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(54) LUBRICANT CONTAINING THIADIAZOLE DERIVATIVES

SCHMIERMITTEI MIT THIADIAZOI DERIVATEN

1. UBRIFIANT CONTENANT DES DÉRIVÉS DE THIADIAZOLES

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Description**FIELD**

5 [0001] This disclosure relates to novel additive compositions and lubricating compositions, in particular lubricating compositions for use in driveline, transmission, gears or axles. Furthermore, the disclosure describes the use of an additive composition and a lubricant composition for enhancing FZG test performance.

BACKGROUND

10 [0002] Different applications of lubricants require different properties and performance characteristics, often leading to a delicate balancing of components. The difficulties are multiplied by the fact that some components may, to the detriment of the lubricant's performance, chemically interact with each other. Further challenges arise from environmental and legal requirements, e.g. setting ever stricter maximum levels of sulfur, phosphorus, and other performance standards.

15 [0003] It is therefore, on the one hand, generally desirable to reduce the levels of sulfur and phosphorus, in particular phosphites, in lubricants exposed to high pressure and load. On the other hand, antiwear and extreme pressure performance is often associated with the presence of sulfur and phosphite additives.

20 [0004] Lubricating compositions for driveline applications, in particular automotive driveline applications, such as transmissions (manual and automatic) clutches, gearboxes, axles, or differentials need to provide antiwear, extreme pressure and loadbearing capacity. Amongst the antiwear properties, anti-scuffing is particularly desirable. Scuffing, can be measured and objectively determined using the CEC L-84-02 industry standard test to evaluate gear scuffing. This test measures anti-scuffing properties of oil for reduction gears, hypoid gears, automatic transmission gears and the like. The test uses a FZG A10-type pinion with a width of 10 mm, and a wheel width of 20 mm. The motor is run at a wheel rotational speed of 2880 rpm and a circumferential speed of 16.6 m/s for a total run duration of 7 minutes and 30 seconds

25 at an initial lubricant oil temperature of 90°C. The results reported include load stage failure. Typically, better results are obtained for lubricants reporting a higher load stage failure.

[0005] Dimercaptothiadiazole (DMTD, Formula (I) with R=H) is a known additive in lubricating compositions, providing antiwear performance. DMTD, however, has the disadvantage of low solubility in lubricating oils, requiring premixing with a dispersant before adding to an additive package or lubricating composition. Still, DMTD tends to drop out of solution.

30 [0006] Another class of known additives with better oil solubility is 2,5-bis (hydrocarbyldithio)-1,3,4-thiadiazole and 2-hydrocarbyldithio-5-mercaptop-1,3,4-thiadiazole. These additives suffer from instability, high reactivity and interaction with other components, leading to reduced performance. Therefore, Automatic Transmission Fluids (ATFs) relying on those additives may experience decreased performance in many areas.

35 [0007] Various classes of thiadiazole-derived compounds including above mentioned 2,5-bis (hydrocarbyldithio)-1,3,4-thiadiazole and 2-hydrocarbyldithio-5-mercaptop-1,3,4-thiadiazole are suggested for use as components in complex transmission fluids by US 2016/0168505 A1. However, as an essential component, phosphites are required, and total sulfur levels are not disclosed.

40 [0008] US 5,656,577 discloses a fluid composition for a fluid coupling, which is excellent in viscosity stability and torque stability, and comprises a polyorganosiloxane base oil having a viscosity of 3,000-500,000 mm²/sec at 25 DEG C. and at least one 5-membered heterocyclic compound incorporated in a proportion of 0.01-3.0 wt. % based on the total weight of the composition, said 5-membered heterocyclic compound being selected from the group consisting of thiadiazole derivatives and thiazole derivatives, both, having at least one monovalent group represented by the formula -Sx-R6 in which R6 is a saturated or unsaturated monovalent group or atom composed of at least one atom selected from a carbon atom, a hydrogen atom, an oxygen atom, a nitrogen atom and a sulfur atom, and x is a number of 1 or greater.

45 [0009] US 5,585,338 discloses an aviation turbo oil having improved load carrying ability (extreme pressure capacity) comprising a major portion of a base oil stock and a minor portion of a mercaptobenzoic acid or mixture of mercaptobenzoic acids.

50 [0010] US 5,801,130 discloses synthetic based turbo oils, preferably polyol ester-based turbo oils which exhibit exceptional load-carrying capacity by use of a synergistic combination of sulfur (S)-based and phosphorous (P)-based load additives. The S-containing additives of the present invention are DMTD and its derivative including the capped DMTD and the DMTD dimer, and the P-containing component is one or more amine phosphates. The turbo oil composition consisting of the dual P/S additives of the present invention achieves an excellent load-carrying capacity, which is better than that obtained when each additive was used alone at a treat rate higher than or comparable to the total combination additive treat rate, and the lower concentration requirement of the P-based additive allows the turbo oil composition to meet US Navy MIL-L-23699 requirement on the Si seal compatibility.

55 [0011] It is an object of the present invention to provide an additive for a driveline lubricant, or a driveline lubricant, that is low in sulfur content, low in phosphite content and it is an object of the invention to provide enhanced anti-wear, specifically gear anti-scuffing properties to a driveline lubricating composition of low total sulfur content and very little,

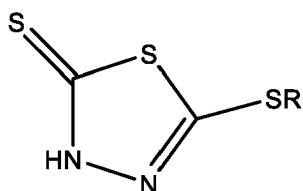
or no phosphite present.

SUMMARY

5 [0012] One or more of said objects is solved by a lubricating composition comprising

- a major part of a base oil of lubricating viscosity wherein the base oil is selected from API Group I, II, III, IV, V, or mixtures thereof,
- 10 b) a total of 0.001 to 0.536 wt.%, based on the total lubricating composition, of one or more monohydrocarbyl-substituted dimercaptothiadiazole derivatives according to Formula I or a tautomer or salt thereof below

Formula I



wherein R is methyl or C₂ to C₄ alkyl,
wherein the total lubricating composition has a sulfur content of up to 2,500 ppm (wt.),

25

- less than 0.1 wt% phosphite;
- dispersant.

30 [0013] The use of the monohydrocarbyl-substituted dimercaptothiadiazole of Formula (I) according to the invention leads to more stable lubricating compositions, allowing reduced total sulfur at equal or improved gear scuffing resistance.

35 [0014] In particular, the gear scuffing resistance is surprisingly improved compared to conventional agents such as dimercaptodiazole (Formula (I) with R=H) or 2,5-bis (hydrocarbyldithio)-1,3,4-thiadiazole and 2-hydrocarbyldithio-5-mercaptop-1,3,4-thiadiazole. Furthermore, a surprising synergy exists using a mixture of 2,5-bis (hydrocarbyldithio)-1,3,4-thiadiazole and 2-hydrocarbyldithio-5-mercaptop-1,3,4-thiadiazole with monohydrocarbyl-substituted dimercaptothiadiazole of Formula (I) according to the invention, allowing even lower sulfur limits and lower overall treat rates at optimal wear resistance, including gear scuffing resistance.

40 [0015] The skilled person understands that monohydrocarbyl-substituted dimercaptothiadiazole derivatives of Formula (I) according to the invention may be present in a tautomeric equilibrium and in salted forms when exposed to other additives in a lubricant composition.

45 [0016] In the present disclosure, in all cases wherein it is referred to monohydrocarbyl-substituted dimercaptothiadiazole derivatives of the present invention, those of Formula (I) are meant, and the tautomeric forms and salted forms are herein treated as synonyms. Thus, e.g. 5-hydrocarbylthio-1,3,4-thiadiazol-2-thiol, 2-hydrocarbylthio-1,3,4-thiadiazol-5-thiol, 2-hydrocarbylthio-5-mercaptop-1,3,4-thiadiazole or 5-(hydrocarbylthio)-1,3,4-thiadiazole-2(3H)-thione all describe the same compound.

50 [0017] The lubricating composition according to the invention contains less than preferably 0.05 wt.% phosphite or less than 0.01 wt.% phosphite, more preferably less than 0.001 wt.%. In the most preferred embodiment, the composition is essentially free of phosphite.

55 [0018] Preferably, the lubricating composition according to the invention has a sulfur content of less than 2,500 ppm (wt.), 2,000 ppm (wt.) or 1,800 ppm (wt.), up to 1,500, in particular less than 1,500 ppm (wt.) or up to 1,200, in particular less than 1200 ppm (wt.) and specifically up to 1,000 or less than 1,000 ppm (wt.).

[0019] Particularly preferred are combinations of low sulfur and low phosphite, such as less than 2500 ppm (wt.) sulfur and less than 0.1 wt% phosphite, or 2,000 ppm (wt.) sulfur and less than 0.01 wt.% phosphite or less than 2,000 ppm (wt.) sulfur and less than 0.001 wt.% phosphite, or preferably less than 1,800 ppm (wt.) sulfur and less than 0.01 wt.% phosphite or less than 1,800 ppm (wt.) sulfur and less than 0.001 wt.% phosphite or even less than 1,500 ppm (wt.) sulfur and less than 0.01 wt.% phosphite or less than 1,500 ppm (wt.) sulfur and less than 0.001 wt.% phosphite or even less than 1,000 ppm (wt.) sulfur and less than 0.01 wt.% phosphite or less than 1,000 ppm (wt.) sulfur and less than 0.001 wt.% phosphite.

[0020] In a preferred embodiment of the invention, the monohydrocarbyl-substituted dimercaptothiadiazole deriva-

tive(s) according to Formula (I) are present in a total of 0.001 to 0.4 wt.% or 0.001 to 0.40 wt.% or, more preferably, 0.005 to 0.400 wt.%, in particular 0.01 to 0.3 or 0.05 to 0.2 wt.%, based on the total lubricating composition.

