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(54) **LUBRICATING OIL CONTAINING ALKYL PHOSPHONIC ACID**

SCHMIERSTOFFZUSAMMENSETZUNG ENTHALTEND ALKYLPHOSPHONSÄURE

COMPOSITION LUBRIFIANTE CONTENANT UN ACIDE PHOSPHONIQUE ALKYLÉ

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Description

TECHNICAL FIELD

[0001] This disclosure relates to lubricating oil additives and lubricating oil compositions containing the same. More specifically, this disclosure describes zinc-free additives that impart anti-wear properties to lubricating oil compositions.

BACKGROUND

[0002] Zinc dialkyldithiophosphate (ZnDTP) has long been used as a wear inhibitor in various lubricating fluids such as automotive engine oil. At least one drawback is that ZnDTP can decompose due to high temperature, oxidative deterioration, or hydrolysis in the presence of water. The result of the decomposition is a sludge that decreases friction coefficient and/or clogs important moving parts.

[0003] When ZnDTP is used in automatic transmission fluids (ATF), the decomposition products can accumulate in the pores of the paper material that forms the wet clutch, which can lead to clogging. Consequently, the cooling performance and durability of the clutch are significantly reduced.

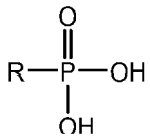
[0004] US patent application 2006/264340 discloses a zinc-free transmission lubricating oil composition comprising an ashless succinimide dispersant, a friction modifier and a phosphonate or phosphonic acid anti-wear additive.

[0005] Thus, there exists a need for alternative zinc-free wear inhibitors that can be used in various lubricating fluids.

SUMMARY

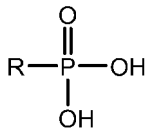
[0006] The invention is defined in the appended claims.

[0007] In one aspect, there is provided a lubricating oil composition comprising: a major amount of an oil of lubricating viscosity having a kinematic viscosity at 100°C in a range of about 1.5 to about 35 mm^2/s; and an anti-wear mixture comprising: one or more ashless dispersants and an alkyl phosphonic acid having a structure given by



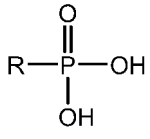
wherein R is a C_3-C_{20} hydrocarbyl group; initial pH of the anti-wear mixture is between 5.0-9.5 as measured by ASTM D664; and wherein the lubricating oil composition is free of zinc.

[0008] In another aspect, there is provided a lubricating oil composition comprising: a major amount of an oil of lubricating viscosity having a kinematic viscosity at 100°C in a range of about 1.5 to about 35 mm^2/s; and an anti-wear mixture comprising: one or more polyisobutenyl succinimide dispersants and an alkyl phosphonic acid having a structure given by



wherein R is a C_3-C_{20} hydrocarbyl group; initial pH of the anti-wear mixture is between 5.0 - 9.5 as measured by ASTM D664; and wherein the lubricating oil composition is free of zinc.

[0009] In yet another aspect, there is provided a method of reducing wear of a transmission or gear comprising: lubricating the transmission or gear with a lubricating oil composition comprising: a major amount of an oil of lubricating viscosity having a kinematic viscosity at 100°C in a range of about 1.5 to about 35 mm2/s; and an anti-wear mixture comprising: one or more ashless dispersants and an alkyl phosphonic acid of the following formula:



wherein R is a C_3-C_{20} hydrocarbyl group; wherein the initial pH of the anti-wear mixture is between 5.0 - 9.5 when measured by the ASTM D664 method; and wherein the lubricating oil composition is free of zinc.

DETAILED DESCRIPTION

Definitions

[0010] The term "succinimide" is understood in the art to include many of the amide, imide, and amidine species which may be formed by the reaction of a succinic anhydride with an amine. The predominant product, however, is a succinimide and this term has been generally accepted as meaning the product of a reaction of an alkenyl- or alkyl-substituted succinic acid or anhydride with an amine. Alkenyl or alkyl succinimides are disclosed in numerous references and are well known in the art. Certain fundamental types of succinimides and related materials encompassed by the term of art "succinimide" are taught in U.S. Patent Nos. 2,992,708; 3,018,291; 3,024,237; 3,100,673; 3,219,666; 3,172,892; and 3,272,746.

[0011] The term "hydrocarbyl" refers to a chemical group or moiety derived from hydrocarbons including saturated and unsaturated hydrocarbons. Examples of hydrocarbyl groups include alkenyl, alkyl, polyalkenyl, polyalkyl, phenyl, and the like.

[0012] The terms 'oil-soluble' or 'oil-dispersible' as used herein do not necessarily indicate that the compounds or additives are soluble, dissolvable, miscible or capable of being suspended in the oil in all proportions. These do mean, however, that they are, for instance, 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.

[0013] It is understood that when combinations, subsets, groups, etc. of elements are disclosed (e.g., combinations of components in a composition, or combinations of steps in a method), that while specific reference of each of the various individual and collective combinations and permutations of these elements may not be explicitly disclosed, each is specifically contemplated and described herein.

[0014] A dispersant is an essential lubricant additive, particularly in engine oil and automatic transmission fluid, for preventing sludge generation and increasing friction coefficient of wet clutch. However, dispersants can often reduce the effects of anti-wear agents (e.g., ZnDTP) and extreme pressure (EP) additives particularly in sulfur phosphorus (S-P) type gear oils and automatic transmission fluids.

[0015] The present invention describes wear inhibitors (or anti-wear agents) that can impart anti-wear properties to lubricating oil compositions. In some embodiments, the present invention describes a wear inhibitor system comprising a succinimide and a phosphonic acid. The wear inhibitor system of the present invention is zinc-free (present in less than about 10 ppm) and therefore avoids at least some of the performance issues associated with conventional zinc anti-wear agents.

