraphs, wherein the functionalized polymer is an amide or imide functionalized partially or fully saturated homo-polyisoprene having:

    (i) an Mw/Mn of less than 1.8,
    (ii) a Functionality Distribution (Fd) value of 2.5 or less,
    (iii) an average functionality (Fv) of 4 to 10 functional group grafts/polymer chain, and
    (iv) an Mn of from 20,000 g/mol to 50,000 g/mol (GPC-PS) of the polymer prior to functionalization.

12. The additive concentrate of the preceding paragraphs, wherein the functionalized polymer is an amide or imide functionalized partially or fully saturated homo-polyisoprene having:

    (i) an Mw/Mn of less than 1.5,
    (ii) a Functionality Distribution (Fd) value of 2.1 or less,

(iii) an average functionality (Fv) of 6 to 8 functional group grafts/polymer chain, and
(iv) an Mn of from 30,000 g/mol to 40,000 g/mol (GPC-PS) of the polymer prior to functionalization.

13. The additive concentrate of any of the preceding paragraphs, wherein the functionalized polymer is an amide or imide functionalized partially or fully saturated homo-polyisoprene having:

(i) an Mw/Mn of about 1.2,
(ii) a Functionality Distribution (Fd) value of about 1.9,
(iii) an average functionality (Fv) of about 7 functional group grafts/polymer chain, and
(iv) an Mn of about 35,140 g/mol (GPC-PS) of the polymer prior to functionalization.

14. The additive concentrate of the preceding paragraphs, wherein the functionalized polymer is derived from a homo-polyisoprene that has been acylated with maleic anhydride or maleic acid and further reacted with an N-phenylphenylene diamine (NPPDA), such as 4-amino-diphenylamine (ADPA).
15. The additive concentrate of the preceding paragraphs, further comprising one or more antioxidant(s).
16. The additive concentrate of paragraph 15, wherein the one or more antioxidant(s) is at least one or more amine antioxidant(s).
17. The additive concentrate of paragraph 15 or 16, wherein the one or more antioxidant(s) is a mixture of one or more amine antioxidant(s) and one or more phenol antioxidant(s).
18. The additive concentrate of paragraphs 15-17, wherein the one or more amine antioxidant(s) and the one or more phenol antioxidant(s) are present at a ratio of about 5:2 to about 9:5, such as about 2:1.
19. The additive concentrate of the preceding paragraphs, comprising no or substantially no sulphurised methyl ester antioxidants, such as less than 2.5 mass%, such as less than 2.2 mass%, such as less than 1.5 mass%, such as less than 0.5 mass% based on the total mass of the additive concentrate.
20. The additive concentrate of the preceding paragraphs, wherein:

(a) the dispersant mixture is present at 15-40 mass%, such as 20-32 mass%, such as 25-30 mass% based upon the total mass of the additive concentrate; and
(b) one or more antioxidant(s) is optionally present at 5-25 mass%, such as 10-22 mass%, such as 14-20 mass% based upon the total mass of the additive concentrate.

21. The additive concentrate of the preceding paragraphs, further comprising one or more additional additive(s) selected from the group consisting of detergents, friction modifiers, anti-foam agents, corrosion inhibitors/anti-rust agents, and anti-wear agents.
22. The additive concentrate of the preceding paragraphs, further comprising one or more detergent(s) selected from the group consisting of oil-soluble neutral or overbased sulfonates and phenates of an alkali or alkaline earth metal.
23. The additive concentrate of the preceding paragraphs, further comprising one or more detergent(s) selected from the group consisting of oil-soluble neutral or overbased sulfonates of calcium or magnesium.
24. The additive concentrate of the preceding paragraphs, comprising no or substantially no phenate detergent, such as less than 1.2 mass%, such as less than 1.0 mass%, such as less than 0.5 mass% based on the total mass of the additive concentrate.
25. The additive concentrate of the preceding paragraphs, further comprising one or more detergent(s), wherein:
(c) the one or more detergent(s) is present at 0.1-5 mass%, such as 0.5-4 mass%, such as 1-3 mass% based upon the total mass of the additive concentrate.
26. The additive concentrate of the preceding paragraphs, further comprising one or more friction modifier(s), wherein:
(d) the one or more friction modifier(s) is present at 0.01-1 mass%, such as 0.02-0.5 mass%, such as 0.05-0.2 mass% based upon the total mass of the additive concentrate.
27. The additive concentrate of the preceding paragraphs, further comprising one or more anti foam agent(s), wherein:
(e) the one or more anti-foam agent(s) is present at 0.001-0.5 mass%, such as 0.01-0.1 mass%, such as 0.02-0.04 mass% based upon the total mass of the additive concentrate.
28. The additive concentrate of the preceding paragraphs, further comprising one or more corrosion inhibitor(s)/anti-rust agent(s) selected from the group consisting of liquid triazole derivatives, such as liquid triazole amines.
29. The additive concentrate of the preceding paragraphs, further comprising one or more corrosion inhibitor(s)/anti-rust agent(s), wherein:
(f) the one or more corrosion inhibitor(s)/anti-rust agent(s) is present at 0.01-2 mass%, such as 0.05-1.5 mass% such as 0.1-0.5 mass% based upon the total mass of the additive concentrate.

30. The additive concentrate of the preceding paragraphs, further comprising one or more anti-wear agent(s), wherein:
(g) the one or more anti-wear agent(s) is present at 0.1-5 mass%, such as 1-2.4 mass%, such as 1.5-2.2 mass% based upon the total mass of the additive concentrate.
31. **A lubricating oil composition** comprising or resulting from the admixing of:

(A) at least 50 mass% of one or more base oil(s), based upon the total mass of the lubricating oil composition; and
(B) an additive concentrate of the preceding paragraphs.

32. The lubricating oil composition of paragraph 31, wherein the one or more base oil(s) comprise one or more group III base oil(s) and optionally one or more group II base oil(s).
33. The lubricating oil composition of paragraph 31 or 32, wherein the one or more base oil(s) comprise a mixture of one or more group III base oil(s) and one or more group II base oil(s).
34. The lubricating oil composition of paragraphs 31-33, wherein the one or more group III base oil(s) and the one or more group II base oil(s) are present at a ratio of about 70:30 to about 30:70, such as about 65:35 to about 40:60, such as about 60:40 to about 45:55, such as about 55:45 to about 50:50.
35. The lubricating oil composition of paragraphs 31-34, comprising 50-95 mass%, such as 60-90 mass%, such as 65-85 mass% of one or more base oil(s) based upon the total mass of the lubricating oil composition.
36. The lubricating oil composition of paragraphs 31-35, comprising:

(A) (a) 25-65 mass%, such as 30-55 mass%, such as 34-48 mass% of one or more group III base oil(s) based upon the total mass of the lubricating oil composition; and
(b) 20-60 mass%, such as 28-48 mass%, such as 30-38 mass% of one or more group II base oil(s) based upon the total mass of the lubricating oil composition.

37. The lubricating oil composition of paragraphs 31-36, comprising:

(B) (a) 1-12 mass%, such as 3-10 mass%, such as 6-8 mass% of dispersant mixture based upon the total mass of the lubricating oil composition;
(b) optionally, 0.1-10 mass%, such as 3-8 mass%, such as 3.5-5 mass% of one or more antioxidants(s) based upon the total mass of the lubricating oil composition;
(c) optionally, 0.01-3 mass%, such as 0.1-1 mass%, such as 0.2-0.6 mass% of one or more detergent(s) based upon the total mass of the lubricating oil composition;
(d) optionally, 0.001-0.2 mass%, such as 0.01-0.06 mass%, such as 0.02-0.04 mass% of one or more friction modifier(s) based upon the total mass of the lubricating oil composition;
(e) optionally, 0.001-0.1 mass%, such as 0.003-0.03 mass%, such as 0.005-0.01 mass% of one or more anti-foam agent(s) based upon the total mass of the lubricating oil composition;
(f) optionally, 0.001-1 mass%, such as 0.01-0.5 mass%, such as 0.05-0.1 mass% of one or more corrosion inhibitor(s)/anti-rust agent(s) based upon the total mass of the lubricating oil composition;
(g) optionally, 0.01-1.5 mass%, such as 0.05-1 mass%, such as 0.06-0.6 mass% of one or more anti-wear agent(s) based upon the total mass of the lubricating oil composition.

38. The lubricating oil composition of paragraphs 31-37, further comprising:
(C) (a) 0.001-1 mass%, such as 0.01-0.5 mass%, such as 0.05-0.2 mass% of one or more pour point depressant(s) based upon the total mass of the lubricating oil composition.
39. The lubricating oil composition of paragraphs 31-38, further comprising:
(C) (b) 0.001-0.5 mass%, such as 0.05-0.3 mass%, such as 0.1-0.22 mass% of one or more viscosity modifier(s) based upon the total mass of the lubricating oil composition.
40. The lubricating oil composition of paragraph 39, wherein the one or more viscosity modifier(s) are selected from olefin copolymer viscosity modifiers.
41. The lubricating oil composition of paragraphs 31-40, comprising:

(A) (a) the one or more group III base oil(s) are present at 38-42 mass% of based upon the total mass of the lubricating oil composition;
(b) the one or more group II base oil(s) are present at 33-37 mass% of based upon the total mass of the lubricating oil composition;
(B) (a) (1) the functionalized polymer is present at 0.2-1 mass% based upon the total mass of the lubricating oil composition;

(2) the one or more chloro dispersant(s) are present at 4-6 mass% based upon the total mass of the lubricating oil composition;
(3) the one or more thermal dispersant(s) are present at 0.5-2 mass% based upon the total mass of the lubricating oil composition;
(b) the one or more antioxidants(s) are present at 3.5-5 mass% of based upon the total mass of the lubricating oil composition;
(c) the one or more detergent(s) are present at 0.2-0.6 mass% of based upon the total mass of the lubricating oil composition;
(d) the one or more friction modifier(s) are present at 0.02-0.04 mass% of based upon the total mass of the lubricating oil composition;
(e) the one or more anti-foam agent(s) are present at 0.005-0.01 mass% of based upon the total mass of the lubricating oil composition;
(f) the one or more corrosion inhibitor(s)/anti-rust agent(s) are present at 0.05-0.1 mass% of based upon the total mass of the lubricating oil composition;
(g) the one or more anti-wear agent(s) are present at 0.06-0.6 mass% of based upon the total mass of the lubricating oil composition;
(C) (a) the one or more pour point depressant(s) are present at 0.05-0.2 mass% of based upon the total mass of the lubricating oil composition; and
(b) the one or more viscosity modifier(s) are present at 0.1-0.22 mass% of based upon the total mass of the lubricating oil composition.