[0021] As described above, the monohydrocarbyl-substituted dimercaptothiadiazole derivative(s) used in the present invention are monoalkyl dimercaptothiadiazole derivative(s). Herein, the alkyl group may be methyl, or it may be ethyl, propyl or butyl, or any combination of C₁ to C₄ alkyl. It is, however preferred that the alkyl group be C₁.

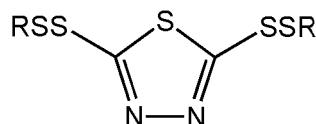
[0022] Advantageously, the monohydrocarbyl-substituted dimercaptothiadiazole derivative(s) contributes 200 to 1,500, in particular 400 to 1,000 ppm sulfur to the lubricating composition.

[0023] The lubricating composition of the present invention contains a dispersant. Preferably, the lubricating composition contains 0.001 to 10 wt.%, based on the total lubricating composition, of a dispersant. The dispersant is preferably present in an amount of 0.01 to 8 wt.%, in particular 0.1 to 5 wt.% in the lubricating composition, based on the total weight of the lubricating composition.

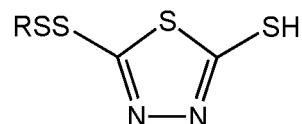
[0024] Particularly preferred for use in the present invention are dispersants selected from the group consisting of ashless dispersants, borated ashless dispersants, ash-containing dispersants, dispersant viscosity index improvers, in particular wherein the dispersant is an ashless dispersant selected from succinimide dispersants, polyisobutylene dispersants, and ethylene-propylene copolymers, specifically a succinimide dispersant.

[0025] As mentioned above, a synergy in gear scuffing resistance is observed, if 0.001 to 0.20 wt.% of one or more monohydrocarbyl-substituted dimercaptothiadiazole derivative(s) are combined with 0.01 to 0.40 wt.% mono- and/or bishydrocarbylthio-substituted dimercaptothiadiazole(s) of Formula II/IIa. Even more preferred is a combination of 0.01 to 0.15 wt.% of one or more monohydrocarbyl-substituted dimercaptothiadiazole derivative(s) with 0.05 to 0.20 wt.% mono- and/or bishydrocarbylthio-substituted dimercaptothiadiazole(s).

Formula (II)



Formula (IIa)



30 wherein R is independently, C₅-C₁₅ alkyl.

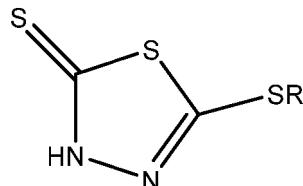
[0026] The lubricating composition according to the invention may further comprise one or more additives selected from the group consisting of extreme-pressure agents, anti-wear agents, friction modifiers, metal deactivators, detergents, viscosity index improvers, antioxidants, corrosion inhibitors, foam inhibitors, demulsifiers, pour point depressants, seal swelling agents, and mixtures thereof.

[0027] In an aspect of the invention, the lubricating composition is used for lubricating a driveline, a transmission, in particular a manual or automated transmission, a gear, an automated gear, or an axle.

[0028] In another aspect of the invention, the lubricating composition is used for enhanced FZG test performance.

[0029] A further aspect of the invention is the use of a total of 0.001 to 0.536 wt.%, based on the total lubricating composition, of one or more monohydrocarbyl-substituted dimercaptothiadiazole derivative(s) according to Formula (I) or a tautomer or salt thereof below

Formula (I)

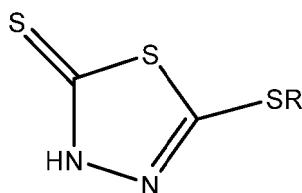


50 wherein R is methyl or C₂ to C₄ alkyl, in a lubricating composition comprising a major part of a base oil of lubricating viscosity wherein the base oil is selected from API Group I, II, III, IV, V, or mixtures thereof, wherein the total lubricating composition has a sulfur content of up to 2,500 ppm (wt.), to enhance the gear scuffing resistance of the lubricating composition. It is to be understood that this aspect contemplates all options and limitations described in connection with the lubricating composition of the invention, individually or in combination. For example, the invention also relates to the use of any of the amounts of one or more monohydrocarbyl-substituted dimercaptothiadiazole derivative(s) according to Formula (I) or a tautomer or salt thereof in a lubricating composition of the invention to enhance the gear scuffing resistance of the lubricating composition.

[0030] A further aspect of the invention is a method of preparing a lubricant comprising blending a base oil of lubricating viscosity wherein the base oil is selected from API Group I, II, III, IV, V, or mixtures thereof with one or more monohydrocarbyl-substituted dimercaptodiadiazole derivative(s) according to Formula (I) or a tautomer thereof

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wherein R is methyl or C₂ to C₄ alkyl to form a lubricant having a sulfur content of up to 2,500 ppm (wt.) and containing less than 0.1 wt% phosphite, in particular wherein the lubricating composition comprises a major part of the base oil and a total of 0.001 to 0.536 wt.%, based on the total lubricating composition, of the one or more monohydrocarbyl-substituted dimercaptodiadiazole derivative(s) according to Formula (I) or a tautomer thereof.

[0031] The method may involve dissolving the compound according to Formula (I) in the base oil in the presence of a dispersant. Viscosity may eventually be adjusted by addition of oil of lubricating viscosity.

20 DETAILED DESCRIPTION

[0032] Transmission lubricants are described that provide improved FZG anti-wear properties. The lubricants are particularly suited for automatic transmissions, such as but not limited to, dual clutch transmissions with a wet-clutch friction disc. Such results were obtained not by increasing the levels of sulfur and phosphorus, but by discovering compounds that more effectively deliver sulfur to the metal surface. Such compounds were not previously expected to affect FZG wear properties in such a dramatic fashion within transmission lubricants. In one aspect, the lubricants include a major amount of a base or lubricating oil(s) and select amounts of a thiadiazole derivative of Formula I.

[0033] As used herein, the terms "oil composition," "lubrication composition," "lubricating oil composition," "lubricating oil," "lubricant composition," "fully formulated lubricant composition," and "lubricant" are considered synonymous, fully interchangeable terminology referring to the finished lubrication product comprising a major amount of a base or lubricating oil plus minor amounts of the select dispersants and detergents noted herein. The lubricant may also include optional additives as further described below.

[0034] As used herein, the term "hydrocarbyl substituent" or "hydrocarbyl group" is used in its ordinary sense, which is well-known to those skilled in the art. Specifically, it refers to a group having a carbon atom directly attached to the remainder of the molecule and having predominantly hydrocarbon character. Examples of hydrocarbyl groups include: (a) hydrocarbon substituents, that is, aliphatic (e.g., alkyl or alkenyl), alicyclic (e.g., cycloalkyl, cycloalkenyl) substituents, and aromatic-, aliphatic-, and alicyclic-substituted aromatic substituents, as well as cyclic substituents wherein the ring is completed through another portion of the molecule (e.g., two substituents together form an alicyclic moiety); (b) substituted hydrocarbon substituents, that is, substituents containing non-hydrocarbon groups which, in the context of this disclosure, do not alter the predominantly hydrocarbon substituent (e.g., halo (especially chloro and fluoro), hydroxy, alkoxy, mercapto, alkylmercapto, nitro, nitroso, amino, alkylamino, and sulfoxy); and (c) hetero substituents, that is, substituents which, while having a predominantly hydrocarbon character, in the context of this disclosure, contain other than carbon in a ring or chain otherwise composed of carbon atoms. Heteroatoms may include sulfur, oxygen, and nitrogen, and encompass substituents such as pyridyl, furyl, thienyl, and imidazolyl. In general, no more than two, for example, no more than one, non-hydrocarbon substituent will be present for every ten carbon atoms in the hydrocarbyl group; typically, there will be no non-hydrocarbon substituents in the hydrocarbyl group.

Base Oil or Lubricating Oil

[0035] As used herein, the term "base oil" or "lubricating oil" generally refers to oils categorized by the American Petroleum Institute (API) category groups Group I-V oils as well as animal oils, vegetable oils (e.g. castor oil and lard oil), petroleum oils, mineral oils, synthetic oils, and oils derived from coal or shale. The American Petroleum Institute has categorized these different basestock types as follows:

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Base oil Category	Sulfur (%)		Saturates (%)	Viscosity Index
Group I	> 0.03	and/or	<90	80 to 120

(continued)

Base oil Category	Sulfur (%)		Saturates (%)	Viscosity Index
Group II	≤0.03	and	≥90	80 to 120
Group III	≤0.03	and	≥90	≥120
Group IV	All polyalphaolefins (PAOs)			
Group V	All others not included in Groups I, II, III, or IV			

[0036] Groups I, II, and III are mineral oil process stocks. Hydrotreated basestocks and catalytically dewaxed basestocks, because of their low sulfur and aromatics content, generally fall into the Group II and Group III categories. Group IV base oils contain true synthetic molecular species, which are produced by polymerization of olefinically unsaturated hydrocarbons and are substantially free of sulfur and aromatics. Many Group V base oils are also true synthetic products and may include diesters, polyol esters, polyalkylene glycols, alkylated aromatics, polyphosphate esters, polyvinyl ethers, and/or polyphenyl ethers, and the like, but may also be naturally occurring oils, such as vegetable oils. It should be noted that although Group III base oils are derived from mineral oil, the rigorous processing that these fluids undergo causes their physical properties to be very similar to some true synthetics, such as PAOs. Therefore, oils derived from Group III base oils may be referred to as synthetic fluids in the industry.

[0037] The base oil used in the disclosed lubricating oil composition may be a mineral oil, animal oil, vegetable oil, synthetic oil, or mixtures thereof. Suitable oils may be derived from hydrocracking, hydrogenation, hydrofinishing, unrefined, refined, and re-refined oils, and mixtures thereof.