[0016] The wear inhibitor system of the present invention may be added to any compatible lubricating oil such as engine oil, hydraulic fluid, slide way lubricant, automatic transmission fluid (ATF), continuously variable transmission (CVT) fluid, battery electric vehicle (BEV), hybrid electric vehicle (HEV) transmission fluid, and gear oil.

Succinimide Dispersants

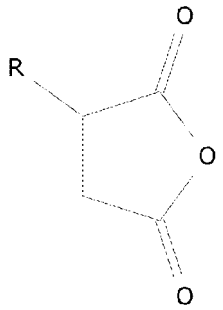
[0017] The succinimide dispersant can be prepared by any known method such as those described in, for example, U.S. Patent Publication No. 20180034635 and U.S. Patent No. 7,091,306,

[0018] In accordance with the present invention, the succinimide is a hydrocarbyl succinimide obtained as the product of a reaction of alkyl-substituted succinic anhydrides with a polyamine. In lubricating oil applications, the succinic anhydrides are typically substituted in alpha position by an alkyl chain such as polyisobutylene (PIBSA) or PIBSA-type moiety. However, any alkyl group compatible with the present invention may be contemplated.

[0019] For lubricating oil application, polyalkylene polyamine is commonly used as the polyamine. However, any polyamine compatible with the present invention may be contemplated.

[0020] The polyamine can react with the alkyl-substituted succinic anhydride to produce, according to their molar ratio, mono-succinimides, bis-succinimides, tris-succinimides or mixtures of thereof.

[0021] In one embodiment, a hydrocarbyl bis-succinimide can be obtained by reacting a hydrocarbyl-substituted succinic anhydride of structure II



Structure II

(wherein R is a hydrocaryl substituent is derived from a polyalkene group having a number average molecular weight of from about 500 to about 3000) with a polyamine.

[0022] In one embodiment, R is a hydrocarbyl substituent is derived from a polyalkene group having a number average molecular weight of from about 1000 to about 2500. In one embodiment, R is a polyisobutenyl substituent derived from a polyisobutene having a number average molecular weight of from about 500 to about 3000 (such as from 850 to 1700). In another embodiment, R is a polyisobutenyl substituent derived from a polyisobutene having a number average molecular weight of from about 1000 to about 2500.

[0023] Suitable polyamines can have a straight- or branched-chain structure and may be cyclic, acylic, or combinations thereof.

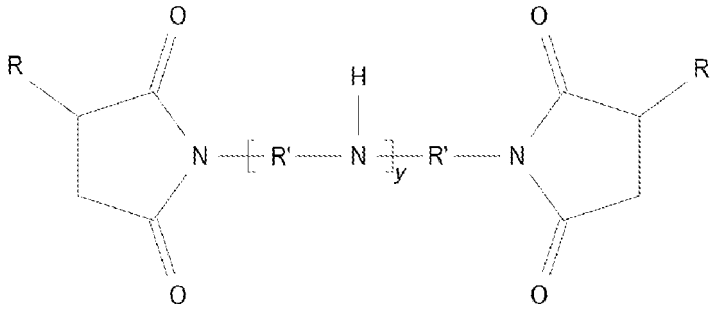
[0024] In some embodiments, polyalkylene polyamines may be used to prepare the bis-succinimide dispersants. Such polyalkylene polyamines will typically contain about 2 to about 12 nitrogen atoms and about 2 to 24 carbon atoms. Particularly suitable polyalkylene polyamines include those having the formula: H_2N-(R'NH)$_x$-H wherein R' is a straight- or branched-chain alkylene group having 2 or 3 carbon atoms and x is 1 to 9. Representative examples of suitable polyalkylene polyamines include diethylenetriamine (DETA), triethylenetetramine (TETA), tetraethylenepentamine (TEPA), pentaethylene hexamine (PEHA), and heavier poly-alkylene-amines (HPA).

[0025] In some embodiments, the polyamine may contain cyclic groups. Specific examples include N, N'-bis-(2-aminoethyl)piperazine) (Bis AEP), N-[(2-aminoethyl) 2-aminoethyl]piperazine) (PEEDA), 1-(2-aminoethyl)-4-[(2-aminoethyl)amino]ethyl]-piperazine) (AEPEEDA) and 1-[2-[[2-[(2-aminoethyl)amino]ethyl]amino]ethyl]-piperazine) (PEDETA).

[0026] Many of the polyamines suitable for use in the present invention are commercially available and others may be prepared by methods which are well known in the art. For example, methods for preparing amines and their reactions are detailed in Sidgewick's "The Organic Chemistry of Nitrogen", Clarendon Press, Oxford, 1966; Noller's "Chemistry of Organic Compounds", Saunders, Philadelphia, 2nd Ed., 1957; and Kirk-Othmer's "Encyclopedia of Chemical Technology", 2nd Ed., especially Volume 2, pp. 99 116.

[0027] Generally, the hydrocarbyl-substituted succinic anhydride is reacted with the polyamine at a temperature of about 130°C to 220°C (e.g., 140°C to 200°C, 145°C to 175°C, etc.). The reaction can be carried out under an inert atmosphere, such as nitrogen or argon. Generally, a suitable molar charge of polyamine to polyalkenyl-substituted succinic anhydride is from about 0.35:1 to about 1:1 (e.g., 0.4:1 to 0.75:1). As used herein, the "molar charge of polyamine to polyalkenyl-substituted succinic anhydride" means the ratio of the number of moles of polyamine to the number of succinic groups in the succinic anhydride reactant.

[0028] One class of suitable hydrocarbyl succinimides may be represented by the following structure:



Structure III

wherein R and R' are as described herein above and y is 1 to 11.

