

LUBRICANTS WITH IMPROVED SEAL COMPATIBILITY

Field of the Invention

5 **[0001]** The present invention relates to lubricating compositions and particularly gear oil compositions that include a minimum level of a specific antioxidant component, where the antioxidant component includes (i) a phenolic antioxidant, (ii) an aminic antioxidant, or (iii) a combination thereof, where the antioxidant component is present in the lubricating composition at 1.0 percent by weight or
10 higher. Such compositions provide surprisingly good seal compatibility compared to compositions with other triazoles and/or alternative additives.

Background of the Invention

[0002] In many industrial applications lubricating compositions come into contact with seals within the equipment in which they are used. Seals are made out
15 of various materials, including nitrile-butadiene rubber (NBR) due to its relatively low cost and high availability, as well as fluorinated elastomers, silicones, and polycarbonates. It is essential that the lubricating composition used has good compatibility with the seals otherwise seals are degraded over time to the point that they fail, leading to fluid leakage increasing maintenance costs, longer down time
20 for the equipment, and even the risk of equipment damage.

[0003] Seals, particularly those made using NBR, break down over time under even normal operating conditions. High temperatures in particular can be very detrimental to some seals. In other cases seals can sometimes be susceptible to attack by chemical additive components of some lubricating compositions, including
25 those used frequently in industrial applications, including some extreme-pressure agents like sulfurized olefins, rust inhibitors like aminic compounds, antiwear agents like phosphates, phosphites, phosphate esters, and phosphate amine salts. In some cases even the base oil itself can attack seal materials including NBR.

[0004] There is an on-going need for industrial lubricating compositions that can
30 provide the required performance and protection for the equipment, but which also protect the seals attack or degradation thus reducing the risk of lubricant leakage, down time and ultimately equipment damage or failure.

[0005] Wind turbines in particular represent an industrial application that requires lubricating compositions with good seal compatibility. Wind turbines as an alternative renewable energy source are attracting more interest, since they produce electricity by converting clean wind energy to electrical energy. A gear box, which is typically situated between the rotor of the wind turbine and the generator, requires a lubricant. The high torque puts a large amount of stress on the gears and bearings in the gear box of these wind turbines, placing high performance requirements on the lubricating composition. In addition, the gear boxes are located in nacelles of the wind turbine high off the ground and the unit themselves are often in remote areas. Thus the gear boxes are often inaccessible or only accessible with great cost and difficulty such that a long service life with limited maintenance is desired. Lubricating compositions with improved seal compatibility but which still provide good lubricating performance are expected to reduce maintenance and down time caused by failed seals. Thus there is a need for lubricating compositions with improved seal compatibility, that still provide good lubricating performance in wind turbines and similar applications.

Summary of the Invention

[0006] The invention provides an industrial lubricating composition comprising an oil of lubricating viscosity and an antioxidant component comprising: (i) a phenolic antioxidant, (ii) an aminic antioxidant, or (iii) a combination thereof where the antioxidant component is present in the lubricating composition at 0.4 percent by weight or higher, and in other embodiments at 1.0 percent by weight or higher,

[0007] The phenolic antioxidant may be present in the lubricating composition from at least 0.2, 0.4, 0.5 or at least 1.0 percent by weight and the aminic antioxidant may be present in the lubricating composition from at least 0.2, 0.4, 0.5 or at least 1.0 percent by weight.

[0008] The invention provides for the described compositions where the oil of lubricating viscosity includes a mineral base oil, where the oil of lubricating viscosity includes a synthetic base oil, and even where the oil of lubricating viscosity includes a combination of a mineral base oil and a synthetic base oil. In some embodiments the oil of lubricating viscosity is substantially free of, or even free of, a synthetic ester base oil.

[0009] The invention provides a method of lubricating a gear assembly comprising supplying to said assembly a lubricating composition comprising an oil of lubricating viscosity and an antioxidant component comprising: (i) a phenolic antioxidant, (ii) an aminic antioxidant, or (iii) a combination thereof where the antioxidant component is present in the lubricating composition at 0.4, 0.5 or 1.0 percent by weight or higher. Any of the antioxidant components described herein may be used in such methods.

[0010] The invention provides for the use of the described antioxidant components in lubricating compositions, at the minimum required level, as a seal protectant, including lubricating compositions for industrial applications. The invention provides even more specifically for wind turbines and other applications that require fatigue or micro-pitting resistant formulations and even applications that have stringent seal compatibility requirements.