42. The lubricating oil composition of paragraphs 31-41, having a phosphorous content of less than 800 ppm, such as less than 550 ppm, such as less than 500 ppm, such as less than 490 ppm based upon the total mass of the lubricating oil composition.
43. The lubricating oil composition of paragraphs 31-42, having a sulfated ash ("SASH") content of less than 0.9 mass%, such as less than 0.6 mass%, such as less than 0.5 mass% based upon the total mass of the lubricating oil composition.
44. The lubricating oil composition of paragraphs 31-43, having a phosphorus content of less than or about 550 ppm and a SASH content of less than or about 0.5 mass%.
45. The lubricating oil composition of paragraph 31-44, exhibiting an SAE viscosity grade of 5W-X, where X represents any one of 8, 12, 16, 20, or 30.
46. The lubricating oil composition of paragraphs 31-45, exhibiting an SAE viscosity grade of 5W-30.
47. The lubricating oil composition of paragraph 31-46, wherein the lubricating oil composition is a heavy-duty diesel engine oil.
48. The lubricating oil composition of paragraphs 31-47, wherein the average piston cleanliness is at least 70 %, such as at least 75 %, such as at least 78 % as determined by CEC L-118-21.
49. The lubricating oil composition of paragraphs 31-48, wherein the average wear on gear train wheels is at least 75 %, such as at least 80 %, such as at least 82 % as determined by CEC L-118-21.
50. The lubricating oil composition of paragraphs 31-49, wherein the average liner wear is less than 8 μm, such as less than 5 μm, such as less than 3 μm as determined by CEC L-118-21.
51. The lubricating oil composition of paragraphs 31-50, wherein the average turbocharger housing deposits are at least 30 %, such as at least 45 %, such as at least 75 % as determined by CEC L-118-21.
52. The lubricating oil composition of paragraphs 31-47, wherein the oxidation is less than 65 A/cm, such as less than 60 A/cm, such as less than 55 A/cm as determined by CEC L-118-21.
53. A **method of lubricating an internal combustion engine** during operation of the engine comprising:

(i) providing to a crankcase of the internal combustion engine the lubricating composition of paragraphs 31-52;
(ii) providing a hydrocarbon fuel in the internal combustion engine; and
(iii) combusting the fuel in the internal combustion engine.

54. The method of paragraph 53, wherein the fuel is one or more of a hydrocarbon fuel, renewable fuel, hydrogen fuel, or any blend thereof.
55. The method of paragraph 53 or 54, wherein the fuel is a hydrocarbon fuel.
56. The method of paragraphs 53-55, wherein the engine is a diesel engine, such as a heavy-duty diesel engine.
57. A **fuel composition** comprising the lubricating composition of paragraphs 31-52 and one or more of hydrocarbon fuel, renewable fuel, hydrogen fuel, or any blend thereof.
58. A **method of increasing the piston cleanliness** of a lubricating oil composition, the method comprising including in the lubricating oil composition a dispersant mixture comprising

(1) 0.01-15 mass% based upon the total mass of the dispersant mixture, of an amide, imide, and/or ester functionalized partially or fully saturated polymer comprising C_{4-5} olefins having:

i) an Mw/Mn of less than 2,
ii) a Functionality Distribution (Fd) value of 3.5 or less, and
iii) an Mn of 10,000 g/mol or more (GPC-PS) of the polymer prior to functionalization; and

(2) 50-90 mass% based upon the total mass of the dispersant mixture, of one or more poly(alkenyl) succinimide(s), which is derived from a polyalkenyl-substituted succinic anhydride prepared using a chlorine-assisted alkylation process and a polyamine ("chloro dispersant(s)"); and

(3) 10-30 mass% based upon the total mass of the dispersant mixture, of one or more poly(alkenyl)succinimide(s), which is derived from a polyalkenyl succinic anhydride prepared using a halogen-free thermal alkylation process and a polyamine ("thermal dispersant(s)").

59. The method of paragraph 58, wherein the average piston cleanliness is increased to at least 70 %, such as at least 75 %, such as at least 78 % as determined by CEC L-118-21.
60. A **method of improving the wear resistance** of a lubricating oil composition, the method comprising including in the lubricating oil composition a dispersant mixture comprising

(1) 0.01-15 mass% based upon the total mass of the dispersant mixture, of an amide, imide, and/or ester functionalized partially or fully saturated polymer comprising C_{4-5} olefins having:

i) an Mw/Mn of less than 2,
ii) a Functionality Distribution (Fd) value of 3.5 or less, and
iii) an Mn of 10,000 g/mol or more (GPC-PS) of the polymer prior to functionalization; and

(2) 50-90 mass% based upon the total mass of the dispersant mixture, of one or more poly(alkenyl) succinimide(s), which is derived from a polyalkenyl-substituted succinic anhydride prepared using a chlorine-assisted alkylation process and a polyamine ("chloro dispersant(s)"); and

(3) 10-30 mass% based upon the total mass of the dispersant mixture, of one or more poly(alkenyl)succinimide(s), which is derived from a polyalkenyl succinic anhydride prepared using a halogen-free thermal alkylation process and a polyamine ("thermal dispersant(s)").

61. The method of paragraph 58, wherein the average wear on gear train wheels is increased to at least 75 %, such as at least 80 %, such as at least 82 % as determined by CEC L-118-21.
62. The method of paragraph 58 or 59, wherein the average liner wear is reduced to less than 8 μm, such as less than 5 μm, such as less than 3 μm as determined by CEC L-118-21.

[0462] This invention further relates to:

A1. An **additive concentrate (or additive package)** comprising a dispersant mixture, the dispersant mixture comprising

(1) 0.01-15 mass% based upon the total mass of the dispersant mixture, of an amide, imide, and/or ester functionalized partially or fully saturated polymer comprising C_{4-5} olefins having:

i) an Mw/Mn of less than 2,
ii) a Functionality Distribution (Fd) value of 3.5 or less, and
iii) an Mn of 10,000 g/mol or more (GPC-PS) of the polymer prior to functionalization; and

(2) 50-90 mass% based upon the total mass of the dispersant mixture, of one or more poly(alkenyl) succinimide(s), which is derived from a polyalkenyl-substituted succinic anhydride prepared using a chlorine-assisted alkylation process and a polyamine ("chloro dispersant(s)"); and
(3) 10-30 mass% based upon the total mass of the dispersant mixture, of one or more poly(alkenyl)succinimide(s), which is derived from a polyalkenyl succinic anhydride prepared using a halogen-free thermal alkylation process and a polyamine ("thermal dispersant(s)").

A2. The additive concentrate of paragraph A1, wherein the one or more thermal dispersant(s) is derived from a polyisobutylene succinic anhydride ("PIBSA") and a polyamine ("PAM"), wherein preferably the PIBSA is based upon a high terminal vinylidene content polyisobutylene (high reactive polyisobutylene, "HR-PIB"), and/or the PIBSA is based upon a polyisobutylene having a Mn of at least 1200 g/mol, such as at least 1500 g/mol, such as at least 1800 g/mol, such as at least 2200 g/mol or at least 2300 g/mol.

A3. The additive concentrate of paragraph A1 or A 2, wherein the dispersant mixture comprises the functionalized polymer at 1-12 mass%, such as 5-11 mass%, such as 7.5-10.5 mass%, such as 8.5-10 mass% based upon the total mass of the dispersant mixture, and/or wherein the dispersant mixture comprises the one or more chloro dispersant(s) at 55-85 mass%, such as 62-82 mass%, such as 68-80 mass%, such as 70-76 mass% based upon the total mass of the dispersant mixture, and/or wherein the dispersant mixture comprises the one or more thermal dispersant(s) at 12-25 mass%, such as 14-22 mass%, such as 15-20 mass%, such as 15.5-17.5 mass% based upon the total mass of the dispersant mixture.

A4. The additive concentrate of the preceding paragraphs A1 to A3, wherein the dispersant mixture comprises the one or more chloro dispersant(s) and the one or more thermal dispersant(s) at a ratio of about 9:1 to about 3:2, such as about 6:1 to about 3:1, such as about 5:1 to about 4:1, in particular at a ratio of about 9:2.

A5. The additive concentrate of the preceding paragraphsA1 to A4, further comprising one or more antioxidant(s), wherein preferably the one or more antioxidant(s) is at least one or more amine antioxidant(s), and wherein more preferably the one or more antioxidant(s) is a mixture of one or more amine antioxidant(s) and one or more phenol antioxidant(s), wherein in particular the one or more amine antioxidant(s) and the one or more phenol antioxidant(s) are present at a ratio of about 5:2 to about 9:5, such as about 2:1.

A6. The additive concentrate of the preceding paragraphs A1 to A5, wherein:

(a) the dispersant mixture is present at 15-40 mass%, such as 20-32 mass%, such as 25-30 mass% based upon the total mass of the additive concentrate; and
(b) one or more antioxidant(s) is optionally present at 5-25 mass%, such as 10-22 mass%, such as 14-20 mass% based upon the total mass of the additive concentrate.

A7. The additive concentrate of the preceding paragraphs A1 to A6, further comprising one or more additional additive(s) selected from the group consisting of detergents, friction modifiers, anti-foam agents, corrosion inhibitors/anti-rust agents (such as one or more triazole amine corrosion inhibitors), and anti-wear agents, in particular further comprising one or more detergent(s).