[0038] Unrefined oils are those derived from a natural, mineral, or synthetic source without or with little further purification treatment. Refined oils are similar to the unrefined oils except that they have been treated in one or more purification steps, which may result in the improvement of one or more properties. Examples of suitable purification techniques are solvent extraction, secondary distillation, acid or base extraction, filtration, percolation, and the like. Oils refined to the quality of an edible may or may not be useful. Edible oils may also be called white oils. In some embodiments, lubricant compositions are free of edible or white oils.

[0039] Re-refined oils are also known as reclaimed or reprocessed oils. These oils are obtained similarly to refined oils using the same or similar processes. Often these oils are additionally processed by techniques directed to removal of spent additives and oil breakdown products.

[0040] Mineral oils may include oils obtained by drilling or from plants and animals or any mixtures thereof. For example such oils may include, but are not limited to, castor oil, lard oil, olive oil, peanut oil, corn oil, soybean oil, and linseed oil, as well as mineral lubricating oils, such as liquid petroleum oils and solvent-treated or acid-treated mineral lubricating oils of the paraffinic, naphthenic or mixed paraffinic-naphthenic types. Such oils may be partially or fully hydrogenated, if desired. Oils derived from coal or shale may also be useful.

[0041] Useful synthetic lubricating oils may include hydrocarbon oils such as polymerized, oligomerized, or interpolymerized olefins (e.g., polybutylenes, polypropylenes, propyleneisobutylene copolymers); poly(1-hexenes), poly(1-octenes), trimers or oligomers of 1-decene, e.g., poly(1-decenes), such materials being often referred to as α -olefins, and mixtures thereof; alkyl-benzenes (e.g. dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di-(2-ethylhexyl)-benzenes); polyphenyls (e.g., biphenyls, terphenyls, alkylated polyphenyls); diphenyl alkanes, alkylated diphenyl alkanes, alkylated diphenyl ethers and alkylated diphenyl sulfides and the derivatives, analogs and homologs thereof or mixtures thereof. Polyalphaolefins are typically hydrogenated materials.

[0042] Other synthetic lubricating oils include polyol esters, diesters, liquid esters of phosphorus-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, and the diethyl ester of decane phosphonic acid), or polymeric tetrahydrofurans. Synthetic oils may be produced by Fischer-Tropsch reactions and typically may be hydroisomerized Fischer-Tropsch hydrocarbons or waxes. In one embodiment oils may be prepared by a Fischer-Tropsch gas-to-liquid synthetic procedure as well as other gas-to-liquid oils.

[0043] The amount of the oil of lubricating viscosity present may be the balance remaining after subtracting from 100 wt. % the sum of the amount of the performance additives inclusive of viscosity index improver(s) and/or pour point depressant(s) and/or other top treat additives. For example, the oil of lubricating viscosity that may be present in a finished fluid may be a major amount, such as greater than about 50 wt. %, greater than about 60 wt. %, greater than about 70 wt. %, greater than about 80 wt. %, greater than about 85 wt. %, or greater than about 90 wt. %.

[0044] The lubricants may also include other optional additives as needed for particular applications as long as the optional components do not affect the basic features of the dispersants and detergents noted above. Several common optional additives are noted herein.

Optional Additive Components

[0045] In addition to the base oil and the thiadizole derivative of Formula I set forth above, the automatic transmission lubricating compositions herein may also include other additives to perform one or more functions required of a lubricating fluid. Further, one or more of the mentioned additives may be multi-functional and provide other functions in addition to or other than the function prescribed herein.

[0046] For example, the compositions herein may include one or more of at least one component selected from the group consisting of a friction modifier, an air expulsion additive, an antioxidant, a corrosion inhibitor, a foam inhibitor, a seal-swell agent, a viscosity index improver, anti-rust agent, extreme pressure additives, and combinations thereof. Other performance additives may also include, in addition to those specified above, one or more of metal deactivators, ashless TBN boosters, demulsifiers, emulsifiers, pour point depressants, and mixtures thereof. Typically, fully-formulated lubricating oils will contain one or more of these performance additives. Examples of some common optional additive components are set forth below.

15 Dispersants

[0047] The lubricating composition of the present invention comprises a dispersant.

[0048] The lubricant composition may include one or more select dispersants or mixtures thereof. Dispersants are often known as ashless-type dispersants because, prior to mixing in a lubricating oil composition, they do not contain ash-forming metals and they do not normally contribute any ash when added to a lubricant. Ashless-type dispersants are characterized by a polar group attached to a relatively high molecular weight hydrocarbon chain. Typical ashless dispersants include N-substituted long chain alkenyl succinimides. N-substituted long chain alkenyl succinimides include polyisobutylene (PIB) substituents with a number average molecular weight of the polyisobutylene substituent in a range of about 800 to about 2500 as determined by gel permeation chromatograph (GPC) using polystyrene (with a number average molecular weight of 180 to about 18,000) as the calibration reference). The PIB substituent used in the dispersant also has a viscosity at 100°C of about 2100 to about 2700 cSt as determined using ASTM D445. Succinimide dispersants and their preparation are disclosed, for instance in U.S. Pat. No. 7,897,696 and U.S. Pat. No. 4,234,435.

[0049] Succinimide dispersants are typically an imide formed from a polyamine, typically a poly(ethyleneamine). The dispersants may include two succinimide moieties joined by a polyamine. The polyamine may be tetra ethylene penta amine (TEPA), tri ethylene tetra amine (TETA), penta ethylene hexa amine (PEHA), other higher nitrogen ethylene diamine species and/or mixtures thereof. The polyamines may be mixtures of linear, branched and cyclic amines. The PIB substituents may be joined to each succinimide moiety.

[0050] In some embodiments the lubricant composition comprises at least one polyisobutylene succinimide dispersant derived from polyisobutylene with number average molecular weight in the range about 350 to about 5000, or about 500 to about 3000, as measured by the GPC method described above. The polyisobutylene succinimide may be used alone or in combination with other dispersants.

[0051] In some embodiments, polyisobutylene (PIB), when included, may have greater than 50 mol. %, greater than 60 mol. %, greater than 70 mol. %, greater than 80 mol. %, or greater than 90 mol. % content of terminal double bonds. Such a PIB is also referred to as highly reactive PIB ("HR-PIB"). HR-PIB having a number average molecular weight ranging from about 800 to about 5000 is suitable for use in embodiments of the present disclosure. Conventional non-highly reactive PIB typically has less than 50 mol. %, less than 40 mol. %, less than 30 mol. %, less than 20 mol. %, or less than 10 mol. % content of terminal double bonds.

[0052] An HR-PIB having a number average molecular weight ranging from about 900 to about 3000, as measured by the GPC method described above, may be suitable. Such an HR-PIB is commercially available, or can be synthesized by the polymerization of isobutene in the presence of a non-chlorinated catalyst such as boron trifluoride, as described in U.S. Pat. No. 4,152,499 and U.S. Pat. No. 5,739,355. When used in the aforementioned thermal ene reaction, HR-PIB may lead to higher conversion rates in the reaction, as well as lower amounts of sediment formation, due to increased reactivity.

[0053] In embodiments the lubricant composition comprises at least one dispersant derived from polyisobutylene succinic anhydride. In an embodiment, the dispersant may be derived from a polyalphaolefin (PAO) succinic anhydride. In an embodiment, the dispersant may be derived from olefin maleic anhydride copolymer. As an example, the dispersant may be described as a poly-PIBSA. In an embodiment, the dispersant may be derived from an anhydride which is grafted to an ethylene-propylene copolymer.

[0054] One class of suitable dispersants may be Mannich bases. Mannich bases are materials that are formed by the condensation of a higher molecular weight, alkyl substituted phenol, a polyalkylene polyamine, and an aldehyde such as formaldehyde. Mannich bases are described in more detail in U.S. Pat. No. 3,634,515.

[0055] A suitable class of dispersants may be high molecular weight esters or half ester amides.

[0056] The dispersants may also be post-treated by conventional methods by reaction with any of a variety of agents.

Among these agents are boron, urea, thiourea, dimercaptothiadiazoles, carbon disulfide, aldehydes, ketones, carboxylic acids, hydrocarbon-substituted succinic anhydrides, maleic anhydride, nitriles, epoxides, carbonates, cyclic carbonates, hindered phenolic esters, and phosphorus compounds. U.S. Pat. No. 7,645,726; U.S. Pat. No. 7,214,649; and U.S. Pat. No. 8,048,831 describes some suitable post-treatment methods and post-treated products.

5 [0057] Suitable boron compounds useful in forming the dispersants herein include any boron compound or mixtures of boron compounds capable of introducing boron-containing species into the ashless dispersant. Any boron compound, organic or inorganic, capable of undergoing such reaction can be used. Accordingly, use can be made of boron oxide, boron oxide hydrate, boron trifluoride, boron tribromide, boron trichloride, HBF_4 boron acids such as boronic acid (e.g. alkyl- $\text{B}(\text{OH})_2$ or aryl- $\text{B}(\text{OH})_2$), boric acid, (i.e., H_3BO_3), tetraboric acid (i.e., $\text{H}_2\text{B}_5\text{O}_7$), metaboric acid (i.e., HBO_2), ammonium salts of such boron acids, and esters of such boron acids. The use of complexes of a boron trihalide with ethers, organic acids, inorganic acids, or hydrocarbons is a convenient means of introducing the boron reactant into the reaction mixture. Such complexes are known and are exemplified by boron trifluoride-diethyl ether, boron trifluoride-phenol, boron trifluoride-phosphoric acid, boron trichloride-chloroacetic acid, boron tribromide-dioxane, and boron trifluoride-methyl ethyl ether.