[0011] The invention further provides for all of the compositions, methods, and uses described herein, where the specified lubricant includes a demulsifier, where the specified lubricant includes a combination of a demulsifier and a sulfurized olefin, where the specified lubricant includes a combination of a substituted triazole and a substituted thiadiazole, where the specified lubricant is essentially free of or even completely free of dithiophosphates including zinc dialkyl dithiophosphates, where the specified lubricant is essentially free of or even completely free of overbased metal-containing detergents, where the specified lubricant is essentially free of or even completely free of zinc, or any combination thereof.

Detailed Description of the Invention

[0012] Various features and embodiments of the invention will be described below by way of non-limiting illustration.

[0013] The invention provides an industrial lubricating composition comprising an oil of lubricating viscosity and an antioxidant component comprising: (i) a phenolic antioxidant, (ii) an aminic antioxidant, or (iii) a combination thereof where the antioxidant component is present in the lubricating composition at 1.0 percent by weight or higher.

The Oil of Lubricating Viscosity

[0014] One component of the compositions of the invention is an oil of lubricating viscosity, which can be present in a major amount, for a lubricant composition, or in a concentrate forming amount, for a concentrate.

5 [0015] Suitable oils include natural and synthetic lubricating oils and mixtures thereof. In a fully formulated lubricant, the oil of lubricating viscosity is generally present in a major amount (i.e. an amount greater than 50 percent by weight). Typically, the oil of lubricating viscosity is present in an amount of 75 to 95 percent by weight, and often greater than 80 percent by weight of the overall composition.

10 The base oil component generally makes up 100 parts by weight (pbw) of the overall composition with the pbw ranges for the other components being provided with this 100 pbw of base oil in mind. In other embodiments the pbw ranges of the various components, including the base oils, are provided such that the total of the pbw of all components is 100, and thus the pbw values are equivalent to percent by weight

15 values. The pbw ranges provided for the various components described below may be taken either way, however in most embodiments they are to be read so as to be equivalent to percent by weight values.

[0016] The oil of lubricating viscosity may include natural and synthetic oils, oil derived from hydrocracking, hydrogenation, and hydrofinishing, unrefined, refined

20 and refined oils or mixtures thereof. Unrefined oils are those obtained directly from a natural or synthetic source generally without (or with little) further purification treatment. Refined oils are similar to the unrefined oils except they have been further treated in one or more purification steps to improve one or more properties. Purification techniques are known in the art and include solvent extraction,

25 secondary distillation, acid or base extraction, filtration, percolation and the like. Re-refined oils are also known as reclaimed or reprocessed oils, and are obtained by processes similar to those used to obtain refined oils and often are additionally processed by techniques directed to removal of spent additives and oil breakdown products.

30 [0017] Natural oils useful as the oil of lubricating viscosity include animal oils, vegetable oils (e.g., castor oil, lard oil), mineral lubricating oils such as liquid petroleum oils and solvent-treated or acid-treated mineral lubricating oils of the

paraffinic, naphthenic or mixed paraffinic naphthenic types and oils derived from coal or shale or mixtures thereof.

[0018] Synthetic oils of lubricating viscosity include hydrocarbon oils such as polymerized and interpolymerised olefins (e.g., polybutylenes, polypropylenes, propyleneisobutylene copolymers); poly(1-hexenes), poly(1-octenes), poly(1-decenes), and mixtures thereof; alkyl-benzenes (e.g., dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di-(2-ethylhexyl)-benzenes); polyphenyls (e.g., biphenyls, terphenyls, alkylated polyphenyls); alkylated biphenyl ethers and alkylated biphenyl sulfides and the derivatives, analogs and homologs thereof or mixtures thereof.

[0019] Another synthetic oil of lubricating viscosity includes polyol esters other than the hydrocarbyl-capped polyoxyalkylene polyol as disclosed herein, dicarboxylic esters, liquid esters of phosphorus-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, and the diethyl ester of decane phosphonic acid), or polymeric tetrahydrofurans. Synthetic conventional oil of lubricating viscosity also include those produced by Fischer-Tropsch reactions and typically may be hydroisomerised Fischer-Tropsch hydrocarbons or waxes. In one embodiment, the oil of lubricating viscosity may be prepared by a Fischer-Tropsch gas-to-liquid synthetic procedure as well as other gas-to-liquid oils.