8. The additive concentrate of paragraph A7, wherein :

i.the one or more detergent(s) is present at 0.1-5 mass%, such as 0.5-4 mass%, such as 1-3 mass% based upon the total mass of the additive concentrate, and/or further comprising one or more friction modifier(s), wherein preferably:
ii. the one or more friction modifier(s) is present at 0.01-1 mass%, such as 0.02-0.5 mass%, such as 0.05-0.2 mass% based upon the total mass of the additive concentrate, and/or further comprising one or more anti foam agent(s), wherein preferably:
iii. the one or more anti-foam agent(s) is present at 0.001-0.5 mass%, such as 0.01-0.1 mass%, such as 0.02-0.04 mass% based upon the total mass of the additive concentrate, and/or further comprising one or more corrosion inhibitor(s)/anti-rust agent(s), wherein preferably:
iv. the one or more corrosion inhibitor(s)/anti-rust agent(s) is present at 0.01-2 mass%, such as 0.05-1.5 mass% such as 0.1-0.5 mass% based upon the total mass of the additive concentrate, and/or further comprising one or more anti-wear agent(s), wherein preferably:
v. the one or more anti-wear agent(s) is present at 0.1-5 mass%, such as 1-2.4 mass%, such as 1.5-2.2 mass% based upon the total mass of the additive concentrate.

A9. A **lubricating oil composition** comprising or resulting from the admixing of:

(A) at least 50 mass% of one or more base oil(s), based upon the total mass of the lubricating oil composition; and
(B) an additive concentrate of any of paragraphsA1 to A8.

A10. The lubricating oil composition of paragraph A9, wherein the one or more base oil(s) comprise one or more group III base oil(s) and optionally one or more group II base oil(s), preferably a mixture of one or more group III base oil(s) and one or more group II base oil(s), wherein in particular the one or more group III base oil(s) and the one or more group II base oil(s) are present at a ratio of about 70:30 to about 30:70, such as about 65:35 to about 40:60, such as about 60:40 to about 45:55, such as about 55:45 to about 50:50.

A11. The lubricating oil composition of paragraph A9 or A10, comprising 50-95 mass%, such as 60-90 mass%, such as 65-85 mass% of one or more base oil(s) based upon the total mass of the lubricating oil composition, and preferably comprising:

(A) (a) 25-65 mass%, such as 30-55 mass%, such as 34-48 mass% of one or more group III base oil(s) based upon the total mass of the lubricating oil composition; and
(b) 20-60 mass%, such as 28-48 mass%, such as 30-38 mass% of one or more group II base oil(s) based upon the total mass of the lubricating oil composition.

A12. The lubricating oil composition of paragraphs 9-11, comprising:

(B) (a) 1-12 mass%, such as 3-10 mass%, such as 6-8 mass% of dispersant mixture based upon the total mass of the lubricating oil composition;

(b) optionally, 0.1-10 mass%, such as 3-8 mass%, such as 3.5-5 mass% of one or more antioxidants(s) based upon the total mass of the lubricating oil composition;
(c) optionally, 0.01-3 mass%, such as 0.1-1 mass%, such as 0.2-0.6 mass% of one or more detergent(s) based upon the total mass of the lubricating oil composition;
(d) optionally, 0.001-0.2 mass%, such as 0.01-0.06 mass%, such as 0.02-0.04 mass% of one or more friction modifier(s) based upon the total mass of the lubricating oil composition;
(e) optionally, 0.001-0.1 mass%, such as 0.003-0.03 mass%, such as 0.005-0.01 mass% of one or more anti-foam agent(s) based upon the total mass of the lubricating oil composition;
(f) optionally, 0.001-1 mass%, such as 0.01-0.5 mass%, such as 0.05-0.1 mass% of one or more corrosion inhibitor(s)/anti-rust agent(s) based upon the total mass of the lubricating oil composition;
(g) optionally, 0.01-1.5 mass%, such as 0.05-1 mass%, such as 0.06-0.6 mass% of one or more anti-wear agent(s) based upon the total mass of the lubricating oil composition, and preferably further comprising:

(C) (a) 0.001-1 mass%, such as 0.01-0.5 mass%, such as 0.05-0.2 mass% of one or more pour point depressant(s) based upon the total mass of the lubricating oil composition, and/or
(b) 0.001-0.5 mass%, such as 0.05-0.3 mass%, such as 0.1-0.22 mass% of one or more viscosity modifier(s) based upon the total mass of the lubricating oil composition.

A13. The lubricating oil composition of paragraphs A9-A12, having a phosphorous content of less than 800 ppm, such as less than 550 ppm, such as less than 500 ppm, such as less than 490 ppm based upon the total mass of the lubricating oil composition, and/or having a sulfated ash ("SASH") content of less than 0.9 mass%, such as less than 0.6 mass%, such as less than 0.5 mass% based upon the total mass of the lubricating oil composition, in particular having a phosphorus content of less than or about 550 ppm and a SASH content of less than or about 0.5 mass%.
A14. The lubricating oil composition of paragraphs A9-A13, wherein the average piston cleanliness is at least 70 %, such as at least 75 %, such as at least 78 % as determined by CEC L-118-21, and/or wherein the average wear on gear train wheels is at least 75 %, such as at least 80 %, such as at least 82 % as determined by CEC L-118-21, and/or wherein the average liner wear is less than 8 μm, such as less than 5 μm, such as less than 3 μm as determined by CEC L-118-21, and/or wherein the average turbocharger housing deposits are at least 30 %, such as at least 45 %, such as at least 75 % as determined by CEC L-118-21, and/or wherein the oxidation is less than 65 A/cm, such as less than 60 A/cm, such as less than 55 A/cm as determined by CEC L-118-21.
A15. A **method of lubricating an internal combustion engine** during operation of the engine comprising:

(i) providing to a crankcase of the internal combustion engine the lubricating composition of paragraphs A9-A14;
(ii) providing a fuel in the internal combustion engine; and
(iii) combusting the fuel in the internal combustion engine,

wherein preferably the fuel is one or more of a hydrocarbon fuel (such as petroleum derived fuel, and or a renewable fuel), and or hydrogen fuel, or any blend thereof, in particular a hydrocarbon fuel, and/or the engine is a diesel engine, such as a heavy-duty diesel engine.
A16. A **fuel composition** comprising the lubricating composition of paragraphs A9-A14 and one or more of hydrocarbon fuel, hydrogen fuel, or any blend thereof (preferably the hydrocarbon fuel comprises a petroleum derived fuel and or a renewable fuel).
A17. A **method of increasing the piston cleanliness** of a lubricating oil composition,
the method comprising including in the lubricating oil composition a dispersant mixture comprising

(1) 0.01-15 mass% based upon the total mass of the dispersant mixture, of an amide, imide, and/or ester functionalized partially or fully saturated polymer comprising C_{4-5} olefins having:

i) an Mw/Mn of less than 2,
ii) a Functionality Distribution (Fd) value of 3.5 or less, and
iv) an Mn of 10,000 g/mol or more (GPC-PS) of the polymer prior to functionalization; and

(2) 50-90 mass% based upon the total mass of the dispersant mixture, of one or more poly(alkenyl) succinimide(s), which is derived from a polyalkenyl-substituted succinic anhydride prepared using a chlorine-assisted alkylation process and a polyamine ("chloro dispersant(s)"); and
(3) 10-30 mass% based upon the total mass of the dispersant mixture, of one or more poly(alkenyl)succinimide(s), which is derived from a polyalkenyl succinic anhydride prepared using a halogen-free thermal alkylation process and a polyamine ("thermal dispersant(s)"),

wherein preferably the average piston cleanliness is increased to at least 70 %, such as at least 75 %, such as at least 78 % as determined by CEC L-118-21.
A18. A **method of improving the wear resistance** of a lubricating oil composition, the method comprising including in the lubricating oil composition a dispersant mixture comprising

(1) 0.01-15 mass% based upon the total mass of the dispersant mixture, of an amide, imide, and/or ester functionalized partially or fully saturated polymer comprising C_{4-5} olefins having:

i) an Mw/Mn of less than 2,
ii) a Functionality Distribution (Fd) value of 3.5 or less, and
v) an Mn of 10,000 g/mol or more (GPC-PS) of the polymer prior to functionalization; and

(2) 50-90 mass% based upon the total mass of the dispersant mixture, of one or more poly(alkenyl) succinimide(s), which is derived from a polyalkenyl-substituted succinic anhydride prepared using a chlorine-assisted alkylation process and a polyamine ("chloro dispersant(s)"); and
(3) 10-30 mass% based upon the total mass of the dispersant mixture, of one or more poly(alkenyl)succinimide(s), which is derived from a polyalkenyl succinic anhydride prepared using a halogen-free thermal alkylation process and a polyamine ("thermal dispersant(s)"),

wherein preferably the average wear on gear train wheels is increased to at least 75 %, such as at least 80 %, such as at least 82 % as determined by CEC L-118-21, and/or the average liner wear is reduced to less than 8 μm, such as less than 5 μm, such as less than 3 μm as determined by CEC L-118-21.

[0463] The following non-limiting examples are provided to illustrate the disclosure.

Experimental

[0464] All molecular weights are number average molecular weights (Mn) reported in g/mol, as determined by gel permeation chromatography using polystyrene standards, unless otherwise noted. "A.I.", "ai", "a.i.", and "ai" are wt% active ingredient, unless otherwise indicated.

Testing Procedures

[0465] **Viscosity index** is measured according to ASTM D2270.
[0466] **High Temperature High Shear Viscosity,** ("**HTHS**" or "**HTHS150**") is determined at 150° C according to ASTM D4683 and is reported in cPs.
[0467] **KV100** is Kinematic viscosity measured at 100° C according to ASTM D445-19a.
[0468] **Cold Cranking Simulator** ("**CCS**"), at -25° C unless otherwise indicated, is a measure of the cold-cranking characteristics of crankcase lubricants and is determined as described in ASTM D5293-92.
[0469] **Noack volatility** ("**Noack**") is determined by the Noack test (ASTM D5800, procedure B).
[0470] **Phosphorus** content is measured by ASTM D4951.
[0471] **Sulfated ash** ("**SASH**") content is measured by ASTM D874.
[0472] **Mack T11 Test** for Soot-Induced Viscosity Control, ASTM D7156-19 was conducted in a Mack E-TECH V-MAC III diesel engine with exhaust gas recirculation. Two, 30-minute oil flushes, followed by 252 hours at constant speed 1800

rpm. The fuel injection timing was adjusted to targets of soot level (thermos-gravimetric analysis (TGA), ASTM D5967) at 96 hours, 192 hours, and 228 hours, specifically a TGA soot level of 2.75 % +/- 0.25 % at 96 h, 5.50 % +/- 0.35 % at 192 h, and 6.53 % +/- 0.44 % at 228 h. Oil samples were taken every 12 hours to measure the soot level (TGA, ASTM D5967) and the kinematic viscosity at 100° C. The performance of the oil was determined by comparing the soot level at which a specified viscosity increase (4 cSt, 12 cSt and 15 cSt) is observed. Also, oil consumption was measured.

