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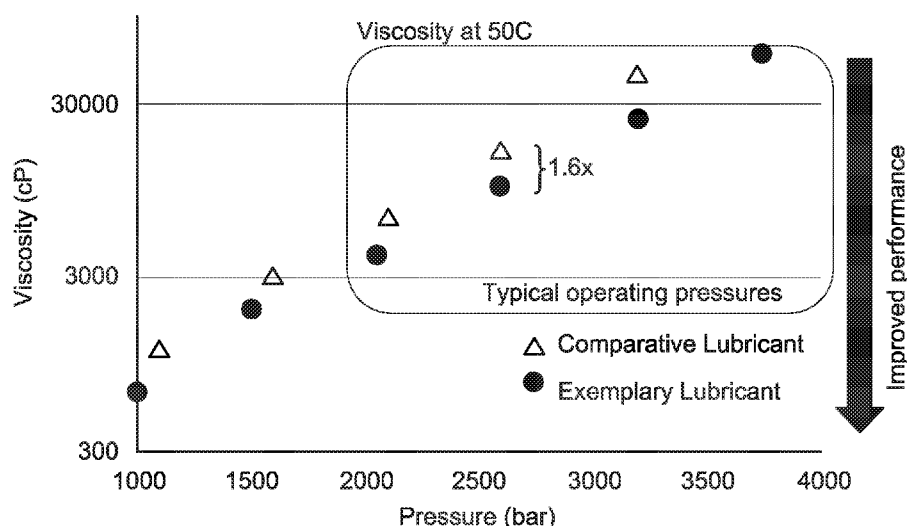
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(54) Title: NOVEL FORMULATION FOR LUBRICATION OF HYPER COMPRESSORS PROVIDING IMPROVED PUMPABILITY UNDER HIGH-PRESSURE CONDITIONS

**FIG. 1**(57) Abstract: The present disclosure provides a lubricating composition with improved high-pressure pumpability and/or reduced viscosity at high pressures, as well as method of making and using the same. The lubricating composition includes a white oil and a polymeric thickener present in an amount equal to or less than about 40 wt% of the lubricating composition. The white oil has a kinematic viscosity of at least one of: about 80 mm²/sec to about 120 mm²/sec at 40°C and/or about 9.5 mm²/sec to about 14 mm²/sec at 100°C.

Declarations under Rule 4.17:

- *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
- *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

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NOVEL FORMULATION FOR LUBRICATION OF HYPER COMPRESSORS
PROVIDING IMPROVED PUMPABILITY UNDER HIGH-PRESSURE CONDITIONS

FIELD

[0001] The present disclosure relates generally to lubricating compositions, as well as methods of making and using the same. More specifically, the present disclosure relates to lubricating compositions with improved high-pressure pumpability and reduced viscosity at high pressures, as well as methods of making and using the same.

BACKGROUND

[0002] The manufacture of high pressure polyolefins, such as high pressure low density polyethylene (HP-LDPE) or ethylene vinyl acetate (EVA), is accomplished by placing the olefinic material under high pressure utilizing at least one hyper compressor. Hyper compressors are capable of reaching operating pressure of, e.g., about 70 to about 350 megapascals (MPa) or about 10,000 to about 50,000 pounds per square inch (PSI). When at operating pressure, the olefinic raw material is converted into a polyolefin (e.g., HP-LDPE) via a catalyst. Often, olefinic raw material is compressed to a pressure of about 35 MPa or less, about 30 MPa or less, about 25 MPa or less, or about 20 MPa or less via a first compressor prior to being compressed by the hyper compressor.

[0003] High pressure compressors, such as hyper compressors, require the use of lubricants to reduce friction between moving parts. However, because of the high operating pressures and unique architecture of high pressure compressors, the cylinders of these compressors require a lubricant with specific lubricity characteristics under the high injection pressure present. Lubricants employed in hyper compressors leak downstream into the polymerization reactor. As such, the lubricants mix with and become part of the reaction mixture, which can interfere with the polymerization of the olefin into high pressure polyolefin or affect the polyolefin properties.

[0004] As a result, mineral oil (white oil or paraffin oil) has been used as a high pressure compressor (e.g., hyper compressor) lubricant because the leakage of mineral oil based lubricants into the reaction mixture has little, if any, adverse effect on high pressure polyolefin formation or the use of the polyolefin in the manufacturing of goods. Furthermore, hyper compressor lubricants often require a food-grade lubricant. Current food grade white oil hyper compressor lubricants utilize a thickener to achieve the required viscosity. As a result, the white oil typically has a kinematic viscosity below 75 mm²/sec at 40°C and a viscosity index greater than 95.

[0005] Polyethylene (PE) is one of the most common polymers utilized in the manufacture of goods, and can be found in a wide range of products, such as plastic bags, medical equipment, artificial human hips, etc. The demand for PE has increased dramatically in the last decade and is

expected to continue to this dramatic growth. As such, there is a need for a lubricant (such as a food grade lubricant) that results in greater flow rates at a given pressure, and that provides superior lubrication and protection for the machinery involved in the production of high pressure olefins.

SUMMARY

[0006] The present disclosure relates to a lubricating composition comprising a white oil and a polymeric thickener. It was surprising and unexpectedly discovered that by utilizing a white oil with a higher kinematic viscosity than previously appreciated, a lower amount of polymeric thickener can be utilized, thereby resulting in a lubricant with greater flow rates and superior lubricating effects. In an aspect, the disclosure provides a lubricating composition comprising: a white oil and a polymeric thickener present in an amount equal to or less than about 40 wt% of the lubricating composition. In an embodiment, the white oil has a kinematic viscosity (which may be determined by, e.g., ASTM D445 or ASTM D7042) of at least one of: about 80 mm²/sec to about 120 mm²/sec at 40°C; about 9.5 mm²/sec to about 14 mm²/sec at 100°C; or a combination thereof.

[0007] In some embodiments, the white oil has a kinematic viscosity of at least one of: about 85 mm²/sec to about 115 mm²/sec at 40°C, about 90 mm²/sec to about 110 mm²/sec at 40°C, about 10 mm²/sec to about 13.5 mm²/sec at 100°C, about 10.5 mm²/sec to about 13 mm²/sec at 100°C, or a combination thereof.

[0008] In some embodiments, the lubricating composition has a kinematic viscosity of about 200 mm²/sec to about 240 mm²/sec (e.g., about 220 mm²/sec).

[0009] In certain embodiments, the white oil is present in an amount of about 50 wt% to about 95 wt% (e.g., about 70 wt% to about 95 wt% or about 75 wt% to about 90 wt%) of the lubricating composition.

[0010] In other embodiments, the polymeric thickener is at least one of a polybutene polymeric thickener, high molecular weight hydrocarbons, polyesters, polymers of methacrylate, copolymers of methacrylate, butadiene, olefins, alkylated styrenes, or combinations thereof.

[0011] In yet another embodiment, the lubricating composition further comprises at least one performance additive. For example, the performance additive may be at least one of a dispersant, an additional detergent, a corrosion inhibitor, a rust inhibitor, a metal deactivator, an additional anti-wear agent, an extreme pressure additive, a pour point depressant, an anti-seizure agent, a wax modifier, a viscosity index improver, a viscosity improver/modifier, a fluid-loss additive, a seal compatibility agent, an additional friction modifier, a lubricity agent, an anti-staining agent, a chromophoric agent, a demulsifier, an emulsifier, a densifier, a wetting agent, a gelling agent, a tackiness agent, a colorant, an antioxidant, an oxidation inhibitor, or a combination thereof.

[0012] In particular embodiments, a total amount of performance additives is equal to or less than 10 wt% (e.g., about 0.5 wt% to about 9 wt% or about 0.5 wt% to about 8 wt%) of the lubricating composition.

[0013] In another aspect, the present disclosure provides a method of making a lubricating composition with at least one of improved high-pressure pumpability, reduced viscosity at high pressures, or a combination thereof. The method comprises mixing: a white oil with a kinematic viscosity of at least one of: about 80 mm²/sec to about 120 mm²/sec at 40°C; about 9.5 mm²/sec to about 14 mm²/sec at 100°C; or a combination thereof; and a polymeric thickener present in an amount equal to or less than about 40 wt% of the lubricating composition.

[0014] In some embodiments, the white oil has a kinematic viscosity of at least one of: about 85 mm²/sec to about 115 mm²/sec at 40°C, about 90 mm²/sec to about 110 mm²/sec at 40°C, about 10 mm²/sec to about 13.5 mm²/sec at 100°C, about 10.5 mm²/sec to about 13 mm²/sec at 100°C, or a combination thereof.

[0015] In further embodiments, the method further comprises mixing the white oil and the polymeric thickener with at least one performance additive.

[0016] In a further aspect, the disclosure provides a lubricating composition produced according to the method of making the lubricating composition of the present disclosure.

[0017] In yet another aspect, the present disclosure provides a method of lubricating a compressor, the method comprising applying the lubricating composition of the present disclosure to the compressor.

[0018] In some embodiments, the compressor is a high-pressure compressor.

[0019] In other embodiments, the compressor is a hyper compressor.

[0020] In an aspect, the present disclosure provides a method of pressurizing an olefin (e.g., ethylene). The method comprises: introducing the olefin into a compressor that is lubricated by the lubricating composition of the present disclosure; and pressurizing the olefin with the compressor, wherein the compressor is at least one of a high pressure compressor, a hyper compressor, or both.

[0021] In yet a further aspect, the present disclosure provides a method of making a high pressure olefin, the method comprising: pressurizing an olefin with a high pressure compressor that is lubricated with the lubricating composition of the present disclosure; and reacting the pressurized olefin to form the high pressure olefin.

[0022] In some embodiments, at least one of the olefin is ethylene, the high pressure olefin is high pressure low density polyethylene, or a combination thereof.

[0023] Where applicable or not specifically disclaimed, any one of the embodiments described herein are contemplated to be able to combine with any other one or more embodiments or aspects, even though the embodiments are described under different aspects of the disclosure. These and other embodiments are disclosed or are obvious from and encompassed by, the following Detailed Description, including the Drawings and Examples herein.

BRIEF DESCRIPTION OF THE DRAWINGS

[0024] The following detailed description, given by way of example, but not intended to limit the disclosure solely to the specific embodiments described, may best be understood in conjunction with the accompanying drawings.

[0025] FIG. 1 illustrates the kinematic viscosities of an exemplary lubricant and a comparative lubricant at pressures ranging from 1000 bar to 3750 bar.

[0026] FIGS. 2A and 2B illustrate the test methods for examining pumpability or flow rates of lubricants.

[0027] FIG. 3 illustrates the flow rates of an exemplary lubricant and a comparative lubricant at 50°C with 100% pump scaling at pressures ranging from 1000 bar to 3000 bar.

[0028] FIG. 4 illustrates flow rates of an exemplary lubricant and a comparative lubricant at 50°C and 2000 bar with pump scaling ranging from 30% to 100%.

DETAILED DESCRIPTION

[0029] The specification relates, in part, to the surprising discovery that the compositions of the present disclosure surprisingly and unexpectedly provide disproportionate improvements in pump flow rates for pumps that are set to run at a wide range of reduced oil flow rates (pump scaling). A synergistic effect is achieved by the combination of ingredients in the composition of the present disclosure, thereby providing energy efficiency gains, reduced maintenance costs for the pumping system, and an ability to efficiently operate under conditions of reduced oil consumption.

[0030] The following is a detailed description of the present disclosure provided to aid those skilled in the art in practicing the present disclosure. Those of ordinary skill in the art may make modifications and variations in the embodiments described herein without departing from the spirit or scope of the present disclosure. Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this disclosure belongs. The terminology used in the description of the disclosure herein is for describing particular embodiments only and is not intended to be limiting of the disclosure. All publications, patent applications, patents, figures and other references mentioned herein are

expressly incorporated by reference in their entirety and may be employed in the practice of the present disclosure.

[0031] Although any methods and materials similar or equivalent to those described herein can also be used in the practice or testing of the present disclosure, the preferred methods and materials are now described. All publications mentioned herein are incorporated herein by reference to disclose and described the methods and/or materials in connection with which the publications are cited.

[0032] The specification relates, in part, to the surprising discovery that the lubricating composition of the present disclosure provides superior lubrication and protection for the machinery, while providing a disproportionate improvements in pump flow rates for pumps that are set to run at a wide range of reduced oil flow rates (pump scaling).

[0033] The following terms may have meanings ascribed to them below, unless specified otherwise. However, it should be understood that other meanings that are known or understood by those having ordinary skill in the art are also possible, and within the scope of the present disclosure. In the case of conflict, the present specification, including definitions, will control. In addition, the materials, methods, and examples are illustrative only and not intended to be limiting.

[0034] The articles "a", "an", and "the" as used herein and in the appended claims are used herein to refer to one or to more than one (i.e., to at least one) of the grammatical object of the article unless the context clearly indicates otherwise. By way of example, "an element" means one element or more than one element.

[0035] The phrase "and/or," as used herein in the specification and in the claims, should be understood to mean "either or both" of the elements so conjoined, i.e., elements that are conjunctively present in some cases and disjunctively present in other cases. Multiple elements listed with "and/or" should be construed in the same fashion, i.e., "one or more" of the elements so conjoined. Other elements may optionally be present other than the elements specifically identified by the "and/or" clause, whether related or unrelated to those elements specifically identified. Thus, as a non-limiting example, a reference to "A and/or B", when used in conjunction with open-ended language such as "comprising" can refer, in one embodiment, to A only (optionally including elements other than B); in another embodiment, to B only (optionally including elements other than A); in yet another embodiment, to both A and B (optionally including other elements); etc.

[0036] As used herein in the specification and in the claims, "or" should be understood to have the same meaning as "and/or" as defined above. For example, when separating items in a list, "or" or "and/or" shall be interpreted as being inclusive, i.e., the inclusion of at least one, but also

including more than one, of a number or list of elements, and, optionally, additional unlisted items. Only terms clearly indicated to the contrary, such as "only one of" or "exactly one of," or, when used in the claims, "consisting of," will refer to the inclusion of exactly one element of a number or list of elements. In general, the term "or" as used herein shall only be interpreted as indicating exclusive alternatives (i.e., "one or the other but not both") when preceded by terms of exclusivity, such as "either," "one of," "only one of," or "exactly one of."

[0037] In the claims, as well as in the specification above, all transitional phrases such as "comprising," "including," "carrying," "having," "containing," "involving," "holding," "composed of," and the like are to be understood to be open-ended, i.e., to mean including but not limited to. Only the transitional phrases "consisting of" and "consisting essentially of" shall be closed or semi-closed transitional phrases, respectively, as set forth in the United States Patent Office Manual of Patent Examining Procedures, Section 2111.03.

[0038] As used herein in the specification and in the claims, the phrase "at least one," in reference to a list of one or more elements, should be understood to mean at least one element selected from anyone or more of the elements in the list of elements, but not necessarily including at least one of each and every element specifically listed within the list of elements and not excluding any combinations of elements in the list of elements. This definition also allows that elements may optionally be present other than the elements specifically identified within the list of elements to which the phrase "at least one" refers, whether related or unrelated to those elements specifically identified. Thus, as a non-limiting example, "at least one of A and B" (or, equivalently, "at least one of A or B," or, equivalently "at least one of A and/or B") can refer, in one embodiment, to at least one, optionally including more than one, A, with no B present (and optionally including elements other than B); in another embodiment, to at least one, optionally including more than one, B, with no A present (and optionally including elements other than A); in yet another embodiment, to at least one, optionally including more than one, A, and at least one, optionally including more than one, B (and optionally including other elements); etc.

[0039] It should also be understood that, in certain methods described herein that include more than one step or act, the order of the steps or acts of the method is not necessarily limited to the order in which the steps or acts of the method are recited unless the context indicates otherwise.

[0040] Unless specifically stated or obvious from context, as used herein, the term "about" is understood as within a range of normal tolerance in the art, for example within 2 standard deviations of the mean. About can be understood as within 10%, 9%, 8%, 7%, 6%, 5%, 4%, 3%, 2%, 1%, 0.5%, 0.1 %, 0.05%, or 0.01% of the stated value. Unless otherwise clear from context,

all numerical values provided in the detailed description and the claims are modified by the term “about.”

[0041] Any compositions or methods provided herein can be combined with one or more of any of the other compositions and methods provided herein.

[0042] Ranges provided herein are understood to be shorthand for all of the values within the range. For example, a range of 1 to 50 is understood to include any number, combination of numbers, or sub-range from the group consisting 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, or 50.

[0043] The term “white oil”, as used herein, refers to a purified mixture of liquid saturated hydrocarbons, which are manufactured from petroleum through several refining purification stages, including catalytic hydrogenation. The white oils used herein may be food-grade (as too may be the lubricating composition of the present disclosure) and meets at least one of the following requirements: United States Federal Drug Administration 21 C.F.R. § 178.3620(a), United States Pharmacopeia, National Sanitation Foundation H1 Registration, European Pharmacopeia, European Regulation (EU) 10/2011, or a combination thereof.

[0044] The term “high pressure compressor”, as used herein, refers to a compressor that is capable of compressing a raw material, such as an olefin (e.g. ethylene), to a pressure of at least 20 MPa, 25 MPa, 30 MPa, or 35 MPa.

[0045] The term “hyper compressor”, as used herein, refers to a compressor that is capable of compressing a raw material, such as an olefin (e.g. ethylene), to a pressure of at least 50 MPa, 55 MPa, 60 MPa, 65 MPa, 70 MPa, 75 MPa, 80 MPa, 85 MPa, 90 MPa, 95 MPa, or 100 MPa.

[0046] The high pressure or hyper compressor may be a horizontal balanced opposed reciprocating compressor. For example, the compressor may be a positive displacement, reciprocating crosshead, multi-stage compressor. The compressor may comprise at least one packed-plunger type cylinder, which may be made of solid tungsten-carbide or a tungsten-carbide coated steel.

[0047] Reference will now be made in detail to exemplary embodiments of the disclosure. While the disclosure will be described in conjunction with the exemplary embodiments, it will be understood that it is not intended to limit the disclosure to those embodiments. To the contrary, it is intended to cover alternatives, modifications, and equivalents as may be included within the spirit and scope of the disclosure as defined by the appended claims.

COMPOSITIONS OF THE PRESENT DISCLOSURE

[0048] In an aspect, the disclosure provides a lubricating composition that has surprising and unexpectedly enhanced lubricating ability and significant improvements in pump flow rates. The lubricating composition comprises: a white oil with a kinematic viscosity of at least one of: about 80 mm²/sec to about 120 mm²/sec at 40°C (e.g., about 85 mm²/sec to about 115 mm²/sec at 40°C or about 90 mm²/sec to about 110 mm²/sec at 40°C); about 9.5 mm²/sec to about 14 mm²/sec at 100°C (e.g., about 10 mm²/sec to about 13.5 mm²/sec at 100°C or about 10.5 mm²/sec to about 13 mm²/sec at 100°C); or a combination thereof; and a polymeric thickener present in an amount equal to or less than about 40 wt% of the lubricating composition. In any aspect or embodiment described herein, the lubricating composition may be an ISO VG 220 lubricant. For example, the lubricating composition may be an ISO VG 220 food-grade lubricant.

[0049] The polymeric thickener may include at least one of a polybutene polymeric thickener, high molecular weight hydrocarbons, polyesters, polymers of methacrylate, copolymers of methacrylate, butadiene, olefins, alkylated styrenes, or combinations thereof. In certain embodiments, the polymeric thickener is present in an amount of ≤ about 40 wt%, ≤ about 35 wt%, ≤ about 30 wt%, ≤ about 25 wt%, ≤ about 20 wt%, ≤ about 15 wt%, ≤ about 10 wt%. For example, the polymeric thickener may be present in the lubricating composition in an amount of: about 3 wt% to about 40 wt%, about 3 wt% to about 35 wt%, about 3 wt% to about 30 wt%, about 3 wt% to about 25 wt%, about 3 wt% to about 20 wt%, about 3 wt% to about 15 wt%, about 3 wt% to about 10 wt%, about 5 wt% to about 40 wt%, about 5 wt% to about 35 wt%, about 5 wt% to about 30 wt%, about 5 wt% to about 25 wt%, about 5 wt% to about 20 wt%, about 5 wt% to about 15 wt%, about 5 wt% to about 10 wt%, about 10 wt% to about 40 wt%, about 10 wt% to about 35 wt%, about 10 wt% to about 30 wt%, about 10 wt% to about 25 wt%, about 10 wt% to about 20 wt%, about 10 wt% to about 15 wt%, about 15 wt% to about 40 wt%, about 15 wt% to about 35 wt%, about 15 wt% to about 30 wt%, about 15 wt% to about 25 wt%, about 15 wt% to about 20 wt%, about 20 wt% to about 40 wt%, about 20 wt% to about 35 wt%, about 20 wt% to about 30 wt%, about 20 wt% to about 25 wt%, about 25 wt% to about 40 wt%, about 25 wt% to about 35 wt%, about 25 wt% to about 30 wt%, about 30 wt% to about 40 wt%, about 30 wt% to about 35 wt%, or about 35 wt% to about 40 wt%. In certain embodiments, the polymeric thickener is present in the lubricating composition in an amount of about 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, or 40 wt%.

[0050] The white oil (or mineral oil or paraffin oil) may be present in the lubricating composition in an amount of about 50 wt% to about 95 wt%. For example, the white oil may be present in the lubricating composition in an amount of about 50 wt% to about 85 wt%, about 50

wt% to about 80 wt%, about 50 wt% to about 75 wt%, about 50 wt% to about 70 wt%, about 50 wt% to about 65 wt%, about 50 wt% to about 60 wt%, about 50 wt% to about 55 wt%, about 55 wt% to about 95 wt%, about 55 wt% to about 90 wt%, about 55 wt% to about 85 wt%, about 55 wt% to about 80 wt%, about 55 wt% to about 75 wt%, about 55 wt% to about 70 wt%, about 55 wt% to about 65 wt%, about 55 wt% to about 60 wt%, about 60 wt% to about 95 wt%, about 60 wt% to about 90 wt%, about 60 wt% to about 85 wt%, about 60 wt% to about 80 wt%, about 60 wt% to about 75 wt%, about 60 wt% to about 70 wt%, about 60 wt% to about 65 wt%, about 65 wt% to about 95 wt%, about 65 wt% to about 90 wt%, about 65 wt% to about 85 wt%, about 65 wt% to about 80 wt%, about 65 wt% to about 75 wt%, about 65 wt% to about 70 wt%, about 70 wt% to about 95 wt%, about 70 wt% to about 90 wt%, about 70 wt% to about 85 wt%, about 70 wt% to about 80 wt%, about 70 wt% to about 75 wt%, about 75 wt% to about 95 wt%, about 75 wt% to about 90 wt%, about 75 wt% to about 85 wt%, about 75 wt% to about 80 wt%, about 80 wt% to about 95 wt%, about 80 wt% to about 90 wt%, about 80 wt% to about 85 wt%, about 85 wt% to about 95 wt%, about 85 wt% to about 90 wt%, or about 90 wt% to about 95 wt%. In certain embodiments, the white oil is present in the lubricating composition in an amount of about 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, or 95 wt%.

[0051] The lubricating composition of the present disclosure may have a kinematic viscosity of about 200 mm²/sec to about 240 mm²/sec. For example, the kinematic viscosity of the lubricating composition may be about 200 mm²/sec to about 230 mm²/sec, about 200 mm²/sec to about 220 mm²/sec, about 200 mm²/sec to about 210 mm²/sec, about 210 mm²/sec to about 240 mm²/sec, about 210 mm²/sec to about 230 mm²/sec, about 210 mm²/sec to about 220 mm²/sec, about 220 mm²/sec to about 240 mm²/sec, about 220 mm²/sec to about 230 mm²/sec, or about 230 mm²/sec to about 240 mm²/sec.

PERFORMANCE ADDITIVES

[0052] The lubricating composition of the present disclosure may further comprise at least one performance additive. For example, the lubricating composition may include at least one of a dispersant, an additional detergent, a corrosion inhibitor, a rust inhibitor, a metal deactivator, an additional anti-wear agent, an extreme pressure additive, an anti-seizure agent, a wax modifier, a viscosity index improver, a viscosity modifier/improver, a fluid-loss additive, a seal compatibility agent, an additional friction modifier, a lubricity agent, an anti-staining agent, a chromophoric agent, a demulsifier, an emulsifier, a pour point depressant, a densifier, a wetting agent, a gelling agent, a tackiness agent, a colorant, an antioxidants, an oxidation inhibitor, or a combination

thereof. The presence or absence of these lubricating oil performance additives does not adversely affect the lubricating compositions of the present disclosure. For a review of many commonly used additives, see Klamann in *Lubricants and Related Products*, Verlag Chemie, Deerfield Beach, FL; ISBN 0 89573 177 0. Reference is also made to "Lubricant Additives" by M. W. Ranney, published by Noyes Data Corporation of Parkridge, NJ (1973) and "Lubricant Additives: Chemistry and Applications" edited by L.R. Rudnick, published by CRC Press of Boca Raton, FL (2009).

[0053] Unless specified otherwise, the performance additive or performance additives listed above are present in a total amount equal to or less than about 10 wt%, equal to or less than about 9.5 wt%, equal to or less than about 9 wt%, equal to or less than about 8.5 wt%, equal to or less than about 8 wt%, equal to or less than about 7.5 wt%, equal to or less than about 7 wt%, equal to or less than about 6.5 wt%, equal to or less than about 6 wt%, equal to or less than about 5.5 wt%, equal to or less than about 5 wt%, equal to or less than about 4.5 wt%, equal to or less than about 4 wt%, equal to or less than about 3.5 wt%, equal to or less than about 3 wt%, equal to or less than about 2.5 wt%, equal to or less than about 2 wt%, equal to or less than about 1.5 wt%, or equal to or less than about 0.5 wt%. For example, the performance additive or performance additives are present in a total amount of about 0.1 to about 10 wt%, about 0.1 to about 9 wt%, about 0.1 to about 8 wt%, about 0.1 to about 7 wt%, about 0.1 to about 6 wt%, about 0.1 to about 5 wt%, about 0.1 to about 4 wt%, about 0.1 to about 3 wt%, about 0.1 to about 2 wt%, about 0.1 to about 1 wt%, about 0.5 to about 10 wt%, about 0.5 to about 9 wt%, about 0.5 to about 8 wt%, about 0.5 to about 7 wt%, about 0.5 to about 6 wt%, about 0.5 to about 5 wt%, about 0.5 to about 4 wt%, about 0.5 to about 3 wt%, about 0.5 to about 2 wt%, about 1 to about 10 wt%, about 1 to about 9 wt%, about 1 to about 8 wt%, about 1 to about 7 wt%, about 1 to about 6 wt%, about 1 to about 5 wt%, about 1 to about 4 wt%, about 1 to about 3 wt%, about 2 to about 10 wt%, about 2 to about 9 wt%, about 2 to about 8 wt%, about 2 to about 7 wt%, about 2 to about 6 wt%, about 2 to about 5 wt%, about 2 to about 4 wt%, about 3 to about 10 wt%, about 3 to about 9 wt%, about 3 to about 8 wt%, about 3 to about 7 wt%, about 3 to about 6 wt%, about 3 to about 5 wt%, about 4 to about 10 wt%, about 4 to about 9 wt%, about 4 to about 8 wt%, about 4 to about 7 wt%, about 4 to about 6 wt%, about 5 to about 10 wt%, about 5 to about 9 wt%, about 5 to about 8 wt%, about 5 to about 7 wt%, about 6 to about 10 wt%, about 6 to about 9 wt%, about 6 to about 8 wt%, about 7 to about 10 wt%, about 7 to about 9 wt%, or about 8 to about 10 wt%.