[0020] Oils of lubricating viscosity may further be defined as specified in the American Petroleum Institute (API) Base Oil Interchangeability Guidelines. The five base oil groups are as follows: Group I (sulfur content >0.03 wt %, and/or <90 wt % saturates, viscosity index 80-120); Group II (sulfur content ≤ 0.03 wt % and ≥ 90 wt % saturates, viscosity index 80-120); Group III (sulfur content ≤ 0.03 wt % and ≥ 90 wt % saturates, viscosity index ≥ 120); Group IV (all polyalphaolefins PAOs such as PAO-2, PAO-4, PAO-5, PAO-6, PAO-7 or PAO-8); and Group V. The oil of lubricating viscosity includes API Group I, Group II, Group III, Group IV, Group V oil or mixtures thereof. In one embodiment, the oil of lubricating viscosity is an API Group I, Group II, Group III, Group IV oil or mixtures thereof. Alternatively, the oil of lubricating viscosity is often an API Group II, Group III or Group IV oil or mixtures thereof.

[0021] The various described oils of lubricating viscosity may be used alone or in combinations. The oil of lubricating viscosity is used in the range of about 70 wt % to about 99 wt %, and in another embodiment, in the range of about 75 wt % to about 98 wt %, in another embodiment in the range of about 88 wt % to about 97 wt % of the lubricant.

[0022] In some embodiments the lubricating oil component of the present invention includes a Group II or Group III base oil, or a combination thereof. These are classifications established by the API (American Petroleum Institute). Group III oils contain < 0.03 percent sulfur and > 90 percent saturates and have a viscosity index of > 120. Group II oils have a viscosity index of 80 to 120 and contain < 0.03 percent sulfur and > 90 percent saturates. The oil can also be derived from the hydroisomerization of wax, such as slack wax or a Fischer-Tropsch synthesized wax. Such "Gas-to-Liquid" oils are typically characterized as Group III.

[0023] The compositions of the present invention may include some amount of Group I base oils, and even Group IV and Group V base oils. Polyalphaolefins are categorized as Group IV. Group V encompasses "all others". However, in some embodiments the lubricating oil component of the invention contains no more than 20, 10, 5, or even 1 percent by weight Group I base oil. These limits may also apply to Group IV or Group V base oils. In other embodiments the lubricating oil present in the compositions of the invention is at least 60, 70, 80, 90, or even 95 percent by weight Group II and/or Group III base oil. In some embodiments the lubricating oil present in the compositions of the invention is essentially only Group II and/or Group III base oil, where small amounts of other types of base oils may be present but not in amounts that significantly impact the properties or performance of the overall composition.

[0024] In some embodiments the compositions of the invention include some amount of Group I and/or Group II base oils. In other embodiments the compositions of the invention are lubricating compositions where the oil of lubricating viscosity is primarily Group I and/or Group II base oils, or even essentially Group I and/or Group II base oils, or even exclusively Group I and/or Group II base oils.

[0025] In some embodiments the compositions of the invention include some amount of Group I base oils. In other embodiments the compositions of the invention are lubricating compositions where the oil of lubricating viscosity is primarily Group I base oils, or even essentially Group I base oils, or even exclusively Group I base oils.

[0026] In some embodiments the compositions of the invention include some amount of Group II base oils. In other embodiments the compositions of the invention are lubricating compositions where the oil of lubricating viscosity is primarily Group II base oils, or even essentially Group II base oils, or even exclusively Group II base oils.

[0027] In some embodiment's the oil of lubricating viscosity may be present in the range from 60 to 99.9, from 88.5 to 99.6, from 96.9 to 99.5, or from 98.2 to 99.4 weight percent of the lubricating oil composition. Each oil of lubricating viscosity described above may be used alone or as mixtures of one or more thereof.

The Antioxidant Component

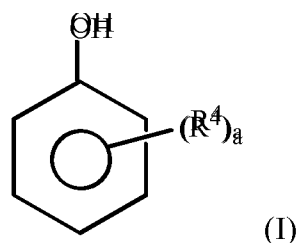
[0028] The present invention requires the described lubricant compositions to include a minimum level of a specific antioxidant component. The antioxidant component includes: (i) a phenolic antioxidant, (ii) an aminic antioxidant, or (iii) a combination thereof. The antioxidant component must be present in the described lubricating compositions at a minimum of 0.4, 0.5 or a minimum 1.0 percent by weight or higher.