10 [0058] Suitable phosphorus compounds for forming the dispersants herein include phosphorus compounds or mixtures of phosphorus compounds capable of introducing a phosphorus-containing species into the ashless dispersant. Any phosphorus compound, organic or inorganic, capable of undergoing such reaction can thus be used. Accordingly, use can be made of such inorganic phosphorus compounds as the inorganic phosphorus acids, and the inorganic phosphorus oxides, including their hydrates. Typical organic phosphorus compounds include full and partial esters of phosphorus acids, such as the mono-, di-, and tri esters of phosphoric acid, thiophosphoric acid, dithiophosphoric acid, trithiophosphoric acid and tetrathiophosphoric acid; the mono-, di-, and tri esters of phosphorous acid, thiophosphorous acid, dithiophosphorous acid and trithiophosphorous acid; the trihydrocarbyl phosphine oxides; the trihydrocarbyl phosphine sulfides; the mono- and dihydrocarbyl phosphonates, ($\text{RPO}(\text{OR}')\text{OR}''$) where R and R' are hydrocarbyl and R'' is a hydrogen atom or a hydrocarbyl group), and their mono-, di- and trithio analogs; the mono- and dihydrocarbyl phosphonites, ($\text{RP}(\text{OR}')\text{OR}''$) where R and R' are hydrocarbyl and R'' is a hydrogen atom or a hydrocarbyl group) and their mono- and dithio analogs; and the like. Thus, use can be made of such compounds as, for example, phosphorous acid (H_3PO_3 , sometimes depicted as $\text{H}_2(\text{HPO}_3)$, and sometimes called ortho-phosphorous acid or phosphonic acid), phosphoric acid (H_3PO_4 , sometimes called orthophosphoric acid), hypophosphoric acid ($\text{H}_4\text{P}_2\text{O}_6$), metaphosphoric acid (HPO_3), pyrophosphoric acid ($\text{H}_4\text{P}_2\text{O}_7$), hypophosphorous acid (H_3PO_2 , sometimes called phosphinic acid), pyrophosphorous acid ($\text{H}_4\text{P}_2\text{O}_5$, sometimes called pyrophosphonic acid), phosphinous acid (H_3PO), tripolyphosphoric acid ($\text{H}_5\text{P}_3\text{O}_{10}$), tetrapolyphosphoric acid ($\text{H}_5\text{P}_4\text{O}_{13}$), trimetaphosphoric acid ($\text{H}_3\text{P}_3\text{O}_9$), phosphorus trioxide, phosphorus tetraoxide, phosphorus pentoxide, and the like. Partial or total sulfur analogs such as phosphorotetrathioic acid (H_3PS_4), phosphoromonothioic acid ($\text{H}_3\text{PO}_3\text{S}$), phosphorodithioic acid ($\text{H}_3\text{PO}_2\text{S}_2$), phosphorotritioic acid (H_3POS_3), phosphorus sesquisulfide, phosphorus heptasulfide, and phosphorus pentasulfide (P_2S_5 , sometimes referred to as P_4S_{10}) can also be used in forming dispersants for this disclosure. Also usable, though less preferred, are the inorganic phosphorus halide compounds such as PCl_3 , PBr_3 , POCl_3 , PSCl_3 , etc.

15 [0059] Likewise use can be made of such organic phosphorus compounds as mono-, di-, and triesters of phosphoric acid (e.g., trihydrocarbyl phosphates, dihydrocarbyl monoacid phosphates, monohydrocarbyl diacid phosphates, and mixtures thereof), mono-, di-, and triesters of phosphorous acid (e.g., trihydrocarbyl phosphites, dihydrocarbyl hydrogen phosphites, hydrocarbyl diacid phosphites, and mixtures thereof), esters of phosphonic acids (both "primary", $\text{RP}(\text{O})(\text{OR})_2$, and "secondary", $\text{R}_2\text{P}(\text{O})(\text{OR})$), esters of phosphinic acids, phosphonyl halides (e.g., $\text{RP}(\text{O})\text{Cl}_2$ and $\text{R}_2\text{P}(\text{O})\text{Cl}$), halophosphites (e.g., $(\text{RO})\text{PCl}_2$ and $(\text{RO})_2\text{PCl}$), halophosphates (e.g., $\text{ROP}(\text{O})\text{Cl}_2$ and $(\text{RO})_2\text{P}(\text{O})\text{Cl}$), tertiary pyrophosphate esters (e.g., $(\text{RO})_2\text{P}(\text{O})-\text{O}-\text{P}(\text{O})(\text{OR})_2$), and the total or partial sulfur analogs of any of the foregoing organic phosphorus compounds, and the like wherein each hydrocarbyl group contains up to about 100 carbon atoms, preferably up to about 50 carbon atoms, more preferably up to about 24 carbon atoms, and most preferably up to about 12 carbon atoms. Also usable, although less preferred, are the halophosphine halides (e.g., hydrocarbyl phosphorus tetrahalides, dihydrocarbyl phosphorus trihalides, and trihydrocarbyl phosphorus dihalides), and the halophosphines (monohalophosphines and dihalophosphines).

20 [0060] The lubricants herein may include mixtures of one or more boronated and phosphorylated dispersants set forth above combined with non-boronated and non-phosphorylated dispersants.

25 [0061] In one embodiment the lubricating oil composition may include at least one borated dispersant, wherein the dispersant is the reaction product of an olefin copolymer or a reaction product of an olefin copolymer with succinic anhydride, and at least one polyamine. The ratio of PIBSA:polyamine may be from 1:1 to 10:1, preferably, 1:1 to 5:1, or 4:3 to 3:1 or 4:3 to 2:1. A particularly useful dispersant contains a polyisobutylene group of the PIBSA having a number average molecular weight (M_n) in the range of from about 500 to 5000, as determined by the GPC method described above, and a (B) polyamine having a general formula $\text{H}_2\text{N}(\text{CH}_2)_m-\text{[NH}(\text{CH}_2)_m\text{]}_n-\text{NH}_2$, wherein m is in the range from 2 to 4 and n is in the range of from 1 to 2.

30 [0062] In addition to the above, the dispersant may be post-treated with an aromatic carboxylic acid, an aromatic

polycarboxylic acid, or an aromatic anhydride wherein all carboxylic acid or anhydride group(s) are attached directly to an aromatic ring. Such carboxyl-containing aromatic compounds may be selected from 1,8-naphthalic acid or anhydride and 1,2-naphthalenedicarboxylic acid or anhydride, 2,3-naphthalenedicarboxylic acid or anhydride, naphthalene-1,4-dicarboxylic acid, naphthalene-2,6-dicarboxylic acid, phthalic anhydride, pyromellitic anhydride, 1,2,4-benzene tricarboxylic acid anhydride, diphenic acid or anhydride, 2,3-pyridine dicarboxylic acid or anhydride, 3,4-pyridine dicarboxylic acid or anhydride, 1,4,5,8-naphthalenetetracarboxylic acid or anhydride, perylene-3,4,9,10-tetracarboxylic anhydride, pyrene dicarboxylic acid or anhydride, and the like. The moles of this post-treatment component reacted per mole of the polyamine may range from about 0.1:1 to about 2:1. A typical molar ratio of this post-treatment component to polyamine in the reaction mixture may range from about 0.2:1 to about 2:1. Another molar ratio of this post-treatment component to the polyamine that may be used may range from 0.25:1 to about 1.5:1. This post-treatment component may be reacted with the other components at a temperature ranging from about 140° to about 180° C.

[0063] Alternatively, or in addition to the post-treatment described above, the dispersant may be post-treated with a non-aromatic dicarboxylic acid or anhydride. The non-aromatic dicarboxylic acid or anhydride of may have a number average molecular weight of less than 500, as measured by the GPC method described above. Suitable carboxylic acids or anhydrides thereof may include, but are not limited to acetic acid or anhydride, oxalic acid and anhydride, malonic acid and anhydride, succinic acid and anhydride, alkenyl succinic acid and anhydride, glutaric acid and anhydride, adipic acid and anhydride, pimelic acid and anhydride, suberic acid and anhydride, azelaic acid and anhydride, sebacic acid and anhydride, maleic acid and anhydride, fumaric acid and anhydride, tartaric acid and anhydride, glycolic acid and anhydride, 1,2,3,6-tetrahydronaphthalic acid and anhydride, and the like.

[0064] The non-aromatic carboxylic acid or anhydride is reacted at a molar ratio with the polyamine ranging from about 0.1 to about 2.5 moles per mole of polyamine. Typically, the amount of non-aromatic carboxylic acid or anhydride used will be relative to the number of secondary amino groups in the polyamine. Accordingly, from about 0.2 to about 2.0 moles of the non-aromatic carboxylic acid or anhydride per secondary amino group in Component B may be reacted with the other components to provide the dispersant according to embodiments of the disclosure. Another molar ratio of the non-aromatic carboxylic acid or anhydride to polyamine that may be used may range from 0.25:1 to about 1.5:1 moles of per mole of polyamine. The non-aromatic carboxylic acid or anhydride may be reacted with the other components at a temperature ranging from about 140° to about 180° C.

[0065] The weight % actives of the alkenyl or alkyl succinic anhydride can be determined using a chromatographic technique. This method is described in column 5 and 6 in U.S. Pat. No. 5,334,321. The percent conversion of the polyolefin is calculated from the % actives using the equation in column 5 and 6 in U.S. Pat. No. 5,334,321.

[0066] The TBN of a suitable borated dispersant may be from about 10 to about 65 mg KOH/gram composition on an oil-free basis, which is comparable to about 5 to about 30 mg KOH/gram composition TBN if measured on a dispersant sample containing about 50% diluent oil.