[0029] In some embodiments, the succinimide dispersant may be post-treated by a reactive boron compound or organic carbonate.

[0030] Suitable boron compounds that can be used as a source of boron include, for example, boric acid, a boric acid salt, a boric acid ester, and the like. Representative examples of a boric acid include orthoboric acid, metaboric acid, paraboric acid, and the like. Representative examples of a boric acid salt include ammonium borates, such as ammonium metaborate, ammonium tetraborate, ammonium pentaborate, ammonium octaborate, and the like. Representative examples of a boric acid ester include monomethyl borate, dimethyl borate, trimethyl borate, monoethyl borate, diethyl borate, triethyl borate, monopropyl borate, dipropyl borate, tripropyl borate, monobutyl borate, dibutyl borate, tributyl borate, and the like.

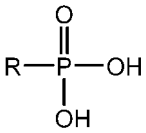
[0031] Suitable organic carbonates include, for example, cyclic carbonates such as 1,3-dioxolan-2-one (ethylene carbonate); 4-methyl-1,3-dioxolan-2-one(propylene carbonate); 4-ethyl-1,3-dioxolan-2-one(butylene carbonate); 4-hydroxymethyl-1,3-dioxolan-2-one; 4,5-dimethyl-1,3-dioxolan-2-one; 4-ethyl-1,3-dioxolan-2-one; 4,4-dimethyl-1,3-dioxolan-2-one; 4-methyl-5-ethyl-1,3-dioxolan-2-one; 4,5-diethyl-1,3-dioxolan-2-one; 4,4-diethyl-1,3-dioxolan-2-one; 1,3-dioxan-2-one; 4,4-dimethyl-1,3-dioxan-2-one; 5,5-dimethyl-1,3-dioxan-2-one; 5,5-dihydroxymethyl-1,3-dioxan-2-one; 5-methyl-1,3-dioxan-2-one; 4-methyl-1,3-dioxan-2-one; 5-hydroxy-1,3-dioxan-2-one; 5-hydroxymethyl-5-methyl-1,3-dioxan-2-one; 5,5-diethyl-1,3-dioxan-2-one; 5-methyl-5-propyl-1,3-dioxan-2-one; 4,6-dimethyl-1,3-dioxan-2-one; 4,4,6-trimethyl-1,3-dioxan-2-one and spiro[1,3-oxa-2-cyclohexanone-5,5'-1',3'-oxa-2'-cyclohexanone]. Other suitable cyclic carbonates may be prepared from saccharides such as sorbitol, glucose, fructose, galactose and the like and from vicinal diols prepared from C_1 to C_{30} olefins by methods known in the art.

Alkyl Phosphonic Acid

[0032] Alkyl phosphonic acid may be described as a hydrocarbyl substituted derivative of a phosphonic acid. Phosphonic acids including alkyl phosphonic acids are generally insoluble in base oil due to their diacid structure. This has limited the use of phosphonic acids in lubricating oils.

[0033] Mixing alkyl phosphonic acids with a basic compound such as the succinimide dispersant of the present invention neutralizes the alkyl phosphonic acid which in turn enhances the oil solubility of the mixture including the alkyl phosphonic acid and/or the alkyl phosphonate.

[0034] In accordance with the present invention, the alkyl phosphonic acid is a monoalkyl phosphonic acid that can be described by the following formula:



Structure IV

wherein R is a C_3-C_{20} hydrocarbyl group. R may be saturated or unsaturated. R may be linear, branched, or cyclic. In some embodiments, R is aliphatic. In some embodiments, R is aromatic. R may be an alkyl, aryl, or alkaryl group. In some embodiments, R may include a heteroatom. In some embodiments, R may include an ether or thioether moiety.

[0035] The phosphonic acid may be obtained by any known compatible method. For example, phosphonic acid may

be obtained via oxidation of phosphinic acid. Another synthetic pathway involves hydrolysis of dialkyl phosphonate to phosphonic acid under acidic conditions. A more detailed discussion can be found in Beilstein J. Org. Chem. 2017, 13, 2186-2213,

[0036] Suitable examples of compatible alkyl phosphonic acids include butyl phosphonic acid, octyl phosphonic acid, decyl phosphonic acid, octadecyl phosphonic acid, and the like.

[0037] In some embodiments, the alkyl phosphonic acid may be pre-mixed with the succinimide dispersant prior to blending with the base oil. The initial pH of such a mixture is between about 5.0 to about 9.5 as measured by ASTM D664. In other embodiments, no pre-mixing is required.

Lubricating Oil

[0038] When employed as lubricant additives, the succinimide is present in the lubricating oil composition in concentrations ranging from about 0.001 to about 20 wt. % (including, but not limited to, 0.01 to 5 wt. %, 0.2 to 4 wt. %, 0.5 to 3 wt. %, 1 to 2 wt. %, and so forth), based on the total weight of the lubricating oil composition.

[0039] The phosphonic acid is present in concentrations ranging from about 0.001 to about 20 wt. % (including, but not limited to, 0.01 to 5 wt. %, 0.02 to 4 wt. %, 0.05 to 3 wt. %, 0.1 to 2 wt. %, and so forth), based on the total weight of the lubricating oil composition.

[0040] Oils used as the base oil will be selected or blended depending on the desired end use and the additives in the finished oil to give the desired grade of engine oil, e.g. a lubricating oil composition having an Society of Automotive Engineers (SAE) Viscosity Grade of 0W, 0W-8, 0W-16, 0W-20, 0W-30, 0W-40, 0W-50, 0W-60, 5W, 5W-20, 5W-30, 5W-40, 5W-50, 5W-60, 10W, 10W-20, 10W-30, 10W-40, 10W-50, 15W, 15W-20, 15W-30, or 15W-40.