[0029] Suitable phenolic antioxidants that may be used in the invention include substituted phenol that contains at least one alkyl substituent group. In some embodiments the phenolic antioxidant includes compounds free of nitrogen which are also ashless. In some embodiments the phenolic antioxidant includes a substituted phenol containing at least two branched alkyl substituent groups. In some embodiments the phenolic antioxidant comprises a substituted phenol containing at least two branched alkyl substituent groups and further containing a ester containing substituent group.

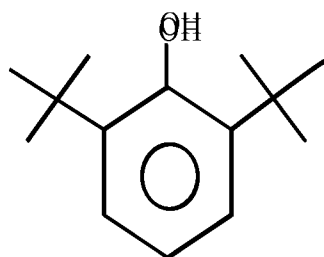
[0030] The phenolic antioxidant can include a sterically hindered phenols that contain an alkyl group ortho to the hydroxyl group, two alkyl groups ortho to the hydroxyl group that occupy the 2-position and 6-position of the phenolic ring, or a

mixture thereof. The alkyl groups can contain 1 to 24 carbon atoms and in other instances 3 to 18 and 3 to 12 carbon atoms. The alkyl groups can be linear, branched to include tertiary alkyl groups, or a mixture thereof. The sterically hindered phenol can also contain one or more additional alkyl groups and/or one or more hydrocarbyl groups such as a propionate ester group. Useful sterically hindered phenols can include ortho-alkylated phenolic compounds such as for example 2,6-ditertbutylphenol, 4-methyl-2,6-di-tertbutylphenol, 2,4,6-tritertbutylphenol, 2-tert-butylphenol, 2,6-diisopropylphenol, 2-methyl-6-tert-butylphenol, 2,4-dimethyl-6-tert-butylphenol, 4-(N,N-dimethylaminomethyl)-2,6-di-tertbutyl phenol, 4-ethyl-2,6-di-tertbutylphenol, and their analogs and homologs. Mixtures of two or more such mononuclear phenol compounds are also suitable.

[0031] In an embodiment of the invention the sterically hindered phenol can be represented by the following formula:

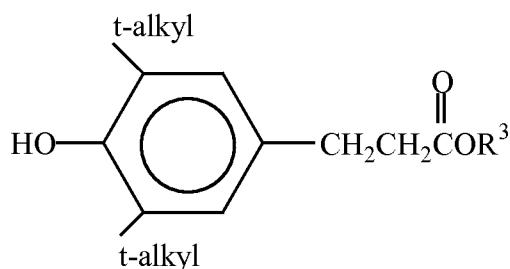


wherein R^4 is an alkyl group containing 1 up to 24 carbon atoms and a is an integer of 1 to 5. In some embodiments R^4 contains 4 to 18 carbon atoms or even from 4 to 12 carbon atoms. R^4 may be either straight chained or branched chained, and in some embodiments is branched. The value for a can be 1 to 4, 1 to 3, or 2, or 3. In some embodiments the phenol is a butyl substituted phenol containing 2 or 3 t-butyl groups. In some embodiments one R^4 group is located in the 4 position on the ring and is hydrogen, a hydrocarbyl such as methyl, ethyl, or dodecyl. In any of these embodiments, when a is 2 and t-butyl groups occupy the 2- and 6-positions of phenol, the phenol is extremely sterically hindered and has the following structure:



(II)

[0032] In one embodiment of the invention the sterically hindered phenol can be represented by the following formula:



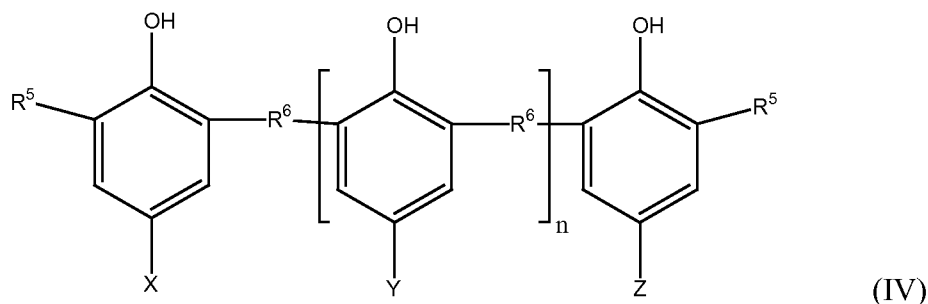
(III)