[0067] Typically, the dispersants described above are provided in about 4.5 to about 25 weight percent and, in other approaches, about 4.5 to about 12 weight percent, and in yet other approaches, about 4.5 to about 7.7 weight percent in the lubricant.

Extreme Pressure Agents

[0068] The lubricating oil compositions herein may also optionally contain one or more extreme pressure agents. Extreme Pressure (EP) agents that are soluble in the oil include sulfur- and chlorosulfur-containing EP agents, chlorinated hydrocarbon EP agents and phosphorus EP agents. Examples of such EP agents include chlorinated wax; organic sulfides and polysulfides such as dibenzyl disulfide, bis(chlorobenzyl) disulfide, dibutyl tetrasulfide, sulfurized methyl ester of oleic acid, sulfurized alkylphenol, sulfurized dipentene, sulfurized terpene, and sulfurized Diels-Alder adducts; phosphosulfurized hydrocarbons such as the reaction product of phosphorus sulfide with turpentine or methyl oleate; phosphorus esters such as the dihydrocarbyl and trihydrocarbyl phosphites, e.g., dibutyl phosphite, diheptyl phosphite, dicyclohexyl phosphite, pentylphenyl phosphite; dipentylphenyl phosphite, tridecyl phosphite, distearyl phosphite and polypropylene substituted phenyl phosphite; metal thiocarbamates such as zinc dioctyldithiocarbamate and barium heptylphenol diacid; amine salts of alkyl and dialkylphosphoric acids, including, for example, the amine salt of the reaction product of a dialkyldithiophosphoric acid with propylene oxide; and mixtures thereof.

[0069] The extreme pressure agents may be present in amount of, for example, from 0 to 3.0 wt. % or from 0.1 to 2.0 wt. %, based on the total weight of the lubricating oil composition.

Friction Modifiers

[0070] The lubricating oil compositions herein may also optionally contain one or more friction modifiers. Suitable friction modifiers may comprise metal containing and metal-free friction modifiers and may include, but are not limited to, imidazolines, amides, amines, succinimides, alkoxylated amines, alkoxylated ether amines, amine oxides, amidoam-

ines, nitriles, betaines, quaternary amines, imines, amine salts, amino guanidine, alkanolamides, phosphonates, metal-containing compounds, glycerol esters, sulfurized fatty compounds and olefins, sunflower oil other naturally occurring plant or animal oils, dicarboxylic acid esters, esters or partial esters of a polyol and one or more aliphatic or aromatic carboxylic acids, and the like.

5 [0071] Suitable friction modifiers may contain hydrocarbyl groups that are selected from straight chain, branched chain, or aromatic hydrocarbyl groups or mixtures thereof, and may be saturated or unsaturated. The hydrocarbyl groups may be composed of carbon and hydrogen or hetero atoms such as sulfur or oxygen. The hydrocarbyl groups may range from 12 to 25 carbon atoms. In some embodiments the friction modifier may be a long chain fatty acid ester. In another embodiment the long chain fatty acid ester may be a mono-ester, or a di-ester, or a (tri)glyceride. The friction modifier

10 [0072] Other suitable friction modifiers may include organic, ashless (metal-free), nitrogen-free organic friction modifiers. Such friction modifiers may include esters formed by reacting carboxylic acids and anhydrides with alkanols and generally include a polar terminal group (e.g. carboxyl or hydroxyl) covalently bonded to an oleophilic hydrocarbon chain. An example of an organic ashless nitrogen-free friction modifier is known generally as glycerol monooleate (GMO) which

15 may contain mono-, di-, and tri-esters of oleic acid. Other suitable friction modifiers are described in U.S. Pat. No. 6,723,685.

20 [0073] Aminic friction modifiers may include amines or polyamines. Such compounds can have hydrocarbyl groups that are linear, either saturated or unsaturated, or a mixture thereof and may contain from 12 to 25 carbon atoms. Further examples of suitable friction modifiers include alkoxylated amines and alkoxylated ether amines. Such compounds may have hydrocarbyl groups that are linear, either saturated, unsaturated, or a mixture thereof. They may contain from about 12 to about 25 carbon atoms. Examples include ethoxylated amines and ethoxylated ether amines.

25 [0074] The amines and amides may be used as such or in the form of an adduct or reaction product with a boron compound such as a boric oxide, boron halide, metaborate, boric acid or a mono-, di- or tri-alkyl borate. Other suitable friction modifiers are described in U.S. Pat. No. 6,300,291.

30 [0075] A friction modifier may optionally be present in ranges such as 0 wt. % to 6 wt. %, or 0.01 wt. % to 4 wt. %, or 0.05 wt. % to 2 wt. %.

Detergents

30 [0076] The lubricant composition also includes one or more select detergents or mixtures thereof to provide specific amounts of metal and soap content to the lubricating composition. By one approach, the detergent is a metal containing detergent, such as neutral to overbased detergents. Suitable detergent substrates include phenates, sulfur containing phenates, sulfonates, calixarates, salixarates, salicylates, carboxylic acids, phosphorus acids, mono- and/or di-thiophosphoric acids, alkyl phenols, sulfur coupled alkyl phenol compounds and methylene bridged phenols. Suitable detergents and their methods of preparation are described in greater detail in numerous patent publications, including U.S. Patent No. 7,732,390, and references cited therein. In one approach, the detergents are neutral to overbased sulfonates, phenates, or carboxylates with an alkali metal or alkaline earth metal salt. The detergents may be linear or branched, such as linear or branched sulfonates. Linear detergents are those that include a straight chain with no side chains attached thereto and typically include carbon atoms bonded only to one or two other carbon atoms. Branched detergents are those with one or more side chains attached to the molecule's backbone and may include carbon atoms bonded to one, two, three, or four other carbon atoms. In one embodiment the sulfonate detergent may be a predominantly linear alkylbenzenesulfonate detergent. In some embodiments the linear alkyl (or hydrocarbyl) group may be attached to the benzene ring anywhere along the linear chain of the alkyl group, but often in the 2, 3, or 4 position of the linear chain, and in some instances predominantly in the 2 position. In other embodiments, the alkyl (or hydrocarbyl) group may be branched, that is, formed from a branched olefin such as propylene or 1-butene or isobutene. Sulfonate detergents having a mixture of linear and branched alkyl groups may also be used.

45 [0077] The detergent substrate may be salted with an alkali or alkaline earth metal such as, but not limited to, calcium, magnesium, potassium, sodium, lithium, barium, or mixtures thereof. In some embodiments, the detergent is free of barium. A suitable detergent may include alkali or alkaline earth metal salts of petroleum sulfonic acids and long chain mono- or di-alkylarylsulfonic acids with the aryl group being one of benzyl, tolyl, and xylyl.

50 [0078] Overbased detergent additives are well known in the art and may be alkali or alkaline earth metal overbased detergent additives. Such detergent additives may be prepared by reacting a metal oxide or metal hydroxide with a substrate and carbon dioxide gas. The substrate is typically an acid, for example, an acid such as an aliphatic substituted sulfonic acid, an aliphatic substituted carboxylic acid, or an aliphatic substituted phenol. In general, the terminology "overbased" relates to metal salts, such as metal salts of sulfonates, carboxylates, and phenates, wherein the amount of metal present exceeds the stoichiometric amount. Such salts may have a conversion level in excess of 100% (i.e., they may comprise more than 100% of the theoretical amount of metal needed to convert the acid to its "normal," "neutral" salt). The expression "metal ratio," often abbreviated as MR, is used to designate the ratio of total chemical equivalents

of metal in the overbased salt to chemical equivalents of the metal in a neutral salt according to known chemical reactivity and stoichiometry. In a normal or neutral salt, the metal ratio is one and in an overbased salt, the MR, is greater than one. Such salts are commonly referred to as overbased, hyperbased, or superbased salts and may be salts of organic sulfur acids, carboxylic acids, or phenols. The detergents may also exhibit a total base number (TBN) of about 27 to about 307 and, in other approaches, about 200 to about 307.

[0079] In transmission fluids, the detergent provides less than about 455 ppm of the metal to the lubricant composition. Higher levels of metal result in failures in one or more of the friction durability or wear tests set forth herein. In other approaches, the detergent provides about 0 to about 281 ppm of metal. In yet other approaches, the detergent provides about 0 to about 100 ppm metal to the lubricant composition.

[0080] The detergent also provides select levels of soap content to the lubricant composition and the provided soap amounts are balanced with the level of metal such that if the metal is not within the desired ranges, then increasing soap content does not achieve desired results, which is discussed in more detail in the Examples herein. By one approach, the detergent provides about 0.02 to about 0.15 percent soap content to the final lubricating composition, such as sulfonate soap, phenate soap, and/or carboxylate soap. In other approaches, the detergent provides about 0.02 to about 0.1 percent soap, and in yet other approaches, about 0.02 to about 0.05 percent soap.

[0081] Soap content generally refers to the amount of neutral organic acid salt and reflects a detergent's cleansing ability, or detergency, and dirt suspending ability. The soap content can be determined by the following formula, using an exemplary calcium sulfonate detergent (represented by $RSO_3)_vCa_w(CO_3)_x(OH)_y$ with v, w, x, and y denoting the number of sulfonate groups, the number of calcium atoms, the number of carbonate groups, and the number of hydroxyl groups respectively):

$$\text{soap content} = \frac{\text{formula weight of } [(RSO_3)_2Ca]}{\text{effective formula weight}} \times 100$$

[0082] Effective formula weight is the combined weight of all the atoms that make up the formula $(RSO_3)_vCa_w(CO_3)_x(OH)_y$ plus that of any other lubricant components. Further discussion on determining soap content can be found in FUELS AND LUBRICANTS HANDBOOK, TECHNOLOGY, PROPERTIES, PERFORMANCE, AND TESTING, George Totten, editor, ASTM International, 2003, relevant portions thereof incorporated herein by reference.