[0041] The oil of lubricating viscosity (sometimes referred to as "base stock" or "base oil") is the primary liquid constituent of a lubricant, into which additives and possibly other oils are blended, for example to produce a final lubricant (or lubricant composition). A base oil, which is useful for making concentrates as well as for making lubricating oil compositions therefrom, may be selected from natural (vegetable, animal or mineral) and synthetic lubricating oils and mixtures thereof.

[0042] Definitions for the base stocks and base oils in this disclosure are the same as those found in American Petroleum Institute (API) Publication 1509 Annex E ("API Base Oil Interchangeability Guidelines for Passenger Car Motor Oils and Diesel Engine Oils," December 2016). Group I base stocks contain less than 90% saturates and/or greater than 0.03% sulfur and have a viscosity index greater than or equal to 80 and less than 120 using the test methods specified in Table E-1. Group II base stocks contain greater than or equal to 90% saturates and less than or equal to 0.03% sulfur and have a viscosity index greater than or equal to 80 and less than 120 using the test methods specified in Table E-1. Group III base stocks contain greater than or equal to 90% saturates and less than or equal to 0.03% sulfur and have a viscosity index greater than or equal to 120 using the test methods specified in Table E-1. Group IV base stocks are polyalphaolefins (PAO). Group V base stocks include all other base stocks not included in Group I, II, III, or IV.

[0043] Natural oils include animal oils, vegetable oils (e.g., castor oil and lard oil), and mineral oils. Animal and vegetable oils possessing favorable thermal oxidative stability can be used. Of the natural oils, mineral oils are preferred. Mineral oils vary widely as to their crude source, for example, as to whether they are paraffinic, naphthenic, or mixed paraffinic-naphthenic. Oils derived from coal or shale are also useful. Natural oils vary also as to the method used for their production and purification, for example, their distillation range and whether they are straight run or cracked, hydrorefined, or solvent extracted.

[0044] Synthetic oils include hydrocarbon oil. Hydrocarbon oils include oils such as polymerized and interpolymerized olefins (e.g., polybutylenes, polypropylenes, propylene isobutylene copolymers, ethylene-olefin copolymers, and ethylene-alphaolefin copolymers). Polyalphaolefin (PAO) oil base stocks are commonly used synthetic hydrocarbon oil. By way of example, PAOs derived from C_8 to C_{14} olefins, e.g., C_8, C_{10}, C_{12}, C_{14} olefins or mixtures thereof, may be utilized.

[0045] Other useful fluids for use as base oils include non-conventional or unconventional base stocks that have been processed, preferably catalytically, or synthesized to provide high performance characteristics.

[0046] Non-conventional or unconventional base stocks/base oils include one or more of a mixture of base stock(s) derived from one or more Gas-to-Liquids (GTL) materials, as well as isomerate/isodewaxate base stock(s) derived from natural wax or waxy feeds, mineral and or non-mineral oil waxy feed stocks such as slack waxes, natural waxes, and waxy stocks such as gas oils, waxy fuels hydrocracker bottoms, waxy raffinate, hydrocrackate, thermal crackates, or other mineral, mineral oil, or even non-petroleum oil derived waxy materials such as waxy materials received from coal liquefaction or shale oil, and mixtures of such base stocks. Other base oils include Coal to liquid (CTL) products and alkyl-naphthalene.

[0047] Base oils for use in the lubricating oil compositions of present disclosure are any of the variety of oils corresponding to API Group I, Group II, 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, more preferably the Group III to Group V base oils due to their exceptional volatility, stability, viscometric and cleanliness features.

[0048] Typically, the base oil will have a kinematic viscosity at 100°C (ASTM D445) in a range of 1.5 to 35 mm^2/s

(e.g., 1.5 to 25 mm^2/s, 2.0 to 20 mm^2/s, or 2.0 to 15 mm^2/s).

[0049] The present lubricating oil compositions may also contain conventional lubricant additives for imparting auxiliary functions to give a finished lubricating oil composition in which these additives are dispersed or dissolved. For example, the lubricating oil compositions can be blended with antioxidants, ashless dispersants, anti-wear agents, detergents such as metal detergents, rust inhibitors, dehazing agents, demulsifying agents, friction modifiers, metal deactivating agents, pour point depressants, viscosity modifiers, antifoaming agents, co-solvents, package compatibilizers, corrosion-inhibitors, dyes, extreme pressure agents and the like and mixtures thereof. A variety of the additives are known and commercially available. These additives, or their analogous compounds, can be employed for the preparation of the lubricating oil compositions of the invention by the usual blending procedures.

[0050] Each of the foregoing additives, when used, is used at a functionally effective amount to impart the desired properties to the lubricant. Thus, for example, if an additive is an ashless dispersant, a functionally effective amount of this ashless dispersant would be an amount sufficient to impart the desired dispersancy characteristics to the lubricant. Generally, the concentration of each of these additives, when used, may range, unless otherwise specified, from about 0.001 to about 20 wt. %, such as about 0.01 to about 10 wt. %.

[0051] The following non-limiting examples are illustrative of the present invention.

EXAMPLES

[0052] Lubricating oil samples (i.e., examples and comparative examples) were evaluated for anti-wear performance. Each sample includes succinimide dispersant, a phosphorus additive (optional in some comparative examples), other lubricating oil additives (friction modifiers, ashless anti-wear additives, antioxidants, metal deactivators, seal swell additives, foam inhibitors, and viscosity modifiers), and base oil.

Succinimide Dispersant

[0053] Borated Succinimide 1 is a boron-modified polyisobutenyl succinimide with a polyisobutylene number average molecular weight of 950 (N: 1.95 wt%; B: 0.63 wt%).

[0054] Borated Succinimide 2 is a boron-modified polyisobutenyl succinimide with a polyisobutylene number average molecular weight of 1,300 (N: 1.88 wt%; B: 0.36 wt%).