5 wherein the t-alkyl groups can have 4 to 8 carbon atoms, and R³ is a straight chain or branched chain alkyl group containing 2 to 22, 2 to 8, 2 to 6 carbon atoms or even just 4 carbon atoms. R³ is desirably a 2-ethylhexyl group or an n-butyl group. Hindered, ester-substituted phenols such as those of formula (III) can be prepared by heating a 2,6-dialkylphenol with an acrylate ester under
 10 base catalysis conditions such as aqueous KOH as described in International Publication No. WO01/74978. In another embodiment of this invention the sterically hindered phenol is an alkylation reaction product of an alkylphenol such as a dodecylphenol and isobutylene to form a product containing a di-t-butylated alkylphenol. An embodiment of the invention is a sterically hindered
 15 phenol having two or more alkyl substituents that contain 1 to 24 carbon atoms and that occupy the 2-position and 6-position of the phenolic ring.

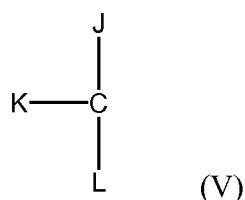
[0033] The phenolic antioxidant can also include an alkylene or alkylidene coupled sterically hindered phenol oligomer. The coupled sterically hindered phenol oligomer can contain two or more phenolic rings where each ring is
 20 occupied at the 2-, 4- and 6-positions by an alkyl group such as a methyl or t-butyl group or an arylalkyl group such as a 3,5-di-t-butyl-4-hydroxybenzyl group. The alkylene and alkylidene coupling groups can be respectively methylene and ethylidene groups. The alkyl groups can have 1 to 24 carbon

atoms and in other instances can have 3 to 18 and 3 to 12 carbon atoms. The alkyl groups can be linear, branched to include tertiary alkyl groups, or a mixture thereof. The coupled sterically hindered phenol oligomer can include a mixture of two or more oligomers where each oligomer contains a different number of phenolic rings. The coupling of the phenolic rings in an oligomer can be at ortho ring positions, at para ring positions, or at a mixture of ortho and para ring positions.

[0034] In an embodiment of the invention the phenolic antioxidant is a coupled alkylphenol which can be represented by the formula:



wherein each R^5 is independently a tertiary alkyl group containing from 4 to about 8 carbon atoms, each of X, Y and Z is independently hydrogen or a hydrocarbon radical, each R^6 is independently an alkylene or alkylidene group, and n is a number ranging from zero to about 4. Each R^5 group must be a tertiary alkyl group. Tertiary alkyl groups have the general structure:



wherein each of J, K and L is an alkyl group of 1-4 carbon atoms. Representative tertiary alkyl groups are tertiary butyl, tertiary amyl, tertiary hexyl and tertiary octyl. The R^5 groups may be the same or different. In some embodiments all R^5 are the same, and in still further embodiments are all tertiary butyl groups. Each R^6 is independently a divalent group such as an alkylene or an alkylidene group. These groups may be substituted for example by various hydrocarbyl groups such as alkyl and aryl groups. Representative examples of suitable R^6 groups are methylene, ethylene, propylene, phenyl substituted methylene, methyl substituted methylene,

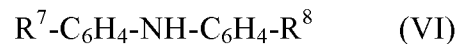
5 methyl substituted ethylene and the like. Typically, each R⁶ contains from one to about 10 carbon atoms, or from one to about three carbon atoms. In one embodiment, R⁶ is phenyl substituted methylene. In another embodiment, each is methylene, that is a group of the formula -CH₂-. Each X, Y and Z is independently
10 hydrogen or a hydrocarbon-based group. These groups may be the same or different. In one embodiment, each of X, Y and Z is independently an aliphatic hydrocarbon group. Thus each of these groups will contain at least one carbon atom, but may contain more. In still further embodiments they contain from 1 to about 500 carbon atoms, from 4 to about 100 carbon atoms, or even from about 4 to about 30 carbon atoms.

[0035] In an embodiment of the invention the phenolic antioxidant is a methylene coupled oligomer of a sterically hindered phenol such as for example 4,4'-methylene-bis(6-tert-butyl-2-methylphenol), 4,4'-methylene-bis(2-tert-amyl-6-methylphenol), 2,2'-methylene-bis(4-methyl-6-tert-butylphenol), 4,4'methylene-bis(2,6-di-tert-butylphenol), and similar compounds. In an embodiment of this
15 invention a methylene coupled oligomer of a sterically hindered phenol is 2,2'-methylene-bis(6-tert-butyl-4-dodecylphenol) as described in U.S. Patent No. 6,002,051 regarding its preparation and use.