[0473] **Caterpillar 1N Test** for Piston Deposits was performed according to ASTM D6750-19. Oil consumption was also measured. The test was conducted in a single cylinder Caterpillar 1Y540 diesel engine (The engine was run under conditions detailed in Table A14.1 in ASTM D6750-19 for a 60-minute break-in period followed by 252 hours of test conditions). The piston was then removed and rated according to the procedures outlined in ASTM Deposit Rating Manual 20. Note that ASTM D6750 covers both the 1K procedure with 0.4% Fuel Sulfur and the 1N procedure with 0.04% Fuel Sulfur.

[0474] **Cummins ISM Engine Test.** Valve train wear protection was determined according to the Cummins ISM engine test, ASTM D7468-21 in a 10.8L 6-cyl diesel engine equipped with exhaust gas recirculation. The Cummins ISB test covers a heavy-duty diesel engine test procedure conducted under high soot conditions to evaluate oil performance with regard to valve train wear, top ring wear, sludge deposits, and oil filter plugging. The engine is operated for 200 hours in four 50 hours stages. Stages A and B test conditions operate at 1800 RPM at rated power with retarded fuel injection timing to generate soot, and stages B and D test conditions operate at 1600 RPM at peak torque to promote and evaluate wear to the injector adjusting screws, crossheads, and top piston ring. Oil performance was assessed by evaluating injector adjusting screw, crosshead, top ring wear, oil filter plugging, oil pan and valve cover sludge formation. These parameters are combined to establish a total merit result in accordance with ASTM D7468.

[0475] **Cummins ISB Engine Test.** Valve train wear protection was determined according to the Cummins ISB engine test, ASTM D7484-21 in a 5.9L 6-cyl diesel engine equipped with exhaust gas recirculation. The Cummins ISB test is a two-stage test. Stage A, for 100 hours, the engine was operated with retarded fuel-injection timing to generate excess soot according to the ASTM Protocol. During Stage B, for 250 hours, the engine was operated at cyclic conditions according to the ASTM Protocol to induce valve-train wear. Oil performance was determined by assessing crosshead weight loss (mg) measured as detailed in Section 8.1.5 in ASTM D7484-21, tappet weight loss (mg) measured as detailed in section 8.1.6 in ASTM D7484-21, and camshaft wear (μm) averaged over the 12 lobes measured with a Mitutoyo Snap Gauge and Mitutoyo Digital Indicator as detailed in Section 8.1.7 in ASTM D7484-21.

[0476] **Daimler OM471 FE1 Performance Test** was performed according to CEC L-118-21 at APL (Oil D, Oil E and Comparative Oil B 1) or ISP (Oil F) in Germany under this Daimler/Mercedes-Benz In-House test method. The OM471 is a EURO VI, 12.8L 6-cyl engine developing 375 kilowatts peak power and 2500 Newton meters peak torque. The test is designed to test the performance of lubricating oils against piston deposits. It is an extensive (over 600 hours) HDD engine test required to meet various OEM and Industry specification including DTFR 15C130. At the end of the test, there are several key test parameters that need to meet the limits set by Daimler in order to pass the test including: sludge in oil mist separator ($\geq$ 95 %), piston cleanliness, grooves (average $\geq$74 %), liner wear (average $\leq$8 μm), turbocharger housing deposits (average $\geq$30 %), wear on gear train wheels (single $\geq$70 %, average $\geq$75 %), oxidation ($\leq$ 65 A/cm μm), and specific oil consumption ($\leq$8 g/h).

[0477] The moments of **molecular weight** (**Mw**, **Mn, Mz**) were determined by Gel Permeation Chromatography ("GPC-PS") using polystyrene standards (Acquity™ APC Polystyrene High MW Calibration Kit, 266-1,760,000 Da) and the software provided by the vendor (Empower™ 3, version 7.41.00.00) as follows.

Molecular weights [number average molecular weight (Mn), weight average molecular weight (Mw), and z-average molecular weight (Mz)] are determined using an Agilent Acuity P-SM-FTN and P-15m high temperature GPC-SEC (gel permeation/size exclusion chromatograph) equipped with an on-line differential refractive index (DRI) detector and a PDA UV detector for 215,254 and 304 wavelengths. The GPC uses 3 Agilent PLgel 10 micron Mixed B LS columns. The column separation is performed using a flow rate of 0.25mL/min and a nominal injection volume of 10 microliters. The detectors and columns are maintained at 30° C when in low flow mode(idle) and heated up to 35° C when preparing to run samples. The stream emerging from the SEC columns is directed into the optical flow cell and then into the DRI detector. Solvent for the SEC experiment is un-inhibited THF(tetrahydrofuran). Polymer solutions are prepared by placing dry polymer in a glass container, adding the desired amount of THF. Once the sample is added to machine it is given time to reach 35° C before the run begins. The GPC runs a pre-run programmed equilibrium of approx 1.5 hours. Samples are agitated for 2 to 15 hours depending on solubility. Samples are filtered after the agitation and before being run. All quantities are measured gravimetrically. The THF densities used to express the polymer concentration in mass/volume units are 0.887 g/mL at 68° C. The injection sample concentration is 3 mg/mL. Prior to running each sample, the DRI detector and the injector are purged. Flow rate in the apparatus is then increased from 0.01 to 0.25 mL/minute, and the DRI is allowed to stabilize for 4 to 5 hours before injecting the first sample. Software used to run the GPC and prepare reports is Empower™ 3, version 7.41.00.00.

[0478] "FG" means functional group.

[0479] **Average functionality** [also referred to as Average Functionality Value (**Fv**)] and **Functionality Distribution**

(**Fd**) value are determined as follows.

[0480] A simplified non-polymeric material bearing the ADPA-imide functional group (ODSA-ADPA) was prepared according to the procedure below; and subsequently used as a reference material and calibrant for the functional group GPC analysis described further below.

[0481] 268 g of octadecenylsuccinic anhydride (mixture of isomers, 0.094 mol) was added to a four-necked, round-bottom flask, equipped with an air-powered stirrer, a thermocouple connected to temperature controller and electric heating mantle, and a nitrogen inlet. The material was heated to 170° C with constant stirring and under a continuous nitrogen sweep through the reactor headspace.

[0482] 17.2 g of 4-aminodiphenylamine (ADPA, 0.094 mol) was added portionwise to the hot reaction mixture, allowing time for any foaming to subside as the amine addition continued. The mixture was heated until the reaction was determined to be complete by FTIR analysis of the anhydride and imide peaks at ca. 1780 and 1700 cm-1, respectively (the anhydride peak was completely consumed, and the imide peak no longer increasing - approx. 2-3h). The material was allowed to partially cool (below 100° C) before being drained out of the reactor. It was used directly as the GPC calibrant without further purification.

[0483] A GPC calibration curve (shown as Figure 1 of USSN 18/480,571 filed October 4, 2023 claiming priority to USSN 63/379,006, filed October 11, 2022) was prepared from ODSA-ADPA samples at 0.01, 0.02, 0.03, 0.04, and 0.05 mg/ml, according to the GPC procedure described above, and integrated in the UV 304 nm channel.

[0484] Samples of the functional polymer were prepared and submitted for GPC analysis as described above. The chromatogram was integrated by drawing a flat baseline across the base of each of the peaks, in line with the solvent baseline. When the chromatogram peaks were not resolved to the baseline (baseline indicated by triangle in Figure 2 abscissa), a vertical cut was made at the minimum point between them (shown as the diamond in Figure 2 abscissa in USSN 18/480,571 filed October 4, 2023 claiming priority to USSN 63/379,006, filed October 11, 2022). The minimum point is the inflection point in the GPC trace where the second derivative of the curve changes in sign (*e.g.*, from negative to positive or vice versa). For the purposes of the Average Functionality Value (Fv) and Functionality Distribution (Fd) calculations, any chain-coupled and chain-fragmented polymer resolved from the main polymer peak should be included in all calculations (Mn, Mw, PDI (Mw/Mn), and any subsequent calculations) as part of the main peak. A representative chromatogram for GPC analysis is shown as Figure 2 of USSN 18/480,571 filed October 4, 2023 claiming priority to USSN 63/379,006, filed October 11, 2022.

[0485] The Average Functionality Value (Fv) of the sample is defined as the average number of functional groups per polymer chain across the entire sample and is calculated via Eq 1:

$$Fv = \frac{moles_{amine\,FG}}{moles_{polymer}} = \frac{(UV304\ int_{total})}{(FG\ cal\ slope)} * \frac{Mn}{(poly\ mg/ml)} \qquad (1)$$

where,

Fv = the average functionality in units of FG grafts/polymer chain calculated across the total sample,
UV304 int_{total} = the total polymer peak integration in the UV304 channel,
FG Cal Slope = the slope of the UV304 calibration curve from ODSA-ADPA,
Mn = the polymer peak number average molecular weight (using polystyrene standard), and
Poly mg/ml = the concentration of polymer (excluding functional groups) in the total sample in units of mg/ml, measured gravimetrically during sample preparation.