[0083] The treat rates of the detergent may be about 0.08 weight percent to about 1 weight percent based on the total weight of the lubricant composition. In some approaches, the metal containing detergent is not boronated such that the boron in the lubricant is solely provided by the dispersant.

[0084] The total amount of detergent that may be present in the lubricating oil composition may be from 0 wt. % to 2 wt. %, or from about 0 wt. % to about 0.5 wt. %, or about 0 wt. % to about 0.15 wt.

Viscosity Index Improvers

[0085] The lubricating oil compositions herein also may optionally contain one or more viscosity index improvers. Suitable viscosity index improvers may include polyolefins, olefin copolymers, ethylene/propylene copolymers, polyisobutenes, hydrogenated styrene-isoprene polymers, styrene/maleic ester copolymers, hydrogenated styrene/butadiene copolymers, hydrogenated isoprene polymers, alpha-olefin maleic anhydride copolymers, polymethacrylates, polyacrylates, polyalkyl styrenes, hydrogenated alkenyl aryl conjugated diene copolymers, or mixtures thereof. Viscosity index improvers may include star polymers and suitable examples are described in US Publication No. 20120101017A1.

[0086] The lubricating oil compositions herein also may optionally contain one or more dispersant viscosity index improvers in addition to a viscosity index improver or in lieu of a viscosity index improver. Suitable viscosity index improvers may include functionalized polyolefins, for example, ethylene-propylene copolymers that have been functionalized with the reaction product of an acylating agent (such as maleic anhydride) and an amine; polymethacrylates functionalized with an amine, or esterified maleic anhydride-styrene copolymers reacted with an amine.

[0087] The total amount of viscosity index improver and/or dispersant viscosity index improver may be 0 wt. % to 20 wt. %, 0.1 wt. % to 15 wt. %, 0.25 wt. % to 12 wt. %, or 0.5 wt. % to 10 wt. %, of the lubricating composition.

Antioxidants

[0088] The lubricating oil compositions herein also may optionally contain one or more antioxidants. Antioxidant compounds are known and include for example, phenates, phenate sulfides, sulfurized olefins, phosphosulfurized terpenes, sulfurized esters, aromatic amines, alkylated diphenylamines (e.g., nonyl diphenylamine, di-nonyl diphenylamine, octyl diphenylamine, dioctyl diphenylamine), phenyl-alpha-naphthylamines, alkylated phenyl-alpha-naphthylamines, hindered non-aromatic amines, phenols, hindered phenols, oil-soluble molybdenum compounds, macromolecular antioxidants,

or mixtures thereof. Antioxidant compounds may be used alone or in combination.

[0089] Useful antioxidants may include diarylamines and high molecular weight phenols. In an embodiment, the lubricating oil composition may contain a mixture of a diarylamine and a high molecular weight phenol, such that each antioxidant may be present in an amount sufficient to provide up to about 5%, by weight, based upon the final weight of the lubricating oil composition. In an embodiment, the antioxidant may be a mixture of 0.3 to 2% diarylamine and 0.4 to 2% high molecular weight phenol, by weight, based upon the final weight of the lubricating oil composition.

[0090] The one or more antioxidant(s) may be present in ranges 0 wt. % to 5 wt. %, or 0.01 wt. % to 5 wt. %, or 0.1 wt. % to 3 wt. %, or 0.8 wt. % to 2 wt. %, of the lubricating composition.

10 Corrosion Inhibitors

[0091] The automatic transmission lubricants may further include additional corrosion inhibitors (it should be noted that some of the other mentioned components may also have copper corrosion inhibition properties). Suitable additional inhibitors of copper corrosion include ether amines, polyethoxylated compounds such as ethoxylated amines and ethoxylated alcohols, imidazolines, monoalkyl and dialkyl thiadiazole, and the like

[0092] Thiazoles, triazoles and thiadiazoles may also be used in the lubricants. Examples include benzotriazole; tolyltriazole; octyltriazole; decyltriazole; dodecyltriazole; 2-mercaptopbenzothiazole; 2,5-dimercapto-1,3,4-thiadiazole; 2-mercaptop-5-hydrocarbylthio-1,3,4-thiadiazoles; and 2-mercaptop-5-hydrocarbyldithio-1,3,4-thiadiazoles. The preferred compounds are the 1,3,4-thiadiazoles, especially the 2-hydrocarbyldithio-5-mercaptop-1,3,4-dithiadiazoles, a number of which are available as articles of commerce.

[0093] The corrosion inhibitor, if present, can be used in an amount sufficient to provide 0 wt. % to 5 wt. %, 0.01 wt. % to 3 wt. %, 0.1 wt. % to 2 wt. %, based upon the final weight of the lubricating oil composition.

25 Foam Inhibitors/Anti Foam Agents

[0094] Anti-foam/Surfactant agents may also be included in a fluid according to the present invention. Various agents are known for such use. Especially preferred are copolymers of ethyl acrylate and hexyl ethyl acrylate, such as PC-1244, available from Solutia. Preferred are silicone fluids, such as 4% DCF. Mixtures of anti-foam agents are especially preferred.

30 Anti-Rust Agents

[0095] Various known anti-rust agents or additives are known for use in transmission fluids, and are suitable for use in the fluids according to the present disclosure. Especially preferred are alkyl polyoxyalkylene ethers, such as Mazawet® 77, C-8 acids such as Neofat® 8, oxyalkyl amines such as Tomah PA-14, 3-decyloxypropylamine, and polyoxypropylene-polyoxyethylene block copolymers such as Pluronic® L-81.

Pour Point Depressants

[0096] Suitable pour point depressants may include polymethylmethacrylates or mixtures thereof. Pour point depressants may be present in an amount sufficient to provide from 0 wt.% to 1 wt.%, 0.01 wt.% to 0.5 wt.%, or 0.02 wt.% to 0.04 wt.%, based upon the total weight of the lubricating composition.

45 Seal-Swell Agents

[0097] The automatic transmission fluids of the present disclosure may further include seal swell agents. Seal swell agents such as esters, adipates, sebacates, azelates, phthalates, sulfones, alcohols, alkylbenzenes, substituted sulfolanes, aromatics, or mineral oils cause swelling of elastomeric materials used as seals in engines and automatic transmissions.

[0098] Alcohol-type seal swell agents are generally low volatility linear alkyl alcohols, such as decyl alcohol, tridecyl alcohol and tetradecyl alcohol. Alkylbenzenes useful as seal swell agents include dodecylbenzenes, tetradecylbenzenes, dinonyl-benzenes, di(2-ethylhexyl)benzene, and the like. Substituted sulfolanes (e.g. those described in U.S. Pat. No. 4,029,588, incorporated herein by reference) are likewise useful as seal swell agents in compositions according to the present invention. Mineral oils useful as seal swell agents in the present invention include low viscosity mineral oils with high naphthenic or aromatic content. Aromatic seal swell agents include the commercially available Exxon Aromatic 200 ND seal swell agent. Commercially available examples of mineral oil seal swell agents include Exxon® Necton®-37 (FN 1380) and Exxon® Mineral Seal Oil (FN 3200).

[0099] In general terms, a suitable lubricant may include additive components in the ranges listed in Table 1.

TABLE 1

Component	Suitable Ranges, Weight Percent	Preferred Ranges, Weight Percent
Monohydrocarbyl-substituted dimercaptothiadiazole derivatives according to Formula I or tautomers or salted versions thereof	0.001-4	0.1-3
Dispersants	0 to 10.0	1.0-8.0
Detergents	0.01 to 1	0.08 to 0.4
Friction Modifiers	0 to 6	0.005 to 4
Viscosity Modifiers	0 to 20	0 to 15
Antioxidants	0 to 5.0	0.05 to 3.0
Rust inhibitors	0 to 1	0.005 to 0.5
Corrosion Inhibitors	0 to 1.2	0.005 to 0.8
Anti-wear agents	0 to 5	0 to 3
Seal Swell Agents	0 to 20	0 to 10
Antifoam Agents	0 to 1	0.001 to 0.15
Extreme pressure agents	0 to 2	0 to 1
Lubricating Base Oils	Balance	Balance
Total	100	100

[0100] Additives used in formulating the compositions described herein may be blended into the base oil individually or in various sub-combinations. However, it may be suitable to blend all of the components concurrently using an additive concentrate (i.e., additives plus a diluent, such as a hydrocarbon solvent).

[0101] A better understanding of the present disclosure and its many advantages may be clarified with the following examples. The following examples are illustrative and not limiting thereof in either scope or spirit. Those skilled in the art will readily understand that variations of the components, methods, steps, and devices described in these examples can be used. Unless noted otherwise, all percentages, ratios, and parts noted in this disclosure are by weight.

Examples

[0102] Lubricating compositions according to examples 1 to 5 as well as comparative examples 1 to 3 as shown in Table 2 have been prepared.

[0103] Synthesis example A was prepared by mixing 266g of succinimide dispersant with 5.0 g DMTD and 46g PAO-4, stirring under nitrogen protection at 110 °C for 1h, then 130 °C for 1h, and 140 °C for 1h to give a dark brown oil.

[0104] Synthesis example B was prepared by mixing 221.3g of succinimide dispersant with 8.27g of a compound of Formula I, or a tautomer thereof, wherein R is methyl, (also referred to as 5-(methylthio)-3,4-thiadiazole-2(3H)-thione), stirring under nitrogen protection at 80 °C for 1.5h, then 105 °C for 1h to give a light brown oil.