Viscosity Improver(s) or Modifier(s).

[0054] The viscosity improver, viscosity modifier, or Viscosity Index (VI) modifier increases the viscosity of the lubricating composition at elevated temperatures, thereby increasing film thickness, and having limited effects on the viscosity of the lubricating composition at low temperatures. In certain embodiments, the lubricating composition comprises at least one viscosity improver (e.g., 1, 2, 3, 4, 5, 6, or more viscosity improver(s)). Any viscosity improver that is known or that becomes known in the art may be utilized in the lubricating composition of the present disclosure. Exemplary viscosity improvers include high molecular weight hydrocarbons, polyesters and viscosity index improver dispersants that function as both a viscosity index improver and a dispersant. The molecular weight of these polymers can range from about 1,000 to about 1,500,000 (e.g., about 20,000 to about 1,200,000 or about 50,000 to about 1,000,000). In a particular embodiment, the molecular weights of these polymers can range from about 1,000 to about 1,000,000 (e.g., about 1,200 to about 500,000 or about 1,200 to about 5,000).

[0055] In certain embodiments, the viscosity improver is at least one of linear or star-shaped polymers of methacrylate, linear or star-shaped copolymers of methacrylate, butadiene, olefins, alkylated styrenes, polyisobutylene, polymethacrylate (e.g., copolymers of various chain length alkyl methacrylates), copolymers of ethylene and propylene, hydrogenated block copolymers of styrene and isoprene, or combinations thereof. For example, the viscosity improver may include styrene-isoprene or styrene-butadiene based polymers of about 50,000 to about 200,000 molecular weight.

[0056] Olefin copolymers are commercially available from Chevron Oronite Company LLC under the trade designation "PARATONE®" (such as "PARATONE® 8921" and "PARATONE® 8941"); from Afton Chemical Corporation under the trade designation "HiTEC®" (such as "HiTEC® 5850B"); and from The Lubrizol Corporation under the trade designation "Lubrizol® 7067C". Hydrogenated polyisoprene star polymers are commercially available from Infineum International Limited, e.g., under the trade designation "SV200" and "SV600". Hydrogenated diene-styrene block copolymers are commercially available from Infineum International Limited, e.g., under the trade designation "SV 50".

[0057] The polymethacrylate or polyacrylate polymers can be linear polymers which are available from Evnolk Industries under the trade designation "Viscoplex®" (e.g., Viscoplex 6-954) or star polymers which are available from Lubrizol Corporation under the trade designation Asteric™ (e.g., Lubrizol 87708 and Lubrizol 87725).

[0058] Illustrative vinyl aromatic-containing polymers useful in the present disclosure may be derived predominantly from vinyl aromatic hydrocarbon monomer. Illustrative vinyl aromatic-

containing copolymers useful in the present disclosure may be represented by the following formula:



wherein A is a polymeric block derived predominantly from vinyl aromatic hydrocarbon monomer, and B is a polymeric block derived predominantly from conjugated diene monomer.

[0059] Although their presence is not required to obtain the benefit of the composition of the present disclosure, viscosity modifiers may be used in an amount of less than about 10 weight percent (e.g. less than about 7 weight percent or less than about 4 weight percent). In certain embodiments, the viscosity improver is present in an amount less than 2 weight percent, less than about 1 weight percent, or less than about 0.5 weight percent, based on the total weight of the lubricating composition. Viscosity modifiers are generally added as concentrates, in large amounts of diluent oil.

[0060] As used herein, the viscosity modifier concentrations are given on an “as delivered” basis. The active polymer may be delivered with a diluent oil. The “as delivered” viscosity modifier may contain from about 20 weight percent to about 75 weight percent of an active polymer for polymethacrylate or polyacrylate polymers, or from about 8 weight percent to about 20 weight percent of an active polymer for olefin copolymers, hydrogenated polyisoprene star polymers, or hydrogenated diene-styrene block copolymers, in the “as delivered” polymer concentrate.

Antioxidant(s).

[0061] In certain embodiments, the lubricating composition comprises at least one antioxidant (e.g., 1, 2, 3, 4, 5, 6, or more antioxidant(s)). The antioxidant(s) may be added to retard the oxidative degradation of base oils during service. Such degradation may result in deposits on metal surfaces, the presence of sludge, or a viscosity increase in the lubricant. One skilled in the art knows a wide variety of oxidation inhibitors that are useful in lubricating oil compositions. See, Klamann in *Lubricants and Related Products*, op cite, and U.S. Patent Nos. 4,798,684 and 5,084,197, for example. Any antioxidant that is known or that becomes known in the art may be utilized in the lubricating composition of the present disclosure.

[0062] Two general types of oxidation inhibitors are those that react with the initiators, peroxy radicals, and hydroperoxides to form inactive compounds, and those that decompose these materials to form less active compounds. Examples are hindered (alkylated) phenols, e.g. 6-di(tert-butyl)-4-methylphenol [2,6-di(tert-butyl)-p-cresol, DBPC], and aromatic amines, e.g. N-phenyl- α -naphthalamine. These oxidation inhibitors are used in turbine, circulation, and hydraulic oils that are intended for extended service.

[0063] The antioxidant or antioxidants may be present in an amount equal to or less than about 6 wt%, equal to or less than about 5.75 wt%, equal to or less than about 5.5 wt%, equal to or less than about 5.25 wt%, equal to or less than about 5 wt%, equal to or less than about 4.75 wt%, equal to or less than about 4.5 wt%, equal to or less than about 4.25 wt%, equal to or less than about 4 wt%, equal to or less than about 3.75 wt%, equal to or less than about 3.5 wt%, equal to or less than about 3.25 wt%, equal to or less than about 3 wt%, equal to or less than about 2.75 wt%, equal to or less than about 2.5 wt%, equal to or less than about 2.25 wt%, equal to or less than about 2 wt%, equal to or less than about 1.75 wt%, equal to or less than about 1.5 wt%, equal to or less than about 1.25 wt%, equal to or less than about 1 wt%, equal to or less than about 0.75 wt%, equal to or less than about 0.50 wt%, or equal to or less than about 0.25 wt% on an as-received basis. For example, the antioxidant or antioxidants may be present in an amount of about 0.1 wt% to about 6 wt %, about 0.1 wt% to about 5 wt %, about 0.1 wt% to about 4 wt %, about 0.1 wt% to about 3 wt %, about 0.1 wt% to about 2 wt %, about 0.1 wt% to about 1.5 wt %, about 0.1 wt% to about 1 wt %, about 0.1 wt% to about 0.75 wt %, about 0.1 wt% to about 0.5 wt %, about 0.2 wt% to about 6 wt %, about 0.2 wt% to about 5 wt %, about 0.2 wt% to about 4 wt %, about 0.2 wt% to about 3 wt %, about 0.2 wt% to about 2 wt %, about 0.2 wt% to about 1.5 wt %, about 0.2 wt% to about 1 wt %, about 0.2 wt% to about 0.75 wt %, about 0.2 wt% to about 0.5 wt %, about 0.3 wt% to about 6 wt %, about 0.3 wt% to about 5 wt %, about 0.3 wt% to about 4 wt %, about 0.3 wt% to about 3 wt %, about 0.3 wt% to about 2 wt %, about 0.3 wt% to about 1.5 wt %, about 0.3 wt% to about 1 wt %, about 0.3 wt% to about 0.75 wt %, about 0.3 wt% to about 0.5 wt %, about 0.5 wt% to about 6 wt %, about 0.5 wt% to about 5 wt %, about 0.5 wt% to about 4 wt %, about 0.5 wt% to about 3 wt %, about 0.5 wt% to about 2 wt %, about 0.5 wt% to about 1.5 wt %, about 0.5 wt% to about 1 wt %, about 0.5 wt% to about 0.75 wt %, about 0.5 wt% to about 0.5 wt %, about 1 wt% to about 6 wt %, about 1 wt% to about 5 wt %, about 1 wt% to about 4 wt %, about 1 wt% to about 3 wt %, about 2 wt% to about 6 wt %, about 2 wt% to about 5 wt %, about 2 wt% to about 4 wt %, about 3 wt% to about 6 wt %, about 3 wt% to about 5 wt %, about 4 wt% to about 6 wt %, or about 5 wt% to about 6 wt % on an as-received basis. In an embodiment, the antioxidant include at least one of a food-grade phenolic antioxidant, a food-grade aminic antioxidant, or a combination thereof.

[0064] The below discussion of phenolic antioxidants is presented only by way of example, and is not limiting on the type of phenolic antioxidants that can be utilized in the lubricating composition of the present disclosure.

[0065] Useful antioxidants include hindered phenols. These phenolic antioxidants may be ashless (metal-free) phenolic compounds or neutral or basic metal salts of certain phenolic compounds. In an embodiment, the phenolic antioxidant compounds or compounds are hindered phenolics which are the ones which contain a sterically hindered hydroxyl group, such as those that are derivatives of dihydroxy aryl compounds in which the hydroxyl groups are in the o- or p-position to each other. In certain embodiments, the phenolic antioxidant or antioxidants are hindered phenols substituted with C₆+ alkyl groups and the alkylene coupled derivatives of these hindered phenols. Examples of phenolic materials of this type 2-t-butyl-4-heptyl phenol; 2-t-butyl-4-octyl phenol; 2-t-butyl-4-dodecyl phenol; 2,6-di-t-butyl-4-heptyl phenol; 2,6-di-t-butyl-4-dodecyl phenol; 2-methyl-6-t-butyl-4-heptyl phenol; and 2-methyl-6-t-butyl-4-dodecyl phenol. Other useful hindered mono-phenolic antioxidants may include for example hindered 2,6-di-alkyl-phenolic propionic ester derivatives. Bis-phenolic antioxidants may also be advantageously used in combination with the composition of the present disclosure. Examples of ortho-coupled phenols include: 2,2'-bis(4-heptyl-6-t-butyl-phenol); 2,2'-bis(4-octyl-6-t-butyl-phenol); and 2,2'-bis(4-dodecyl-6-t-butyl-phenol). Para-coupled bisphenols include for example 4,4'-bis(2,6-di-t-butyl phenol) and 4,4'-methylene-bis(2,6-di-t-butyl phenol).

[0066] Further examples of phenol-based antioxidants include 2-t-butylphenol, 2-t-butyl-4-methylphenol, 2-t-butyl-5-methylphenol, 2,4-di-t-butylphenol, 2,4-dimethyl-6-t-butylphenol, 2-t-butyl-4-methoxyphenol, 3-t-butyl-4-methoxyphenol, 2,5-di-t-butylhydroquinone (manufactured by the Kawaguchi Kagaku Co. under trade designation "Antage DBH"), 2,6-di-t-butylphenol and 2,6-di-t-butyl-4-alkylphenols such as 2,6-di-t-butyl-4-methylphenol and 2,6-di-t-butyl-4-ethylphenol; 2,6-di-t-butyl-4-alkoxyphenols such as 2,6-di-t-butyl-4-methoxyphenol and 2,6-di-t-butyl-4-ethoxyphenol, 3,5-di-t-butyl-4-hydroxybenzylmercaptooctyl acetate, alkyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionates such as n-octyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate (manufactured by the Yoshitomi Seiyaku Co. under the trade designation "Yonox SS"), n-dodecyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate and 2'-ethylhexyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate; 2,6-di-t-butyl-alpha-dimethylamino-p-cresol, 2,2'-methylenebis(4-alkyl-6-t-butylphenol) compounds such as 2,2'-methylenebis(4-methyl-6-t-butylphenol) (manufactured by the Kawaguchi Kagaku Co. under the trade designation "Antage W-400") and 2,2'-methylenebis(4-ethyl-6-t-butylphenol) (manufactured by the Kawaguchi Kagaku Co. under the trade designation "Antage W-500"); bisphenols such as 4,4'-butylidenebis(3-methyl-6-t-butylphenol) (manufactured by the Kawaguchi Kagaku Co. under the trade designation "Antage W-

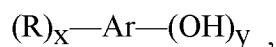
300"), and 4,4'-methylenebis(2,6-di-t-butylphenol) (manufactured by Laporte Performance Chemicals under the trade designation "Ionox 220AH").

[0067] Other examples of phenol-based antioxidants include 4,4'-bis(2,6-di-t-butylphenol), 2,2-(di-p-hydroxyphenyl)propane (Bisphenol A), 2,2-bis(3,5-di-t-butyl-4-hydroxyphenyl)propane, 4,4'-cyclohexylidenebis(2,6-di-t-butylphenol), hexamethylene glycol bis[3, (3,5-di-t-butyl-4-hydroxyphenyl)propionate] (manufactured by the Ciba Speciality Chemicals Co. under the trade designation "Irganox L109"), triethylene glycol bis[3-(3-t-butyl-4-hydroxy-5-methylphenyl)propionate] (manufactured by the Yoshitomi Seiyaku Co. under the trade designation "Tominox 917"), 2,2'-thio[diethyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate] (manufactured by the Ciba Speciality Chemicals Co. under the trade designation "Irganox L115"), 3,9-bis{1,1-dimethyl-2-[3-(3-t-butyl-4-hydroxy-5-methylphenyl)propionyloxy]ethyl}2,4,8,10-tetraoxaspiro[5,5]undecane (manufactured by the Sumitomo Kagaku Co. under the trade designation "Sumilizer GA80") and 4,4'-thiobis(3-methyl-6-t-butylphenol) (manufactured by the Kawaguchi Kagaku Co. under the trade designation "Antage RC"), 2,2'-thiobis(4,6-di-t-butylresorcinol); polyphenols, such as tetrakis[methylene-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionato]methane (manufactured by the Ciba Speciality Chemicals Co. under the trade designation "Irganox L101"), 1,1,3-tris(2-methyl-4-hydroxy-5-t-butylphenyl)butane (manufactured by the Yoshitomi Seiyaku Co. under the trade designation "Yoshinox 930"), 1,3,5-trimethyl-2,4,6-tris(3,5-di-t-butyl-4-hydroxybenzyl)benzene (manufactured by Ciba Speciality Chemicals under the trade designation "Irganox 330"), bis[3,3'-bis(4'-hydroxy-3'-t-butylphenyl)butyric acid] glycol ester, 2-(3',5'-di-t-butyl-4-hydroxyphenyl)-methyl-4-(2",4"-di-t-butyl-3"-hydroxyphenyl)methyl-6-t-butylphenol and 2,6-bis(2'-hydroxy-3'-t-butyl-5'-methylbenzyl)-4-methylphenol; and phenol/aldehyde condensates, such as the condensates of p-t-butylphenol and formaldehyde and the condensates of p-t-butylphenol and acetaldehyde.

[0068] The phenolic antioxidant or phenolic type antioxidant include sulfurized and non-sulfurized phenolic antioxidants. Phenolic antioxidants include compounds having one or more than one hydroxyl group bound to an aromatic ring which may itself be mononuclear (e.g., benzyl) or poly-nuclear (e.g., naphthyl and spiro aromatic compounds). Thus, phenol type antioxidants include phenol per se, catechol, resorcinol, hydroquinone, naphthol, etc., as well as alkyl or alkenyl and sulfurized alkyl or alkenyl derivatives thereof, and bisphenol type compounds including such bi-phenol compounds linked by alkylene bridges sulfuric bridges or oxygen bridges. Alkyl phenols may include mono- and poly-alkyl or alkenyl phenols, the alkyl or alkenyl group containing from about 3 to about 100 carbons (e.g., about 4 to about 50 carbons) and sulfurized derivatives thereof.

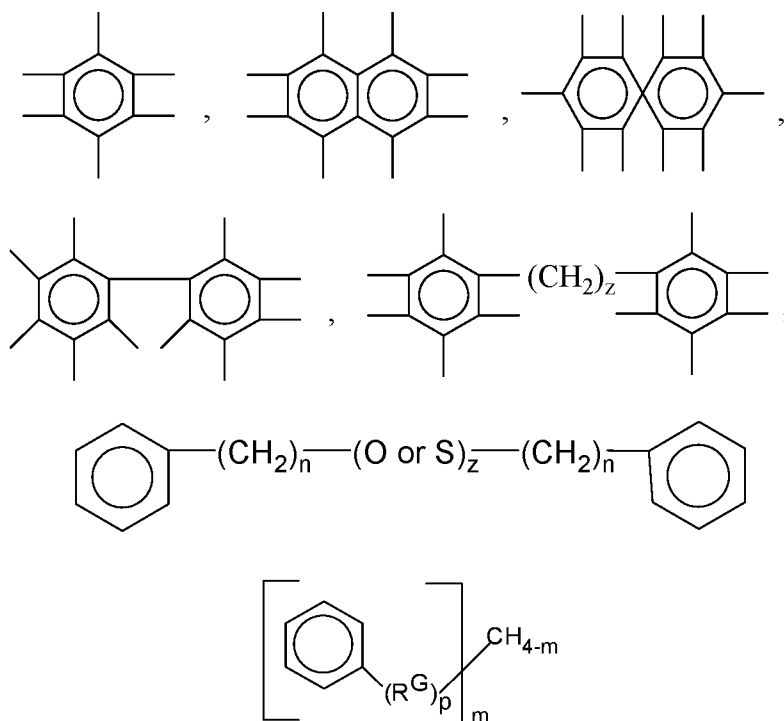
The number of alkyl or alkenyl groups present in the aromatic ring may range from 1 up to the available unsatisfied valences of the aromatic ring remaining after counting the number of hydroxyl groups bound to the aromatic ring.

[0069] For example, the phenolic antioxidant may be represented by the following formula:



wherein:

Ar is selected from the group consisting of:



wherein:

R is a C_3 - C_{100} alkyl or alkenyl group, a sulfur substituted alkyl or alkenyl group (e.g., a C_4 - C_{50} alkyl or alkenyl group or sulfur substituted alkyl or alkenyl group, a C_3 - C_{100} alkyl or sulfur substituted alkyl group, or a C_4 - C_{50} alkyl group);

R^G is a C_1 - C_{100} alkylene or sulfur substituted alkylene group (e.g., a C_2 - C_{50} alkylene or sulfur substituted alkylene group or a C_2 - C_2 alkylene or sulfur substituted alkylene group);

y is at least 1 to up to the available valences of Ar;

x ranges from 0 to up to the available valences of Ar-y;

z ranges from 1 to 10;

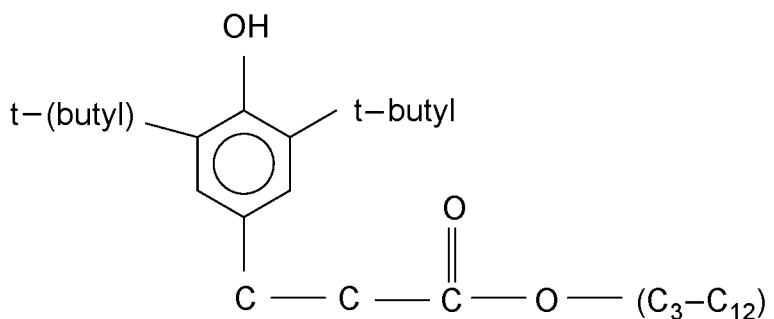
n ranges from 0 to 20;

m is 0 to 4; and

p is 0 or 1,

[0070] In certain embodiments, at least one of: R is C₄-C₅₀ alkyl group, R^g is a C₂-C₂₀ alkylene or sulfur substituted alkylene group, y ranges from 1 to 3, x ranges from 0 to 3, z ranges from 1 to 4, n ranges from 0 to 5, p is 0, or a combination thereof.

[0071] In particular embodiments, the phenolic antioxidant include hindered phenolics and phenolic esters that contain a sterically hindered hydroxyl group. For example, the phenolic antioxidant can include derivatives of dihydroxy aryl compounds in which the hydroxyl groups are in the o- or p-position to each other. The phenolic antioxidant may include the hindered phenols substituted with C₁+ alkyl groups and the alkylene coupled derivatives of these hindered phenols, such as: 2-t-butyl-4-heptyl phenol; 2-t-butyl-4-octyl phenol; 2-t-butyl-4-dodecyl phenol; 2,6-di-t-butyl-4-heptyl phenol; 2,6-di-t-butyl-4-dodecyl phenol; 2-methyl-6-t-butyl-4-heptyl phenol; 2-methyl-6-t-butyl-4-dodecyl phenol; 2,6-di-t-butyl-4 methyl phenol; 2,6-di-t-butyl-4-ethyl phenol; 2,6-di-t-butyl 4 alkoxy phenol; and/or



[0072] In certain embodiments, the phenolic type antioxidant is at least one of Ethanox® 4710, Irganox® 1076, Irganox® L1035, Irganox® 1010, Irganox® L109, Irganox® L118, Irganox® L135, or a combination thereof.

[0073] The phenolic antioxidant or antioxidants may be present in an amount of about 0.05 wt% to about 3 wt%, about 0.05 wt% to about 2.5 wt%, about 0.05 wt% to about 2 wt%, about 0.05 wt% to about 1.5 wt%, about 0.05 wt% to about 1 wt%, about 0.05 wt% to about 0.75 wt%, about 0.05 wt% to about 0.5 wt%, about 0.05 wt% to about 0.3 wt%, about 0.1 wt% to about 3 wt%, about 0.1 wt% to about 2.5 wt%, about 0.1 wt% to about 2 wt%, about 0.1 wt% to about 1.5 wt%, about 0.1 wt% to about 1 wt%, about 0.1 wt% to about 0.75 wt%, about 0.1 wt% to about 0.5 wt%, about 0.1 wt% to about 0.3 wt%, about 0.5 wt% to about 3 wt%, about 0.5 wt% to about 2.5 wt%, about 0.5 wt% to about 2 wt%, about 0.5 wt% to about 1.5 wt%, about 0.5 wt% to about 1 wt%, about 1 wt% to about 3 wt%, about 1 wt% to about 2.5 wt%, about 1 wt% to about 2 wt%, about 1 wt% to about 1.75 wt%, about 1 wt% to about 1.5 wt%, , about 1.5 wt% to about 3 wt%,

about 1.5 wt% to about 2.5 wt%, about 1.5 wt% to about 2 wt%, about 2 wt% to about 3 wt%, about 2 wt% to about 2.5 wt%, or about 2.5 wt% to about 3 wt%, on an as-received basis.

[0074] Effective amounts of one or more catalytic antioxidants may be used. The catalytic antioxidants comprise an effective amount of a) one or more oil soluble polymetal organic compounds; and, effective amounts of b) one or more substituted N,N'-diaryl-o-phenylenediamine compounds or c) one or more hindered phenol compounds; or a combination of both b) and c). Catalytic antioxidants are more fully described in U.S. Patent No. 8, 048,833, which is incorporated herein by reference in its entirety.

[0075] Non-phenolic oxidation inhibitors that may be used in the composition of the present disclosure include aromatic amine antioxidants, which may be used either as such or in combination with phenolic antioxidants.

[0076] An exemplary aromatic amine antioxidant include alkylated and non-alkylated aromatic amines, such as aromatic monoamines of the formula



wherein:

R^1 is an aliphatic, aromatic or substituted aromatic group;

R^2 is an aromatic or a substituted aromatic group;

R^3 is H, alkyl, aryl or $R^4S(O)_xR^5$;

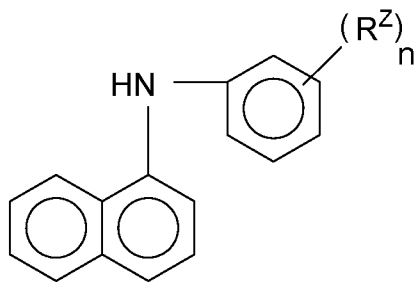
R^4 is an alkylene, alkenylene, or aralkylene group;

R^5 is a higher alkyl group, or an alkenyl, aryl, or alkaryl group; and

x is 0, 1 or 2.

[0077] The aliphatic group R^1 may contain from 1 to about 20 carbon atoms (e.g. from about 6 to 12 carbon atoms). The aliphatic group may be a saturated aliphatic group. In certain embodiments, both R^1 and R^2 are aromatic or substituted aromatic groups, and the aromatic group may be a fused ring aromatic group such as naphthyl. Aromatic groups R^1 and R^2 may be joined together with other groups such as S.

[0078] The aminic antioxidant may be an aromatic amine antioxidant, such as an phenyl- α -naphthyl amine (e.g., Irganox[®] L06) which is described by the following chemical structure:



wherein:

R^Z is hydrogen or a C_1 to C_{14} linear or C_3 to C_{14} branched alkyl group; and

n is an integer ranging from 1 to 5 (e.g. 1).

[0079] In certain embodiments, at least one of: R^Z is C_1 to C_{10} linear or C_3 to C_{10} branched alkyl group; n is 1; or a combination thereof.

[0080] In another embodiment, R^Z is a linear or branched C_6 to C_8 .

[0081] In certain embodiments, the aromatic amine antioxidant can have at least 6 carbon atoms substituted with an alkyl groups. Examples of aliphatic groups include hexyl, heptyl, octyl, nonyl, and decyl. In an embodiments, the aliphatic groups will not contain more than about 14 carbon atoms. Additional amine antioxidants include diphenylamines, phenyl naphthylamines, phenothiazines, imidodibenzyls, and diphenyl phenylene diamines. In a particular embodiment, a mixture of two or more (e.g., 2, 3, 4, 5, or more) aromatic amine antioxidants are present in the lubricating composition. Polymeric amine antioxidants can also be used. Particular examples of aromatic amine antioxidants useful in the composition of the present disclosure include: p,p'-dioctyldiphenylamine; t-octylphenyl-alpha-naphthylamine; phenyl-alphanaphthylamine; and p-octylphenyl-alpha-naphthylamine.

[0082] Further examples of amine-based antioxidants include dialkyldiphenylamines, such as p,p'-dioctyldiphenylamine (manufactured by the Seiko Kagaku Co. under the trade designation "Nonflex OD-3"), p,p'-di-alpha-methylbenzyl- diphenylamine and N-p-butylphenyl-N-p'-octylphenylamine; monoalkyldiphenylamines, such as mono-t-butylphenylamine, and monooctyldiphenylamine; bis(dialkylphenyl)amines such as di(2,4-diethylphenyl)amine and di(2-ethyl-4-nonylphenyl)amine; alkylphenyl-1-naphthylamines, such as octylphenyl-1-naphthylamine and N-t-dodecylphenyl-1-naphthylamine; aryl-naphthylamines, such as 1-naphthylamine, phenyl-1-naphthylamine, phenyl-2-naphthylamine, N-hexylphenyl-2-naphthylamine and N-octylphenyl-2-naphthylamine, phenylenediamines such as N,N'-diisopropyl-p-phenylenediamine and N,N'-diphenyl-p-phenylenediamine, and phenothiazines such as phenothiazine (manufactured by the Hodogaya Kagaku Co.: Phenothiazine) and 3,7-dioctylphenothiazine.