[0486] The Functionality Distribution (Fd) value represents the range of functionalities across the MW distribution in the sample (*i.e.,* the difference in functionality between high MW and low MW fractions in the sample). Fd is calculated via eq. 2:

$$Fd = PDI * \frac{F_{max} - F_{min}}{Fv} \qquad (2)$$

where,

PDI = polydispersity index of the total polymer peak, calculated from Mn/Mw,
Fmax = the maximum functionality value between the 10th and 90th cumulative percentile (by RI) of the polymer peak,
F_{min} = the minimum functionality value between the 10th and 90th cumulative percentile (by RI) of the polymer peak, and
Fv = Average Functionality Value for the entire sample.

[0487] To calculate the individual functionalities across the sample, a detailed GPC slice report (exported with equal time in each slice, approx. 0.003 minutes per slice) containing data for slice retention time, MW, slice area, and cumulative % was exported for the polymer peak in both the refractive index (RI) and UV304 channel chromatograms.

[0488] The exported data for both channels were aligned at the same retention time, then offset by 6.0 seconds based on the measured retention time difference between the RI and UV detectors (i.e., the time it takes for the material to travel from one detector to the other - this was determined by the retention time (RT) difference for polystyrene (PS) peaks in the calibration curve).

[0489] To verify the exported slice data matches the original data sufficiently, the sum of peak slice areas should be within ± 5 % of the total integrated peak area for both the RI and UV304 channel polymer peaks.

[0490] The polymer concentration in each slice of the RI channel data was determined by equation 3: (the functional polymer dn/dc doesn't need to be known, but it is assumed assumption here that dn/dc does not change with MW.)

$$poly\ mol/L_{slice} = \frac{poly\ mg/ml * \frac{RI\ int_{slice}}{RI\ int_{total}}}{Mn_{slice}} \qquad (3)$$

where,

Poly mol/L_{slice} = the concentration of polymer (excluding functional groups) in units of mol/L calculated to be in a single MW slice of the RI chromatogram,
Poly mg/ml = the concentration of polymer (excluding functional groups) in units of mg/ml in the total sample, measured gravimetrically during sample preparation,
RI int_{slice} = the integration area of an individual slice in the RI chromatogram,
RI int_{total} = the total polymer peak integration in the RI chromatogram, and
Mn_{slice} = the MW of the polymer peak slice in the RI chromatogram.

[0491] The amine concentration in each slice of the UV304 channel data was determined via equation 4:

$$Amine\ FG\ mol/L_{slice} = \frac{UV304\ int_{slice}}{FG\ cal\ slope} \qquad (4)$$

where,

Amine FG mo/L_{slice} = the concentration of amine functional groups in units of mol/L calculated to be in a single slice of the UV 304 chromatogram,
UV304 int_{slice} = the integration area of an individual slice in the UV304 chromatogram, and FG Cal Slope = the slope of the UV304 calibration curve from ODSA-ADPA.

[0492] From the polymer and amine FG slice concentrations calculated above, the functionality of the individual chromatogram slices can be calculated according to equation 5:

$$F_{slice} = \frac{amine\ FG\ mol/L_{slice}}{poly\ mol/L_{slice}} \qquad (5)$$

where,

F_{slice} = the functionality in units of FG grafts/polymer chain calculated for an individual slice of the RI/UV304 chromatograms,
Poly mol/L_{slice} = the concentration of polymer (excluding functional groups) in units of mol/L calculated to be in a single MW slice of the RI chromatogram, and
Amine FG mo/L_{slice} = the concentration of amine functional groups in units of mol/L calculated to be in a single slice of the UV 304 chromatogram.

[0493] The calculations are completed for each slice of the exported chromatograms. The maximum and minimum functionality values between the 10th and 90th cumulative percentile of the polymer peak are selected as Fmax and Fmin, respectively, and used to calculate Fd as described above.

Materials

[0494] F-H-PI is 7.0-F-H-Polyisoprene-A. Amine functionalized hydrogenated isoprene polymer having an average functionality (Fv) of 7.0 was prepared using SA-H-Polyisoprene-A (succinate functionality of 7.0) by adding one equivalent of amine (4-amino-diphenylamine, ADPA) per succinate unit (as determined by SAP, ASTM D94) at 170° C under nitrogen. The reaction is allowed to continue and heat soak for up to two hours, after which it is diluted with additional oil (Group III, 4 cSt (Yubase™ 4) and allowed to cool to ambient temperature. During cooling the material is combined with ethoxylated alcohol (such as Berol™ 1214 or Surfonic™ L24-4, Huntsman) at 10 wt % of reaction mixture. The 7.15-F-H-Polyisoprene-A had a Functionality Distribution (Fd) value of 1.76, an Mw/Mn of 1.239, an Mn of 31629 g/mol, an Mz of 47835 g/mol, and was used as a blend in oil with an ai of 0.5 wt %, unless otherwise indicated.

[0495] PIB is polyisobutylene.

[0496] PIBSA is polyisobutylene succinic anhydride.

[0497] PIBSA-PAM is polyisobutylene succinic anhydride - polyalkylene amine.

Component Chart

[0498]

Lubricating Oil Components	Description
F-H-PI (1)/(2) PF2024L001/EP	Functionalised hydrogenated polyisoprene in oil, ai -27.7 (1) or ai ~40 (2), having an Fv of about 7, an Fd of about 1.9, an Mw/Mn of about 1.2 and an Mn of about 35,140 g/mol (GPC-PS) produced according to methods similar to those described inlJSSN 18/480,571 filed October 4, 2023 and claiming priority to USSN 63/379,006, filed Oct 11, 2022
Borated PIBSA-PAM	Polyisobutylene succinimide having 1 to 3 mass % boron, based upon a PIB having an Mn of about 950 g/mol in oil, ai -50
PIBSA-PAM 950 Mn	Polyisobutylene succinimide based upon a PIB having an Mn of about 950 g/mol in oil, ai -55
PIBSA-PAM 2200 Mn	Polyisobutylene succinimide based upon a PIB having an Mn of about 2200 g/mol in oil
PIBSA-ester	PIBSA ester of hydrocarbyl-bridged naphthyloxy alcohol in oil, ai ~40, prepared in a manner similar to Example 1 of U.S. 2009/0203559
HR-PIBSA-PAM	Polyisobutylene succinimide based upon a highly reactive PIB (HR_PIB) having an Mn of about 2300 g/mol in oil, ai ~54
Calcium sulfonate	Calcium sulfonate detergent having a TBN of approximately 300 mgKOH/g (on an as diluted basis) in oil, ai -55
Magnesium sulfonate	Magnesium sulfonate detergent having a TBN of approximately 400 mgKOH/g (on an as diluted basis) in oil, ai ~57
Magnesium salicylate/sulfonate	Magnesium salicylate/sulfonate detergent combination having a TBN of approximately 350 mgKOH/g (on an as diluted basis) in oil
Calcium phenate	Calcium phenate detergent having a TBN of approximately 150 mgKOH/g (on an as diluted basis) in oil, ai -55
ZDDP	Zinc dialkyl dithiophosphate in oil, where the alkyl groups are derived from a mixture of 1° and 2° alcohols, ai -75
Mo Friction modifier	Trimeric Mo dialkyldithiocarbamate compound in oil, ~45 ai
DPA antioxidant	Alkylated diphenylamine antioxidant
Phenol antioxidant	Hindered phenol antioxidant
Sulphurised alkyl methyl ester	Sulphurised rapeseed methyl ester
Corrosion inhibitor	N,N-bis(2-ethylhexyl)-((1,2,4)-triazol-1-yl)methyl)amine
Anti-foamant	Polydimethylsiloxane

(continued)

Lubricating Oil Components	**Description**
PIBSA	Polyisobutylene succinate having an Mn of about 950 g/mol in oil, ai ~72
PIB	Polyisobutylene having an Mn of about 950 g/mol
Diluent (1)/(2)	Group I base oil diluent
Lube oil flow improver (LOFI)	C_{12-18} dialkylfumarate/vinyl acetate copolymer, ai ~50, available as Infineum V387™ from Infineum USA LP, Linden NJ, USA
Viscosity modifier (1)	Semi-crystalline olefin copolymer viscosity modifier, 20 SSI
Viscosity modifier (2)	Olefin copolymer viscosity modifier, 24 SSI, in group II base oil available as Oronite Paratone® 24EX from Chevron Oronite, San Ramon CA, USA, ai ~10.2
Group II 4.5 cSt base oil	Lubricating oil basestock having a KV_{100} of about 4.4-4.7 cSt available as ExxonMobil EHC™ 45 from ExxonMobil Lubricants & Petroleum Specialties Company, Spring TX, USA
Group II 5.0 cSt base oil	Lubricating oil basestock having a KV_{100} of about 5.2-5.6 cSt available as ExxonMobil EHC™ 65 from ExxonMobil Lubricants & Petroleum Specialties Company, Spring TX, USA
Group II 6.5 cSt base oil	Lubricating oil basestock having a KV_{100} of about 6.3-6.6 cSt available as ExxonMobil EHC™ 65 from ExxonMobil Lubricants & Petroleum Specialties Company, Spring TX, USA
Group II 11.0 cSt base oil	Lubricating oil basestock having a KV_{100} of about 10.0-11.0 cSt available as ExxonMobil EHC™ 65 from ExxonMobil Lubricants & Petroleum Specialties Company, Spring TX, USA
Group III 4 cSt base oil	Lubricating gas-to-liquids oil basestock having a a KV_{100} of about 4 cSt available as Qatar GTL QHVI 4 from Shell, London, UK
Group III 8 cSt base oil	Lubricating gas-to-liquids oil basestock having a KV_{100} of about 8 cSt available as Qatar GTL QHVI 8 from Shell London, UK

[0499] In the following tables of the Examples, the amounts indicated for the individual materials refer to the amounts of the *components* (which contain a certain amount of active ingredient in oil, as indicated in the Component Chart above). For example, the component F-H-PI has an active ingredient (a.i.) content of about 27.7 wt%, the remainder of the component being diluent oil (see the Component Chart above). This means for example that the *active ingredient content* of the functionalized polymer in Oil F (see TABLE 2.1 below, indicating a content of 2.150 mass% of the F-H-PI *component*) is 0.596 mass% (i.e., 2.150 mass% × 0.277). Likewise, the *active ingredient content* of the thermal dispersant in Oil F (indicating a content of 2 mass% of the HR-PIBS-PAM *component*) is 1.08 mass% (i.e., 2 mass% × 0.54) and the *active ingredient content* of the chloro dispersants in Oil F (indicating a content of 2 mass% of the borated PIBSA-PAM *component,* a content of 3 mass% of the PIBSA-PAM 950 Mn *component* and a content of 4 mass% of the PIBSA-PAM 2200 Mn *component*) is 4.85 mass% (i.e., 2 mass% × 0.5 + (3 + 4 mass%) × 0.55). In this OIL F, the *ratio* of the chloro dispersants to the thermal dispersant is thus 4.85/1.08 = 4.49. The ratio of the chloro dispersants to the thermal dispersant of the other oils can be calculated analogously, based on the mass% of the respective components indicated in the example tables below and using the active ingredient content (%) as indicated for the respective component in the Component Chart above.