[0055] Succinimide 1 is a polyisobutenyl succinimide with a polyisobutylene number average molecular weight of 950 (N: 2.15 wt%).

[0056] Succinimide 2 is a polyisobutenyl succinimide with a polyisobutylene number average molecular weight of 950 (N: 2.0 wt%).

[0057] Succinimide 3 is a low molecular weight alkenyl succinimide (N: 4.6 wt%).

Phosphorus Additive

[0058] Phosphorus additive is a phosphorus-containing compound.

[0059] Monoalkyl phosphonic acid includes butyl phosphonic acid (P: 22.4 wt%), octyl phosphonic acid (P: 15.7 wt%), and octadecyl phosphonic acid (P: 9.3 wt%).

[0060] Phosphorus compound 1 is inorganic phosphoric acid H_3PO_4 (P: 27.0 wt%).

[0061] Phosphorus compound 2 is 2-ethylhexyl phosphate ester (P: 11.1 wt%).

[0062] Phosphorus compound 3 is 3-bis(2-methylpropoxy)phosphinothioylthio-2-methyl-propanoic acid, commercially available from BASF under the trade name Irgalube® 353 (P: 9.3 wt%).

[0063] Phosphorus compound 4 is trilauryl trithiophosphite (P: 4.9 wt%)

[0064] Phosphorus compound 5 is a mixture of C12, C14, and C18 phosphate ester (P: 8.3 wt%).

[0065] Phosphorus compound 6 is isotridecyl phosphate ester (P: 8.2 wt%).

[0066] Phosphorus compound 7 is dimethyl octadecyl phosphonate (P: 8.6 wt%)

[0067] The examples and comparative examples were prepared from the above-mentioned additives in the ratios described in Table 1 and Table 2. The initial pH of the mixture of succinimide dispersant (A) and phosphorus additive (B) was measured by ASTM D664 method and reported in Table 1.

Wear Test

[0068] The anti-wear performance of each lubricating oil compositions was determined using the 4 ball wear scar test (ASTM D4172) at 1200 rpm and 1800 rpm, oil temperature of 80°C, and load of 392N for 60 min. After testing, the test balls were removed and the wear scars were measured. The wear scar diameters are reported in mm in Table 1 and Table 2. A smaller wear scar diameter indicates better anti-wear performance.

Table 1

	Comp. ex. 1	Comp. ex. 2	Comp. ex. 3	Comp. ex. 4	Comp. ex. 5	Comp. ex. 6	Comp. ex. 7	Comp. ex. 8
(A) Dispersants								
Borated succinimide 1 (950)	1.24	1.24	1.24	1.24	1.24	1.24	1.24	1.24
Succinimide 1 (XC180000144)	0.74	0.74	0.74	0.74	0.74	0.74	0.74	0.74
(8) Phosphorus additives								
Butylphosphonic acid								
Octyl phosphonic acid								
Octadecyl phosphonic acid								
P. compound 1		0.08						
P. compound 2			0.18					
P. compound 3				0.22				
P. compound 4					0.41			
P. compound 5						0.25		
P. compound 6							0.25	
P. compound 7								0.24
Initial pH of A+B mixture	10.0	7.7	6.7	8.3	9.6	6.6	6.6	7.9
Phosphorus content from B (ppm)	0	216	200	205	201	208	206	205
Other additives	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Base oil	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance
Wear and Deposit test								
Wear scar diameter @ 1200rpm (μm)	0.48	0.48	0.53	0.51	0.45	0.49	0.49	0.42
Wear scar diameter @ 1800rpm (μm)	0.54	0.61	0.64	0.56	0.53	0.62	0.63	0.54

Table 1 cont.

	Example 1	Example 2	Example 3	Example 4
(A) Dispersants				
Borated succinimide 1 (950)	1.24	1.24	1.24	1.24

(continued)

	Example 1	Example 2	Example 3	Example 4
(A) Dispersants				
Succinimide 1 (XC180000144)	0.74	0.74	0.74	0.74
(B) Phosphorus additives				
Butyl phosphonic acid	0.09			
Octyl phosphonic acid		0.13	0.30	
Octadecyl phosphonic acid				0.22
P. compound 1				
P. compound 2				
P. compound 3				
P. compound 4				
P. compound 5				
P. compound 6				
P. compound 7				
Initial pH of A+B mixture	7.6	7.5	6.9	7.2
Phosphorus content from B (ppm)	202	204	471	204
Other additives	2.0	2.0	2.0	2.0
Base oil	Balance	Balance	Balance	Balance
Wear and Deposit test				
Wear scar diameter @ 1200rpm (μm)	0.44	0.38	0.33	0.33
Wear scar diameter @ 1800rpm (μm)	0.49	0.38	0.34	0.36

[0069] Comparative examples 1-8 which contain succinimide but do not contain alkyl phosphonic acid showed poor anti-wear performance. By contrast, inventive examples 1-4 which contain succinimide and C_4-C_{18} alkyl phosphonic acids showed superior anti-wear performance.

[0070] The anti-wear property of alkyl phosphonic acid was also evaluated with different succinimide mixtures. Table 2 below shows the 4-ball wear scar results for comparative examples 9-10 and inventive examples 5-6.