[0083] A sulfur-containing antioxidant may be any and every antioxidant containing sulfur, for example, including dialkyl thiodipropionates such as dilauryl thiodipropionate and distearyl thiodipropionate, dialkyldithiocarbamic acid derivatives (excluding metal salts), bis(3,5-di-*t*-butyl-4-hydroxybenzyl)sulfide, mercaptobenzothiazole, reaction products of phosphorus pentoxide and olefins, and dicetyl sulfide. For example, the sulfur-containing antioxidant is a dialkyl thiodipropionate, such as dilauryl thiodipropionate and distearyl thiodipropionate.

[0084] Additional examples of sulphur-based antioxidants include dialkylsulphides, such as didodecylsulphide and dioctadecylsulphide; thiodipropionic acid esters, such as didodecyl thiodipropionate, dioctadecyl thiodipropionate, dimyristyl thiodipropionate and dodecyloctadecyl thiodipropionate, and 2-mercaptobenzimidazole. In an embodiment, the antioxidant is a sulfurized alkyl phenols, or an alkali or alkaline earth metal salt thereof.

[0085] In certain embodiments, the lubricating composition includes at least one aminic antioxidant (e.g., 1, 2, 3, 4, 5, or more) present in an amount equal to or less than about 6 wt%, equal to or less than about 5.75 wt%, equal to or less than about 5.5 wt%, equal to or less than about 5.25 wt%, equal to or less than about 5 wt%, equal to or less than about 4.75 wt%, equal to or less than about 4.5 wt%, equal to or less than about 4.25 wt%, equal to or less than about 4 wt%, equal to or less than about 3.75 wt%, equal to or less than about 3.5 wt%, equal to or less than about 3.25 wt%, equal to or less than about 3 wt%, equal to or less than about 2.75 wt%, equal to or less than about 2.5 wt%, equal to or less than about 2.25 wt%, equal to or less than about 2 wt%, equal to or less than about 1.75 wt%, equal to or less than about 1.5 wt%, equal to or less than about 1.25 wt%, equal to or less than about 1 wt%, equal to or less than about 0.75 wt%, equal to or less than about 0.50 wt%, or equal to or less than about 0.25 wt% on an as-received basis. For example, the aminic antioxidant or antioxidants may be present in an amount of about 0.1 wt% to about 6 wt %, about 0.1 wt% to about 5 wt %, about 0.1 wt% to about 4 wt %, about 0.1 wt% to about 3 wt %, about 0.1 wt% to about 2 wt %, about 0.1 wt% to about 1.5 wt %, about 0.1 wt% to about 1 wt %, about 0.1 wt% to about 0.75 wt %, about 0.1 wt% to about 0.5 wt %, about 0.2 wt% to about 6 wt %, about 0.2 wt% to about 5 wt %, about 0.2 wt% to about 4 wt %, about 0.2 wt% to about 3 wt %, about 0.2 wt% to about 2 wt %, about 0.2 wt% to about 1.5 wt %, about 0.2 wt% to about 1 wt %, about 0.2 wt% to about 0.75 wt %, about 0.2 wt% to about 0.5 wt %, about 0.3 wt% to about 6 wt %, about 0.3 wt% to about 5 wt %, about 0.3 wt% to about 4 wt %, about 0.3 wt% to about 3 wt %, about 0.3 wt% to about 2 wt %, about 0.3 wt% to about 1.5 wt %, about 0.3 wt% to about 1 wt %, about 0.3 wt% to about 0.75 wt %, about 0.3 wt% to about 0.5 wt %, about 0.5 wt% to about 6 wt %, about 0.5 wt% to about 5 wt %, about 0.5 wt% to about 4 wt %, about 0.5 wt% to

about 3 wt %, about 0.5 wt% to about 2 wt %, about 0.5 wt% to about 1.5 wt %, about 0.5 wt% to about 1 wt %, about 0.5 wt% to about 0.75 wt %, about 0.5 wt% to about 0.5 wt %, about 1 wt% to about 6 wt %, about 1 wt% to about 5 wt %, about 1 wt% to about 4 wt %, about 1 wt% to about 3 wt %, about 2 wt% to about 6 wt %, about 2 wt% to about 5 wt %, about 2 wt% to about 4 wt %, about 3 wt% to about 6 wt %, about 3 wt% to about 5 wt %, about 4 wt% to about 6 wt %, or about 5 wt% to about 6 wt % on an as-received basis.

[0086] Other oxidation inhibitors that have proven useful in lubricating compositions are chlorinated aliphatic hydrocarbons such as chlorinated wax; organic sulfides and polysulfides such as benzyl disulfide, bis(chlorobenzyl)disulfide, dibutyl tetrasulfide, sulfurized methyl ester of oleic acid, sulfurized alkylphenol, sulfurized dipentene, and sulfurized terpene; phosphosulfurized hydrocarbons such as the reaction product of a phosphorus sulfide with turpentine or methyl oleate, phosphorus esters including principally dihydrocarbon and trihydrocarbon phosphites such as dibutyl phosphite, diheptyl phosphite, dicyclohexyl phosphite, pentylphenyl phosphite, dipentylphenyl phosphite, tridecyl phosphite, distearyl phosphite, dimethyl naphthyl phosphite, oleyl 4-pentylphenyl phosphite, polypropylene (molecular weight 500)-substituted phenyl phosphite, diisobutyl-substituted phenyl phosphite; metal thiocarbamates, such as zinc dioctyldithiocarbamate, and barium heptylphenyl dithiocarbamate; Group II metal phosphorodithioates such as zinc dicyclohexylphosphorodithioate, zinc dioctylphosphorodithioate, barium di(heptylphenyl)(phosphorodithioate, cadmium dinonylphosphorodithioate, and the reaction of phosphorus pentasulfide with an equimolar mixture of isopropyl alcohol, 4-methyl-2-pentanol, and n-hexyl alcohol.

[0087] Another class of antioxidants which may be used in the lubricating oil compositions disclosed herein are oil soluble copper compounds. Any oil soluble suitable copper compound may be blended into the lubricating composition. Examples of suitable copper antioxidants include copper dihydrocarbyl thio- or dithio-phosphates and copper salts of carboxylic acid (naturally occurring or synthetic). Other suitable copper salts include copper dithiacarbamates, sulphonates, phenates, and acetylacetonates. Basic, neutral, or acidic copper Cu(I) and or Cu(II) salts derived from alkenyl succinic acids or anhydrides are known to be particularly useful.

[0088] In an embodiment, the antioxidants includes hindered phenols, arylamines, or a combination thereof. These antioxidants may be used individually by type or in combination with one another.

Pour Point Depressant(s).

[0089] In other embodiments, the lubricating composition comprises at least one pour point depressant or a lube oil flow improver. Pour point depressant may be added to lower the minimum temperature at which the fluid will flow or can be poured. Any pour point depressant or lube oil flow improved that is known or that becomes known in the art may be utilized in the lubricating composition of the present disclosure. In certain embodiments, the pour point depressant includes at least one (e.g., 1, 2, 3, 4, or more) pour point depressant or lube oil flow improver, such as at least one of alkylated naphthalenes polymethacrylates (e.g., copolymers of various chain length alkyl methacrylates), polyacrylates, polyarylamides, condensation products of haloparaffin waxes and aromatic compounds, vinyl carboxylate polymers, terpolymers of dialkylfumarates, vinyl esters of fatty acids, allyl vinyl ethers, or combinations thereof. U.S. Patent Nos. 1,815,022; 2,015,748; 2,191,498; 2,387,501; 2,655, 479; 2,666,746; 2,721,877; 2,721,878; and 3,250,715 describe useful pour point depressants and/or the preparation thereof. The pour point depressant or depressants may be present in an amount equal to or less than about 5 wt%, for example about 0.01 to about 1.5 wt%. For example, the pour point depressant or depressants may be present in an amount equal to or less than about 5 wt%, equal to or less than about 4.75 wt%, equal to or less than about 4.5 wt%, equal to or less than about 4.25 wt%, equal to or less than about 4 wt%, equal to or less than about 3.75 wt%, equal to or less than about 3.5 wt%, equal to or less than about 3.25 wt%, equal to or less than about 3 wt%, equal to or less than about 2.75 wt%, equal to or less than about 2.5 wt%, equal to or less than about 2.25 wt%, equal to or less than about 2 wt%, equal to or less than about 1.75 wt%, equal to or less than about 1.5 wt%, equal to or less than about 1.25 wt%, equal to or less than about 1 wt%, equal to or less than about 0.75 wt%, equal to or less than about 0.50 wt%, or equal to or less than about 0.25 wt% of the lubricating composition. For example, the pour point depressant or depressants may be present in an amount of about 0.1 wt% to about 5 wt %, about 0.1 wt% to about 4 wt %, about 0.1 wt% to about 3 wt %, about 0.1 wt% to about 2 wt %, about 0.1 wt% to about 1.5 wt %, about 0.1 wt% to about 1 wt %, about 0.1 wt% to about 0.75 wt %, about 0.1 wt% to about 0.5 wt %, about 0.2 wt% to about 5 wt %, about 0.2 wt% to about 4 wt %, about 0.2 wt% to about 3 wt %, about 0.2 wt% to about 2 wt %, about 0.2 wt% to about 1.5 wt %, about 0.2 wt% to about 1 wt %, about 0.2 wt% to about 0.75 wt %, about 0.2 wt% to about 0.5 wt %, about 0.3 wt% to about 5 wt %, about 0.3 wt% to about 4 wt %, about 0.3 wt% to about 3 wt %, about 0.3 wt% to about 2 wt %, about 0.3 wt% to about 1.5 wt %, about 0.3 wt% to about 1 wt %, about 0.3 wt% to about 0.75 wt %, about 0.3 wt% to about 0.5 wt %, about 0.5 wt% to about 5 wt %, about 0.5 wt% to about 4 wt %, about 0.5 wt% to about 3 wt %, about 0.5 wt% to about 2 wt %, about 0.5 wt% to about 1.5 wt %, about 0.5 wt% to about 1 wt %, about 0.5

wt% to about 0.75 wt %, about 0.5 wt% to about 0.5 wt %, about 1 wt% to about 5 wt %, about 1 wt% to about 4 wt %, about 1 wt% to about 3 wt %, about 2 wt% to about 5 wt %, about 2 wt% to about 4 wt %, or about 3 wt% to about 5 wt % of the lubricating composition.

Seal Compatibility Agent(s).

[0090] In other embodiments, the lubricating composition comprises at least one (e.g., 1, 2, 3, 4, or more) seal compatibility agent. The seal compatibility agent(s) may be added to help swell elastomeric seals by causing a chemical reaction in the fluid or physical change in the elastomer. Any seal compatibility agent that is known or that becomes known may be utilized in the lubricating composition of the present disclosure. For example, the seal compatibility agent or agents may include at least one of organic phosphates, aromatic esters, aromatic hydrocarbons, esters (e.g. butylbenzyl phthalate), polybutenyl succinic anhydride, or sulfolane-type seal swell agents (e.g. Lubrizol 730-type seal swell additives), or combinations thereof. Although their presence is not required to obtain the benefit of the present disclosure, seal compatibility additives may be present in an amount of zero to about 3 weight percent (e.g., about 0.01 to about 2 weight percent) of the lubricating composition.

Antifoam Agent(s).

[0091] In other embodiments, the lubricating composition comprises at least one (e.g., 1, 2, 3, 4, or more) antifoam agent. The antifoam agent(s) may be added to retard the formation of stable foams. Any antifoam agent that is known or that becomes known may be utilized in the lubricating composition of the present disclosure. Foam inhibitors include polymers of alkyl methacrylate especially useful poly alkyl acrylate polymers where alkyl may be understood to be methyl, ethyl, propyl, isopropyl, butyl, or iso butyl and polymers of dimethylsilicone which form materials called dimethylsiloxane polymers in the viscosity range of 100 cSt to 100,000 cSt. Silicone polymers, which have been post reacted with various carbon containing moieties, are the most widely used defoamers. Organic polymers are sometimes used as defoamers although much higher concentrations are required.

[0092] Antifoam agents are commercially available and may be used in conventional minor amounts along with other additives such as demulsifiers. Although their presence is not required to obtain the benefit of the present disclosure, the antifoam agent or agents may be present in a combined amount less than 1 weight percent (e.g. less than 0.1 weight percent) of the lubricating composition.

Demulsifier(s).

[0093] In other embodiments, the lubricating composition comprises at least one (e.g., 1, 2, 3, 4, or more) demulsifier. The demulsifier may be added to separate emulsions (e.g., water-in-oil). Any demulsifier that is known or that becomes known may be utilized in the lubricating composition of the present disclosure. An illustrative demulsifying component is described in EP-A-330,522. This exemplary demulsifying agent is obtained by reacting an alkylene oxide with an adduct obtained by reaction of a bis-epoxide with a polyhydric alcohol. Demulsifiers are commercially available and may be used in conventional minor amounts along with other additives such as antifoam agents. Although their presence is not required to obtain the benefit of the present disclosure, the emulsifier or emulsifiers may be present a combined amount less than 1 weight percent (e.g. less than 0.1 weight percent).

[0094] In certain embodiments, the demulsifying agent includes at least one of alkoxyated phenols, phenol-formaldehyde resins, synthetic alkylaryl sulfonates (such as metallic dinonylnaphthalene sulfonates), or a combination thereof. In an embodiment, a demulsifying agent is a predominant amount of a water-soluble polyoxyalkylene glycol having a pre-selected molecular weight of any value in the range of between about 450 and about 5000 or more. In an embodiment, the water soluble polyoxyalkylene glycol demulsifier may also be one produced from alkoxylation of n-butanol with a mixture of alkylene oxides to form a random alkoxyated product.

[0095] Polyoxyalkylene glycols useful in the present disclosure may be produced by a well-known process for preparing polyalkylene oxide having hydroxyl end-groups by subjecting an alcohol or a glycol ether and one or more alkylene oxide monomers, such as ethylene oxide, butylene oxide, or propylene oxide, to form block copolymers in addition polymerization, while employing a strong base, such as potassium hydroxide as a catalyst. In such a process, the polymerization is commonly carried out under a catalytic concentration of about 0.3 to about 1.0% by mole of potassium hydroxide to the monomer(s) and at high temperature of about 100°C to about 160°C. It is well known that the catalyst potassium hydroxide is, for the most part, bonded to the chain-end of the produced polyalkylene oxide in a form of alkoxide in the polymer solution so obtained.

[0096] The soluble polyoxyalkylene glycol emulsifier(s) useful in the compositions of the present disclosure may also be one produced from alkoxylation of n-butanol with a mixture of alkylene oxides to form a random alkoxyated product.

Corrosion Inhibitor or Anti-rust Additive.

[0097] In other embodiments, the lubricating composition comprises at least one (e.g. 1, 2, 3, 4, or more) corrosion inhibitor or anti-rust additive. The corrosion inhibitor or anti-rust additive

may be added to protect lubricated metal surfaces against chemical attack by water or other contaminants. A wide variety of corrosion inhibitors are commercially available, and any corrosion inhibitor or anti-rust additive that is known or that becomes known may be utilized in the lubricating composition of the present disclosure. In an embodiment, the corrosion inhibitor can be a polar compound that wets the metal surface protecting it with a film of oil. In another embodiment, the anti-rust additive may absorb water by incorporating it in a water-in-oil emulsion so that only the oil touches the surface. In yet a further embodiment, the corrosion inhibitor chemically adheres to the metal to produce a non-reactive surface. In certain embodiments, the anti-rust additive or corrosion inhibitor is at least one zinc dithiophosphates, metal phenolates, basic metal sulfonates, a fatty acid, a fatty acid mixture, amines, or a combination thereof.

[0098] Antirust additives may include (short-chain) alkenyl succinic acids, partial esters thereof and nitrogen-containing derivatives thereof; and synthetic alkarylsulfonates, such as metal dinonylnaphthalene sulfonates. Antirust agents include, for example, monocarboxylic acids which have from 8 to 30 carbon atoms, alkyl or alkenyl succinates or partial esters thereof, hydroxy-fatty acids, which have from 12 to 30 carbon atoms and derivatives thereof, sarcosines which have from 8 to 24 carbon atoms and derivatives thereof, amino acids and derivatives thereof, naphthenic acid and derivatives thereof, lanolin fatty acid, mercapto-fatty acids, and/or paraffin oxides.

[0099] Examples of monocarboxylic acids (C8-C30), include, for example, caprylic acid, pelargonic acid, decanoic acid, undecanoic acid, lauric acid, myristic acid, palmitic acid, stearic acid, arachic acid, behenic acid, cerotic acid, montanic acid, melissic acid, oleic acid, docosanic acid, erucic acid, eicosenic acid, beef tallow fatty acid, soy bean fatty acid, coconut oil fatty acid, linolic acid, linoleic acid, tall oil fatty acid, 12-hydroxystearic acid, laurylsarcosinic acid, myritylsarcosinic acid, palmitylsarcosinic acid, stearyl sarcosinic acid, oleylsarcosinic acid, alkylated (C8-C20) phenoxyacetic acids, lanolin fatty acid, and C8-C24 mercapto-fatty acids.

[0100] Examples of polybasic carboxylic acids include, for example, the alkenyl (C10-C100) succinic acids indicated in CAS No. 27859-58-1 and ester derivatives thereof, dimer acid, N-acyl-N-alkyloxyalkyl aspartic acid esters (U.S. Patent No. 5,275,749).

[0101] Examples of the alkylamines that function as antirust additives or as reaction products with the above carboxylates to give amides and the like are represented by primary amines, such as laurylamine, coconut-amine, n-tridecylamine, myristylamine, n-pentadecylamine, palmitylamine, n-heptadecylamine, stearylamine, n-nonadecylamine, n-eicosylamine, n-heneicosylamine, n-docosylamine, n-tricosylamine, n-pentacosylamine, oleylamine, beef tallow-

amine, hydrogenated beef tallow-amine and soy bean-amine. Examples of the secondary amines include dilaurylamine, di-coconut-amine, di-n-tridecylamine, dimyristylamine, di-n-pentadecylamine, dipalmitylamine, di-n-pentadecylamine, distearylamine, di-n-nonadecylamine, di-n-eicosylamine, di-n-heneicosylamine, di-n-docosylamine, di-n-tricosylamine, di-n-pentacosylamine, dioleylamine, di-beef tallow-amine, di-hydrogenated beef tallow-amine and di-soy bean-amine.

[0102] Examples of the aforementioned N-alkylpolyalkylenediamines include: ethylenediamines, such as laurylethylenediamine, coconut ethylenediamine, n-tridecylethylenediamine, myristylethylenediamine, n-pentadecylethylenediamine, palmitylethylenediamine, n-heptadecylethylenediamine, stearylethylenediamine, n-nonadecylethylenediamine, n-eicosylethylenediamine, n-heneicosylethylenediamine, n-docosylethylenediamine, n-tricosylethylenediamine, n-pentacosylethylenediamine, oleylethylenediamine, beef tallow-ethylenediamine, hydrogenated beef tallow-ethylenediamine and soy bean-ethylenediamine; propylenediamines such as laurylpropylenediamine, coconut propylenediamine, n-tridecylpropylenediamine, myristylpropylenediamine, n-pentadecylpropylenediamine, palmitylpropylenediamine, n-heptadecylpropylenediamine, stearylpropylenediamine, n-nonadecylpropylenediamine, n-eicosylpropylenediamine, n-heneicosylpropylenediamine, n-docosylpropylenediamine, n-tricosylpropylenediamine, n-pentacosylpropylenediamine, diethylene triamine (DETA) or triethylene tetramine (TETA), oleylpropylenediamine, beef tallow-propylenediamine, hydrogenated beef tallow-propylenediamine and soy bean-propylenediamine; butylenediamines such as laurylbutylenediamine, coconut butylenediamine, n-tridecylbutylenediamine, myristylbutylenediamine, n-pentadecylbutylenediamine, stearylbutylenediamine, n-eicosylbutylenediamine, n-heneicosylbutylenediamine, n-docosylbutylenediamine, n-tricosylbutylenediamine, n-pentacosylbutylenediamine, oleylbutylenediamine, beef tallow-butylene-diamine, hydrogenated beef tallow-butylene-diamine and soy bean butylene-diamine; and pentylenediamines such as laurylpentylenediamine, coconut pentylenediamine, myristylpentylenediamine, palmitylpentylenediamine, stearyl-pentylenediamine, oleylpentylenediamine, beef tallow-pentylenediamine, hydrogenated beef tallow-pentylenediamine and soy bean pentylenediamine.

[0103] The corrosion inhibitor or anti-rust additive may be present in an amount equal to or less than about 5 wt%, for example about 0.01 to 5 wt%, on an as-received basis. For example, the corrosion inhibitor may be present in an amount equal to or less than 4 wt%, equal or less than

3 wt%, equal to or less than 2 wt%, or equal to or less than 1 wt% on an as-received basis. By way of further example, the corrosion inhibitor may be present in an amount of about 0.01 to about 5 wt%, about 0.01 to about 4 wt%, about 0.01 to about 3 wt%, about 0.01 to about 2 wt%, about 0.05 to about 5 wt%, about 0.05 to about 4 wt%, about 0.05 to about 3 wt%, about 0.05 to about 2 wt%, about 0.1 to about 5 wt%, about 0.1 to about 4 wt%, about 0.1 to about 3 wt%, about 0.1 to about 2 wt%, about 1 to about 5 wt%, about 1 to about 4 wt%, about 1 to about 3 wt%, about 2 to about 5 wt%, about 2 to about 4 wt%, or about 3 to about 5 wt%, on an as-received basis.

Metal Passivator(s), Deactivator(s) and Corrosion Inhibitor(s).

[0104] This type of component includes 2,5-dimercapto-1,3,4-thiadiazoles and derivatives thereof, mercaptobenzothiazoles, alkyltriazoles and benzotriazoles. Examples of dibasic acids useful as anti-corrosion agents, other than sebacic acids, which may be used in the present disclosure, are adipic acid, azelaic acid, dodecanedioic acid, 3-methyladipic acid, 3-nitrophthalic acid, 1,10-decanedicarboxylic acid, and fumaric acid. The anti-corrosion combination is a straight or branch-chained, saturated or unsaturated monocarboxylic acid or ester thereof which may optionally be sulphurized in an amount up to 35% by weight. In an embodiment, the acid is a C4 to C22 straight chain unsaturated monocarboxylic acid. The monocarboxylic acid may be a sulphurized oleic acid. However, other suitable materials are oleic acid itself, valeric acid and erucic acid. A component of the anti-corrosion combination is a triazole as previously defined. In an embodiment, the triazole is tolyltriazole, which may be included in the compositions of the disclosure include triazoles, thiazoles and certain diamine compounds which are useful as metal deactivators or metal passivators. Examples include triazole, benzotriazole and substituted benzotriazoles, such as alkyl substituted derivatives. The alkyl substituent may contain up to 1.5 carbon atoms, e.g. up to 8 carbon atoms. The triazoles may contain other substituents on the aromatic ring such as halogens, nitro, amino, mercapto, etc. Examples of suitable compounds are benzotriazole and the tolyltriazoles, ethylbenzotriazoles, hexylbenzotriazoles, octylbenzotriazoles, chlorobenzotriazoles and nitrobenzotriazoles. In a particular embodiment, the compound is benzotriazole and/or tolyltriazole.

[0105] Illustrative substituents include, for example, alkyl that is straight or branched chain, for example, methyl, ethyl, n-propyl, iso-propyl, n-butyl, sec-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl, 2-ethylhexyl, n-nonyl, n-decyl, n-dodecyl, n-tetradecyl, n-hexadecyl, n-octadecyl or n-eicosyl; alkenyl that is straight or branched chain, for example, prop-2-enyl, but-2-enyl, 2-methylprop-2-enyl, pent-2-enyl, hexa-2,4-dienyl, dec-10-enyl or eicos-2-enyl; cycloalkyl that is, for example, cyclopentyl, cyclohexyl, cyclooctyl, cyclodecyl, adamantyl or cyclododecyl; aralkyl that

is, for example, benzyl, 2-phenylethyl, benzhydryl or naphthylmethyl; aryl that is, for example, phenyl or naphthyl; heterocyclic group that is, for example, a morpholine, pyrrolidine, piperidine or a perhydroazepine ring; alkylene moieties that include, for example, methylene, ethylene, 1:2- or 1:3-propylene, 1:4-butylene, 1:6-hexylene, 1:8-octylene, 1:10-decylene and 1:12-dodecylene.

[0106] Illustrative arylene moieties include, for example, phenylene and naphthylene. 1-(or 4)-(dimethylaminomethyl) triazole, 1-(or 4)-(diethylaminomethyl) triazole, 1-(or 4)-(diisopropylaminomethyl) triazole, 1-(or 4)-(di-n-butylaminomethyl) triazole, 1-(or 4)-(di-n-hexylaminomethyl) triazole, 1-(or 4)-(di-isooctylaminomethyl) triazole, 1-(or 4)-(di-(2-ethylhexyl)aminomethyl) triazole, 1-(or 4)-(di-n-decylaminomethyl) triazole, 1-(or 4)-(di-n-dodecylaminomethyl) triazole, 1-(or 4)-(di-n-octadecylaminomethyl) triazole, 1-(or 4)-(di-n-eicosylaminomethyl) triazole, 1-(or 4)-[di-(prop-2'-enyl)aminomethyl] triazole, 1-(or 4)-[di-(but-2'-enyl)aminomethyl] triazole, 1-(or 4)-[di-(eicos-2'-enyl)aminomethyl] triazole, 1-(or 4)-(dicyclohexylaminomethyl) triazole, 1-(or 4)-(di-benzylaminomethyl) triazole, 1-(or 4)-(diphenylaminomethyl) triazole, 1-(or 4)-(4'-morpholinomethyl) triazole, 1-(or 4)-(1'-pyrrolidinomethyl) triazole, 1-(or 4)-(1'-piperidinomethyl) triazole, 1-(or 4)-(1'-perhydroazepinomethyl) triazole, 1-(or 4)-(2',2''-dihydroxyethyl)aminomethyl] triazole, 1-(or 4)-(dibutoxypropyl-aminomethyl) triazole, 1-(or 4)-(dibutylthiopropyl-aminomethyl) triazole, 1-(or 4)-(di-butylaminopropyl-aminomethyl) triazole, 1-(or 4)-(1-methanamine)-N,N-bis(2-ethylhexyl)-methyl benzotriazole, N,N-bis-(1- or 4-triazolylmethyl) laurylamine, N,N-bis-(1- or 4-triazolylmethyl) oleylamine, N,N-bis-(1- or 4-triazolylmethyl) ethanolamine and N,N,N',N'-tetra(1- or 4-triazolylmethyl) ethylene diamine.