Examples

Example 1: Pre-Tests.

[0500] Oil A, Comparative Oils B1 and B2, and Comparative Oils C1 to C4 were prepared as indicated in Table 1.1 below.

TABLE 1.1

	Oil A mass %	**Comparative Oil B1/B2** mass %	**Comparative Oil C1/C2 and C3/C4** mass %	
Component				
F-H-PI (2)	---	1.560	---	---

(continued)

	Oil A mass %	**Comparative Oil B1/B2** mass %	**Comparative Oil C1/C2 and C3/C4** mass %	
Component				
F-H-PI (1)	2.540	---	---	---
Borated PIBSA-PAM	2.000	0.500	0.500	0.500
PIBSA-PAM 950 Mn	3.000	4.000	---	---
PIBSA-PAM 2200 Mn	4.000	4.000	8.500	8.500
PIBSA-ester	---	1: 0.500 2: 0.300	1: 1.560 2: 1.400	3:1.365 4: 1.300
HR-PIBSA-PAM	2.000	---	---	---
Calcium sulfonate	0.550	0.333	1.320	1.320
Magnesium sulfonate	0.460	0.475	---	---
Magnesium salicylate/sulfonate	---	---	0.640	0.640
Calcium phenate	---	0.447	0.150	0.150
ZDDP	0.640	0.640	1.000	1.000
Mo Friction modifier	0.060	0.120	0.075	0.075
DPA antioxidant	2.600	1: 2.000 2: 1.700	0.250	0.250
Phenol antioxidant	---	---	2.500	2.500
Sulphurised alkyl methyl ester	0.420	0.530	---	---
Corrosion inhibitor	0.100	0.100	---	---
Anti-foamant	0.008	0.008	0.007	0.007
PIBSA	0.300	0.300	0.100	0.100
PIB	1.300	1.600	0.150	0.150
Diluent (1)	2.724	2.062	---	---
Diluent (2)	---	---	2.108	2.108
Lube oil flow improver (LOFI)	0.200	0.200	0.300	0.300
Viscosity modifier (2)	2.000	1: 1.500 2: 1.305	3.500	1.200
Group II 4.5 cSt base oil	---	1: 59.125 2: 55.000	---	59.900
Group II 5.0 cSt base oil	---	---	1: 26.840 2: 26.900	---
Group II 6.5 cSt base oil	---	1: 20.000 2: 24.820	-	3: 19.935 4: 20.000
Group II 11.0 cSt base oil	---	---	1: 50.500 2: 50.600	---
Group III 4 cSt base oil	60.098	---	---	---
Group III 8 cSt base oil	15.000	---	---	---

(continued)

Property				
SAE viscosity grade	5W-30	10W-30	15W-40	10W-30
HTHS150 (cP)	3.15	1: 3.13 2: 3.10	1: 4.1 2: 4.13	3: 3.07 4: 3.06
KV_{100}	10.34	1: 9.76 2: 9.96	1: 13.98 2: 14.19	3: 9.51 4: 9.54
CCS at -30 °C	5164	1: 5438 2: 5770	1: 6320 2: 6564	3: 5121 4: 4900
NOACK	9.8	1: 11.7 2: 10.8	1: 12 2: 11.52	3: 12 4: 12.04
Phosphorus ppm	500	1: 494 2: 500	800	800
SASH mass %	0.52	1: 0.52 2: 0.5	1: 0.93 2: 0.9	3: 0.94 4: 0.9

[0501] Oil A is characterized by comprising a dispersant mixture comprising about 10.5 mass% of functionalized polymer, about 73 mass% of chloro dispersants and about 16.5 mass% of thermal dispersant, while Comparative Oils B1 and B2 comprise no thermal dispersant, and Comparative Oils C1 to C4 comprise chloro dispersants only.

[0502] Further, the content of detergents and ZDDP is reduced in Oil A and Comparative Oils B1 and B2 compared to Comparative Oils C1 to C4, thus enabling Oil A and Comparative Oils B1 and B2 to contain only about 500 ppm phosphorus and only about 0.5 mass% SASH, in contrast to about 800 ppm phosphorus and about 0.9 mass% SASH in Comparative oils C1 to C4.

(1) Mack T11 Test for Soot-Induced Viscosity Control.

[0503] Oil A and Comparative Oil C1 were tested for soot-induced viscosity according to the Mack T-11 engine test described above. The data are reported in Table 1.2 below.

[0504] An oil with better soot dispersancy would be able to hold a higher level of soot at the specified viscosity increase. At all three specified viscosity increase levels (4 cSt, 12 cSt and 15 cSt), Oil A, containing the dispersant mixture according to the invention and thus functionalized polymer and thermal dispersant in addition to chloro dispersants, can hold more soot, indicating it has surprisingly better soot dispersancy.

TABLE 1.2

	Oil A mass %	**Comparative Oil C1** mass %
Mack T11 Test Results		
Soot at 4 cSt Viscosity Increase (%)	7.07	5.15
Soot at 12 cSt Viscosity Increase (%)	>7.33	5.94
Soot at 15 cSt Viscosity Increase (%)	>7.76	6.45

(2) Caterpillar 1N Test for Piston Deposits.

[0505] Oil A and Comparative Oil C2 were tested for tendency to form piston and ring groove deposits in the Caterpillar 1N engine test described above using the 1N procedure with 0.04% Fuel Sulfur. The piston ratings at the end of each test and oil consumption are given in Table 1.3 below.

[0506] This test quantifies Weighted Total Demerits (WDN) which encompasses piston deposits, ring sticking, ring and cylinder wear, piston, ring and liner scuffing. Higher numbers indicate more severe deposits. Comparative Oil C2, containing no functionalized polymer and no thermal dispersant, performs worse than Oil A, containing the dispersant mixture according to the invention. TGH and TLHC values demonstrate almost similar performance, however the overall cleanliness outlined by the WDN values shows a difference in performance due tot he distinct dispersant system when comparting Oil A to Comparative Oil C2.

TABLE 1.3

	Oil A mass %	**Comparative Oil C2** mass %
Caterpillar 1N Test Results		
Weighted Demerits number (WDN)	237.2	246.5
Top Groove Fill (%)	13	13
Top Land Heavy Carbon (%)	1	0

(3) Cummins ISM Engine Test for Valve Train Wear Protection.

[0507] Comparative Oil B1 and Comparative Oil C3 were tested for valve train wear protection according to the Cummins ISM engine test described above. The data are reported in Table 1.4 below.

[0508] Comparative Oil B1, containing the functionalized polymer, demonstrates a distinct and surprising improvement over Comparative Oil C3, which represents a conventional HDD formulation with 800 ppm phosphorous and 0.9 mass% SASH, in the Cummins ISM engine test in all the measurements.

TABLE 1.4

	Comparative Oil B1 mass %	**Comparative Oil C3** mass %
Cummins ISM Engine Test Results		
Top Ring Mass Loss (mg)	19.40	71.60
Total Merits	1908.60	1766.40

(4) Cummins ISB Engine Test for Valve Train Wear Protection.

[0509] Comparative Oil B2 and Comparative Oil C4 were tested for valve train wear protection according to the Cummins ISB engine test described above. The data are reported in Table 1.5 below.

[0510] Comparative Oil B2, containing the functionalized polymer, demonstrates a distinct and surprising improvement over Comparative Oil C4, which represents a conventional HDD formulation with 800 ppm phosphorous and 0.9 mass% SASH, in the Cummins ISB engine test in all the wear measurements, particularly in the parameter for camshaft wear.

TABLE 1.5

	Comparative Oil B2 mass %	**Comparative Oil C4** mass %
Cummins ISB Engine Test Resuls		
Average Camshaft Wear (μm)	30.5	48.8
Average Tappet Weight Loss (mg)	98.4	83.8
Average Crosshead Weight Loss (mg)	6.1	5.0

Example 2: Daimler OM471 FE1 Performance Test.

[0511] Oil D, Oil E and Oil F were prepared as indicated in Table 2.1 below. Additionally, Comparative Oil B1 (see also above) was used.