[0105] Synthesis example C was prepared by mixing 428g of succinimide dispersant with 20.4g of Formula I, or a tautomer thereof, wherein R is methyl (also referred to as 5-(methylthio)-3,4-thiadiazole-2(3H)-thione), stirring under nitrogen at 90 °C for 30 minutes, then 100 °C for 30 minutes, then 105 °C for 1h to give a light brown oil.

[0106] All examples and comparative examples have been formulated to comparable kinematic viscosity at 100 °C (KV100).

TABLE 2

	Comp. Ex. 1	Ex. 1	Ex. 2	Ex. 3	Comp. Ex. 2	Comp. Ex. 3	Ex. 4 a	Ex. 4
Succinimide dispersant ¹	4	-	2	4	4	-	2.3	2.3
Aromatic amine antioxidant	0.4	0.4	0.4	0.4	0.4	-	-	-
Synthesis Example A	-	-	-	-	-	4.77	-	-

(continued)

	Comp. Ex. 1	Ex. 1	Ex. 2	Ex. 3	Comp. Ex. 2	Comp. Ex. 3	Ex. 4 a	Ex. 4								
5	Synthesis Example B	-	4.3	2.2	-	-	-	-								
Synthesis	-	-	-	-	-	-	1.7	1.7								
Example C																
10	Inventive agent delivered without dispersant ²	-	-	-	0.15	0.15	-	-								
Calcium Salicylate Detergent	-	-	-	-	-	-	0.6	-								
Dibutyl hydrogen phosphite	-	-	-	-	0.18	-	-	-								
15	Total succinimide dispersant	4	4.15	4.12	4	4	4	3.92								
Total Inventive agent ²	-	0.15	0.08	0.15	0.15	-	0.08	0.08								
20	Total Conventional agent 1 ³	0.3	-	0.1	-	-	-	-								
Total Conventional agent 2 ⁴	-	-	-	-	-	0.1	-	-								
25	Group V synthetic dibasic ester base oil based on diisooctyl adipate	5	5	5	5	5	5	5								
Base Oil 1 ⁵	43.76	43.76	43.76	43.83	43.75	43.72	43.8	44.1								
Base Oil 2 ⁶	46.54	46.54	46.54	46.62	46.52	46.51	46.6	46.9								
Total	100	100	100	100	100	100	100	100								
30	FZG, FLS ⁷	5	9	9	9	8	3	7								
Total sulfur ⁸	1108	940	824	746	752	498	497	480								
KV100	5.294	5.369	5.341	5.312	5.294	5.33	5.324	5.285								
All amounts shown in wt.%.																
35	1The succinimide dispersant was a 950 MW succinimide dispersant.															
2Inventive agent: 5-(methylthio)-3,4-thiadiazole-2(3H)-thione (R=methyl in Formula (I)) 3Conventional agent 1: 85:15 mixture of 2,5-bis-(hydrocarbyldithio)-1,3,4-thiadiazole and 5-hydrocarbyldithio-2-mercaptop-1,3,4-thiadiazole																
4Conventional agent 2: dimercaptothiadiazole (R=H in Formula (I))																
40	5Base Oil 1: PAO having KV 100= 4 cSt															
6Base Oil 2: PAO having KV 100 = 6 cSt																
7FZG, FLS: FZG(A10/16.6R/90); FLS: Failure Load Stage as determined by CEC L-84-02																
45	8Total Sulfur as determined by Inductively Coupled Plasma (ICP) spectrometry															

[0107] A comparison of Examples 1 and 2 with Comparative Example 1 shows that despite the lower sulfur levels delivered by the inventive agent, the lubricating compositions of the present invention outperform the conventional lubricating composition comprising 2,5-bis-(hydrocarbyldithio)-1,3,4-thiadiazole. A particular synergism is observed in Example 2 wherein the combination of a conventional mixture of 2,5-bis-(hydrocarbyldithio)-1,3,4-thiadiazole and its monohydrocarbyl derivative with the inventive agent leads to the same FZG test performance at even lower sulfur levels.

[0108] A comparison of Example 3 with Comparative Example 2 shows that phosphite has a detrimental influence on FZG test performance.

[0109] A comparison of Comparative Example 3 with Examples 4a and 4 shows that the inventive agent outperforms DMTD and that FZG test performance is even enhanced in the absence of a detergent, in particular a salicylate detergent.

TABLE 3

	Comp. Ex. 5	Ex. 5
Commercial Formulation*	99.84	99.84
Conventional Agent ²	0.16	

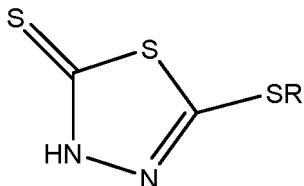
(continued)

	Comp. Ex. 5	Ex. 5
Inventive compound delivered without dispersant		0.16
Total	100	100
FZG, FLS	5	8
S-ICP	1240	1547
kV 100	6.18	6.12

* Commercial Formulation contains: extreme pressure agent, succinimide friction modifiers, aminic friction modifiers, aromatic amine antioxidant, borated and phosphorylated succinimide dispersant, 300 TBN calcium sulfonate detergent, antifoam agents, process oil, polymethacrylate viscosity modifiers, ester base oils, and Group 3 base oils.

Claims**1. Lubricating composition comprising**

a) a major part of a base oil of lubricating viscosity wherein the base oil is selected from API Group I, II, III, IV, V, or mixtures thereof,
 b) a total of 0.001 to 0.536 wt.%, based on the total lubricating composition, of one or more monohydrocarbyl-substituted dimercaptodiadiazole derivative(s) according to Formula (I), or a tautomer or salt thereof, below

Formula Iwherein R is methyl or C₂ to C₄ alkyl,

wherein the total lubricating composition has a sulfur content of up to 2,500 ppm (wt.),

c) less than 0.1 wt% phosphite;
 d) a dispersant.

2. Lubricating composition according to claim 1, wherein the monohydrocarbyl-substituted dimercaptodiadiazole derivative(s) (s) according to Formula (I) are present in a total of 0.005 to 0.400 wt.%, in particular 0.01 to 0.3 or 0.05 to 0.2 wt.% based on the total lubricating composition.

3. Lubricating composition according to claim 1 or 2, wherein the monohydrocarbyl-substituted dimercaptodiadiazole derivative(s) comprise 5-(methylthio)-3,4-thiadiazole-2(3H)-thione, in particular wherein the dimercaptodiadiazole is 5-(methylthio)-3,4-thiadiazole-2(3H)-thione.

4. Lubricating composition according to any one of claims 1 to 3, wherein the monohydrocarbyl-substituted dimercaptodiadiazole derivative(s) contributes 200 to 1,500, in particular 400 to 1,000 ppm sulfur to the lubricating composition.

5. Lubricating composition according to any one of claims 1 to 4 wherein the dispersant is present in an amount of 0.001 to 10 wt.%, based on the total lubricating composition, preferably 0.01 to 8, in particular 0.1 to 5 wt.% in the lubricating composition.

6. Lubricating composition according to any one of claims 1 to 5 wherein the dispersant is selected from the group consisting of ashless dispersants, borated ashless dispersants, ash-containing dispersants, dispersant viscosity

index improvers, in particular wherein the dispersant is an ashless dispersant selected from succinimide dispersants, polyisobutylene dispersants, and ethylene-propylene copolymers.

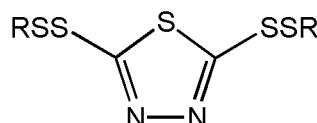
5 7. Lubricating composition according to any one of claims 1 to 6, wherein the total lubricating composition has a sulfur content of less than 2,000 ppm (wt.) or 1,800 ppm (wt.), in particular less than 1500, specifically less than 1200 ppm (wt.).

10 8. Lubricating composition according to any one of claims 1 to 7, further comprising one or more additives selected from the group consisting of extreme-pressure agents, anti-wear agents, friction modifiers, metal deactivators, detergents, viscosity index improvers, antioxidants, corrosion inhibitors, foam inhibitors, demulsifiers, pour point depressants, seal swelling agents, and mixtures thereof.

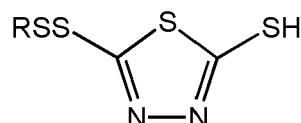
15 9. Lubricating composition according to any one of claims 1 to 8, comprising less than 0.05 wt.%, especially less than 0.01 wt.% phosphite, in particular wherein the composition is free of phosphite.

20 10. Lubricating composition according to any one of claims 1 to 9, comprising 0.001 to 0.20 wt.% of the one or more monohydrocarbyl-substituted dimercaptothiadiazoles and 0.01 to 0.40 wt.% mono- and/or bishydrocarbylthio-substituted dimercaptothiadiazoles of Formulas II/IIa

25 Formula (II)



20 Formula (IIa)



30 wherein R is independently, C₅-C₁₅ alkyl.

35 11. Use of the lubricating composition according any one of claims 1 to 10 for lubricating a driveline, a transmission, in particular a manual or automated transmission, a gear, an automated gear, or an axle.

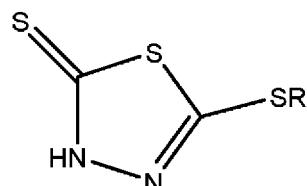
35 Patentansprüche

1. Schmierzusammensetzung, umfassend

40 a) zu einem Großteil ein Basisöl mit Schmierviskosität, wobei das Basisöl aus API-Gruppe I, II, III, IV, V oder Mischungen davon ausgewählt ist,

45 b) zu insgesamt 0,001 bis 0,536 Gew.-%, bezogen auf die Gesamtschmierzusammensetzung, ein oder mehrere monohydrocarbylsubstituierte Dimercaptothiadiazolderivat(e) gemäß der nachstehenden Formel (I) oder ein Tautomer oder Salz davon

45 Formel I



50 55 wobei R Methyl oder C₂- bis C₄-Alkyl ist,
wobei die Gesamtschmierzusammensetzung einen Schwefelgehalt von bis zu 2.500 ppm (Gew.) aufweist,

55 c) zu weniger als 0,1 Gew.-% Phosphit;

d) ein Dispergiermittel.