[0107] The metal deactivating agents which can be used in the lubricating composition of the present disclosure includes, for example, benzotriazole and the 4-alkylbenzotriazoles such as 4-methylbenzotriazole and 4-ethylbenzotriazole; 5-alkylbenzotriazoles such as 5-methylbenzotriazole, 5-ethylbenzotriazole; 1-alkylbenzotriazoles such as 1-dioctylaminomethyl-2,3-benzotriazole; benzotriazole derivatives such as the 1-alkyltolutriazoles, for example, 1-dioctylaminomethyl-2,3-tolotriazole; benzimidazole and benzimidazole derivatives such as 2-(alkyldithio)-benzimidazoles, for example, such as 2-(octyldithio)-benzimidazole, 2-(decyldithio)benzimidazole and 2-(dodecyldithio)-benzimidazole; 2-(alkyldithio)-toluimidazoles such as 2-(octyldithio)-toluimidazole, 2-(decyldithio)-toluimidazole and 2-(dodecyldithio)-toluimidazole; indazole and indazole derivatives of toluimidazoles such as 4-alkylindazole, 5-alkylindazole; benzothiazole, 2-mercaptobenzothiazole derivatives (manufactured by the Chiyoda Kagaku Co. under the trade designation "Thiolite B-3100") and 2-(alkyldithio)benzothiazoles such

as 2-(hexyldithio)benzothiazole and 2-(octyldithio)benzothiazole; 2-(alkyl-dithio)toluthiazoles such as 2-(benzyldithio)toluthiazole and 2-(octyldithio)toluthiazole, 2-(N,N-dialkyldithiocarbamyl)benzothiazoles such as 2-(N,N-diethyldithiocarbamyl)benzothiazole, 2-(N,N-dibutyldithiocarbamyl)- benzotriazole and 2-N,N-dihexyl-dithiocarbamyl)benzotriazole; benzothiazole derivatives of 2-(N,N-dialkyldithiocarbamyl)toluthiazoles such as 2-(N,N-diethyldithiocarbamyl)toluthiazole, 2-(N,N-dibutyldithiocarbamyl)toluthiazole, 2-(N,N-dihexyldithiocarbamyl)- toluthiazole; 2-(alkyldithio)benzoxazoles such as 2-(octyldithio)benzoxazole, 2-(decyldithio)-benzoxazole and 2-(dodecyldithio)benzoxazole; benzoxazole derivatives of 2-(alkyldithio)toluoxazoles such as 2-(octyldithio)toluoxazole, 2-(decyldithio)toluoxazole, 2-(dodecyldithio)toluoxazole; 2,5-bis(alkyldithio)-1,3,4-thiadiazoles such as 2,5-bis(heptyldithio)-1,3,4-thiadiazole, 2,5-bis-(nonyldithio)-1,3,4-thiadiazole, 2,5-bis(dodecyldithio)-1,3,4-thiadiazole and 2,5-bis-(octadecyldithio)-1,3,4-thiadiazole; 2,5-bis(N,N-dialkyl-dithiocarbamyl)-1,3,4-thiadiazoles such as 2,5-bis(N,N-diethyldithiocarbamyl)-1,3,4-thiadiazole, 2,5-bis(N,N-dibutyldithiocarbamyl)-1,3,4-thiadiazole and 2,5-bis(N,N-diocetylthiocarbamyl)1,3,4-thiadiazole; thiadiazole derivatives of 2-N,N-dialkyldithiocarbamyl-5-mercapto-1,3,4-thiadiazoles such as 2-N,N-dibutyldithiocarbamyl-5-mercapto-1,3,4-thiadiazole and 2-N,N-diocetylthiocarbamyl-5-mercapto-1,3,4-thiadiazole, and triazole derivatives of 1-alkyl-2,4-triazoles such as 1-dioctylaminomethyl-2,4-triazole; or concentrates and/or mixtures thereof.

[0108] Although their presence is not required to obtain the benefit of the present disclosure, the metal deactivator(s) and corrosion inhibitor(s) may be present from zero to about 1% by weight (e.g. from 0.01% to about 0.5% by weight) of the total lubricating composition.

Antiwear additive(s) or inhibitor(s).

[0109] In certain embodiments, the lubricating composition comprises at least one antiwear additive or wear inhibitor. Any antiwear additive that is known or that becomes known may be utilized in the lubricating composition of the present disclosure. In certain embodiments, the wear inhibitor is at least one of a food-grade sulfur containing compound, a food-grade phosphorus containing compound, or a combination thereof. The antiwear additive may be an alkyldithiophosphate(s), aryl phosphate(s) and/or phosphite(s). The antiwear additive(s) may be essentially free of metals, or they may contain metal salts.

[0110] In certain embodiments, the antiwear additive is a phosphate ester or salt thereof. A phosphate ester or salt may be a monohydrocarbyl, dihydrocarbyl or a trihydrocarbyl phosphate, wherein each hydrocarbyl group is saturated. In an embodiment, each hydrocarbyl group independently contains from about 8 to about 30, or from about 12 up to about 28, or from about

14 up to about 24, or from about 14 up to about 18 carbons atoms. In an embodiment, the hydrocarbyl groups are alkyl groups. Examples of hydrocarbyl groups include at least one of tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl groups, and mixtures thereof.

[0111] A phosphate ester or salt is a phosphorus acid ester prepared by reacting at least one (e.g., 1, 2, 3, 4, or more) phosphorus acid or anhydride with a saturated alcohol. The phosphorus acid or anhydride can be an inorganic phosphorus reagent, such as phosphorus pentoxide, phosphorus trioxide, phosphorus tetroxide, phosphorous acid, phosphoric acid, phosphorus halide, lower phosphorus esters, or a phosphorus sulfide, including phosphorus pentasulfide, and the like. Lower phosphorus acid esters may contain from 1 to about 7 carbon atoms in each ester group. Alcohols used to prepare the phosphorus acid esters or salts. Examples of commercially available alcohols and alcohol mixtures include Alfol 1218 (a mixture of synthetic, primary, straight-chain alcohols containing 12 to 18 carbon atoms); Alfol 20+ alcohols (mixtures of C18 - C28 primary alcohols having mostly C20 alcohols as determined by GLC (gas-liquid-chromatography)); and Alfol22+ alcohols (C18 - C28 primary alcohols containing primarily C22 alcohols). Alfol alcohols are available from, e.g., Continental Oil Company. Another example of a commercially available alcohol mixture is Adol 60 (about 75% by weight of a straight chain C22 primary alcohol, about 15% of a C20 primary alcohol, and about 8% of C18 and C24 alcohols). The Adol alcohols are marketed by Ashland Chemical.

[0112] The antiwear additive may include at least one (e.g., a mixture of) monohydric fatty alcohol. For example, a mixture of monohydric fatty alcohols derived from naturally occurring triglycerides and ranging in chain length from C8 to C18 may be utilized as an antiwear additive. A variety of monohydric fatty alcohol mixtures are available from Procter & Gamble Company. These mixtures contain various amounts of fatty alcohols containing 12, 14, 16, or 18 carbon atoms. For example, CO-1214 is a fatty alcohol mixture containing 0.5% of C10 alcohol, 66.0% of C12 alcohol, 26.0% of C14 alcohol and 6.5% of C16 alcohol.

[0113] Another group of commercially available alcohol mixtures include the "Neodol" products available from Shell Chemical Co. For example, Neodol 23 is a mixture of C12 and C13 alcohols; Neodol 25 is a mixture of C12 to C15 alcohols; and Neodol 45 is a mixture of C14 to C15 linear alcohols. The phosphate contains from about 14 to about 18 carbon atoms in each hydrocarbyl group. The hydrocarbyl groups of the phosphate may be derived from a mixture of fatty alcohols having from about 14 up to about 18 carbon atoms. The hydrocarbyl phosphate may also be derived from a fatty vicinal diol. Fatty vicinal diols include, but not limited to, those available from Ashland Oil under the general trade designation Adol 114 and Adol 158. The

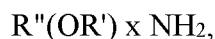
former is derived from a straight chain alpha olefin fraction of C11 - C14, and the latter is derived from a C15 - C18 fraction.

[0114] Phosphate salts may be prepared by reacting an acidic phosphate ester with an amine compound or a metallic base to form an amine or a metal salt. The amines may be monoamines or polyamines. Useful amines include those amines disclosed in U.S. Patent No. 4,234,435.

[0115] Illustrative monoamines may contain a hydrocarbyl group, which contains from 1 to about 30 carbon atoms, or from 1 to about 12, or from 1 to about 6. Examples of primary monoamines useful in the present disclosure include methylamine, ethylamine, propylamine, butylamine, cyclopentylamine, cyclohexylamine, octylamine, dodecylamine, allylamine, cocoamine, stearylamine, and laurylamine. Examples of secondary monoamines include dimethylamine, diethylamine, dipropylamine, dibutylamine, dicyclopentylamine, dicyclohexylamine, methylbutylamine, ethylhexylamine, etc.

[0116] An amine may be a fatty (C8 - C30) amine which includes n-octylamine, n-decylamine, n-dodecylamine, n-tetradecylamine, n-hexadecylamine, n-octadecylamine, oleyamine, etc. Also useful fatty amines include commercially available fatty amines, such as "Armeen" amines (products available from Akzo Chemicals, Chicago, Ill.), e.g. Armeen C, Armeen O, Armeen OL, Armeen T, Armeen HT, Armeen S and Armeen SD, wherein the letter designation relates to the fatty group, such as coco, oleyl, tallow, or stearyl groups.

[0117] Other useful amines include primary ether amines, such as those represented by the formula:



wherein:

R' is a divalent alkylene group having about 2 to about 6 carbon atoms;

x is a number from one to about 150, or from about one to about five, or one; and

R'' is a hydrocarbyl group of about 5 to about 150 carbon atoms.

[0118] An exemplary or illustrative ether amine is available under the name SURFAM® amines produced and marketed by Mars Chemical Company, Atlanta, Ga. Additional exemplary ether amines include those identified as SURFAM P14B (decyloxypropylamine), SURFAM P16A (linear C16), and SURFAM P17B (tridecyloxypropylamine). The carbon chain lengths (i.e., C14, etc.) of the SURFAM ether amines described above and used hereinafter are approximate and include the oxygen ether linkage.

[0119] A further illustrative amine is a tertiary-aliphatic primary amine. For example, the aliphatic group, such as an alkyl group, contains from about 4 to about 30, or from about 6 to about 24, or from about 8 to about 22 carbon atoms. Usually the tertiary alkyl primary amines are monoamines the alkyl group is a hydrocarbonyl group containing from one to about 27 carbon atoms. Such amines are illustrated by tert-butylamine, tert-hexylamine, 1-methyl-1-amino-cyclohexane, tert-octylamine, tert-decylamine, tert-dodecylamine, tert-tetradecylamine, tert-hexadecylamine, tert-octadecylamine, tert-tetracosanylamine, tert-octacosanylamine, and combinations thereof. Mixtures of tertiary aliphatic amines may also be used in preparing the phosphate salt. Illustrative of amine mixtures of this type are "Primene 81R", which is a mixture of C11 - C14 tertiary alkyl primary amines, and "Primene JMT", which is a similar mixture of C18 - C22 tertiary alkyl primary amines (both are available from Rohm and Haas Company). The tertiary aliphatic primary amines and methods for their preparation are known to those of ordinary skill in the art.

[0120] Another illustrative amine is a heterocyclic polyamine. The heterocyclic polyamines include aziridines, azetidines, azolidines, tetra- and dihydropyridines, pyrroles, indoles, piperidines, imidazoles, di- and tetra-hydroimidazoles, piperazines, isoindoles, purines, morpholines, thiomorpholines, N-aminoalkylmorpholines, N-aminoalkylthiomorpholines, N-aminoalkyl-piperazines, N,N'-diaminoalkylpiperazines, azepines, azocines, azonines, azecines and tetra-, di- and perhydro derivatives of each of the above, and mixtures of two or more (e.g., 2, 3, 4, 5, 6, or more) of these heterocyclic amines. In certain embodiments, the heterocyclic amines are saturated 5- and 6-membered heterocyclic amines containing only nitrogen, oxygen and/or sulfur in the hetero ring, especially the piperidines, piperazines, thiomorpholines, morpholines, pyrrolidines, and the like. Piperidine, aminoalkyl substituted piperidines, piperazine, aminoalkyl substituted piperazines, morpholine, aminoalkyl substituted morpholines, pyrrolidine, and aminoalkyl-substituted pyrrolidines, are especially preferred. Usually the aminoalkyl substituents are substituted on a nitrogen atom forming part of the hetero ring. Specific examples of such heterocyclic amines include N-aminopropylmorpholine, N-aminoethylpiperazine, and N,N'-diaminoethylpiperazine. Hydroxy heterocyclic polyamines are also useful. Examples include N-(2-hydroxyethyl)cyclohexylamine, 3-hydroxycyclopentylamine, parahydroxyaniline, N-hydroxyethylpiperazine, and the like.

[0121] The metal salts of the phosphorus acid esters may be prepared by the reaction of a metal base with the acidic phosphorus ester. The metal base may be any metal compound capable of forming a metal salt. Examples of metal bases include metal oxides, hydroxides, carbonates, sulfates, borates, or the like. The metals of the metal base include Group IA, IIA, IB through VIIB,

and VIII metals (CAS version of the Periodic Table of the Elements). These metals include the alkali metals, alkaline earth metals and transition metals. In an embodiment, the metal is a Group IIA metal, such as calcium or magnesium, Group IIB metal, such as zinc, or a Group VIIB metal, such as manganese. In particular embodiments, the metal is magnesium, calcium, manganese or zinc. Examples of metal compounds which may be reacted with the phosphorus acid include zinc hydroxide, zinc oxide, copper hydroxide, copper oxide, etc.

[0122] The lubricating composition of the present disclosure also may include a fatty imidazoline or a reaction product of a fatty carboxylic acid and at least one polyamine. The fatty imidazoline has fatty substituents containing from 8 to about 30, or from about 12 to about 24 carbon atoms. The substituent may be saturated or unsaturated, for example, heptadecenyl derived oleyl groups. In a particular embodiment, the substituents are saturated. In one aspect, the fatty imidazoline may be prepared by reacting a fatty carboxylic acid with a polyalkylenepolyamine. The fatty carboxylic acids can be mixtures of straight and branched chain fatty carboxylic acids containing about 8 to about 30 carbon atoms, or from about 12 to about 24, or from about 16 to about 18. Carboxylic acids include the polycarboxylic acids or carboxylic acids or anhydrides having from 2 to about 4 carbonyl groups, (e.g. 2 carbonyl groups). The polycarboxylic acids include succinic acids and anhydrides and Diels-Alder reaction products of unsaturated monocarboxylic acids with unsaturated carboxylic acids (such as acrylic, methacrylic, maleic, fumaric, crotonic and itaconic acids). In particular embodiments, the fatty carboxylic acids are fatty monocarboxylic acids, having from about 8 to about 30, (e.g. about 12 to about 24 carbon atoms), such as octanoic, oleic, stearic, linoleic, dodecanoic, and tall oil acids. In an embodiment, the fatty carboxylic acid is stearic acid. The fatty carboxylic acid or acids are reacted with at least one polyamine. The polyamines may be aliphatic, cycloaliphatic, heterocyclic or aromatic. Examples of the polyamines include alkylene polyamines and heterocyclic polyamines.

[0123] The antiwear additive according to the present disclosure has very high effectiveness when used in low concentrations and is free of chlorine. For the neutralization of the phosphoric esters, the latter are taken and the corresponding amine slowly added with stirring. The resulting heat of neutralization is removed by cooling. The antiwear additive according to the present disclosure can be incorporated into the respective base liquid with the aid of fatty substances (e.g., tall oil fatty acid, oleic acid, etc.) as solubilizers. The base liquids used are naphthenic or paraffinic base oils, synthetic oils (e.g., polyglycols, mixed polyglycols), polyolefins, carboxylic esters, etc.

[0124] In further embodiments, the lubricating compositions of the present disclosure can contain at least one phosphorus containing antiwear additive. Examples of such additives are

amine phosphate antiwear additives such as that known under the trade name IRGALUBE 349 and/or triphenyl phosphorothionate antiwear additives, such as that known under the trade name IRGALUBE TPPT. Such amine phosphates may be present in an amount of from about 0.01 to about 2% (e.g. about 0.2 to about 1.5%) by weight of the lubricant composition, while such phosphorothionates are suitably present in an amount of from about 0.01 to about 3% (e.g., about 0.5 to about 1.5%) by weight of the lubricating composition. A mixture of an amine phosphate and phosphorothionate may be employed.

[0125] Neutral organic phosphates may be present in an amount from zero to about 4% (e.g., about 0.1 to about 2.5%) by weight of the lubricating composition. The above amine phosphates can be mixed together to form a single component capable of delivering antiwear performance. The neutral organic phosphate is also a conventional ingredient of lubricating oils.

[0126] Phosphates for use in the present disclosure include phosphates, acid phosphates, phosphites, and acid phosphites. The phosphates include triaryl phosphates, trialkyl phosphates, trialkylaryl phosphates, triarylalkyl phosphates, trialkenyl phosphates, or combinations thereof. As specific examples of these, referred to are triphenyl phosphate, tricresyl phosphate, benzyldiphenyl phosphate, ethyldiphenyl phosphate, tributyl phosphate, ethyldibutyl phosphate, cresyldiphenyl phosphate, dicresylphenyl phosphate, ethylphenyldiphenyl phosphate, diethylphenylphenyl phosphate, propylphenyldiphenyl phosphate, dipropylphenylphenyl phosphate, triethylphenyl phosphate, tripropylphenyl phosphate, butylphenyldiphenyl phosphate, dibutylphenylphenyl phosphate, tributylphenyl phosphate, trihexyl phosphate, tri(2-ethylhexyl) phosphate, tridecyl phosphate, trilauryl phosphate, trimyristyl phosphate, tripalmityl phosphate, tristearyl phosphate, trioleyl phosphate, or combinations thereof.

[0127] The acid phosphates include, for example, 2-ethylhexyl acid phosphate, ethyl acid phosphate, butyl acid phosphate, oleyl acid phosphate, tetracosyl acid phosphate, isodecyl acid phosphate, lauryl acid phosphate, tridecyl acid phosphate, stearyl acid phosphate, isostearyl acid phosphate, or combinations thereof.

[0128] The phosphites include, for example, triethyl phosphite, tributyl phosphite, triphenyl phosphite, tricresyl phosphite, tri(nonylphenyl) phosphite, tri(2-ethylhexyl) phosphite, tridecyl phosphite, trilauryl phosphite, triisooctyl phosphite, diphenylisodecyl phosphite, tristearyl phosphite, trioleyl phosphite, or combinations thereof.

[0129] The acid phosphites include, for example, dibutyl hydrogenphosphite, dilauryl hydrogenphosphite, dioleyl hydrogenphosphite, distearyl hydrogenphosphite, diphenyl hydrogenphosphite, or combinations thereof.

[0130] Amines that form amine salts with such phosphates include, for example, mono-substituted amines, di-substituted amines and tri-substituted amines. Examples of the mono-substituted amines include butylamine, pentylamine, hexylamine, cyclohexylamine, octylamine, laurylamine, stearylamine, oleylamine and benzylamine; and those of the di-substituted amines include dibutylamine, dipentylamine, dihexylamine, dicyclohexylamine, dioctylamine, dilaurylamine, distearylamine, dioleylamine, dibenzylamine, stearyl monoethanolamine, decyl monoethanolamine, hexyl monopropylamine, benzyl monoethanolamine, phenyl monoethanolamine, and tolyl monopropylamine. Examples of tri-substituted amines include tributylamine, tripentylamine, trihexylamine, tricyclohexylamine, trioctylamine, trilaurylamine, tristearylamine, trioleylamine, tribenzylamine, dioleyl monoethanolamine, dilauryl monopropylamine, dioctyl monoethanolamine, dihexyl monopropylamine, dibutyl monopropylamine, oleyl diethanolamine, stearyl dipropylamine, lauryl diethanolamine, octyl dipropylamine, butyl diethanolamine, benzyl diethanolamine, phenyl diethanolamine, tolyl dipropylamine, xylyl diethanolamine, triethanolamine, and tripropylamine. Phosphates or their amine salts are added to the base oil in an amount from zero to about 5% by weight, (e.g. from about 0.1 to about 2% by weight) relative to the total weight of the lubricating composition.

[0131] Illustrative carboxylic acids to be reacted with amines include, for example, aliphatic carboxylic acids, dicarboxylic acids (dibasic acids), aromatic carboxylic acids, or combinations thereof. The aliphatic carboxylic acids have from 8 to 30 carbon atoms, and may be saturated or unsaturated, and linear or branched. Specific examples of the aliphatic carboxylic acids include pelargonic acid, lauric acid, tridecanoic acid, myristic acid, palmitic acid, stearic acid, isostearic acid, eicosanoic acid, behenic acid, triacontanoic acid, caproic acid, undecylenic acid, oleic acid, linolenic acid, erucic acid, linoleic acid, or combinations thereof. Specific examples of the dicarboxylic acids include octadecylsuccinic acid, octadecenylsuccinic acid, adipic acid, azelaic acid, sebacic acid, or combinations thereof. One example of the aromatic carboxylic acids is salicylic acid. Illustrative amines to be reacted with carboxylic acids include, for example, polyalkylene-polyamines, such as diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine, hexaethyleneheptamine, heptaethyleneoctamine, dipropylenetriamine, tetrapropylenetriamine, hexabutyleneheptamine, or combinations thereof; and alkanolamines, such as monoethanolamine and diethanolamine. Of these, preferred are a

combination of isostearic acid, tetraethylenepentamine, or combinations thereof; and a combination of oleic acid and diethanolamine. Reaction products of carboxylic acids and amines may be added to the base oil in an amount of from zero to about 5% by weight (e.g. from about 0.03 to about 3% by weight) relative to the total weight of the lubricating composition.

[0132] Other illustrative antiwear additives include phosphites, thiophosphites, phosphates, and thiophosphates, including mixed materials having, for instance, one or two sulfur atoms, i.e., monothio- or dithio compounds. 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.

[0133] Specific examples of some phosphites and thiophosphites within the scope of the disclosure include phosphorous acid, mono-, di- or tri-thiophosphorous acid, mono-, di- or tri-propyl phosphite or mono-, di- or tri-thiophosphite; mono-, di- or tri-butyl phosphite or mono-, di- or tri-thiophosphite; mono-, di- or tri-amyl phosphite or mono-, di- or tri-thiophosphite; mono-, di- or tri-hexyl phosphite; or mono-, di- or tri-thiophosphite; mono-, di- or tri-phenyl phosphite; or mono-, di- or tri-thiophosphite; mono-, di- or tri-tolyl phosphite; or mono-, di- or tri-thiophosphite; mono-, di- or tri-cresyl phosphite; or mono-, di- or tri-thiophosphite; dibutyl phenyl phosphite; or mono-, di- or tri-phosphite; amyl dicresyl phosphite; or mono-, di- or tri-thiophosphite, and any of the above with substituted groups, such as chlorophenyl or chlorobutyl.

[0134] Specific examples of the phosphates and thiophosphates within the scope of the disclosure include phosphoric acid, mono-, di-, or tri-thiophosphoric acid, mono-, di-, or tri-propyl phosphate or mono-, di-, or tri-thiophosphate; mono-, di-, or tri-butyl phosphate or mono-, di-, or tri-thiophosphate; mono-, di-, or tri-amyl phosphate or mono-, di-, or tri-thiophosphate; mono-, di-, or tri-hexyl phosphate or mono-, di-, or tri-thiophosphate; mono-, di-, or tri-phenyl phosphate or mono-, di-, or tri-thiophosphate; mono-, di-, or tritolyl phosphate or mono-, di-, or trithiophosphate; mono-, di-, or tri-cresyl phosphate or mono-, di-, or tri-thiophosphate; dibutyl phenyl phosphate or mono-, di-, or tri-phosphate, amyl dicresyl phosphate or mono-, di-, or tri-thiophosphate, and any of the above with substituted groups, such as chlorophenyl or chlorobutyl.

[0135] These phosphorus compounds may be prepared by well-known reactions. For example, the reaction of an alcohol or a phenol with phosphorus trichloride or by a transesterification reaction. Alcohols and phenols can be reacted with phosphorus pentoxide to provide a mixture of an alkyl or aryl phosphoric acid and a dialkyl or diaryl phosphoric acid. Alkyl phosphates can also

be prepared by the oxidation of the corresponding phosphites. Thiophosphates can be prepared by the reaction of phosphites with elemental sulfur. In any case, the reaction can be conducted with moderate heating. Moreover, various phosphorus esters can be prepared by reaction using other phosphorus esters as starting materials. Thus, medium chain (C9 to C22) phosphorus esters have been prepared by reaction of dimethylphosphite with a mixture of medium-chain alcohols by means of a thermal transesterification or an acid- or base-catalyzed transesterification. *See*, for example, U.S. Patent No. 4,652,416. Most such materials are also commercially available; for instance, triphenyl phosphite is available from Albright and Wilson as Duraphos TPP™; di-n-butyl hydrogen phosphite from Albright and Wilson as Duraphos DBHP™; and triphenylthiophosphate from Ciba Specialty Chemicals as Irgalube TPPT™.

[0136] Examples of esters of the dialkylphosphorodithioic acids include esters obtained by reaction of the dialkyl phosphorodithioic acid with an alpha, beta-unsaturated carboxylic acid (e.g., methyl acrylate) and, optionally an alkylene oxide such as propylene oxide.

[0137] One or more of the above-identified metal dithiophosphates may be used from about zero to about 2% by weight (e.g., from about 0.1 to about 1% by weight) based on the weight of the total composition.

[0138] The hydrocarbyl in the dithiophosphate may be alkyl, cycloalkyl, aralkyl or alkaryl groups, or a substantially hydrocarbon group of similar structure. Illustrative alkyl groups include isopropyl, isobutyl, n-butyl, sec-butyl, the various amyl groups, n-hexyl, methylisobutyl, heptyl, 2-ethylhexyl, diisobutyl, isooctyl, nonyl, behenyl, decyl, dodecyl, tridecyl, etc. Illustrative lower alkylphenyl groups include butylphenyl, amylphenyl, heptylphenyl, etc. Cycloalkyl groups likewise are useful and these include chiefly cyclohexyl and the lower alkyl-cyclohexyl radicals. Many substituted hydrocarbon groups may also be used, e.g., chloropentyl, dichlorophenyl, and dichlorodecyl.

[0139] The phosphorodithioic acids from which the metal salts useful in this disclosure are prepared are well known. Examples of dihydrocarbylphosphorodithioic acids and metal salts, and processes for preparing such acids and salts are found in, for example U.S. Patent Nos. 4,263,150; 4,289,635; 4,308,154; and 4,417,990. These patents are hereby incorporated by reference.

[0140] The phosphorodithioic acids may be prepared by the reaction of a phosphorus sulfide with an alcohol or phenol or mixtures of alcohols. An exemplary reaction involves four moles of the alcohol or phenol and one mole of phosphorus pentasulfide, and may be carried out within the temperature range from about 50°C to about 200°C. Thus, the preparation of O,O-di-n-hexyl

phosphorodithioic acid involves the reaction of a mole of phosphorus pentasulfide with four moles of n-hexyl alcohol at about 100°C for about two hours. Hydrogen sulfide is liberated and the residue is the desired acid. The preparation of the metal salts of these acids may be effected by reaction with metal compounds as well known in the art.

[0141] The metal salts of dihydrocarbyldithiophosphates, which are useful in the present disclosure, include those salts containing Group I metals, Group II metals, aluminum, lead, tin, molybdenum, manganese, cobalt, and nickel. The Group II metals, aluminum, tin, iron, cobalt, lead, molybdenum, manganese, nickel and copper are among the preferred metals. Zinc and copper are especially useful metals. Examples of metal compounds which may be reacted with the acid include lithium oxide, lithium hydroxide, sodium hydroxide, sodium carbonate, potassium hydroxide, potassium carbonate, silver oxide, magnesium oxide, magnesium hydroxide, calcium oxide, zinc hydroxide, strontium hydroxide, cadmium oxide, cadmium hydroxide, barium oxide, aluminum oxide, iron carbonate, copper hydroxide, lead hydroxide, tin butylate, cobalt hydroxide, nickel hydroxide, nickel carbonate, and the like.