TABLE 2.1

	Comparative Oil B1 mass %	**Oil D** mass %	**Oil E** mass %	**Oil F** mass %
Component				
F-H-PI (2)	1.560	1.560	---	---
F-H-PI (1)	---	---	2.100	2.150
Borated PIBSA-PAM	0.500	0.500	1.000	2.000
PIBSA-PAM 950 Mn	4.000	4.000	3.500	3.000

(continued)

	Comparative Oil B1 mass %	**Oil D** mass %	**Oil E** mass %	**Oil F** mass %
Component				
PIBSA-PAM 2200 Mn	4.000	4.000	4.000	4.000
PIBSA-ester	0.500	0.500	0.500	---
HR-PIBSA-PAM	---	2.000	2.000	2.000
Calcium sulfonate	0.333	0.333	0.550	0.550
Magnesium sulfonate	0.475	0.475	0.468	0.468
Calcium phenate	0.447	0.447	---	---
ZDDP	0.640	0.640	0.640	0.640
Mo Friction modifier	0.120	0.120	0.120	0.060
DPA antioxidant	2.000	2.250	2.600	2.500
Phenol antioxidant	---	---	---	1.200
Sulphurised alkyl methyl ester	0.530	0.530	0.530	---
Corrosion inhibitor	0.100	0.100	0.100	0.095
Anti-foamant	0.008	0.008	0.008	0.008
PIBSA	0.300	0.300	0.300	0.300
PIB	1.600	1.600	1.500	1.400
Diluent (1)	2.062	2.062	2.724	2.734
Lube oil flow improver (LOFI)	0.200	0.200	0.200	0.200
Viscosity modifier (1)	1.500	---	---	---
Viscosity modifier (2)	---	2.400	2.000	2.000
Group II 4.5 cSt base oil	59.125	55.600	---	34.695
Group II 6.5 cSt base oil	20.000	20.375	---	---
Group III 4 cSt base oil	---	---	65.160	40.000
Group III 8 cSt base oil	---	---	10.000	---
Property				
SAE viscosity grade	10W-30	10W-30	5W-30	5W-30
HTHS150 (cP)	3.13	3.54	3.05	3.08
KV_{100}	9.76	11.64	9.8	9.74
CCS at -30 °C	5438	6925	4563	6140
NOACK	11.7	11.75	10.7	12
Phosphorus ppm	494	530	510	480
SASH mass %	0.52	0.49	0.48	0.49

[0512] Comparative Oil B1 illustrates the baseline formulation, the dispersant system of which comprises functionalized polymer in addition to chloro dispersants. Oil D introduces thermal dispersant in the dispersant system and uses a higher content of amine antioxidant. Oil E dispenses with phenate detergent, and the content of amine antioxidant is further increased. In Oil F, phenol antioxidant is used in addition to amine antioxidant, and sulphurised methyl ester antioxidant as well as PIBSA ester is removed.

[0513] Moreover, Oil E and Oil F are targeted to be a 5W-30 oil formulation, in contrast to the 10W-30 oil formulation according to Oil D as well as Comparative Oil B1. In addition, Oil E uses a mixture of Group III base oils transitioning from the Group II formulation as shown in Oil D. Finally, Oil F changes the mixture of Group III base oils using only 40 % of Group III base oil and restocking with Group II base oil.

[0514] Comparative Oil B1, Oil D, Oil E and Oil F were tested in the Daimler OM471 FE1 performance test described above. The data are reported in Table 2.2 below.

[0515] Oil D as well as Comparative Oil B1 did not pass the test and were unable to reach the end of test without prematurely replacing the turbocharger due to excess temperature in the turbocharger return line. However, Oil D shows notable improvement over Comparative Oil B1, as significantly improving the piston cleanliness as well as oxidation.

[0516] For Oil E, all the parameters were met including piston cleanliness, turbocharger housing deposits, and oxidation. Oil E is thus able to pass the test, indicating that using a mixture of Group III base oils and thus a credit for the turbocharger performance is evident in the passing result.

[0517] Oil F demonstrates strong pass in all the key parameters set by the test. Thus, even when using a mixture of Group III and Group II base oils and thus a more cost competitive solution, the test may be passed by switching sulphurised methyl ester antioxidant to phenol antioxidant which contributes to further improvement in the turbocharger performance. The remaining parameters still passes due to the robustness of the dispersant system containing functionalized polymer, chloro dispersant and thermal dispersants.

TABLE 2.2

	Comparative Oil B1 mass %	**Oil D** mass %	**Oil E** mass %	**Oil F** mass %
Daimler OM471 FE1 Test Results				
Sludge in oil mist separator, % (≥95)	95	97	96	98
Piston Cleanliness (Grooves and Piston Bottoms, average), % (≥74)	65	73	76	80.8
Liner wear (6 Cylinders, average), μm (≤8)	3	5	1	2
Turbocharger Housing Deposits (1st TC), % (≥50)	38	40	60	85
Turbocharger Housing Deposits (1st and 2nd TC, average), % (≥30)	32*	31**	45	77.5
Wear on gear train wheels (single), % (≥70)	79	80	82	76
Wear on gear train wheels (average), % (≥75)	80	82	83	82.5
Oxidation (IR at End of Test), A/cm (≤65)	73	49	38	50.4
Specific oil consumption, g/h (≤30)	25	25	24	24.9
*3rd TC changed at 518 h, **3rd TC changed at 573 h				

[0518] The term "comprising" herein is considered synonymous with the term "including." Likewise, whenever a composition, an element, or a group of elements is preceded with the transitional phrase "comprising," it is understood that we also contemplate the same composition or group of elements with transitional phrases "consisting essentially of," "consisting of," "selected from the group of consisting of," or "is" preceding the recitation of the composition, element, or elements and vice versa.

Claims

1. An additive concentrate comprising a dispersant mixture, the dispersant mixture comprising

(1) 0.01-15 mass% based upon the total mass of the dispersant mixture, of an amide, imide, and/or ester functionalized partially or fully saturated polymer comprising C_{4-5} olefins having:

i) an Mw/Mn of less than 2,
ii) a Functionality Distribution (Fd) value of 3.5 or less, and
iii) an Mn of 10,000 g/mol or more (GPC-PS) of the polymer prior to functionalization; and

(2) 50-90 mass% based upon the total mass of the dispersant mixture, of one or more poly(alkenyl) succinimide(s), which is derived from a polyalkenyl-substituted succinic anhydride prepared using a chlorine-assisted alkylation process and a polyamine, hereinafter termed "chloro dispersant(s)"; and

(3) 10-30 mass% based upon the total mass of the dispersant mixture, of one or more poly(alkenyl)succini-

mide(s), which is derived from a polyalkenyl succinic anhydride prepared using a halogen-free thermal alkylation process and a polyamine, hereinafter termed "thermal dispersant(s)".

2. The additive concentrate of claim 1, wherein the one or more thermal dispersant(s) is derived from a polyisobutylene succinic anhydride "PIBSA" and a polyamine "PAM", wherein the PIBSA is based upon a high terminal vinylidene content polyisobutylene, hereinafter termed high reactive polyisobutylene "HR-PIB", and the PIBSA is based upon a polyisobutylene having a Mn of at least 1200 g/mol.

3. The additive concentrate of claim 1 or 2, wherein the dispersant mixture comprises: 1) the functionalized polymer at 1 to 12 mass%, based upon the total mass of the dispersant mixture, 2) one or more chloro dispersant(s) at 55 to 85 mass%, based upon the total mass of the dispersant mixture, and 3) one or more thermal dispersant(s) at 12 to 25 mass%, based upon the total mass of the dispersant mixture.

4. The additive concentrate of claim 1, 2, or 3 wherein the dispersant mixture comprises the one or more chloro dispersant(s) and the one or more thermal dispersant(s) at a ratio of about 9:1 to about 3:2.

5. The additive concentrate of any of claims 1 to 4, further comprising one or more antioxidant(s), wherein: 1) the one or more antioxidant(s) is at least one or more amine antioxidant(s), or 2) the one or more antioxidant(s) is a mixture of one or more amine antioxidant(s) and one or more phenol antioxidant(s), wherein the one or more amine antioxidant(s) and the one or more phenol antioxidant(s) are present at a ratio of about 5:2 to about 9:5.

6. The additive concentrate of any of claims 1 to 5, wherein:

(a) the dispersant mixture is present at 15 to 40 mass%, based upon the total mass of the additive concentrate; and
(b) one or more antioxidant(s) is optionally present at 5 to 25 mass%, based upon the total mass of the additive concentrate.

7. The additive concentrate of any of claims 1 to 6, further comprising one or more additional additive(s) selected from the group consisting of detergents, friction modifiers, anti-foam agents, corrosion inhibitors/anti-rust agents, and anti-wear agents.

8. The additive concentrate of any of claims 1 to 7, further comprising one or more triazole amine corrosion inhibitors.

9. The additive concentrate of any of claims 1 to 8, wherein:

i. one or more detergent(s) is present at 0.1-5 mass%, based upon the total mass of the additive concentrate, and
ii. optionally one or more friction modifier(s) is present at 0.01-1 mass%, based upon the total mass of the additive concentrate, and/or
iii. optionally, one or more anti-foam agent(s) is present at 0.001-0.5 mass%, based upon the total mass of the additive concentrate, and/or
iv. one or more corrosion inhibitor(s)/anti-rust agent(s) is present at 0.01-2 mass%, based upon the total mass of the additive concentrate, and/or
v. optionally, one or more anti-wear agent(s) is present at 0.1-5 mass%, based upon the total mass of the additive concentrate.

10. A lubricating oil composition comprising or resulting from the admixing of:

(A) at least 50 mass% of one or more base oil(s), based upon the total mass of the lubricating oil composition; and
(B) the additive concentrate of any of claims 1 to 9.

11. The lubricating oil composition of claim 10, wherein the one or more base oil(s) comprise one or more group III base oil(s) and optionally one or more group II base oil(s).

12. The lubricating oil composition of claim 10 or 11, comprising 50-95 mass% of one or more base oil(s), based upon the total mass of the lubricating oil composition, comprising:

(a) 25-65 mass% of one or more group III base oil(s) based upon the total mass of the lubricating oil composition;

and
(b) 20-60 mass%, of one or more group II base oil(s) based upon the total mass of the lubricating oil composition.

13. The lubricating oil composition of any of claims 10 to 12, comprising:

(a) 1-12 mass% of dispersant mixture based upon the total mass of the lubricating oil composition;
(b) optionally, 0.1-10 mass% of one or more antioxidants(s) based upon the total mass of the lubricating oil composition;
(c) optionally, 0.01-3 mass% of one or more detergent(s) based upon the total mass of the lubricating oil composition;
(d) optionally, 0.001-0.2 mass% of one or more friction modifier(s) based upon the total mass of the lubricating oil composition;
(e) optionally, 0.001-0.1 mass% of one or more anti-foam agent(s) based upon the total mass of the lubricating oil composition;
(f) optionally, 0.001-1 mass% of one or more corrosion inhibitor(s)/anti-rust agent(s) based upon the total mass of the lubricating oil composition;
(g) optionally, 0.01-1.5 mass% of one or more anti-wear agent(s) based upon the total mass of the lubricating oil composition;
(h) optionally, 0.001-1 mass% of one or more pour point depressant(s) based upon the total mass of the lubricating oil composition, and/or
(i) optionally, 0.001-0.5 mass% of one or more viscosity modifier(s) based upon the total mass of the lubricating oil composition.