Table 2

	Comp. ex. 9	Example 5	Comp. ex. 10	Example 6
(A) Dispersants				
Borated succinimide 1 (950)	1.24	1.24		
Borated succinimide 2 (1300)			1.20	1.20
Succinimide 2 (11001)			0.80	0.80
Succinimide 3 (CP4809)	0.35	0.35		
(B) Phosphorus additives				
Octyl phosphonic acid		0.13		0.13
Initial pH of A+B mixture	9.9	7.2	10.5	7.9
Phosphorus content from B (ppm)	0	204	0	204
Other additives	2.0	2.0	2.0	2.0
Base oil	Balance	Balance	Balance	Balance

(continued)

	Comp. ex. 9	Example 5	Comp. ex. 10	Example 6
(A) Dispersants				
Wear and Deposit test				
Wear scar diameter @ 1200rpm (μm)	0.48	0.41	0.78	0.41
Wear scar diameter @ 1800rpm (μm)	0.57	0.44	0.64	0.49

[0071] Inventive examples 5 and 6 which contain octyl phosphonic acid in addition to succinimide, exhibited superior performance compared to comparative examples 9-10, further demonstrating the antiwear capabilities of alkyl phosphonic acids.

Volume Resistivity

[0072] The electrical insulating ability of the lubricating oil compositions was determined in accordance with JIS C2101-1999-24. The volume resistivity values of several examples were measured at an applied voltage of 250 V and reported in units of Ω·cm in Table 3. A volume resistivity of greater than 1×10^8 Ω·cm at 80°C is preferred for adequate insulating properties in transmission fluids.

Table 3

	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6
Volume Resistivity						
Volume Resistivity @ 40°C (Ω·cm)	4.2×10^9	1.4×10^9	3.3×10^9	3.3×10^9	5.6×10^9	1.1×10^9
Volume Resistivity @ 80°C (Ω·cm)	1.2×10^9	0.4×10^9	1.1×10^9	1.0×10^9	1.4×10^9	0.3×10^9

[0073] For the sake of brevity, only certain ranges are explicitly disclosed herein. However, ranges from any lower limit may be combined with any upper limit to recite a range not explicitly recited, as well as, ranges from any lower limit may be combined with any other lower limit to recite a range not explicitly recited, in the same way, ranges from any upper limit may be combined with any other upper limit to recite a range not explicitly recited. Additionally, within a range includes every point or individual value between its end points even though not explicitly recited. Thus, every point or individual value may serve as its own lower or upper limit combined with any other point or individual value or any other lower or upper limit, to recite a range not explicitly recited.

[0074] Likewise, the term "comprising" 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.

[0075] The terms "a" and "the" as used herein are understood to encompass the plural as well as the singular.

[0076] Various terms have been defined above. To the extent a term used in a claim is not defined above, it should be given the broadest definition persons in the pertinent art have given that term as reflected in at least one printed publication or issued patent.

[0077] The foregoing description of the disclosure illustrates and describes the present disclosure. Additionally, the disclosure shows and describes only the preferred embodiments but, as mentioned above, it is to be understood that the disclosure is capable of use in various other combinations, modifications, and environments and is capable of changes or modifications within the scope of the concept as expressed herein, commensurate with the above teachings and/or the skill or knowledge of the relevant art. While the foregoing is directed to embodiments of the present disclosure, other and further embodiments of the disclosure may be devised without departing from the basic scope thereof, and the scope thereof is determined by the claims that follow.

[0078] It is understood that when combinations, subsets, groups, etc. of elements are disclosed (e.g., combinations of components in a composition, or combinations of steps in a method), that while specific reference of each of the various individual and collective combinations and permutations of these elements may not be explicitly disclosed, each

is specifically contemplated and described herein.

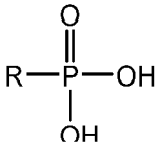
[0079] The embodiments described hereinabove are further intended to explain best modes known of practicing it and to enable others skilled in the art to utilize the disclosure in such, or other, embodiments and with the various modifications required by the particular applications or uses. Accordingly, the description is not intended to limit it to the form disclosed herein.

Claims

1. A lubricating oil composition comprising:

a major amount of an oil of lubricating viscosity having a kinematic viscosity at 100°C in a range of 1.5 to 35 mm^2/s; and

an anti-wear mixture comprising: 0.001 to 20 wt. % of one or more ashless succinimide dispersants, based on the total weight of the lubricating oil composition, and 0.001 to 20 wt. % of an alkyl phosphonic acid having a structure given by



wherein R is a C_3-C_{20} hydrocarbyl group, based on the total weight of the lubricating oil composition; initial pH of the anti-wear mixture is between 5.0 - 9.5 as measured by ASTM D664;

wherein the lubricating oil composition is free of zinc.

2. The lubricating oil composition of claim 1, wherein the one or more ashless dispersants include a hydrocarbyl succinimide.

3. The lubricating oil composition of claim 1, wherein the one or more ashless dispersant include a borated hydrocarbyl succinimide.

4. The lubricating oil composition of claim 1, wherein the anti-wear mixture comprises one or more polyisobutenyl succinimide dispersants.

5. The lubricating oil composition of claim 4, wherein the one or more polyisobutenyl succinimide is borated.

6. The lubricating oil composition of claim 5, wherein at least one of the one or more polyisobutenyl succinimide has a polyisobutylene group with a number average molecular weight of about 850 or greater.

7. The lubricating oil composition of claim 1 or claim 4, wherein the volume resistivity is greater than 1×10^8 Ω·cm at 80°C.

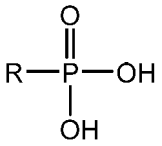
8. The lubricating oil composition of claim 1 or claim 4, wherein the lubricating oil composition is a hydraulic fluid, slide way lubricant, automatic transmission fluid, continuously variable transmission fluid, battery electric vehicle, hybrid electric vehicle transmission fluid, or gear oil.

9. The lubricating oil composition of claim 1 or claim 4, further comprising:
a friction modifier, ashless anti-wear additive, antioxidant, metal deactivator, seal swell additive, foam inhibitor, or viscosity modifier.