[0142] In some instances, the incorporation of certain ingredients such as small amounts of the metal acetate or acetic acid in conjunction with the metal reactant will facilitate the reaction and result in an improved product. For example, the use of up to about 5% of zinc acetate in combination with the required amount of zinc oxide facilitates the formation of a zinc phosphorodithioate with potentially improved performance properties.

[0143] Especially useful metal phosphorodithioates can be prepared from phosphorodithioic acids, which in turn are prepared by the reaction of phosphorus pentasulfide with mixtures of alcohols. In addition, the use of such mixtures enables the utilization of less expensive alcohols, which individually may not yield oil-soluble phosphorodithioic acids. Thus, a mixture of isopropyl and hexylalcohols can be used to produce a very effective, oil-soluble metal phosphorodithioate. For the same reason mixtures of phosphorodithioic acids can be reacted with the metal compounds to form less expensive, oil-soluble salts.

[0144] The mixtures of alcohols may be mixtures of different primary alcohols, mixtures of different secondary alcohols, or mixtures of primary and secondary alcohols. Examples of useful mixtures include: n-butanol and n-octanol; n-pentanol and 2-ethyl-1-hexanol; isobutanol and n-hexanol; isobutanol and isoamyl alcohol; isopropanol and 2-methyl-4-pentanol; isopropanol and sec-butyl alcohol; isopropanol and isooctyl alcohol; and the like.

[0145] Organic triesters of phosphorus acids are also employed in lubricants. Exemplary esters include triarylphosphates, trialkyl phosphates, neutral alkylaryl phosphates, alkoxyalkyl phosphates, triaryl phosphite, trialkylphosphite, neutral alkyl aryl phosphites, neutral phosphonate esters and neutral phosphine oxide esters. In one embodiment, the long chain dialkyl phosphonate esters are used. For example, the dimethyl-, diethyl-, and/or dipropyl-oleyl phosphonates can be used. Neutral acids of phosphorus acids are the triesters rather than an acid (HO-P) or a salt of an acid.

[0146] Any C4 to C8 alkyl or higher phosphate ester may be employed in the disclosure. For example, tributyl phosphate (TBP) and tri isooctyl phosphate (TOF) can be used. The specific triphosphate ester or combination of esters can easily be selected by one skilled in the art to adjust the density, viscosity, etc., of the formulated fluid. Mixed esters, such as dibutyl octyl phosphate or the like may be employed rather than a mixture of two or more trialkyl phosphates.

[0147] A trialkyl phosphate is often useful to adjust the specific gravity of the formulation, but it is desirable that the specific trialkyl phosphate be a liquid at low temperatures. Consequently, a mixed ester containing at least one partially alkylated with a C3 to C4 alkyl group is very desirable, for example, 4-isopropylphenyl diphenyl phosphate or 3-butylphenyl diphenyl phosphate. Even more desirable is a triaryl phosphate produced by partially alkylating phenol with butylene or propylene to form a mixed phenol which is then reacted with phosphorus oxychloride as taught in U.S. Patent No. 3,576,923.

[0148] Any mixed triaryl phosphate (TAP) esters may be used as cresyl diphenyl phosphate, tricresyl phosphate, mixed xylyl cresyl phosphates, lower alkylphenyl/phenyl phosphates, such as mixed isopropylphenyl/phenyl phosphates, t-butylphenyl phenyl phosphates. These esters are used extensively as plasticizers, functional fluids, gasoline additives, flame-retardant additives and the like.

[0149] A metal alkylthiophosphate and more particularly a metal dialkyl dithio phosphate in which the metal constituent is zinc, or zinc dialkyl dithio phosphate (ZDDP) can be a useful component of the lubricating oils of this disclosure. ZDDP can be derived from primary alcohols, secondary alcohols or mixtures thereof. ZDDP compounds are of the formula:



wherein R1 and R2 are C1 – C18 alkyl groups (e.g. C2 - C12 alkyl groups).

[0150] These alkyl groups may be straight chain or branched. Alcohols used in the ZDDP can be propanol, 2-propanol, butanol, secondary butanol, pentanols, hexanols such as 4-methyl-2-

pentanol, n-hexanol, n-octanol, 2-ethyl hexanol, alkylated phenols, and the like. Mixtures of secondary alcohols or of primary and secondary alcohol can be utilized. Alkyl aryl groups may also be used.

[0151] Exemplary zinc dithiophosphates that are commercially available include secondary zinc dithiophosphates, such as those available from for example, The Lubrizol Corporation under the trade designations “LZ 677A”, “LZ 1095” and “LZ 1371”, from for example Chevron Oronite under the trade designation “OLOA 262”, and from for example Afton Chemical under the trade designation “HITEC 7169”.

[0152] Although their presence is not required to obtain the benefit of this disclosure, ZDDP is may be used in amounts of from about zero to about 3 weight percent (e.g. from about 0.05 weight percent to about 2 weight percent, from about 0.1 weight percent to about 1.5 weight percent, or from about 0.1 weight percent to about 1 weight percent) based on the total weight of the lubricating composition, although more or less can often be used advantageously. A secondary ZDDP may be present in an amount of from zero to about 1 weight percent of the total weight of the lubricating composition.

Extreme Pressure Agent(s).

[0153] In other embodiments, the lubricating composition comprises at least one extreme pressure agent. Any extreme pressure agent that is known or that becomes know may be utilized in the lubricating composition of the present disclosure. In certain embodiments, the extreme pressure agent includes at least two (e.g., 2, 3, 4, or more) extreme pressure agents.

[0154] The extreme pressure agents can be at least one sulfur-based extreme pressure agents, such as sulfides, sulfoxides, sulfones, thiophosphinates, thiocarbonates, sulfurized fats and oils, sulfurized olefins, the like, or combinations thereof; at least one phosphorus-based extreme pressure agents, such as phosphoric acid esters (e.g., tricresyl phosphate (TCP) and the like), phosphorous acid esters, phosphoric acid ester amine salts, phosphorous acid ester amine salts, the like, or combinations thereof; halogen-based extreme pressure agents, such as chlorinated hydrocarbons, the like, or combinations thereof; organometallic extreme pressure agents, such as thiophosphoric acid salts (e.g., zinc dithiophosphate (ZnDTP) and the like), thiocarbamic acid salts, or combinations thereof; and the like.

[0155] The phosphoric acid ester, thiophosphoric acid ester, and amine salts thereof functions to enhance the lubricating performances, and can be selected from known compounds conventionally employed as extreme pressure agents. For example, phosphoric acid esters, a

thiophosphoric acid ester, or an amine salt thereof which has an alkyl group, an alkenyl group, an alkylaryl group, or an aralkyl group, any of which contains approximately 3 to 30 carbon atoms, may be employed.

[0156] Examples of the phosphoric acid esters include aliphatic phosphoric acid esters such as triisopropyl phosphate, tributyl phosphate, ethyl dibutyl phosphate, trihexyl phosphate, tri-2-ethylhexyl phosphate, trilauryl phosphate, tristearyl phosphate, and trioleyl phosphate; and aromatic phosphoric acid esters such as benzyl phenyl phosphate, allyl diphenyl phosphate, triphenyl phosphate, tricresyl phosphate, ethyl diphenyl phosphate, cresyl diphenyl phosphate, dicresyl phenyl phosphate, ethylphenyl diphenyl phosphate, diethylphenyl phenyl phosphate, propylphenyl diphenyl phosphate, dipropylphenyl phenyl phosphate, triethylphenyl phosphate, tripropylphenyl phosphate, butylphenyl diphenyl phosphate, dibutylphenyl phenyl phosphate, and tributylphenyl phosphate. In an embodiment, the phosphoric acid ester is a trialkylphenyl phosphate.

[0157] Examples of the thiophosphoric acid esters include aliphatic thiophosphoric acid esters such as triisopropyl thiophosphate, tributyl thiophosphate, ethyl dibutyl thiophosphate, trihexyl thiophosphate, tri-2-ethylhexyl thiophosphate, trilauryl thiophosphate, tristearyl thiophosphate, and trioleyl thiophosphate; and aromatic thiophosphoric acid esters such as benzyl phenyl thiophosphate, allyl diphenyl thiophosphate, triphenyl thiophosphate, tricresyl thiophosphate, ethyl diphenyl thiophosphate, cresyl diphenyl thiophosphate, dicresyl phenyl thiophosphate, ethylphenyl diphenyl thiophosphate, diethylphenyl phenyl thiophosphate, propylphenyl diphenyl thiophosphate, dipropylphenyl phenyl thiophosphate, triethylphenyl thiophosphate, tripropylphenyl thiophosphate, butylphenyl diphenyl thiophosphate, dibutylphenyl phenyl thiophosphate, and tributylphenyl thiophosphate. In an embodiment, the thiophosphoric acid ester is a trialkylphenyl thiophosphate.

[0158] Also employable are amine salts of the above-mentioned phosphates and thiophosphates. Amine salts of acidic alkyl or aryl esters of the phosphoric acid and thiophosphoric acid are also employable. In an embodiment, the amine salt is an amine salt of trialkylphenyl phosphate or an amine salt of alkyl phosphate.

[0159] One or any combination of the compounds selected from the group consisting of a phosphoric acid ester, a thiophosphoric acid ester, and an amine salt thereof may be used.

[0160] The phosphorus acid ester and/or its amine salt function to enhance the lubricating performance of the composition, and can be selected from known compounds conventionally

employed as extreme pressure agents. For example, the extreme pressure agent can be a phosphorus acid ester or an amine salt thereof, which has an alkyl group, an alkenyl group, an alkylaryl group, or an aralkyl group, any of which contains approximately 3 to 30 carbon atoms.

[0161] Examples of phosphorus acid esters that may be used includes aliphatic phosphorus acid esters, such as triisopropyl phosphite, tributyl phosphite, ethyl dibutyl phosphite, trihexyl phosphite, tri-2-ethylhexylphosphite, trilauryl phosphite, tristearyl phosphite, and trioleyl phosphite; and aromatic phosphorus acid esters such as benzyl phenyl phosphite, allyl diphenylphosphite, triphenyl phosphite, tricresyl phosphite, ethyl diphenyl phosphite, tributyl phosphite, ethyl dibutyl phosphite, cresyl diphenyl phosphite, dicresyl phenyl phosphite, ethylphenyl diphenyl phosphite, diethylphenyl phenyl phosphite, propylphenyl diphenyl phosphite, dipropylphenyl phenyl phosphite, triethylphenyl phosphite, tripropylphenyl phosphite, butylphenyl diphenyl phosphite, dibutylphenyl phenyl phosphite, and tributylphenyl phosphite. Also favorably employed are dilauryl phosphite, dioleyl phosphite, dialkyl phosphites, and diphenyl phosphite. In certain embodiments, the phosphorus acid ester is a dialkyl phosphite or a trialkyl phosphite.

[0162] The phosphate salt may be derived from a polyamine, such as alkoxyated diamines, fatty polyamine diamines, alkylenepolyamines, hydroxy containing polyamines, condensed polyamines arylpolyamines, and heterocyclic polyamines. Examples of these amines include Ethoduomeen T/13 and T/20, which are ethylene oxide condensation products of N-tallowtrimethylenediamine containing 3 and 10 moles of ethylene oxide per mole of diamine, respectively.

[0163] In another embodiment, the polyamine is a fatty diamine. The fatty diamine may include mono- or dialkyl, symmetrical or asymmetrical ethylene diamines, propane diamines (1,2 or 1,3), and polyamine analogs of the above. Suitable commercial fatty polyamines are Duomeen C (N-coco-1,3-diaminopropane), Duomeen S (N-soya-1,3-diaminopropane), Duomeen T (N-tallow-1,3-diaminopropane), and Duomeen O (N-oleyl-1,3-diaminopropane). "Duomeens" are commercially available from Armak Chemical Co., Chicago, Ill.

[0164] Such alkylenepolyamines include methylenepolyamines, ethylenepolyamines, butylenepolyamines, propylenepolyamines, pentylenepolyamines, etc. The higher homologs and related heterocyclic amines, such as piperazines and N-amino alkyl-substituted piperazines, are also included. Specific examples of such polyamines are ethylenediamine, triethylenetetramine, tris-(2-aminoethyl)amine, propylenediamine, trimethylenediamine, tripropylenetetramine,

tetraethylenepentamine, hexaethyleneheptamine, pentaethylenehexamine, etc. Higher homologs obtained by condensing two or more of the above-noted alkyleneamines are similarly useful as are mixtures of two or more of the aforescribed polyamines.

[0165] In one embodiment the polyamine is an ethylenepolyamine. Such polyamines are described in detail under the heading Ethylene Amines in Kirk Othmer's "Encyclopedia of Chemical Technology", 2nd Edition, Vol. 7, pages 22-37, Interscience Publishers, New York (1965). Ethylenepolyamines can be a complex mixture of polyalkylenepolyamines, including cyclic condensation products.

[0166] Other useful types of polyamine mixtures are those resulting from stripping of the above-described polyamine mixtures to leave, as residue, what is often termed "polyamine bottoms". The alkylenepolyamine bottoms can be characterized as having less than 2%, usually less than 1% (by weight) material boiling below about 200°C. An exemplary sample of such ethylene polyamine bottoms obtained from the Dow Chemical Company of Freeport, Tex. designated "E-100". These alkylenepolyamine bottoms include cyclic condensation products, such as piperazine, and higher analogs of diethylenetriamine, triethylenetetramine and the like. These alkylenepolyamine bottoms can be reacted solely with the acylating agent or they can be used with other amines, polyamines, or mixtures thereof. Another useful polyamine is a condensation reaction between at least one hydroxy compound with at least one polyamine reactant containing at least one primary or secondary amino group. In an embodiment, the hydroxy compounds are alcohols and amines. The polyhydric alcohols are described below. In one embodiment, the hydroxy compounds are polyhydric amines. Polyhydric amines include any of the above-described monoamines reacted with an alkylene oxide (e.g., ethylene oxide, propylene oxide, butylene oxide, etc.) having from two to about 20 carbon atoms, or from two to about four. Examples of polyhydric amines include tri-(hydroxypropyl)amine, tris-(hydroxymethyl)amino methane, 2-amino-2-methyl-1,3-propanediol, N,N,N',N'-tetrakis(2-hydroxypropyl)ethylenediamine, and N,N,N',N'-tetrakis(2-hydroxyethyl)ethylenediamine. IN an embodiment, the polyhydric amin is tris(hydroxymethyl)aminomethane (THAM).

[0167] Polyamines which react with the polyhydric alcohol or amine to form the condensation products or condensed amines, are described above. In an embodiment, the polyamine include at least one of triethylenetetramine (TETA), tetraethylenepentamine (TEPA), pentaethylenehexamine (PEHA), and mixtures of polyamines, such as the above-described "amine bottoms".

[0168] In some embodiments, the extreme pressure additive or additives includes sulphur-based extreme pressure additives, such as dialkyl sulphides, dibenzyl sulphide, dialkyl polysulphides, dibenzyl disulphide, alkyl mercaptans, dibenzothiophene, 2,2'-dithiobis(benzothiazole), or combinations thereof; phosphorus-based extreme pressure additives, such as trialkyl phosphates, triaryl phosphates, trialkyl phosphonates, trialkyl phosphites, triaryl phosphites, dialkylhydrozine phosphites, or combinations thereof; and/or phosphorus- and sulphur-based extreme pressure additives, such as zinc dialkyldithiophosphates, dialkylthiophosphoric acid, trialkyl thiophosphate esters, acidic thiophosphate esters, trialkyl trithiophosphates, or combinations thereof. Extreme pressure additives can be used individually or in the form of mixtures, conveniently in an amount within the range from zero to about 2 % by weight of the lubricating composition.

Dispersant(s).

[0169] In other embodiments, the lubricating composition comprises at least one dispersant. During machine operation, oil-insoluble oxidation byproducts are produced. The dispersant may be added to help keep these byproducts in solution, thus diminishing their deposition on metal surfaces. Any dispersant that is known or that becomes known may be utilized in the lubricating composition of the present disclosure. In certain embodiments, the dispersant includes at least two (e.g., 2, 3, 4, or more) dispersants.

[0170] In some embodiments, the dispersants is ashless or ash-forming in nature. In an embodiment, the dispersant is an ashless. So called ashless are organic materials that form substantially no ash upon combustion. For example, non-metal-containing or borated metal-free dispersants are considered ashless. In contrast, metal-containing detergents form ash upon combustion.

[0171] Suitable dispersants may contain a polar group attached to a relatively high molecular weight hydrocarbon chain (e.g., about 50 to about 400 carbon atoms). In certain embodiments, the polar group contains at least one element of nitrogen, oxygen, or phosphorus.

[0172] A particularly useful class of dispersants are the (poly)alkenylsuccinic derivatives, which may be produced by the reaction of a long chain hydrocarbyl substituted succinic compound, e.g. a hydrocarbyl substituted succinic anhydride, with a polyhydroxy or polyamino compound. The long chain hydrocarbyl group constituting the oleophilic portion of the molecule, which confers solubility in the oil, is normally a polyisobutylene group. Many examples of this type of dispersant are well known commercially and in the literature. Exemplary U.S. patents describing such dispersants are U.S. Patent Nos. 3,172,892; 3,2145,707; 3,219,666; 3,316,177; 3,341,542;

3,444,170; 3,454,607; 3,541,012; 3,630,904; 3,632,511; 3,787,374 and 4,234,435. Other types of dispersant are described in U.S. Patent Nos. 3,036,003; 3,200,107; 3,254,025; 3,275,554; 3,438,757; 3,454,555; 3,565,804; 3,413,347; 3,697,574; 3,725,277; 3,725,480; 3,726,882; 4,454,059; 3,329,658; 3,449,250; 3,519,565; 3,666,730; 3,687,849; 3,702,300; 4,100,082; 5,705,458. A further description of dispersants may be found, for example, in European Patent Application No. 471 071, to which reference is made for this purpose.

[0173] Hydrocarbyl-substituted succinic acid and hydrocarbyl-substituted succinic anhydride derivatives are useful dispersants. In particular, succinimide, succinate esters, or succinate ester amides prepared by the reaction of a hydrocarbon-substituted succinic acid compound (e.g., a hydrocarbon-substituted succinic acid compound having at least 50 carbon atoms in the hydrocarbon substituent) with at least one equivalent of an alkylene amine are particularly useful.

[0174] Succinimides are formed by the condensation reaction between hydrocarbyl substituted succinic anhydrides and amines. Molar ratios can vary depending on the polyamine. For example, the molar ratio of hydrocarbyl substituted succinic anhydride to TEPA can vary from about 1:1 to about 5:1. Representative examples are shown in U.S. Patent Nos. 3,087,936; 3,172,892; 3,219,666; 3,272,746; 3,322,670; and 3,652,616, 3,948,800; and Canada Patent No. 1,094,044.

[0175] Succinate esters may be formed by the condensation reaction between hydrocarbyl substituted succinic anhydrides and alcohols or polyols. Molar ratios can vary depending on the alcohol or polyol used. For example, the condensation product of a hydrocarbyl substituted succinic anhydride and pentaerythritol is a useful dispersant.

[0176] Succinate ester amides may be formed by condensation reaction between hydrocarbyl substituted succinic anhydrides and alkanol amines. For example, suitable alkanol amines include ethoxylated polyalkylpolyamines, propoxylated polyalkylpolyamines and polyalkenylpolyamines, such as polyethylene polyamines. One example is propoxylated hexamethylenediamine. Representative examples are shown in U.S. Patent No. 4,426,305.

[0177] The molecular weight of the hydrocarbyl substituted succinic anhydrides used in the preceding paragraphs can range between about 800 and about 2,500 or more. The above products can be post-reacted with various reagents such as sulfur, oxygen, formaldehyde, carboxylic acids, such as oleic acid. The above products can also be post reacted with boron compounds, such as boric acid, borate esters or highly borated dispersants, to form borated dispersants, which may have from about 0.1 to about 5 moles of boron per mole of dispersant reaction product.

[0178] Mannich base dispersants are made from the reaction of alkylphenols, formaldehyde, and amines. See U.S. Patent No. 4,767,551, which is incorporated herein by reference. Process aids and catalysts, such as oleic acid and sulfonic acids, can also be part of the reaction mixture. Molecular weights of the alkylphenols may range from about 800 to about 2,500. Representative examples are shown in U.S. Patent Nos. 3,697,574; 3,703,536; 3,704,308; 3,751,365; 3,756,953; 3,798,165; and 3,803,039.

[0179] High molecular weight aliphatic acid modified Mannich condensation products useful in this disclosure can be prepared from high molecular weight alkyl-substituted hydroxyaromatics or HNR₂ group-containing reactants, wherein each R is independently selected from hydrogen, C1-C18 alkyl, aryl, alkenyl, alkaryl group.

[0180] Hydrocarbyl substituted amine ashless dispersant additives are well known to one skilled in the art; see, for example, U.S. Patent Nos. 3,275,554; 3,438,757; 3,565,804; 3,755,433, 3,822,209, and 5,084,197.

[0181] In certain embodiments, the dispersants include borated and/or non-borated succinimides, including those derivatives from mono-succinimides, bis-succinimides, and/or mixtures of mono- and bis-succinimides, wherein the hydrocarbyl succinimide is derived from a hydrocarbylene group such as polyisobutylene having a Mn of from about 500 to about 5000, or from about 1000 to about 3000, or about 1000 to about 2000, or a mixture of such hydrocarbylene groups, often with high terminal vinylic groups. Other dispersants include succinic acid-esters and amides, alkylphenol-polyamine-coupled Mannich adducts, their capped derivatives, and other related components.

[0182] Polymethacrylate or polyacrylate derivatives are another class of dispersants. These dispersants may be prepared by reacting a nitrogen containing monomer and a methacrylic or acrylic acid esters containing about 5 to about 25 carbon atoms in the ester group. Representative examples are shown in U.S. Patent Nos. 2,100,993, and 6,323,164. Polymethacrylate and polyacrylate dispersants may be used as multifunctional viscosity modifiers. The lower molecular weight versions can be used as lubricant dispersants or fuel detergents.

[0183] Illustrative dispersants useful in this disclosure include those derived from polyalkenyl-substituted mono- or dicarboxylic acid, anhydride or ester, wherein the polyalkenyl moiety has an average molecular weight of at least about 900 and from greater than 1.3 to 1.7 (e.g. from greater than 1.3 to 1.6 or from greater than 1.3 to 1.5) functional groups (mono- or dicarboxylic acid

producing moieties) per polyalkenyl moiety (a medium functionality dispersant). Functionality (F) can be determined according to the following formula:

$$F = (SAP \times Mn) / ((112,200 \times A.I.) - (SAP \times 98)),$$

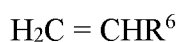
wherein SAP is the saponification number (i.e., the number of milligrams of KOH consumed in the complete neutralization of the acid groups in one gram of the succinic-containing reaction product, as determined according to ASTM D94); Mn is the number average molecular weight of the starting olefin polymer; and A.I. is the percent active ingredient of the succinic-containing reaction product (the remainder being unreacted olefin polymer, succinic anhydride and diluent).

[0184] The polyalkenyl moiety of the dispersant may have a number average molecular weight of at least about 900 or suitably at least about 1500, such as between about 1800 and about 3000 (e.g. between about 2000 and about 2800, from about 2100 to about 2500, or from about 2200 to about 2400). The molecular weight of a dispersant is generally expressed in terms of the molecular weight of the polyalkenyl moiety. This is because the precise molecular weight range of the dispersant depends on numerous parameters including the type of polymer used to derive the dispersant, the number of functional groups, and the type of nucleophilic group employed.

[0185] Polymer molecular weight, specifically Mn, can be determined by various known techniques. One convenient method is gel permeation chromatography (GPC), which additionally provides molecular weight distribution information (see W. W. Yau, J. J. Kirkland and D. D. Bly, "Modern Size Exclusion Liquid Chromatography", John Wiley and Sons, New York, 1979). Another useful method for determining molecular weight, particularly for lower molecular weight polymers, is vapor pressure osmometry (e.g., ASTM D3592).

[0186] In an embodiment, the polyalkenyl moiety in a dispersant has a narrow molecular weight distribution (MWD), also referred to as polydispersity, as determined by the ratio of weight average molecular weight (Mw) to number average molecular weight (Mn). Polymers having a Mw/Mn of less than 2.2 (e.g. less than 2.0) are most desirable. Suitable polymers have a polydispersity of from about 1.5 to 2.1 (e.g. from about 1.6 to about 1.8).

[0187] Suitable polyalkenes employed in the formation of the dispersants include homopolymers, interpolymers or lower molecular weight hydrocarbons. One family of such polymers comprise polymers of ethylene and/or at least one C3 to C26 alpha-olefin having the formula



wherein R⁶ is a straight or branched chain alkyl radical comprising 1 to 26 carbon atoms and wherein the polymer contains carbon-to-carbon unsaturation, and a high degree of terminal ethenylidene unsaturation. In an embodiment, such polymers comprise interpolymers of ethylene and at least one alpha-olefin of the above formula, wherein R⁶ is alkyl of from 1 to 18 carbon atoms (e.g. from 1 to 8 carbon atoms or from 1 to 2 carbon atoms).

[0188] Another useful class of polymers is polymers prepared by cationic polymerization of monomers such as isobutene and styrene. For example, the polymer(s) can be polyisobutenes obtained by polymerization of a C4 refinery stream having a butene content of 35 to 75% by wt., and an isobutene content of 30 to 60% by wt. Petroleum feedstreams, such as Raffinate II, can be a source of monomer for making poly-n-butenes. These feedstocks are disclosed in the art such as in U.S. Pat. No. 4,952,739. Certain embodiments utilize polyisobutylene prepared from a pure isobutylene stream or a Raffinate I stream to prepare reactive isobutylene polymers with terminal vinylidene olefins. Polyisobutene polymers that may be employed may be based on a polymer chain of from about 1500 to about 3000.

[0189] In yet further embodiments, the dispersant(s) are non-polymeric (e.g., mono- or bis-succinimides). Such dispersants can be prepared by conventional processes, such as those disclosed in U.S. Patent Application Publication No. 2008/0020950, the disclosure of which is incorporated herein by reference.

[0190] The dispersant(s) can be borated by conventional means, as generally disclosed in U.S. Patent Nos. 3,087,936, 3,254,025 and 5,430,105.

[0191] Dispersants may be used in an amount of zero to about 10 weight percent or about 0.01 to about 8 weight percent (e.g. about 0.1 to about 5 weight percent or about 0.5 to about 3 weight percent). Or such dispersants may be used in an amount of zero to about 8 weight percent (e.g. about 0.01 to about 5 weight percent or about 0.1 to about 3 weight percent). On an active ingredient basis, such additives may be used in an amount of zero to about 10 weight percent (e.g. about 0.3 to about 3 weight percent). The hydrocarbon portion of the dispersant atoms can range from about C60 to about C1000, or from about C70 to about C300, or from about C70 to about C200. These dispersants may contain both neutral and basic nitrogen, and mixtures thereof. Dispersants can be end-capped by borates and/or cyclic carbonates. Nitrogen content in the finished oil can vary from about zero to about 2000 ppm by weight (e.g. from about 100 ppm by weight to about 1200 ppm by weight). Basic nitrogen can vary from about zero to about 1000 ppm by weight (e.g. from about 100 ppm by weight to about 600 ppm by weight).