14. The lubricating oil composition of any of claims 10 to 13, having a phosphorous content of less than 800 ppm, alternately less than 550 ppm, based upon the total mass of the lubricating oil composition, and/or having a sulfated ash ("SASH") content of less than 0.9 mass%, alternately less than 0.5 mass%.

15. The lubricating oil composition of any of claims 10 to 14 wherein:

1) the average piston cleanliness is at least 70 % as determined by CEC L-118-21, and/or
2) wherein the average wear on gear train wheels is greater than 75 % as determined by CEC L-118-21, and/or wherein
3) the average liner wear is less than 8 μm, as determined by CEC L-118-21, and/or
4) wherein the average turbocharger housing deposits are at least 30 % as determined by CEC L-118-21, and/or
5) wherein the oxidation is less than 65 A/cm as determined by CEC L-118-21.

16. A method of lubricating an internal combustion engine during operation of the engine comprising:

(i) providing to a crankcase of the internal combustion engine the lubricating composition of any of claims claim 10 to 15;
(ii) providing a fuel in the internal combustion engine; and
(iii) combusting the fuel in the internal combustion engine,

wherein the fuel is one or more of a hydrocarbon fuel, renewable fuel, hydrogen fuel, or any blend thereof.

17. The method of claim 16, wherein the fuel comprises a hydrocarbon fuel and/or the engine is a diesel engine.

18. A fuel composition comprising the lubricating composition any of claims claim 10 to 15 and one or more of hydrocarbon fuel hydrogen fuel, or any blend thereof.

19. The fuel composition of claim 18, wherein the hydrocarbon fuel comprises a petroleum derived fuel and or a renewable fuel.

20. A method of increasing the piston cleanliness of a lubricating oil composition, the method comprising including in the lubricating oil composition the additive concentrate of any of claims 1 to 9, wherein preferably the average piston cleanliness is increased to at least 70 % as determined by CEC L-118-21.

22. A method of improving the wear resistance of a lubricating oil composition, the method comprising including in the lubricating oil composition the additive concentrate of any of claims 1 to 9, wherein preferably the average wear on gear train wheels is at least 75 % as determined by CEC L-118-21, and/or the average liner wear is less than 8 μm, as determined by CEC L-118-21.

Europäisches Patentamt
European Patent Office
Office européen des brevets

EUROPEAN SEARCH REPORT

Application Number
EP 25 15 0792

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	US 2013/310287 A1 (GIESELMAN MATTHEW D [US] ET AL) 21 November 2013 (2013-11-21) * paragraphs [0002], [0017], [0018], [0036] - [0039], [0043], [0045], [0046] * * paragraphs [0075] - [0078], [0081], [0082], [0088], [0092] * * paragraphs [0142] - [0146]; claims 1, 8, 10, 14, 15, 17; examples * -----	1-22	INV. C10M161/00 ADD. C10N10/04 C10N10/12 C10N20/04 C10N30/04 C10N30/06 C10N30/10 C10N30/00 C10N40/25
A	US 2015/005210 A1 (JONES CRAIG J [GB] ET AL) 1 January 2015 (2015-01-01) * claims; examples * * paragraphs [0004], [0007] - [0009], [0016]; table 1 * -----	1-22	
A	US 2014/024567 A1 (MCDOUGALL PATRICK J [US] ET AL) 23 January 2014 (2014-01-23) * all examples with the amine-functionalized acylated polyisoprene PIP-1; paragraphs [0001], [0152], [0153], [0166], [0167]; example 6; tables * -----	1-22	**TECHNICAL FIELDS SEARCHED (IPC)** C10M C10N

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	7 May 2025	Bork, Ana-Maria

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
&. : member of the same patent family, corresponding document

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 25 15 0792

07-05-2025

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2013310287 A1	21-11-2013	CA 2753414 A1	02-09-2010
		CN 102414300 A	11-04-2012
		EP 2401348 A1	04-01-2012
		EP 2431448 A1	21-03-2012
		JP 5735434 B2	17-06-2015
		JP 5840245 B2	06-01-2016
		JP 2012519222 A	23-08-2012
		JP 2014111794 A	19-06-2014
		KR 20110132394 A	07-12-2011
		US 2012046206 A1	23-02-2012
		US 2013310287 A1	21-11-2013
		US 2016075966 A1	17-03-2016
		WO 2010099136 A1	02-09-2010
US 2015005210 A1	01-01-2015	CA 2864262 A1	22-08-2013
		CN 104145007 A	12-11-2014
		CN 106893629 A	27-06-2017
		EP 2814920 A2	24-12-2014
		US 2015005210 A1	01-01-2015
		WO 2013122898 A2	22-08-2013
US 2014024567 A1	23-01-2014	CA 2875957 A1	23-01-2014
		CN 104411809 A	11-03-2015
		EP 2875105 A1	27-05-2015
		JP 6275130 B2	07-02-2018
		JP 2015522694 A	06-08-2015
		SG 11201500255T A	27-02-2015
		US 2014024567 A1	23-01-2014
		WO 2014014561 A1	23-01-2014

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- US 48057123 **[0009] [0057] [0483] [0484]**
- US 63379006 **[0009] [0057] [0483] [0484] [0498]**
- US 63584675 **[0009]**
- US 5171908 A **[0151]**
- US 5783531 A **[0151]**
- US 10913916 B **[0160]**
- US 10781397 B **[0160]**
- US 5429758 A **[0218]**
- US 4311628 A **[0219]**
- US 7790661 B **[0239]**
- US 20170073606 A **[0241]**
- EP 2401348 A **[0241]**
- US 6429178 B **[0297]**
- US 6429179 B **[0297]**
- US 6153565 A **[0297]**
- US 6281179 B **[0297]**
- US 2005065045 **[0298]**
- US 7407919 B **[0298]**
- WO 9826030 A **[0329]**
- US 10829712 B **[0335] [0414] [0443]**
- US 4702850 A **[0336]**
- US 4798684 A **[0346]**
- US 5084197 A **[0346]**
- US 8048833 B **[0348]**
- US 10731101 B **[0351]**
- US 1815022 A **[0359]**
- US 2015748 A **[0359]**
- US 2191498 A **[0359]**
- US 2387501 A **[0359]**
- US 2655479 A **[0359]**
- US 2666746 A **[0359]**
- US 2721877 A **[0359]**
- US 2721878 A **[0359]**
- US 3250715 A **[0359]**
- US 20210189283 **[0369]**
- US 3172892 A **[0384] [0386]**
- US 32145707 B **[0384]**
- US 3219666 A **[0384] [0386]**
- US 3316177 A **[0384]**
- US 3341542 A **[0384]**
- US 3444170 A **[0384]**
- US 3454607 A **[0384]**
- US 3541012 A **[0384]**
- US 3630904 A **[0384]**
- US 3632511 A **[0384]**
- US 3787374 A **[0384]**
- US 4234435 A **[0384]**
- US 3036003 A **[0384]**
- US 3200107 A **[0384]**
- US 3254025 A **[0384]**
- US 3275554 A **[0384]**
- US 3438757 A **[0384]**
- US 3454555 A **[0384]**
- US 3565804 A **[0384]**
- US 3413347 A **[0384]**
- US 3697574 A **[0384] [0409]**
- US 3725277 A **[0384]**
- US 3725480 A **[0384]**
- US 3726882 A **[0384]**
- US 4454059 A **[0384]**
- US 3329658 A **[0384]**
- US 3449250 A **[0384]**
- US 3519565 A **[0384]**
- US 3666730 A **[0384]**
- US 3687849 A **[0384]**
- US 3702300 A **[0384]**
- US 4100082 A **[0384]**
- US 5705458 A **[0384]**
- EP 0471071 A **[0384]**
- EP 0451380 A **[0384]**
- US 4873009 A **[0386]**
- US 3087936 A **[0386]**
- US 3272746 A **[0386]**
- US 3322670 A **[0386]**
- US 3652616 A **[0386]**
- US 3948800 A **[0386]**
- US 6821307 B **[0386]**
- CA 1094044 **[0386]**
- US 4152499 A **[0387]**
- EP 0355895 A **[0387]**
- US 4426305 A **[0390]**
- US 7485603 B **[0391] [0414]**
- US 4767551 A **[0409]**
- US 10899986 B **[0409]**
- US 3703536 A **[0409]**
- US 3704308 A **[0409]**
- US 3751365 A **[0409]**
- US 3756953 A **[0409]**
- US 3798165 A **[0409]**
- US 3803039 A **[0409]**
- US 4231759 A **[0409]**
- US 9938479 B **[0409]**
- US 7491248 B **[0409]**
- WO 0142399 A **[0409]**
- US 2100993 A **[0410]**
- US 6323164 B **[0410]**
- US 2719125 A **[0420]**
- US 2719126 A **[0420]**

- US 3087937 A **[0420]**
- US 2760933 A **[0421]**
- US 2836564 A **[0421]**
- US 3663561 A **[0422] [0424]**
- EP 330522 A **[0443]**
- US 18480571 B **[0498]**
- US 20090203559 A **[0498]**

Non-patent literature cited in the description

- *CHEMICAL AND ENGINEERING NEWS*, 1985, vol. 63 (5), 27 **[0020]**
- American Petroleum Institute Publication 1509. January 2021 **[0149] [0162]**
- Synthetic Lubricants and High-Performance Functional Fluids. Marcel Dekker, Inc, 1999, vol. 1-52 **[0151]**
- **IMADA et al.** *J Am. Chem. Soc.*, 2005, vol. 127, 14544-14545 **[0213]**
- Kirk-Othmer Encyclopedia of Chemical Technology, vol. 14, 477-526 **[0292]**
- **M. BELZER**. *Journal of Tribology*, 1992, vol. 114, 675-682 **[0336]**
- **M. BELZER** ; **S. JAHANMIR**. *Lubrication Science*, 1988, vol. 1, 3-26 **[0336]**
- **KLAMANN**. Lubricants and Related Products. Wiley VCH, 1984 **[0346]**