2. Schmierzusammensetzung nach Anspruch 1, wobei die monohydrocarbylsubstituierten Dimercaptothiadiazolderivat(e) gemäß Formel (I) zu insgesamt 0,005 bis 0,400 Gew.-%, insbesondere 0,01 bis 0,3 oder 0,05 bis 0,2 Gew.-%, bezogen auf die Gesamtschmierzusammensetzung, vorliegen.

3. Schmierzusammensetzung nach Anspruch 1 oder 2, wobei das bzw. die monohydrocarbylsubstituierten Dimercaptothiadiazolderivat(e) 5-(Methylthio)-3,4-thiadiazol-2(3H)-thion umfassen, insbesondere wobei das Dimercaptothiadiazol 5-(Methylthio)-3,4-thiadiazol-2(3H)-thion ist.

4. Schmierzusammensetzung nach einem der Ansprüche 1 bis 3, wobei das bzw. die monohydrocarbylsubstituierten Dimercaptothiadiazolderivat(e) 200 bis 1.500, insbesondere 400 bis 1.000 ppm Schwefel zu der Schmierzusammensetzung beitragen.

5. Schmierzusammensetzung nach einem der Ansprüche 1 bis 4, wobei das Dispergiermittel in einer Menge von 0,001 bis 10 Gew.-%, bezogen auf die Gesamtschmierzusammensetzung, vorzugsweise 0,01 bis 8, insbesondere 0,1 bis 5 Gew.-% in der Schmierzusammensetzung vorhanden ist.

6. Schmierzusammensetzung nach einem der Ansprüche 1 bis 5, wobei das Dispergiermittel ausgewählt ist aus der Gruppe bestehend aus aschelosen Dispergiermitteln, borierten aschelosen Dispergiermitteln, aschehaltigen Dispergiermitteln, dispergierenden Viskositätsindexverbesserern, insbesondere wobei das Dispergiermittel ein ascheloses Dispergiermittel ist, das aus Succinimid-Dispergiermitteln, Polyisobutylene-Dispergiermitteln und Ethylen-Propylen-Copolymeren ausgewählt ist.

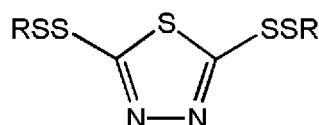
7. Schmierzusammensetzung nach einem der Ansprüche 1 bis 6, wobei die Gesamtschmierzusammensetzung einen Schwefelgehalt von weniger als 2.000 ppm (Gew.) oder 1.800 ppm (Gew.), insbesondere weniger als 1.500, insbesondere weniger als 1.200 ppm (Gew.) aufweist.

8. Schmierzusammensetzung nach einem der Ansprüche 1 bis 7, ferner umfassend einen oder mehrere Zusatzstoffe, die ausgewählt sind aus der Gruppe bestehend aus Höchstdruckmitteln, Verschleißschutzmitteln, Reibungsmodifizierungsmitteln, Metaldeaktivatoren, Detergenzien, Viskositätsindexverbesserern, Antioxidationsmitteln, Korrosionsschutzmitteln, Schaumunterdrückern, Demulgatoren, Stockpunktsenkern, Dichtungsquellmitteln und Mischungen davon.

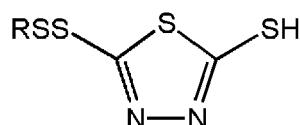
9. Schmierzusammensetzung nach einem der Ansprüche 1 bis 8, die weniger als 0,05 Gew.-%, insbesondere weniger als 0,01 Gew.-% Phosphit umfasst, insbesondere wobei die Zusammensetzung frei von Phosphit ist.

10. Schmierzusammensetzung nach einem der Ansprüche 1 bis 9, umfassend zu 0,001 bis 0,20 Gew.-% das eine oder die mehreren monohydrocarbylsubstituierten Dimercaptothiadiazole und zu 0,01 bis 0,40 Gew.-% Mono- und/oder bishydrocarbylthiosubstituierte Dimercaptothiadiazole der Formeln II/IIa

Formel (II)



Formel (IIa)



50 wobei R unabhängig C₅-C₁₅-Alkyl ist.

55 11. Verwendung der Schmierzusammensetzung nach einem der Ansprüche 1 bis 10 zum Schmieren eines Antriebsstrangs, einer Übertragung, insbesondere einer manuellen oder automatisierten Übertragung, eines Getriebes, eines automatisierten Getriebes oder einer Achse.

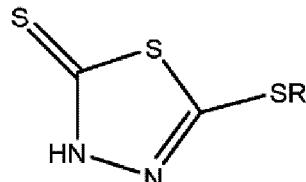
Revendications

1. Composition lubrifiante comprenant

5 a) une majeure partie d'une huile de base de viscosité lubrifiante dans laquelle l'huile de base est sélectionnée parmi le Groupe I, II, III, IV, V API, ou des mélanges de ceux-ci,
 b) un total de 0,001 à 0,536 % en poids, sur la base de la composition lubrifiante totale, d'un ou plusieurs dérivé(s) de dimercaptothiadiazole à substitution monohydrocarbyle selon la Formule (I), ou d'un tautomère ou d'un sel de celui-ci, ci-dessous

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Formule I



dans laquelle R est un méthyle ou un alkyle en C_2 à C_4 ,
 dans laquelle la composition lubrifiante totale a une teneur en soufre allant jusqu'à 2500 ppm (en poids),

25 c) moins de 0,1 % en poids de phosphite ;
 d) un dispersant.

2. Composition lubrifiante selon la revendication 1, dans laquelle les dérivés de dimercaptothiadiazole à substitution monohydrocarbyle selon la Formule (I) sont présents dans un total de 0,005 à 0,400 % en poids, en particulier de 0,01 à 0,3 ou de 0,05 à 0,2 % en poids sur la base de la composition lubrifiante totale.

30 3. Composition lubrifiante selon la revendication 1 ou 2, dans laquelle le ou les dérivés de dimercaptothiadiazole à substitution monohydrocarbyle comprennent 5-(méthylthio)-3,4-thiadiazole-2(3H)-thione, en particulier dans laquelle le dimercaptothiadiazole est 5-(méthylthio)-3,4-thiadiazole-2(3H)-thione.

35 4. Composition lubrifiante selon l'une quelconque des revendications 1 à 3, dans laquelle le ou les dérivés de dimercaptothiadiazole à substitution monohydrocarbyle apportent de 200 à 1500, en particulier de 400 à 1000 ppm de soufre à la composition lubrifiante.

40 5. Composition lubrifiante selon l'une quelconque des revendications 1 à 4, dans laquelle le dispersant est présent en une quantité de 0,001 à 10 % en poids, sur la base de la composition lubrifiante totale, de préférence de 0,01 à 8, en particulier de 0,1 à 5 % en poids dans la composition lubrifiante.

45 6. Composition lubrifiante selon l'une quelconque des revendications 1 à 5, dans laquelle le dispersant est sélectionné parmi le groupe constitué de dispersants sans cendres, dispersants boratés sans cendres, dispersants contenant des cendres, dispersants améliorant l'indice de viscosité, en particulier dans laquelle le dispersant est un dispersant sans cendre choisi parmi des dispersants succinimide, dispersants polyisobutylène et copolymères éthylène-propylène.

50 7. Composition lubrifiante selon l'une quelconque des revendications 1 à 6, dans laquelle la composition lubrifiante totale a une teneur en soufre inférieure à 2000 ppm (en poids) ou 1800 ppm (en poids), en particulier inférieure à 1500, spécifiquement inférieure à 1200 ppm (en poids).

55 8. Composition lubrifiante selon l'une quelconque des revendications 1 à 7, comprenant en outre un ou plusieurs additifs choisi parmi le groupe constitué d'agents extrême-pression, agents anti-usure, modificateurs de friction, désactivateurs de métaux, détergents, améliorants d'indice de viscosité, antioxydants, inhibiteurs de corrosion, inhibiteurs de mousse, agents désémulsifiants, abaisseurs de point d'écoulement, agents de gonflement des joints et mélanges de ceux-ci.

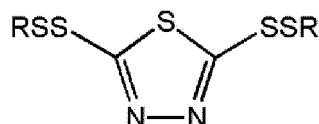
9. Composition lubrifiante selon l'une quelconque des revendications 1 à 8, comprenant moins de 0,05 % en poids, en particulier moins de 0,01 % en poids de phosphite, en particulier dans laquelle la composition est exempte de phosphite.

5 10. Composition lubrifiante selon l'une quelconque des revendications 1 à 9, comprenant de 0,001 à 0,20 % en poids du ou des dimercaptothiadiazoles à substitution monohydrocarbyle et de 0,01 à 0,40 % en poids de dimercaptothiadiazoles à substitution mono- et/ou bishydrocarbylethio de Formules II/IIa

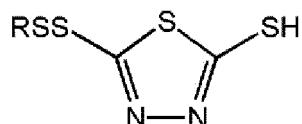
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Formule (II)

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Formule (IIa)



dans laquelle R est indépendamment, un alkyle en C₅-C₁₅.

20 11. Utilisation de la composition lubrifiante selon l'une quelconque des revendications 1 à 10 pour la lubrification d'une chaîne cinématique, d'une transmission, en particulier d'une transmission manuelle ou automatisée, d'un engrenage, d'un engrenage automatisé ou d'un essieu.

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REFERENCES CITED IN THE DESCRIPTION

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