[0192] Dispersants as described herein are beneficially useful with the compositions of the present disclosure. Further, in one embodiment, preparation of the compositions of the present disclosure using one or more (e.g. 1, 2, 3, 4, or more) dispersants is achieved by combining ingredients of the present disclosure, plus optional base stocks and lubricant additives, in a mixture at a temperature above the melting point of such ingredients, particularly that of the one or more M-carboxylates (M = H, metal, two or more metals, mixtures thereof).

[0193] As used herein, the dispersant concentrations are given on an “as delivered” basis. The active dispersant may be delivered with a process oil. The “as delivered” dispersant may contain from about 20 weight percent to about 80 weight percent, or from about 40 weight percent to about 60 weight percent, of active dispersant in the “as delivered” dispersant product.

Detergent(s).

[0194] In other embodiments, the lubricating composition comprises at least one detergent. The detergent may be added to protect lubricated metal surfaces against chemical attack by water or other contaminants. Any detergent that is known or that becomes known may be utilized in the lubricating composition of the present disclosure. In certain embodiments, the detergent includes at least two (e.g., 2, 3, 4, or more) detergents.

[0195] Illustrative detergents useful in this disclosure include, for example, alkali metal detergents, alkaline earth metal detergents, or mixtures of one or more alkali metal detergents and one or more alkaline earth metal detergents. In an embodiment, the detergent is an anionic material that contains a long chain hydrophobic portion of the molecule and a smaller anionic or oleophobic hydrophilic portion of the molecule. The anionic portion of the detergent may be derived from an organic acid, such as a sulfur-containing acid, carboxylic acid (e.g., salicylic acid), phosphorus-containing acid, phenol, or mixtures thereof. The counterion may be an alkaline earth or alkali metal. The detergent can be overbased as described herein.

[0196] In other embodiments, the detergent is a metal salt of an organic or inorganic acid, a metal salt of a phenol, or mixtures thereof. The metal may be selected from an alkali metal, an alkaline earth metal, and mixtures thereof. The organic or inorganic acid may be selected from an aliphatic organic or inorganic acid, a cycloaliphatic organic or inorganic acid, an aromatic organic or inorganic acid, and mixtures thereof.

[0197] In certain embodiments, the metal is selected from an alkali metal, an alkaline earth metal, and mixtures thereof. In another embodiment, the metal is selected from calcium (Ca), magnesium (Mg), and mixtures thereof.

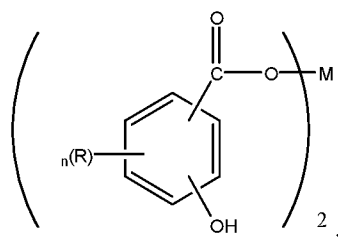
[0198] The organic acid or inorganic acid may be selected from a sulfur-containing acid, a carboxylic acid, a phosphorus-containing acid, and mixtures thereof.

[0199] In a particular embodiment, the metal salt of an organic or inorganic acid or the metal salt of a phenol comprises at least one of calcium phenate, calcium sulfonate, calcium salicylate, magnesium phenate, magnesium sulfonate, magnesium salicylate, an overbased detergent, or mixtures thereof.

[0200] Salts that contain a substantially stoichiometric amount of the metal are described as neutral salts and have a total base number (TBN, as measured by ASTM D2896) of from 0 to 80. Many compositions are overbased, containing large amounts of a metal base that is achieved by reacting an excess of a metal compound (a metal hydroxide or oxide, for example) with an acidic gas (such as carbon dioxide). Useful detergents can be neutral, mildly overbased, or highly overbased. These detergents can be used in mixtures of neutral, overbased, highly overbased calcium salicylate, sulfonates, phenates and/or magnesium salicylate, sulfonates, phenates. The TBN ranges can vary from low, medium to high TBN products, including as low as 0 to as high as 600. In an embodiment, the TBN delivered by the detergent is between 1 and 20 (e.g. between 1 and 12). Mixtures of low, medium, high TBN can be used, along with mixtures of calcium and magnesium metal based detergents, and including sulfonates, phenates, salicylates, and carboxylates. A detergent mixture with a metal ratio of 1, in conjunction with a detergent with a metal ratio of 2, and as high as a detergent with a metal ratio of 5, can be used. Borated detergents can also be used.

[0201] Alkaline earth phenates are another useful class of detergent. These detergents can be made by reacting alkaline earth metal hydroxide or oxide (CaO, Ca(OH)₂, BaO, Ba(OH)₂, MgO, Mg(OH)₂, for example) with an alkyl phenol or sulfurized alkylphenol. Useful alkyl groups include straight chain or branched C1 – C30 alkyl groups (e.g. C4 – C20 alkyl groups) or mixtures thereof. Examples of suitable phenols include isobutylphenol, 2-ethylhexylphenol, nonylphenol, dodecyl phenol, and the like. It should be noted that starting alkylphenols may contain more than one alkyl substituent that are each independently straight chain or branched and can be used from about 0.5 to about 6 weight percent. When a non-sulfurized alkylphenol is used, the sulfurized product may be obtained by methods well known in the art. These methods include heating a mixture of alkylphenol and sulfurizing agent (including elemental sulfur, sulfur halides, such as sulfur dichloride, and the like) and then reacting the sulfurized phenol with an alkaline earth metal base.

[0202] In some embodiments, the detergent is a metal salts of carboxylic acids. These carboxylic acid detergents may be prepared by reacting a basic metal compound with at least one carboxylic acid and removing free water from the reaction product. These compounds may be overbased to produce the desired TBN level. Detergents made from salicylic acid are one class of detergents derived from carboxylic acids. Useful salicylates include long chain alkyl salicylates. One useful family of compositions is of the formula:



wherein: R is an alkyl group having about 1 to about 30 carbon atoms, n is an integer from 1 to 4, and M is an alkaline earth metal. In certain embodiments, the R group or groups are alkyl chains of at least C11 (e.g. at least C13). R may be optionally substituted with substituents that do not interfere with the detergent's function. In an embodiment, the M is calcium, magnesium, barium, or mixtures thereof. In a particular embodiment, the M is calcium.

[0203] Hydrocarbyl-substituted salicylic acids may be prepared from phenols by the Kolbe reaction (see U.S. Patent No. 3,595,791). The metal salts of the hydrocarbyl-substituted salicylic acids may be prepared by double decomposition of a metal salt in a polar solvent, such as water or alcohol.

[0204] Alkaline earth metal phosphates are also used as detergents and are known in the art.

[0205] Detergents may be simple detergents or what is known as hybrid or complex detergents. The latter detergents can provide the properties of two detergents without the need to blend separate materials. See U.S. Patent No. 6,034,039.

[0206] In an embodiment, the detergent or detergents (e.g., 1, 2, 3, 4, or more detergents) includes calcium sulfonates, magnesium sulfonates, calcium salicylates, magnesium salicylates, calcium phenates, magnesium phenates, and other related components (including borated detergents), or mixtures thereof. For example, a mixture of detergents may include magnesium sulfonate and calcium salicylate, magnesium sulfonate and calcium sulfonate, magnesium sulfonate and calcium phenate, calcium phenate and calcium salicylate, calcium phenate and calcium sulfonate, calcium phenate and magnesium salicylate, or calcium phenate and magnesium phenate. Overbased detergents may also be utilized in the lubricating composition of the present disclosure.

[0207] Although their presence is not required to obtain the benefit of this disclosure, detergent concentration in the lubricating oils of this disclosure can range from zero to about 6.0 weight percent (e.g. zero to 5.0 weight percent or from about 0.01 weight percent to about 3.0 weight percent) based on the total weight of the lubricating oil.

[0208] As used herein, the detergent concentrations are given on an “as delivered” basis. The active detergent may delivered with a process oil. The “as delivered” detergent can contain from about 20 weight percent to about 100 weight percent, or from about 40 weight percent to about 60 weight percent, of active detergent in the “as delivered” detergent product.

Friction Modifier(s).

[0209] In other embodiments, the lubricating composition comprises at least one (e.g., 1, 2, 3, 4, or more) friction modifier. A friction modifier is any material or materials that can alter the coefficient of friction of a surface lubricated by any lubricant or fluid containing such material(s). Friction modifiers, also known as friction reducers, or lubricity agents or oiliness agents, and other such agents that change the ability of base oils, formulated lubricant compositions, or functional fluids, to modify the coefficient of friction of a lubricated surface may be effectively used in combination with the base oils or lubricant compositions of the present disclosure if desired. Friction modifiers that lower the coefficient of friction are particularly advantageous in combination with the base oils and lube compositions of this disclosure. Any friction modifier that is known or that becomes known may be utilized in the lubricating composition of the present disclosure.

[0210] Friction modifiers may include, for example, organometallic compounds or materials, or mixtures thereof. Illustrative organometallic friction modifiers useful in the lubricating turbine oil formulations of this disclosure include, for example, molybdenum amine, molybdenum diamine, an organotungstenate, a molybdenum dithiocarbamate, molybdenum dithiophosphates, molybdenum amine complexes, molybdenum carboxylates, and the like, and mixtures thereof. In an embodiment, tungsten-based compounds are utilized.

[0211] Other illustrative friction modifiers useful in the lubricating formulations of the present disclosure include, for example, alkoxylated fatty acid esters, alkanolamides, polyol fatty acid esters, borated glycerol fatty acid esters, fatty alcohol ethers, and mixtures thereof.

[0212] Illustrative alkoxylated fatty acid esters include, for example, polyoxyethylene stearate, fatty acid polyglycol ester, and the like. These can include polyoxypropylene stearate,

polyoxybutylene stearate, polyoxyethylene isostearate, polyoxypropylene isostearate, polyoxyethylene palmitate, and the like.

[0213] Illustrative alkanolamides include, for example, lauric acid diethylalkanolamide, palmitic acid diethylalkanolamide, and the like. These can include oleic acid diethylalkanolamide, stearic acid diethylalkanolamide, oleic acid diethylalkanolamide, polyethoxylated hydrocarbylamides, polypropoxylated hydrocarbylamides, and the like.

[0214] Illustrative polyol fatty acid esters include, for example, glycerol mono-oleate, saturated mono-, di-, and tri-glyceride esters, glycerol mono-stearate, and the like. These can include polyol esters, hydroxyl-containing polyol esters, and the like.

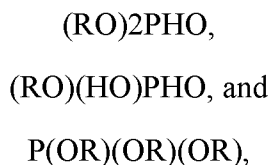
[0215] Illustrative borated glycerol fatty acid esters include, for example, borated glycerol mono-oleate, borated saturated mono-, di-, and tri-glyceride esters, borated glycerol mono-stearate, and the like. In addition to glycerol polyols, these can include trimethylolpropane, pentaerythritol, sorbitan, and the like. These esters can be polyol monocarboxylate esters, polyol dicarboxylate esters, and on occasion polyoltricarboxylate esters. In certain embodiments, the friction modifier is glycerol mono-oleates, glycerol dioleates, glycerol trioleates, glycerol monostearates, glycerol distearates, and glycerol tristearates and the corresponding glycerol monopalmitates, glycerol dipalmitates, glycerol tripalmitates, or the respective isostearates, linoleates, and the like, or combinations thereof. In an embodiment, the friction modifier is a glycerol esters or mixtures containing any of these. Ethoxylated, propoxylated, butoxylated fatty acid esters of polyols, especially using glycerol as underlying polyol can be utilized.

[0216] Illustrative fatty alcohol ethers include, for example, stearyl ether, myristyl ether, and the like. Alcohols, including those that have carbon numbers from C3 to C50, can be ethoxylated, propoxylated, or butoxylated to form the corresponding fatty alkyl ethers. The underlying alcohol portion can be, e.g., stearyl, myristyl, C11 – C13 hydrocarbon, oleyl, isosteryl, and the like.

[0217] Other friction modifiers could be optionally included in addition to the fatty phosphites and fatty imidazolines. A useful list of such other friction modifier additives is included in U.S. Patent No. 4,792,410. U.S. Patent No. 5,110,488 discloses metal salts of fatty acids and especially zinc salts, useful as friction modifiers. Fatty acids are also useful friction modifiers. A list of other suitable friction modifiers includes at least one of: (i) fatty phosphonates; (ii) fatty acid amides; (iii) fatty epoxides; (iv) borated fatty epoxides; (v) fatty amines; (vi) glycerol esters; (vii) borated glycerol esters; (viii) alkoxylated fatty amines; (ix) borated alkoxylated fatty amines; (x) metal salts of fatty acids; (xi) sulfurized olefins; (xii) condensation products of carboxylic acids or

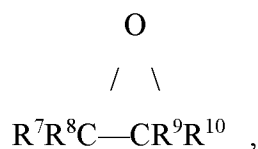
equivalents and polyalkylene-polyamines; (xiii) metal salts of alkyl salicylates; (xiv) amine salts of alkylphosphoric acids; (xv) fatty esters; (xvi) condensation products of carboxylic acids; or equivalents with polyols and mixtures thereof.

[0218] Representatives of each of these types of friction modifiers are known and are commercially available. For instance, (i) includes components of the formulas:



wherein, in these structures, the each “R” is conventionally referred to as an alkyl group, but may also be hydrogen. It is, of course, possible that the alkyl group is actually alkenyl and thus the terms “alkyl” and “alkylated,” as used herein, will embrace other than saturated alkyl groups within the component. The component should have sufficient hydrocarbyl groups to render it substantially oleophilic. In some embodiments, the hydrocarbyl groups are substantially unbranched. Many suitable such components are available commercially and may be synthesized as described in U.S. Patent No. 4,752,416. In some embodiments, the component contains 8 to 24 carbon atoms in each of the R groups. In other embodiments, the component may be a fatty phosphite containing 12 to 22 carbon atoms in each of the fatty radicals, or 16 to 20 carbon atoms. In one embodiment the fatty phosphite can be formed from oleyl groups, thus having 18 carbon atoms in each fatty radical.

[0219] The (iv) borated fatty epoxides are known from Canadian Patent No. 1,188,704. These oil-soluble boron- containing compositions are prepared by reacting, at a temperature from 80°C to 250°C, boric acid or boron trioxide with at least one fatty epoxide having the formula:



wherein each of R⁷, R⁸, R⁹ and R¹⁰ is independently hydrogen or an aliphatic radical, or any two thereof together with the epoxy carbon atom or atoms to which they are attached, form a cyclic radical. In an embodiment, the fatty epoxide contains at least 8 carbon atoms.

[0220] The borated fatty epoxides can be characterized by the method for their preparation which involves the reaction of two materials. Reagent A can be boron trioxide or any of the various forms of boric acid including metaboric acid (HBO₂), orthoboric acid (H₃BO₃) and tetraboric acid

(H₂B₄O₇). In an embodiment, Reagent A is boric acid, such as orthoboric acid. Reagent B can be at least one fatty epoxide having the above formula. In the formula, each of the R groups is most often hydrogen or an aliphatic radical with at least one being a hydrocarbyl or aliphatic radical containing at least 6 carbon atoms. The molar ratio of reagent A to reagent B may be about 1:0.25 to about 1:4 (e.g. about 1:1 to about 1:3 or about 1:2). The borated fatty epoxides can be prepared by merely blending the two reagents and heating them at temperature of about 80°C to about 250°C, such as about 100°C to about 200°C, for a period of time sufficient for reaction to take place. If desired, the reaction may be effected in the presence of a substantially inert, normally liquid organic diluent. During the reaction, water is evolved and may be removed by distillation.

[0221] The (iii) non-borated fatty epoxides, corresponding to Reagent B above, are also useful as friction modifiers.

[0222] Borated amines are generally known from U.S. Patent No. 4,622,158. Borated amine friction modifiers (including (ix) borated alkoxyated fatty amines) can be prepared by the reaction of a boron compounds, as described above, with the corresponding amines. The amine can be a simple fatty amine or hydroxy containing tertiary amines. The borated amines can be prepared by adding the boron reactant, as described above, to an amine reactant and heating the resulting mixture at about 50°C to about 300°C (e.g. about 100°C to about 250°C or about 130°C to about 180°C) with stirring. The reaction is continued until by-product water ceases to evolve from the reaction mixture indicating completion of the reaction.

[0223] Among the amines useful in preparing the borated amines are commercial alkoxyated fatty amines known by the trademark "ETHOMEEN" and available from Akzo Nobel. Representative examples of these ETHOMEEN™ materials is ETHOMEEN™ C/12 (bis[2-hydroxyethyl]-coco-amine); ETHOMEEN™ C/20 (polyoxyethylene-[10]cocoamine); ETHOMEEN™ S/12 (bis[2-hydroxyethyl]-soyamine); ETHOMEEN™ T/12 (bis[2-hydroxyethyl]-tallow-amine); ETHOMEEN™ T/15 (polyoxyethylene-[5]tallowamine); ETHOMEEN™ O/12 (bis[2-hydroxyethyl]oleyl-amine); ETHOMEEN™ 18/12 (bis[2—hydroxyethyl]-octadecylamine); and ETHOMEEN™ 18/25 (polyoxyethylene[15]-octadecylamine). Fatty amines and ethoxylated fatty amines are also described in U.S. Patent No. 4,741,848. Dihydroxyethyl tallowamine (commercially sold as ENT-12™) is included in these types of amines.

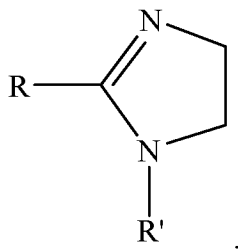
[0224] The (viii) alkoxyated fatty amines, and (v) fatty amines themselves (such as oleylamine and dihydroxyethyl tallowamine) may be useful as friction modifiers in this disclosure. Such amines are commercially available.

[0225] Both borated and unborated fatty acid esters of glycerol can be used as friction modifiers. The (vii) borated fatty acid esters of glycerol are prepared by borating a fatty acid ester of glycerol with boric acid with removal of the water of reaction. In an embodiment, there is sufficient boron present such that each boron will react with from 1.5 to 2.5 hydroxyl groups present in the reaction mixture. The reaction may be carried out at a temperature in the range of about 60°C to about 135°C, in the absence or presence of any suitable organic solvent, such as methanol, benzene, xylenes, toluene, or oil.

[0226] The (vi) fatty acid esters of glycerol themselves can be prepared by a variety of methods well known in the art. Many of these esters, such as glycerol monooleate and glycerol tallowate, are manufactured on a commercial scale. In a particular embodiment, the esters are oil-soluble and prepared from C8 to C22 fatty acids or mixtures thereof, such as are found in natural products and as are described in greater detail below. In an embodiment, fatty acid monoesters of glycerol used, although, mixtures of mono- and diesters may be used. For example, commercial glycerol monooleate may contain a mixture of 45% to 55% by weight monoester and 55% to 45% diester.

[0227] Fatty acids can be used in preparing the above glycerol esters; they can also be used in preparing their (x) metal salts, (ii) amides, and (xii) imidazolines, any of which can also be used as friction modifiers. In an embodiment, the fatty acids are those containing 10 to 24 carbon atoms, such as those containing 12 to 18 carbon atoms. The acids can be branched or straight-chain, saturated or unsaturated. In some embodiments, the acids are straight-chain acids. In other embodiments, the acids are branched. Suitable acids include decanoic, oleic, stearic, isostearic, palmitic, myristic, palmitoleic, linoleic, lauric, and linolenic acids, and the acids from the natural products tallow, palm oil, olive oil, peanut oil, corn oil, coconut oil and Neat's foot oil. In certain embodiments, the acid is oleic acid. In other embodiments, the metal salts include zinc and calcium salts. Examples are overbased calcium salts and basic oleic acid-zinc salt complexes, such as zinc oleate, which can be represented by the formula $Zn_4Oleate_6O_1$. In an embodiment, the amides are those prepared by condensation with ammonia or with primary or secondary amines such as ethylamine and diethanolamine. Fatty imidazolines are the cyclic condensation product of an acid with a diamine or polyamine, such as a polyethylenepolyamine. The imidazolines may be represented by the structure:

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wherein: R is an alkyl group; and R' is hydrogen or a hydrocarbyl group or a substituted hydrocarbyl group, including $-(\text{CH}_2\text{CH}_2\text{NH})_n-$ groups, wherein n is an integer from 1 to 4. In an embodiment, the friction modifier is the condensation product of a C10 to C24 fatty acid with a polyalkylene polyamine, and in particular, the product of isostearic acid with tetraethylenepentamine.

[0228] The condensation products of carboxylic acids and polyalkyleneamines (xiii) may be imidazolines or amides. They may be derived from any of the carboxylic acids described above and any of the polyamines described herein.

[0229] Sulfurized olefins (xi) are well known commercial materials used as friction modifiers. A particularly sulfurized olefin utilized herein is one which is prepared in accordance with the detailed teachings of U.S. Patent Nos. 4,957,651 and 4,959,168. Described therein is a co-sulfurized mixture of 2 or more reactants selected from the group consisting of (1) at least one fatty acid ester of a polyhydric alcohol, (2) at least one fatty acid, (3) at least one olefin, and (4) at least one fatty acid ester of a monohydric alcohol. Reactant (3), the olefin component, comprises at least one olefin. This olefin may be an aliphatic olefin, which usually will contain 4 to 40 carbon atoms, e.g. from 8 to 36 carbon atoms. For example, terminal olefins, or alpha-olefins, including those having from 12 to 20 carbon atoms, may be utilized. Mixtures of these olefins are commercially available, and such mixtures are contemplated for use in this disclosure. The co-sulfurized mixture of two or more of the reactants, is prepared by reacting the mixture of appropriate reactants with a source of sulfur. The mixture to be sulfurized can contain about 10 to about 90 parts of Reactant (1), or about 0.1 to about 15 parts by weight of Reactant (2); or about 10 to about 90 parts (e.g. about 15 to about 60 parts or about 25 to about 35 parts) by weight of Reactant (3), or about 10 to about 90 parts by weight of reactant (4). The mixture, in the present disclosure, includes Reactant (3) and at least one other member of the group of reactants identified as Reactants (1), (2) and (4). The sulfurization reaction may be effected at an elevated temperature with agitation and optionally in an inert atmosphere and in the presence of an inert solvent. The sulfurizing agents useful in the process of the present disclosure include elemental sulfur, which may be hydrogen sulfide, sulfur halide plus sodium sulfide, and a mixture of hydrogen sulfide and

sulfur or sulfur dioxide. For example, about 0.5 to about 3 moles of sulfur are employed per mole of olefinic bonds. Sulfurized olefins may also include sulfurized oils, such as vegetable oil, lard oil, oleic acid and olefin mixtures.

[0230] Metal salts of alkyl salicylates (xiii) include calcium and other salts of long chain (e.g. C12 to C16) alkyl-substituted salicylic acids.

[0231] Amine salts of alkylphosphoric acids (xiv) include salts of oleyl and other long chain esters of phosphoric acid, with amines as described below. Useful amines in this regard are tertiary-aliphatic primary amines, sold under the tradename Primene™.

[0232] In some embodiments, the friction modifier is a fatty acid or fatty oil, a metal salt of a fatty acid, a fatty amide, a sulfurized fatty oil or fatty acid, an alkyl phosphate, an alkyl phosphate amine salt; a condensation product of a carboxylic acid and a polyamine, a borated fatty epoxide, a fatty imidazoline, or combinations thereof.

[0233] In other embodiments, the friction modifier may be the condensation product of isostearic acid and tetraethylene pentamine, the condensation product of isostearic acid and 1-[tris(hydroxymethyl)]methylamine, borated polytetradecyloxirane, zinc oleate, hydroxyethyl-2-heptadecenyl imidazoline, dioleyl hydrogen phosphate, C14 - C18 alkyl phosphate or the amine salt thereof, sulfurized vegetable oil, sulfurized lard oil, sulfurized oleic acid, sulfurized olefins, oleyl amide, glycerol monooleate, soybean oil, or mixtures thereof.

[0234] In still other embodiments, the friction modifier may be glycerol monooleate, oleylamide, the reaction product of isostearic acid and 2-amino-2-hydroxymethyl-1,3-propanediol, sorbitan monooleate, 9-octadecenoic acid, isostearyl amide, isostearyl monooleate or combinations thereof.

[0235] Although their presence is not required to obtain the benefit of the present disclosure, friction modifiers may be present in an amount from zero to about 2 wt% (e.g., about 0.01 wt% to about 1.5 wt%) of the lubricating composition. These ranges may apply to the amounts of individual friction modifier present in the composition or to the total friction modifier component in the compositions, which may include a mixture of two or more friction modifiers.

[0236] Many friction modifiers tend to also act as emulsifiers. This is often due to the fact that friction modifiers often have non-polar fatty tails and polar head groups.

[0237] The lubricating composition of the present disclosure exhibit desired properties, e.g., wear control, in the presence or absence of a friction modifier.

[0238] Although their presence is not required to obtain the benefit of this disclosure, the friction modifier or friction modifiers may be present in an amount of about 0.01 weight percent to about 5 weight percent (e.g. about 0.1 weight percent to about 2.5 weight percent, or about 0.1 weight percent to about 1.5 weight percent, or about 0.1 weight percent to about 1 weight percent). Concentrations of molybdenum-containing materials are often described in terms of Mo metal concentration. Advantageous concentrations of Mo may range from about 25 ppm to about 700 ppm or more (e.g. about 50 to about 200 ppm). Friction modifiers of all types may be used alone or in mixtures with the materials of this disclosure. Often mixtures of two or more friction modifiers, or mixtures of friction modifier(s) with alternate surface active material(s), are also desirable.

Molybdenum-Containing Compounds (Friction Reducers).

[0239] Illustrative molybdenum-containing friction reducers useful in the disclosure include, for example, an oil-soluble decomposable organo molybdenum compound, such as Molyvan™ 855 which is an oil soluble secondary diarylamine defined as substantially free of active phosphorus and active sulfur. The Molyvan™ 855 is described in Vanderbilt's Material Data and Safety Sheet as a organomolybdenum compound having a density of 1.04 and viscosity at 100°C of 47.12 cSt. The organo molybdenum compounds may be useful because of their superior solubility and effectiveness.

[0240] Another illustrative molybdenum-containing compound is Molyvan™ L, which is sulfonated oxymolybdenum dialkyldithiophosphate described in U.S. Patent No. 5,055,174 hereby incorporated by reference.

[0241] Molyvan™ A made by R. T. Vanderbilt Company, Inc., New York, N.Y., USA, is also an illustrative molybdenum-containing compound, which contains about 28.8 wt. % Mo, 31.6 wt. % C, 5.4 wt. % H., and 25.9 wt. % S. Also useful are Molyvan™ 855, Molyvan™ 822, Molyvan™ 856, and Molyvan™ 807.

[0242] Also useful is Sakura Lube™ 500, which is more soluble Mo dithiocarbamate containing lubricant additive obtained from Asahi Denki Corporation and comprised of about 20.2 wt. % Mo, 43.8 wt. % C, 7.4 wt. % H, and 22.4 wt. % S. Sakura Lube™ 300, a low sulfur molybdenum dithiophosphate having a molybdenum to sulfur ratio of 1:1.07, is a molybdenum-containing compound useful in this disclosure.