10. The lubricating oil composition of claim 1 or claim 4, wherein R is a linear alkyl group.

11. A method of reducing wear of a transmission or gear comprising:
lubricating the transmission or gear with a lubricating oil composition comprising:

a major amount of an oil of lubricating viscosity having a kinematic viscosity at 100°C in a range of 1.5 to 35 mm^2/s; and
an anti-wear mixture comprising: 0.001 to 20 wt. % of one or more ashless succinimide dispersants, based on the total weight of the lubricating oil composition, and 0.001 to 20 wt. % of an alkyl phosphonic acid of the following formula:



wherein R is a C_3-C_{20} hydrocarbyl group, based on the total weight of the lubricating oil composition;
wherein the initial pH of the anti-wear mixture is between 5.0 - 9.5 when measured by the ASTM D664 method;

wherein the lubricating oil composition is free of zinc.

12. The method of claim 11, wherein the one or more ashless dispersants include a hydrocarbyl succinimide, for example, a borated hydrocarbyl succinimide.

13. The method of claim 11, wherein the volume resistivity is greater than $1 \times 10^8 \Omega \cdot cm$ at 80°C.

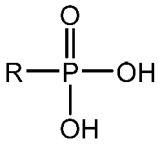
14. The method of claim 11, wherein the lubricating oil composition further comprises:
a friction modifier, ashless anti-wear additive, antioxidant, metal deactivator, seal swell additive, foam inhibitor, or viscosity modifier.

15. The method of claim 11, wherein R is a linear alkyl group.

Patentansprüche

1. Schmierölzusammensetzung, umfassend:

eine Hauptmenge an einem Öl mit schmierender Viskosität mit einer kinematischen Viskosität bei 100 °C in einem Bereich von 1,5 bis 35 mm^2/s; und
eine Verschleißschutzmischung, umfassend: 0,001 bis 20 Gew.% von einem oder mehreren aschefreien Succinimiddispergiermitteln, bezogen auf das Gesamtgewicht der Schmierölzusammensetzung, und 0,001 bis 20 Gew.% einer Alkylphosphonsäure, die eine Struktur aufweist, die gegeben ist durch:



wobei R eine C_3-C_{20}-Hydrocarbylgruppe ist, bezogen auf das Gesamtgewicht der Schmierölzusammensetzung;
wobei der anfängliche pH-Wert der Verschleißschutzmischung zwischen 5,0 und 9,5 liegt, gemessen gemäß ASTM D664;
wobei die Schmierölzusammensetzung frei von Zink ist.

2. Schmierölzusammensetzung gemäß Anspruch 1, wobei das eine oder die mehreren aschefreien Dispergiermittel ein Hydrocarbylsuccinimid einschließt/einschließen.

3. Schmierölzusammensetzung gemäß Anspruch 1, wobei das eine oder die mehreren aschefreien Dispergiermittel ein boriertes Hydrocarbylsuccinimid einschließt/einschließen.

4. Schmierölzusammensetzung gemäß Anspruch 1, wobei die Verschleißschutzmischung ein oder mehrere Polyisobutenylsuccinimid-Dispergiermittel umfasst.

5. Schmierölzusammensetzung gemäß Anspruch 4, wobei das eine oder die mehreren Polyisobutenylsuccimimid(e) boriert ist/sind.

6. Schmierölzusammensetzung nach Anspruch 5, wobei mindestens eines von dem einen oder den mehreren Polyisobutenylsuccinimid(en) eine Polyisobutylengruppe mit einem durchschnittlichen Molekulargewicht (Zahlenmittel) von etwa 850 oder mehr aufweist.

7. Schmierölzusammensetzung nach Anspruch 1 oder Anspruch 4, wobei der spezifische Volumenwiderstand größer als $1 \times 10^8\ \Omega \cdot$ cm bei 80 °C ist.

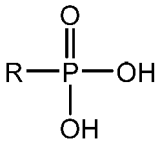
8. Schmierölzusammensetzung nach Anspruch 1 oder Anspruch 4, wobei es sich bei der Schmierölzusammensetzung um eine Hydraulikflüssigkeit, ein Gleitbahnschmiermittel, eine Automatikgetriebeflüssigkeit, eine Flüssigkeit für ein stufenloses Getriebe, ein batteriebetriebenes Fahrzeug, eine Hybridfahrzeuggetriebeflüssigkeit oder ein Getriebeöl handelt.

9. Schmierölzusammensetzung nach Anspruch 1 oder Anspruch 4, ferner umfassend:
einen Reibungsmodifikator, ein aschefreies Verschleißschutzadditiv, ein Antioxidans, einen Metalldesaktivator, ein Dichtungsquelladditiv, einen Schauminhibitor oder einen Viskositätsmodifikator.

10. Schmierölzusammensetzung nach Anspruch 1 oder Anspruch 4, wobei R eine lineare Alkylgruppe ist.

11. Verfahren zum Verringern von Verschleiß eines Getriebes oder Zahnrads, umfassend:
Schmieren des Getriebes oder Zahnrads mit einer Schmierölzusammensetzung, umfassend:

eine Hauptmenge an einem Öl mit schmierender Viskosität mit einer kinematischen Viskosität bei 100 °C in einem Bereich von 1,5 bis 35 mm^2/s; und
eine Verschleißschutzmischung, umfassend: 0,001 bis 20 Gew.% von einem oder mehreren aschefreien Succinimiddispergiermitteln, bezogen auf das Gesamtgewicht der Schmierölzusammensetzung, und 0,001 bis 20 Gew.% einer Alkylphosphonsäure mit der folgenden Formel:



wobei R eine C_3-C_{20}-Hydrocarbylgruppe ist, bezogen auf das Gesamtgewicht der Schmierölzusammensetzung;
wobei der anfängliche pH-Wert der Verschleißschutzmischung zwischen 5,0 und 9,5 liegt, gemessen gemäß dem Verfahren von ASTM D664;
wobei die Schmierölzusammensetzung frei von Zink ist.