[0243] Also useful is Molyvan™ 807, a mixture of about 50 wt. % molybdenum ditridecyldithiocarbonate, and about 50 wt. % of an aromatic oil having a specific gravity of about

38.4 SUS and containing about 4.6 wt. % molybdenum, also manufactured by R. T. Vanderbilt and marketed as an antioxidant and antiwear additive.

[0244] Other sources are molybdenum $\text{Mo}(\text{Co})_6$, and molybdenum octoate, $\text{MoO}(\text{C}_7\text{H}_{15}\text{CO}_2)_2$ containing about 8 wt-% Mo marketed by Aldrich Chemical Company, Milwaukee, Wis. and molybdenum naphthenethiooctoate marketed by Shephard Chemical Company, Cincinnati, Ohio.

[0245] Inorganic molybdenum compounds, such as molybdenum sulfide and molybdenum oxide, are substantially less preferred than the organic compounds as described in Molyvan™ 855, Molyvan™ 822, Molyvan™ 856, and Molyvan™ 807.

[0246] Illustrative molybdenum-containing compounds useful in this disclosure are disclosed, for example, in U.S. Patent Application Publication No. 2003/0119682, which is incorporated herein by reference.

[0247] Organo molybdenum-nitrogen complexes may also be included in the formulations of the present disclosure. The term “organo molybdenum nitrogen complexes” embraces the organo molybdenum nitrogen complexes described in U.S. Patent No. 4,889,647. The complexes are reaction products of a fatty oil, dithanolamine and a molybdenum source. Specific chemical structures have not been assigned to the complexes. U.S. Patent No. 4,889,647 reports an infrared spectrum for an exemplary reaction product of that disclosure; the spectrum identifies an ester carbonyl band at 1740 cm^{-1} and an amide carbonyl band at 1620 cm^{-1} . The fatty oils are glyceryl esters of higher fatty acids containing at least 12 carbon atoms up to 22 carbon atoms or more. The molybdenum source is an oxygen-containing compound such as ammonium molybdates, molybdenum oxides and mixtures.

[0248] Other organo molybdenum complexes which can be used in the present disclosure are tri nuclear molybdenum sulfur compounds described in EP 1 040 115 and WO 99/31113, and the molybdenum complexes described in U.S. Patent No. 4,978,464.

[0249] Although their presence is not required to obtain the benefit of the present disclosure, molybdenum-containing additives may be used in an amount of from zero to about 5.0 percent by mass of the lubricating composition. For example, the dosage may be up to about 3,000 ppm by mass, such as from about 100 ppm to about 2,500 ppm by mass, from about 300 to about 2,000 ppm by mass, or from about 300 to about 1,500 ppm by mass of molybdenum.

Borated Ester Compounds.

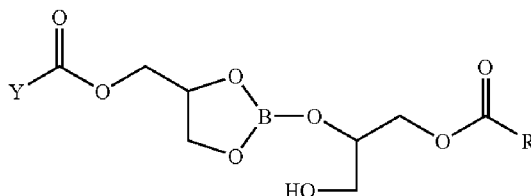
[0250] Illustrative boron-containing compounds useful in the disclosure include, for example, a borate ester, a boric acid, other boron compounds, such as a boron oxide. The boron compound

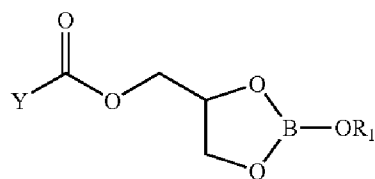
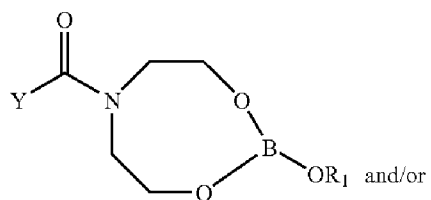
is hydrolytically stable and is utilized for improved antiwear, and performs as a rust and corrosion inhibitor for copper bearings and other metal engine components. The borated ester compound acts as an inhibitor for corrosion of metal to prevent corrosion of either ferrous or non-ferrous metals (e.g. copper, bronze, brass, titanium, aluminum and the like) or both, present in concentrations in which they are effective in inhibiting corrosion.

[0251] Patents describing techniques for making basic salts of sulfonic, carboxylic acids and mixtures thereof include U.S. Patent Nos. 5,354,485; 2,501,731; 2,616,911; 2,777,874; 3,384,585; 3,320,162; 3,488,284; and 3,629,109. The disclosures of these patents are incorporated herein by reference. Methods of preparing borated overbased compositions are found in U.S. Patent Nos. 4,744,920; 4,792,410; and PCT publication WO 88/03144. The disclosures of these references are incorporated herein by reference. The oil-soluble neutral or basic salts of alkali or alkaline earth metals salts may also be reacted with a boron compound.

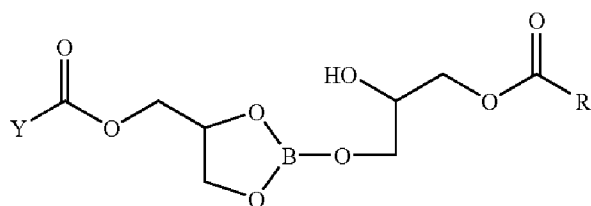
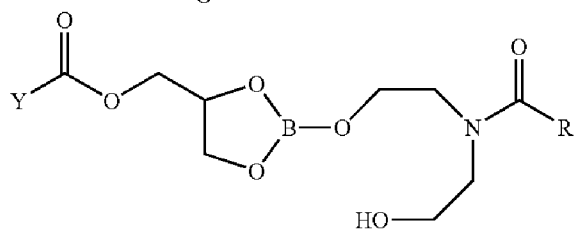
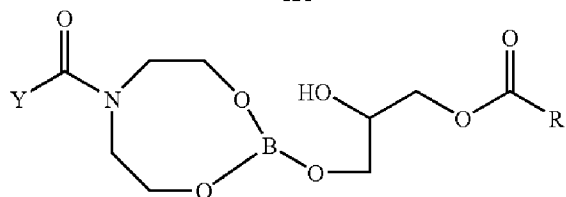
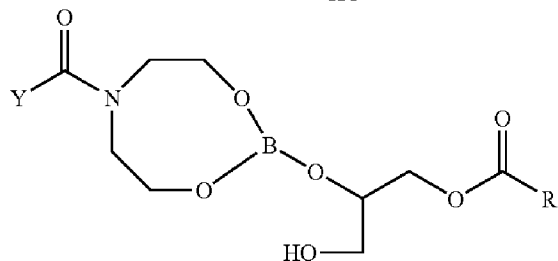
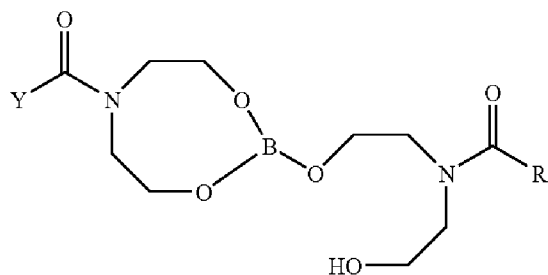
[0252] An illustrative borate ester utilized in this disclosure is manufactured by Exxon-Mobil USA under the product designation of ("MCP 1286") and MOBIL ADC700. Test data show the viscosity at 100°C using the D-445 method is 2.9 cSt; the viscosity at 40°C using the D-445 method is 11.9; the flash point using the D-93 method is 146; the pour point using the D-97 method is -69; and the percent boron as determined by the ICP method is 5.3%. The borated ester (Vanlube™ 289), which is marketed as an antiwear/antiscuff additive and friction reducer, is an exemplary borate ester useful in the disclosure.

[0253] An illustrative borate ester useful in this disclosure is the reaction product obtained by reacting about 1 mole fatty oil, about 1.0 to 2.5 moles diethanolamine followed by subsequent reaction with boric acid to yield about 0.1 to 3 percent boron by mass. It is believed that the reaction products may include one or both of the following two primary components, with the further listed components being possible components when the reaction is pushed toward full hydration:





where R₁ = H or C_xH_y where x = 1 to 60, and y = 3 to 121



wherein Y represents a fatty oil residue. In an embodiment, the fatty oils are glyceryl esters of higher fatty acids containing at least 12 carbon atoms (e.g. 22 carbon atoms or more). Such esters

are commonly known as vegetable and animal oils. Vegetable oils that may be used include oils derived from coconut, corn, cottonseed, linseed, peanut, soybean and sunflower seed. Similarly, animal fatty oils such as tallow may be used.

[0254] The source of boron is boric acid or materials that afford boron and are capable of reacting with the intermediate reaction product of fatty oil and diethanolamine to form a borate ester composition.

[0255] While the above organoborate ester composition is specifically discussed above, it should be understood that other organoborate ester compositions should also function with similar effect in the present disclosure, such as those set forth in U.S. Patent Application Publication No. 2003/0119682, which is incorporated herein by reference. In addition, dispersions of borate salts, such as potassium borate, may also be useful.

[0256] Other illustrative organoborate compositions useful in this disclosure are disclosed, for example, in U.S. Patent Application Publication No. 2008/0261838, which is incorporated herein by reference.

[0257] In addition, other illustrative organoborate compositions useful in this disclosure are disclosed, for example, U.S. Patent No. 4,478,732, U.S. Patent No. 4,406,802, U.S. Patent No. 4,568,472 on borated mixed hydroxyl esters, alkoxyated amides, and amines; U.S. Patent No. 4,298,486 on borated hydroxyethyl imidazolines; U.S. Patent No. 4,328,113 on borated alkyl amines and alkyl diamines; U.S. Patent No. 4,370,248 on borated hydroxyl-containing esters, including GMO; U.S. Patent No. 4,374,032 on borated hydroxyl-containing hydrocarbyl oxazolines; U.S. Patent No. 4,376,712 on borated sorbitan esters; U.S. Patent No. 4,382,006 on borated ethoxylated amines; U.S. Patent No. 4,389,322 on ethoxylated amides and their borates; U.S. Patent No. 4,472,289 on hydrocarbyl vicinal diols and alcohols and ester mixtures and their borates; U.S. Patent No. 4,522,734 on borates of hydrolyzed hydrocarbyl epoxides; U.S. Patent No. 4,537,692 on etherdiamine borates; U.S. Patent No. 4,541,941 on mixtures containing vicinal diols and hydroxyl substituted esters and their borates; U.S. Patent No. 4,594,171 on borated mixtures of various hydroxyl and/or nitrogen containing borates; and U.S. Patent No. 4,692,257 on various borated alcohols/diols, all of which are incorporated herein by reference.

[0258] Although their presence is not required to obtain the benefit of this disclosure, boron-containing compounds may be present in an amount of from zero to about 10.0% percent (e.g. from about 0.01% to about 5% or from about 0.1% to about 3.0 %) by weight of the lubricating composition. An effective elemental boron range of up to about 1000 ppm or less than about 1%

elemental boron. Thus, in an embodiment, a concentration of elemental boron is from about 100 to about 1000 ppm (e.g. from about 100 to about 300 ppm).

[0259] When lubricating oil compositions contain one or more of the additives discussed above, the additive(s) are blended into the composition in an amount sufficient for it to perform its intended function. Exemplary amounts of such additives useful in the present disclosure are shown in Table 1 below.

[0260] It is noted that many of the additives are shipped from the additive manufacturer as a concentrate, containing one or more additives together, with a certain amount of base oil diluents. Accordingly, the weight amounts in Table 1 below, as well as other amounts mentioned herein, are directed to the amount of active ingredient (that is the non-diluent portion of the ingredient). The weight percent (wt%) indicated below is based on the total weight of the lubricating oil composition.

Table 1. Exemplary Amounts of Industrial Lubricating Oil Components

Compound	Approximate wt% (Useful)	Approximate wt% (Exemplary)
Dispersant	0-20	0-3
Detergent	0-20	0-3
Friction Modifier	0-5	0-1.5
Antioxidant	0.1-5	0.1-3
Pour Point Depressant (PPD)	0.0-5	0.01-1.5
Antifoam Agent	0.001-3	0.001-0.3
Demulsifier	0.001-3	0.001-0.15
Viscosity Modifier (solid polymer basis)	0.1-2	0.1-1
Antiwear	0.2-3	0.5-1.5
Inhibitor and Antirust	0.01-5	0.01-2

[0261] The foregoing additives are all commercially available materials. These additives may be added independently but are usually precombined in packages which can be obtained from suppliers of lubricant oil additives. Additive packages with a variety of ingredients, proportions and characteristics are available and selection of the appropriate package will take the requisite use of the ultimate composition into account.

METHODS OF THE PRESENT DISCLOSURE

[0262] One skilled in the art will appreciate that the disclosure throughout the present disclosure regarding the lubricating composition of the present disclosure are similarly contemplated with regard to the methods disclosed herein as well. As such, the amounts, ranges, additives, etc., discussed with regard to the lubricating compositions will not be duplicated with regard to the methods, but are specifically contemplated.

[0263] In a further aspect, the present disclosure provides a method of making a lubricating composition with at least one of improved high-pressure pumpability, reduced viscosity at high pressures, or a combination thereof. The method comprises mixing a white oil and a polymeric thickener present in an amount equal to or less than about 40 wt% of the lubricating composition. The white oil has a kinematic viscosity of at least one of: about 80 mm²/sec to about 120 mm²/sec at 40°C (or any range therein); about 9.5 mm²/sec to about 14 mm²/sec at 100°C (or any range therein); or a combination thereof.

[0264] For example, the kinematic viscosity of the white oil at 40°C may be about 80 mm²/sec to about 120 mm²/sec, about 80 mm²/sec to about 110 mm²/sec, about 80 mm²/sec to about 100 mm²/sec, about 80 mm²/sec to about 90 mm²/sec, about 90 mm²/sec to about 120 mm²/sec, about 90 mm²/sec to about 110 mm²/sec, about 90 mm²/sec to about 100 mm²/sec, about 100 mm²/sec to about 120 mm²/sec, about 100 mm²/sec to about 110 mm²/sec, or about 110 mm²/sec to about 120 mm²/sec. By way of further example, the kinematic viscosity of the white oil at 100°C may be about 9.5 mm²/sec to about 14 mm²/sec, about 9.5 mm²/sec to about 13.5 mm²/sec, about 9.5 mm²/sec to about 13 mm²/sec, about 9.5 mm²/sec to about 12.5 mm²/sec, about 9.5 mm²/sec to about 12 mm²/sec, about 9.5 mm²/sec to about 11.5 mm²/sec, about 9.5 mm²/sec to about 11 mm²/sec, about 9.5 mm²/sec to about 10.5 mm²/sec, about 10 mm²/sec to about 14 mm²/sec, about 10 mm²/sec to about 13.5 mm²/sec, about 10 mm²/sec to about 13 mm²/sec, about 10 mm²/sec to about 12.5 mm²/sec, about 10 mm²/sec to about 12 mm²/sec, about 10 mm²/sec to about 11.5 mm²/sec, about 10 mm²/sec to about 11 mm²/sec, about 10.5 mm²/sec to about 14 mm²/sec, about 10.5 mm²/sec to about 13.5 mm²/sec, about 10.5 mm²/sec to about 13 mm²/sec, about 10.5 mm²/sec to about 12.5 mm²/sec, about 10.5 mm²/sec to about 12 mm²/sec, about 10.5 mm²/sec to about 11.5 mm²/sec, about 11 mm²/sec to about 14 mm²/sec, about 11 mm²/sec to about 13.5 mm²/sec, about 11 mm²/sec to about 13 mm²/sec, about 11 mm²/sec to about 12.5 mm²/sec, about 11 mm²/sec to about 12 mm²/sec, about 11.5 mm²/sec to about 14 mm²/sec, about 11.5 mm²/sec to about 13.5 mm²/sec, about 11.5 mm²/sec to about 13 mm²/sec, about 11.5 mm²/sec to about 12.5 mm²/sec, about 12 mm²/sec to about 14 mm²/sec, about 12 mm²/sec to about 13.5 mm²/sec, about 12

mm²/sec to about 13 mm²/sec, about 12.5 mm²/sec to about 14 mm²/sec, about 12.5 mm²/sec to about 13.5 mm²/sec, or about 13 mm²/sec to about 14 mm²/sec.

[0265] In certain embodiments, the lubricating composition of the present disclosure has a kinematic viscosity of about 200 mm²/sec to about 240 mm²/sec. For example, the kinematic viscosity of the lubricating composition is about 200 mm²/sec to about 230 mm²/sec, about 200 mm²/sec to about 220 mm²/sec, about 200 mm²/sec to about 210 mm²/sec, about 210 mm²/sec to about 240 mm²/sec, about 210 mm²/sec to about 230 mm²/sec, about 210 mm²/sec to about 220 mm²/sec, about 220 mm²/sec to about 240 mm²/sec, about 220 mm²/sec to about 230 mm²/sec, about 230 mm²/sec to about 240 mm²/sec.

[0266] The white oil may be present in an amount of about 50 wt% to about 95 wt% of the lubricating composition. For example, the lubricating composition may comprise white oil in an amount of about 50 wt% to about 85 wt%, about 50 wt% to about 80 wt%, about 50 wt% to about 75 wt%, about 50 wt% to about 70 wt%, about 50 wt% to about 65 wt%, about 50 wt% to about 60 wt%, about 55 wt% to about 95 wt%, about 55 wt% to about 90 wt%, about 55 wt% to about 85 wt%, about 55 wt% to about 80 wt%, about 55 wt% to about 75 wt%, about 55 wt% to about 70 wt%, about 55 wt% to about 65 wt%, about 60 wt% to about 95 wt%, about 60 wt% to about 90 wt%, about 60 wt% to about 85 wt%, about 60 wt% to about 80 wt%, about 60 wt% to about 75 wt%, about 60 wt% to about 70 wt%, about 65 wt% to about 95 wt%, about 65 wt% to about 90 wt%, about 65 wt% to about 85 wt%, about 65 wt% to about 80 wt%, about 65 wt% to about 75 wt%, about 70 wt% to about 95 wt%, about 70 wt% to about 90 wt%, about 70 wt% to about 85 wt%, about 70 wt% to about 80 wt%, about 75 wt% to about 95 wt%, about 75 wt% to about 90 wt%, about 75 wt% to about 85 wt%, about 80 wt% to about 95 wt%, about 80 wt% to about 90 wt%, or about 85 wt% to about 95 wt% of the lubricating composition of the present disclosure.

[0267] The method of preparing the lubricating composition of the present disclosure may further comprise mixing the white oil and the polymeric thickener with at least one (e.g., 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, or more) performance additive. The performance additive may be at least one of a dispersant, an additional detergent, a corrosion inhibitor, a rust inhibitor, a metal deactivator, an additional anti-wear agent, an extreme pressure additive, an anti-seizure agent, a wax modifier, a viscosity index improver, a viscosity modifier, a fluid-loss additive, a seal compatibility agent, an additional friction modifier, a pour point depressant, a lubricity agent, an anti-staining agent, a chromophoric agent, a demulsifier, an emulsifier, a densifier, a wetting agent, a gelling agent, a tackiness agent, a colorant, an antioxidants, an oxidation inhibitor, or a combination thereof. The performance additive or additives can be present in the amounts described herein.

[0268] In a further aspect, the present disclosure comprising a lubricating composition produced, made, or prepared in accordance with the method of the present disclosure.

[0269] In an additional aspect, the present disclosure provides a method of lubricating a compressor. The method comprises applying the lubricating composition of the present disclosure to the compressor. The compressor can be, e.g., a high pressure compressor or a hyper compressor.

[0270] In yet another aspect, the present disclosure provides a method of pressurizing an olefin to a high pressure olefin. The method comprises introducing the olefin into a compressor that is lubricated by the lubricating composition of the present disclosure; and pressurizing the olefin with the compressor, wherein the compressor is at least one of a high pressure compressor, a hyper compressor, or both. In any aspect or embodiment described herein, the olefin is ethylene.

[0271] In a further aspect, the present disclosure provides a method of making high pressure olefin. The method comprises pressurizing an olefin with a high pressure compressor that is lubricated with the lubricating composition of the present disclosure; and reacting the pressured olefin to form the high pressure olefin. In any aspect or embodiment described herein, at least one of the olefin is ethylene, the high pressure olefin is high pressure low density polyethylene, or a combination thereof.

[0272] The lubricating composition of the present disclosure may be utilized in the methods above to lubricate a friction interface of a compressor. For example, the friction interface between at least one stationary part and at least one moving part, or at least two moving parts of the compressor. As such, the lubricating composition of the present disclosure may be utilized in the methods above as a crankcase lubricant, a crosshead lubricant, a cylinder lubricant, cooling, flushing, or a combination thereof, of a compressor. Cylinder lubrication of a compressor may include at least one of lubricating and/or applying to the lubricant composition of the present disclosure to at least one of piston ring(s), valve(s), cylinder wall(s), rod pressure packing, gas seal(s), or a combination thereof. The methods of the present disclosure may further include pumping the lubricating composition of the present disclosure through channels configure and/or arranged to lubricate the compressor as described above.

EXAMPLES

[0273] The present disclosure is further illustrated by the following examples which should not be construed as limiting. The data below demonstrates that the lubricating composition of the present disclosure provides the surprising and unexpected disproportionate improves in pump flow rates in pumps set to a wide range of reduced oil flow rates (pump scaling) and superior lubrication and protection for machinery, as compared to comparative lubricant compositions. Those skilled

in the art will recognize that the present disclosure may be practiced with variations on the disclosed structures, materials, compositions and methods, and such variations are regarded as within the ambit of the disclosure.

[0274] A Comparative ISO VG 220 Lubricant (hereinafter, “Comparative Lubricant”) was prepared with White Oil A, *see* Table 2, and an Exemplary ISO VG220 Lubricant (hereinafter, “Exemplary Lubricant”) was prepared with White Oil B, *see* Table 2, according to the formulations shown in Table 3 below. The Comparative and Exemplary Compositions were prepared with polybutene polymeric thickener having an average molecular weight of about 1000 to about 3000. The resultant compositions were ISO VG 220 food-grade lubricants. As can be seen in Table 3, because White Oil A had a lower viscosity, a greater amount of polymer thickener was required to achieve the necessary viscosity of 200 to 240 mm²/sec.

Table 2. Characteristics of exemplary white oils utilized in the Examples

	White Oil A	White Oil B
Kinematic Viscosity at 40C, mm²/sec	65 to 75	90 to 110
Kinematic Viscosity at 100C, mm²/sec	8.9	11.3
Viscosity Index	104	99
Density, kg/m³	860 to 870	863 to 873
Average molecular weight, amu	Minimum of 480	Minimum of 510
Paraffinic carbon content, %	64	66
Naphthenic carbon content, %	34	34
Aromatic carbon content, %	0	0

Table 3. Comparative composition and Exemplary Composition formulations

	Formulation A (Comparative Composition)	Formulation B (Exemplary Composition)
White oil, wt. %	64% (White oil A)	89% (White oil B)
Polymer thickener, wt. %	27%	10.5%
Other performance additives that do not impact the high-pressure pumpability	9%	0.5%
ISO Viscosity Grade	220 (200 to 240 mm ² /sec)	220 (200 to 240 mm ² /sec)

[0275] Examination of Viscosity Relative to Pressure. The viscosity of the Exemplary Lubricant was examined using ASTM D445 as the pressure was increased from 1000 bar to 3750 bar at 50°C. FIG. 1 shows the viscosities of an Exemplary Lubricant and Comparative Lubricant over operating pressures ranging from 1000 bar to 3750 bar at 50°C. The Exemplary Lubricant resulted in lower viscosities at operating pressures ranging from 1000 bar to 3500 bar, as compared to the Comparative Lubricant. This results in a greater maximum operating pressure for the compressor (such as, an ethylene hyper compressor system), which provides operational

efficiencies and benefits, and increased lubricant flow to the compressor cylinders, which enhances lubricity and wear protection. Similar trends were seen when viscosities were examined at 25°C.

[0276] Examination of High-pressure Pumpability. High-pressure pumpability was measured by recording the volume of a lubricant pumped through a small pipe at high pressures, as shown in FIGS. 1A and 1B. The pipe length was 9 meters, with an inner diameter of 3.18 millimeters. The pipe was immersed in a temperature-controlled water bath to control the temperature of the lubricant being tested. A pressure control valve at the end of the pipe was used to control the lubricant pressure. Pressure transducers were used to monitor the pressure of the lubricant in the pipe.

[0277] The lubricant was pumped by a piston pump. The amount of oil delivered can be controlled by changing the distance travelled by the piston pump, which is referred to as pump scaling. A pump scaling of 100% means that the piston of the pump is travelling the maximum possible distance, while a pump scaling of 50% means that the piston is only travelling half of its maximum possible travel distance.

[0278] Pumpability was measured by recording the volume of oil that flows through the pipe at a given temperature, pressure, and pump setting. The oil was collected at the pipe exit for 60 seconds, and the average flow rate was computed.

[0279] As shown in Figure 3, the decreased viscosity of the Exemplary Lubricant resulted in increased high-pressure pumpability, as compared to the Comparative Lubricant. The increase pumping rate was proportionate to the relative difference in viscosity of the Exemplary Lubricant and Comparative Lubricant. This suggests that the observed improvement in pumpability is achieved through the reduction in the lubricant's viscosity at the operating pressures.

[0280] As shown in Figure 4, the Exemplary Lubricant demonstrated an improved flow rate at high pressure (2000 bar) at intermediate pump piston stroke lengths that is significantly greater than one would expect from the viscosity differences alone. Therefore, although the viscosity of the Exemplary Lubricant is lower than the Comparative Lubricant by a factor of 1.6x at 2000 bar, a 4.2x increase in pump flow rate is observed when the pump is running at reduced scaling. The data demonstrates that lubricants of the present disclosure have disproportionate improvements in pump flow rates for pumps that are set to run at a wide range of reduced oil flow rates (pump scaling). This results in energy efficiency gains, reduced maintenance costs for the pumping system, and an ability to efficiently operate under conditions of reduced oil consumption.

SPECIFIC EMBODIMENTS

[0281] According to an aspect, the present disclosure provides a lubricating composition comprising: a white oil with a kinematic viscosity of at least one of: about 80 mm²/sec to about 120 mm²/sec at 40°C (e.g., about 85 mm²/sec to about 115 mm²/sec at 40°C or about 90 mm²/sec to about 110 mm²/sec at 40°C); about 9.5 mm²/sec to about 14 mm²/sec at 100°C (e.g., about 10 mm²/sec to about 13.5 mm²/sec at 100°C or about 10.5 mm²/sec to about 13 mm²/sec at 100°C); or a combination thereof; and a polymeric thickener present in an amount equal to or less than about 40 wt% of the lubricating composition.

[0282] In any aspect or embodiment described herein, the lubricating composition has a kinematic viscosity of about 200 mm²/sec to about 240 mm²/sec.

[0283] The lubricating composition of claim 1, wherein the white oil is present in an amount of about 50 wt% to about 95 wt% (e.g., about 70 wt% to about 95 wt% or about 75 wt% to about 90 wt%) of the lubricating composition.

[0284] In any aspect or embodiment described herein, the polymeric thickener is at least one of polybutene polymeric thickener, high molecular weight hydrocarbons, polyesters, polymers of methacrylate, copolymers of methacrylate, butadiene, olefins, alkylated styrenes, or combinations thereof.