12. Verfahren nach Anspruch 11, wobei das eine oder die mehreren aschefreien Dispergiermittel ein Hydrocarbylsuccinimid einschließt/einschließen, beispielsweise ein boriertes Hydrocarbylsuccinimid.

13. Verfahren nach Anspruch 11, wobei der spezifische Volumenwiderstand größer als $1 \times 10^8\ \Omega \cdot$cm bei 80 °C ist.

14. Verfahren nach Anspruch 11, wobei die Schmierölzusammensetzung ferner Folgendes umfasst:
einen Reibungsmodifikator, ein aschefreies Verschleißschutzadditiv, ein Antioxidans, einen Metalldesaktivator, ein Dichtungsquelladditiv, einen Schauminhibitor oder einen Viskositätsmodifikator.

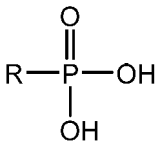
15. Verfahren nach Anspruch 11, wobei R eine lineare Alkylgruppe ist.

Revendications

1. Composition d'huile lubrifiante comprenant :

une quantité principale d'une huile de viscosité lubrifiante ayant une viscosité cinématique à 100 °C dans une

plage de 1,5 à 35 mm^2/s ; et
un mélange antiusure comprenant : 0,001 à 20 % en poids d'un ou plusieurs dispersants sans cendres à base de succinimide, rapporté au poids total de la composition d'huile lubrifiante, et 0,001 à 20 % en poids d'un acide alkylphosphonique ayant une structure donnée par



dans laquelle R est un groupe hydrocarbyle en C_3-C_{20}, rapporté au poids total de la composition d'huile lubrifiante ; le pH initial du mélange antiusure se situant entre 5,0 et 9,5 tel que mesuré par la méthode ASTM D664 ;
la composition d'huile lubrifiante étant dépourvue de zinc.

2. Composition d'huile lubrifiante selon la revendication 1, dans laquelle le ou les dispersants sans cendres comportent un hydrocarbylsuccinimide.

3. Composition d'huile lubrifiante selon la revendication 1, dans laquelle le ou les dispersants sans cendres comportent un hydrocarbylsuccinimide boré.

4. Composition d'huile lubrifiante selon la revendication 1, dans laquelle le mélange antiusure comprend un ou plusieurs dispersants à base de polyisobuténylsuccinimide.

5. Composition d'huile lubrifiante selon la revendication 4, dans laquelle le ou les polyisobuténylsuccinimides sont borés.

6. Composition d'huile lubrifiante selon la revendication 5, dans laquelle le polyisobuténylsuccinimide ou au moins un des polyisobuténylsuccinimides a un groupe polyisobutylène avec un poids moléculaire moyen en nombre d'environ 850 ou plus.

7. Composition d'huile lubrifiante selon la revendication 1 ou la revendication 4, dans laquelle la résistivité volumique est supérieure à 1×10^8 Ω·cm à 80 °C.

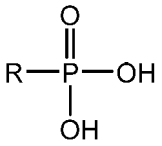
8. Composition d'huile lubrifiante selon la revendication 1 ou la revendication 4, la composition d'huile lubrifiante étant un fluide hydraulique, un lubrifiant pour glissières, un fluide pour transmissions automatiques, un fluide pour transmissions à variation continue, un fluide pour transmissions de véhicules électriques à batterie et de véhicules électriques hybrides, ou une huile pour engrenages.

9. Composition d'huile lubrifiante selon la revendication 1 ou la revendication 4, comprenant en outre :
un modificateur de frottement, un additif antiusure sans cendres, un antioxydant, un désactivateur de métaux, un additif de gonflement des joints, un agent antimousse, ou un modificateur de viscosité.

10. Composition d'huile lubrifiante selon la revendication 1 ou la revendication 4, dans laquelle R est un groupe alkyle linéaire.

11. Procédé de réduction de l'usure d'une transmission ou d'un engrenage comprenant :
la lubrification de la transmission ou de l'engrenage avec une composition d'huile lubrifiante comprenant :

une quantité principale d'une huile de viscosité lubrifiante ayant une viscosité cinématique à 100 °C dans une plage de 1,5 à 35 mm^2/s ; et
un mélange antiusure comprenant : 0,001 à 20 % en poids d'un ou plusieurs dispersants sans cendres à base de succinimide, rapporté au poids total de la composition d'huile lubrifiante, et 0,001 à 20 % en poids d'un acide alkylphosphonique de la formule suivante :



dans laquelle R est un groupe hydrocarbyle en C_3-C_{20}, rapporté au poids total de la composition d'huile lubrifiante ;
dans lequel le pH initial du mélange antiusure se situe entre 5,0 et 9,5 tel que mesuré par la méthode ASTM D664 ;
la composition d'huile lubrifiante étant dépourvue de zinc.

12. Procédé selon la revendication 11, dans lequel le ou les dispersants sans cendres comportent un hydrocarbylsuccinimide, par exemple un hydrocarbylsuccinimide boré.

13. Procédé selon la revendication 11, dans lequel la résistivité volumique est supérieure à 1×10^8 Ω·cm à 80 °C.

14. Procédé selon la revendication 11, dans lequel la composition d'huile lubrifiante comprend en outre :
un modificateur de frottement, un additif antiusure sans cendres, un antioxydant, un désactivateur de métaux, un additif de gonflement des joints, un agent antimousse, ou un modificateur de viscosité.

15. Procédé selon la revendication 11, dans lequel R est un groupe alkyle linéaire.

REFERENCES CITED IN THE DESCRIPTION

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