[0285] In any aspect or embodiment described herein, the lubricating composition further comprises at least one performance additive (e.g., 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10 performance additives).

[0286] In any aspect or embodiment described herein, the at least one performance additive is at least one of a dispersant, an additional detergent, a corrosion inhibitor, a rust inhibitor, a metal deactivator, an additional anti-wear agent, an extreme pressure additive, an anti-seizure agent, a wax modifier, a pour point depressant, a viscosity index improver, a viscosity improver/modifier, a fluid-loss additive, a seal compatibility agent, an additional friction modifier, a lubricity agent, an anti-staining agent, a chromophoric agent, a demulsifier, an emulsifier, a densifier, a wetting agent, a gelling agent, a tackiness agent, a colorant, an antioxidants, an oxidation inhibitor, or a combination thereof.

[0287] In any aspect or embodiment described herein, a total amount of performance additives is equal to or less than 10 wt% (e.g., about 0.5 wt% to about 9 wt% or about 0.5 wt% to about 8 wt%) of the lubricating composition.

[0288] In another aspect, the present disclosure comprises a method of making a lubricating composition with at least one of improved high-pressure pumpability, reduced viscosity at high pressures, or a combination thereof and, the method comprising mixing: a white oil with a

kinematic viscosity of at least one of: about 80 mm²/sec to about 120 mm²/sec at 40°C (e.g., about 85 mm²/sec to about 115 mm²/sec at 40°C or about 90 mm²/sec to about 110 mm²/sec at 40°C); about 9.5 mm²/sec to about 14 mm²/sec at 100°C (e.g., about 10 mm²/sec to about 13.5 mm²/sec at 100°C or about 10.5 mm²/sec to about 13 mm²/sec at 100°C); or a combination thereof; and a polymeric thickener present in an amount equal to or less than about 40 wt% of the lubricating composition.

[0289] In any aspect or embodiment described herein, the lubricating composition has a kinematic viscosity of about 200 mm²/sec to about 240 mm²/sec.

[0290] In any aspect or embodiment described herein, the white oil is present in an amount of about 50 wt% to about 95 wt% of the lubricating composition.

[0291] In any aspect or embodiment described herein, the method further comprises mixing the white oil and the polymeric thickener with at least one performance additive.

[0292] In any aspect or embodiment described herein, the performance additive is at least one of a dispersant, an additional detergent, a corrosion inhibitor, a rust inhibitor, a metal deactivator, an additional anti-wear agent, an extreme pressure additive, an anti-seizure agent, a wax modifier, a viscosity index improver, a pour point depressant, a viscosity improver/modifier, a fluid-loss additive, a seal compatibility agent, an additional friction modifier, a lubricity agent, an anti-staining agent, a chromophoric agent, a demulsifier, an emulsifier, a densifier, a wetting agent, a gelling agent, a tackiness agent, a colorant, an antioxidants, an oxidation inhibitor, or a combination thereof.

[0293] In any aspect or embodiment described herein, a total amount of performance additives is present in an amount equal to or less than 10 wt% of the lubricating composition.

[0294] In yet another aspect, the present disclosure provides a lubricating composition produced according to the method of the present disclosure.

[0295] In yet a further aspect, the present disclosure provides a method of lubricating a compressor, the method comprising applying the lubricating composition of the present disclosure to the compressor.

[0296] In any aspect or embodiment described herein, the compressor is a high-pressure compressor or a hyper compressor.

[0297] In an additional aspect, the present disclosure provides a method of pressurizing an olefin, the method comprising: introducing the olefin into a compressor that is lubricated by the lubricating composition of the present disclosure; and pressurizing the olefin with the compressor, wherein the compressor is at least one of a high pressure compressor, a hyper compressor, or both.

[0298] In any aspect or embodiment described herein, the olefin is ethylene.

[0299] In yet an additional aspect, the present disclosure provides a method of making a high pressure olefin, the method comprising: pressurizing an olefin with a high pressure compressor that is lubricated with the lubricating composition of the present disclosure; and reacting the pressurized olefin to form the high pressure olefin.

[0300] In any aspect or embodiment described herein, at least one of the olefin is ethylene, the high pressure olefin is high pressure low density polyethylene, or a combination thereof.

EQUIVALENTS

[0301] Those skilled in the art will recognize, or be able to ascertain using no more than routine experimentation, many equivalents to the specific embodiments and methods described herein. Such equivalents are intended to be encompassed by the scope of the following claims.

[0302] It is understood that the detailed examples and embodiments described herein are given by way of example for illustrative purposes only, and are in no way considered to be limiting to the disclosure. Various modifications or changes in light thereof will be suggested to persons skilled in the art and are included within the spirit and purview of this application and are considered within the scope of the appended claims. For example, the relative quantities of the ingredients may be varied to optimize the desired effects, additional ingredients may be added, and/or similar ingredients may be substituted for one or more of the ingredients described. Additional advantageous features and functionalities associated with the systems, methods, and processes of the present disclosure will be apparent from the appended claims. Moreover, those skilled in the art will recognize, or be able to ascertain using no more than routine experimentation, many equivalents to the specific embodiments of the disclosure described herein. Such equivalents are intended to be encompassed by the following claims.

PCT/EP Clauses:

[0303] 1. A lubricating composition comprising: a white oil with a kinematic viscosity of at least one of:

80 mm²/sec to 120 mm²/sec at 40°C;

9.5 mm²/sec to 14 mm²/sec at 100°C; or

a combination thereof; and

a polymeric thickener present in an amount equal to or less than 40 wt% of the lubricating composition.

[0304] 2. The lubricating composition of clause 1, wherein the lubricating composition has a kinematic viscosity of 200 mm²/sec to 240 mm²/sec.

- [0305] 3. The lubricating composition of clause 1 or 2, wherein the white oil is present in an amount of 50 wt% to 95 wt% of the lubricating composition.
- [0306] 4. The lubricating composition of any of clauses 1-3, wherein the polymeric thickener is at least one of polybutene polymeric thickener, high molecular weight hydrocarbons, polyesters, polymers of methacrylate, copolymers of methacrylate, butadiene, olefins, alkylated styrenes, or combinations thereof.
- [0307] 5. The lubricating composition of any of clauses 1-4, further comprising at least one performance additive.
- [0308] 6. The lubricating composition of clause 5, wherein the performance additive is at least one of a dispersant, an additional detergent, a corrosion inhibitor, a rust inhibitor, a metal deactivator, an additional anti-wear agent, an extreme pressure additive, an anti-seizure agent, a wax modifier, a viscosity index improver, a pour point depressant, a viscosity improver/modifier, a fluid-loss additive, a seal compatibility agent, an additional friction modifier, a lubricity agent, an anti-staining agent, a chromophoric agent, a demulsifier, an emulsifier, a densifier, a wetting agent, a gelling agent, a tackiness agent, a colorant, an antioxidants, an oxidation inhibitor, or a combination thereof.
- [0309] 7. The lubricating composition of clause 5 or 6, wherein a total amount of performance additives is equal to or less than 10 wt% of the lubricating composition.
- [0310] 8. A method of making a lubricating composition with at least one of improved high-pressure pumpability, reduced viscosity at high pressures, or a combination thereof and, the method comprising mixing:
- a white oil with a kinematic viscosity of at least one of:
 - 80 mm²/sec to 120 mm²/sec at 40°C;
 - 9.5 mm²/sec to 14 mm²/sec at 100°C; or
 - a combination thereof; and
 - a polymeric thickener present in an amount equal to or less than 40 wt% of the lubricating composition.
- [0311] 9. The method of clause 8, further comprising mixing the white oil and the polymeric thickener with at least one performance additive.
- [0312] 10. A lubricating composition produced according to the method of clause 8 or 9.
- [0313] 11. A method of lubricating a compressor, the method comprising applying the lubricating composition of any of clauses 1-7 to the compressor.

[0314] 12. The method of clause 10, wherein the compressor is a high-pressure compressor or a hyper compressor.

[0315] 13. A method of pressurizing an olefin, the method comprising: introducing the olefin into at least one compressor that is lubricated by the lubricating composition of any of clauses 1-7; and pressurizing the olefin with the compressor, wherein the compressor is at least one of a high pressure compressor, a hyper compressor, or both.

[0316] 14. A method of making a high pressure olefin, the method comprising: pressurizing an olefin with a high pressure compressor that is lubricated with the lubricating composition of any of clauses 1-7; and reacting the pressurized olefin to form the high pressure olefin.

[0317] 15. The method of clause 13 or clause 14, wherein at least one of the olefin is ethylene, the high pressure olefin is high pressure low density polyethylene, or a combination thereof.

CLAIMS:

1. A lubricating composition comprising:
a white oil with a kinematic viscosity of at least one of:
80 mm²/sec to 120 mm²/sec at 40°C;
9.5 mm²/sec to 14 mm²/sec at 100°C; or
a combination thereof; and
a polymeric thickener present in an amount equal to or less than 40 wt% of the lubricating composition.
2. The lubricating composition of claim 1, wherein the lubricating composition has a kinematic viscosity of 200 mm²/sec to 240 mm²/sec.
3. The lubricating composition of claim 1 or 2, wherein the white oil is present in an amount of 50 wt% to 95 wt% of the lubricating composition.
4. The lubricating composition of any of claims 1-3, wherein the polymeric thickener is at least one of polybutene polymeric thickener, high molecular weight hydrocarbons, polyesters, polymers of methacrylate, copolymers of methacrylate, butadiene, olefins, alkylated styrenes, or combinations thereof.
5. The lubricating composition of any of claims 1-4, further comprising at least one performance additive.
6. The lubricating composition of claim 5, wherein the performance additive is at least one of a dispersant, an additional detergent, a corrosion inhibitor, a rust inhibitor, a metal deactivator, an additional anti-wear agent, an extreme pressure additive, an anti-seizure agent, a wax modifier, a viscosity index improver, a pour point depressant, a viscosity improver/modifier, a fluid-loss additive, a seal compatibility agent, an additional friction modifier, a lubricity agent, an anti-staining agent, a chromophoric agent, a demulsifier, an emulsifier, a densifier, a wetting agent, a gelling agent, a tackiness agent, a colorant, an antioxidants, an oxidation inhibitor, or a combination thereof.
7. The lubricating composition of claim 5 or 6, wherein a total amount of performance additives is equal to or less than 10 wt% of the lubricating composition.
8. A method of making a lubricating composition with at least one of improved high-pressure pumpability, reduced viscosity at high pressures, or a combination thereof and, the method comprising mixing:
a white oil with a kinematic viscosity of at least one of:

80 mm²/sec to 120 mm²/sec at 40°C;

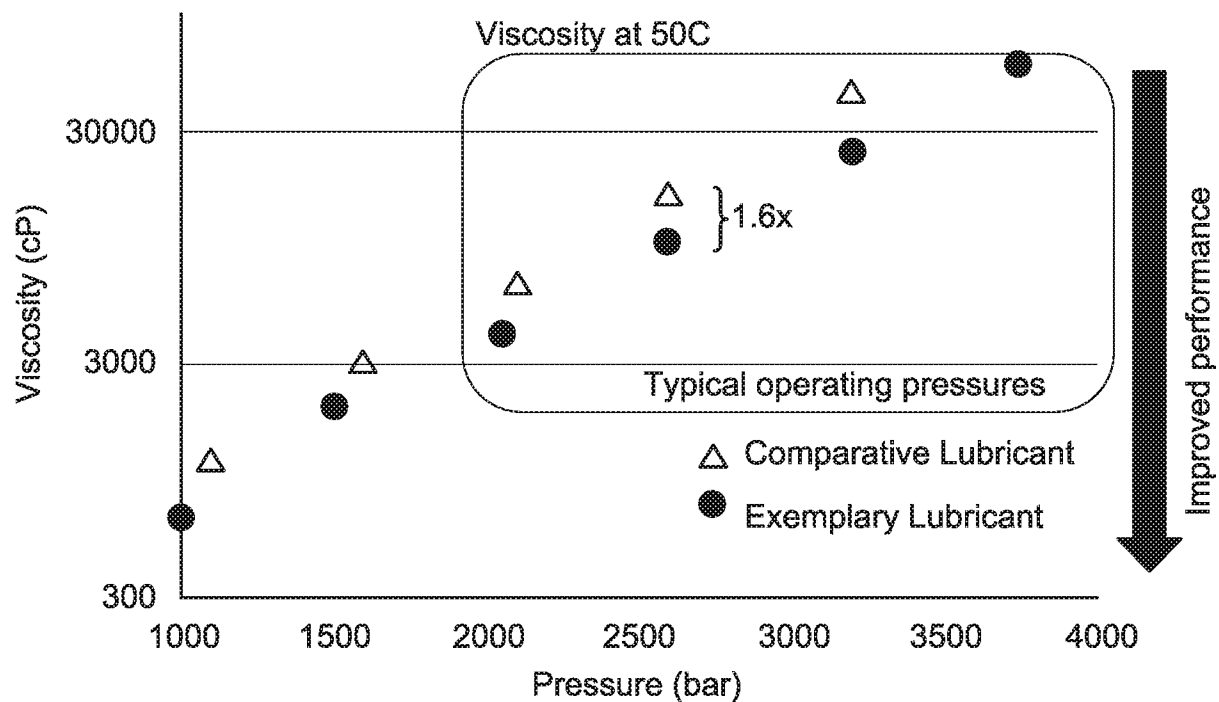
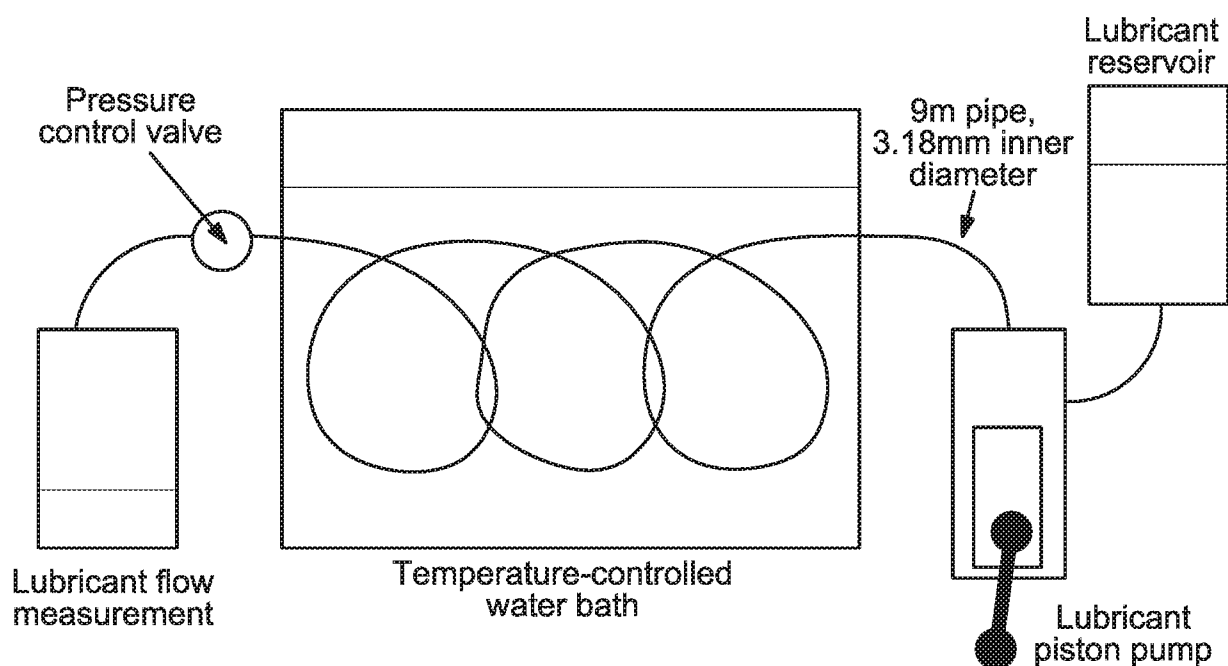
9.5 mm²/sec to 14 mm²/sec at 100°C; or

a combination thereof; and

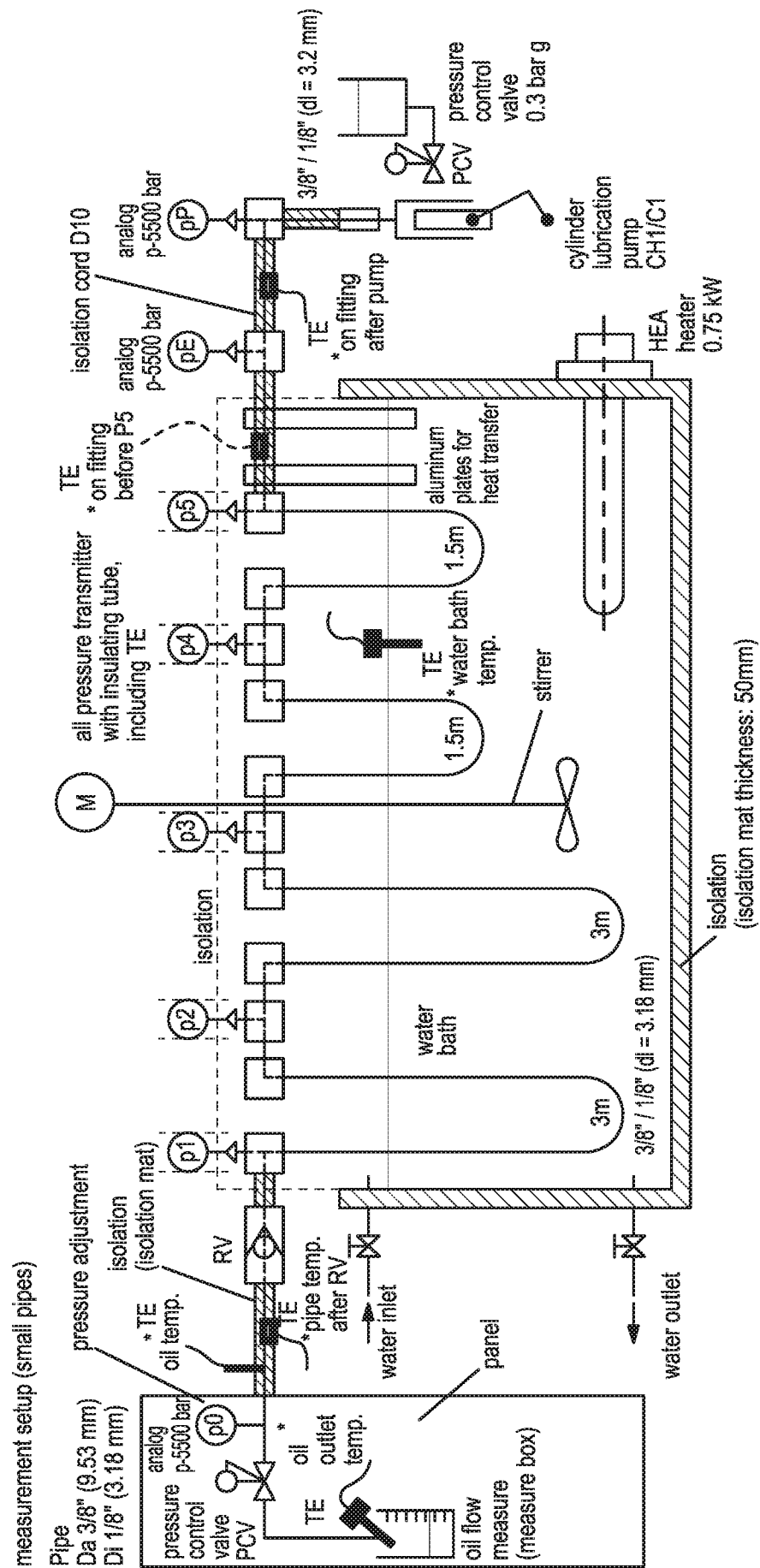
a polymeric thickener present in an amount equal to or less than 40 wt% of the lubricating composition.

9. The method of claim 8, further comprising mixing the white oil and the polymeric thickener with at least one performance additive.
10. A lubricating composition produced according to the method of claim 8 or 9.
11. A method of lubricating a compressor, the method comprising applying the lubricating composition of any of claims 1-7 to the compressor.
12. The method of claim 10, wherein the compressor is a high-pressure compressor or a hyper compressor.
13. A method of pressurizing an olefin, the method comprising:
introducing the olefin into at least one compressor that is lubricated by the lubricating composition of any of clauses 1-7; and
pressurizing the olefin with the compressor, wherein the compressor is at least one of a high pressure compressor, a hyper compressor, or both.
14. A method of making a high pressure olefin, the method comprising:
pressurizing an olefin with a high pressure compressor that is lubricated with the lubricating composition of any of clauses 1-7; and
reacting the pressurized olefin to form the high pressure olefin.
15. The method of claim 13 or claim 14, wherein at least one of the olefin is ethylene, the high pressure olefin is high pressure low density polyethylene, or a combination thereof.

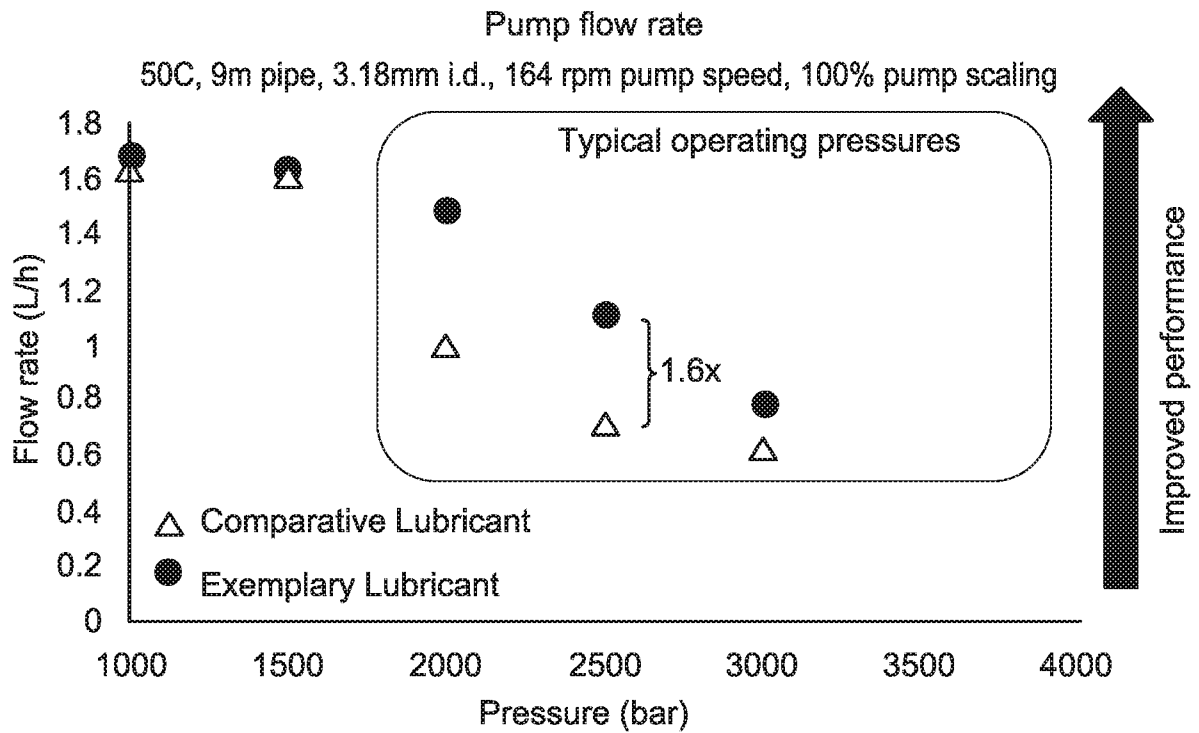
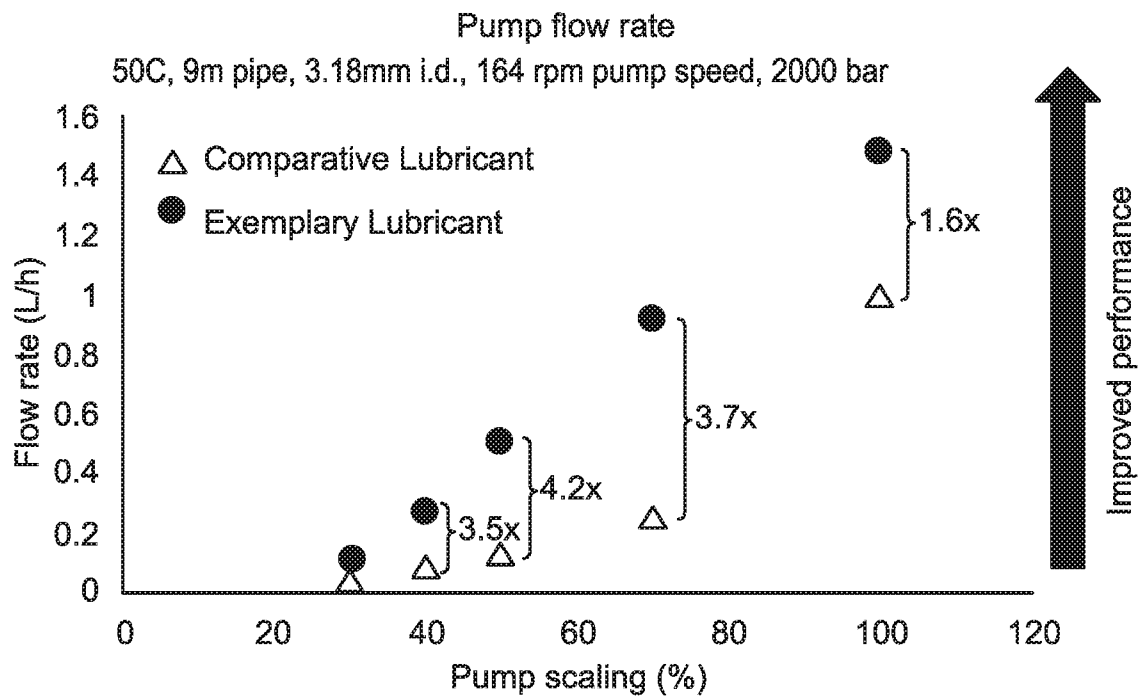
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**FIG. 1****FIG. 2A**

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**FIG. 2B**

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**FIG. 3****FIG. 4**

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2018/045093

A. CLASSIFICATION OF SUBJECT MATTER
INV. C10M169/04
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C10M C10N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, COMPENDEX, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 578 557 A (DOUGAN RODNEY D [US] ET AL) 26 November 1996 (1996-11-26) column 2, line 55 - column 3, line 57 examples column 9, line 8 - line 55 claims; examples -----	1-15
X	GB 1 338 505 A (WITCO CHEMICAL CORP) 28 November 1973 (1973-11-28) page 1, line 12 - page 2, line 26 claims; examples -----	1-14
X	US 2014/357825 A1 (VOLKER KLAUS [DE] ET AL) 4 December 2014 (2014-12-04) paragraph [0033] - paragraph [0040] paragraph [0054] - paragraph [0095] claims; examples -----	1-15

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Further documents are listed in the continuation of Box C.

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See patent family annex.

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Date of the actual completion of the international search

10 October 2018

Date of mailing of the international search report

17/10/2018

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2018/045093

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