[0036] Suitable aminic antioxidants that may be used in the invention include
20 alkaryl amines and in some embodiments the aminic antioxidant is an alkylphenyl amine. Suitable examples include a bis(4-alkylphenyl)amine.

[0037] The aminic antioxidant can include a secondary aromatic amine, typically a monoamine, that contains one aryl group, two aryl groups, or a mixture thereof. An embodiment of the invention is a secondary aromatic amine containing
25 one aryl group such as for example N-methylaniline. The secondary aromatic amine containing one aryl group can also have C₁-C₁₆ alkyl or arylalkyl substituents on the aryl group. In another embodiment of the invention the secondary aromatic amine can be a diarylamine such as for example diphenylamine, N-phenyl-1-naphthylamine or combinations thereof. The diarylamine can contain one, two or
30 more alkyl and/or arylalkyl substituents. The alkyl and arylalkyl substituents can have 1 to 16 carbon atoms and in other instances can have 3 to 14 and 4 to 12 carbon atoms. The alkyl and arylalkyl substituents can be linear, branched, or a mixture

thereof. In an embodiment of the present invention the diarylamine is an alkylated diphenylamine which can be represented by formula:



wherein R^7 and R^8 are independently a hydrogen or an alkyl group containing 1 to 24 carbon atoms. The diphenylamine of formula (VI) can be a mixture of diphenylamine and monoalkylated and dialkylated diphenylamine. R^7 and/or R^8 can be alkyl groups containing from 4 to 20 carbon atoms. In another embodiment of the invention the diphenylamine of formula (VI) is prepared by alkylating diphenylamine with nonenes using well known alkylation methods. Alkylated diarylamines are also commercially available.

[0038] The antioxidant component must be present in the composition at least 1.0 percent by weight. This treat rate is with respect to the final lubricant composition to be used in a mechanical device, but could also be applied to additive packages and concentrates which are then diluted, typically with oil, to produce the final lubricant. The weight percent discussed here are with respect to the overall lubricant composition. Any diluent that may be present in the antioxidant component is generally not considered when determining the percent by weight at which the antioxidant component is present in the composition. In addition, any materials in the antioxidant component other than the phenolic and aminic antioxidants described herein may be excluded when determining the percent by weight at which the antioxidant component is present in the composition, such that the weight percent values discussed only apply to the phenolic and aminic antioxidants.

[0039] Also it is noted that in some embodiments the antioxidant component includes one or more phenolic antioxidants and no aminic antioxidants. In other embodiments the antioxidant component includes one or more aminic antioxidants and no phenolic antioxidants. In still other embodiments the antioxidant component includes a combination of one or more aminic antioxidants and one or more phenolic antioxidants.

[0040] In some embodiments the phenolic antioxidant is present in the lubricating composition from at least 0.5 percent by weight and the aminic antioxidant is present in the lubricating composition from at least 0.5 percent by

weight. In some embodiments the phenolic antioxidant is present in the lubricating composition from at least 1.0 percent by weight and the aminic antioxidant is present in the lubricating composition from at least 1.0 percent by weight or from 0.5 percent by weight.

5 Additional Additives

[0041] Optionally the lubricating compositions of the invention include one or more additional additives, which may be selected from the group including: a foam inhibitor, a demulsifier, a pour point depressant, an antioxidant other than those described above, a dispersant, a metal deactivator (such as a copper deactivator), an
10 antiwear agent, extreme pressure agent, viscosity modifiers, or mixtures thereof. The optional additives may each be present in the range from 0.0005 to 1.3, from 0.00075 to 0.5, from 0.001 to 0.4, or from 0.0015 to 0.3 percent by weight of the lubricating oil composition. However it is noted that some optional additives, including viscosity modifying polymers, which may alternatively be considered
15 as part of the base fluid, may be present in higher amounts including up to 30, 40, or even 50% by weight when considered separate from the base fluid. The optional additives may be used alone or mixtures thereof.

[0042] Antifoams, also known as foam inhibitors, are known in the art and include but are not limited to organic silicones and non-silicon foam inhibitors.
20 Examples of organic silicones include dimethyl silicone and polysiloxanes. Examples of non-silicon foam inhibitors include but are not limited to polyethers, polyacrylates and mixtures thereof as well as copolymers of ethyl acrylate, 2-ethylhexylacrylate, and optionally vinyl acetate. In some embodiments the antifoam is a polyacrylate. Antifoams may be present in the composition from 0.001 to 0.012
25 or 0.004 pbw or even 0.001 to 0.003.

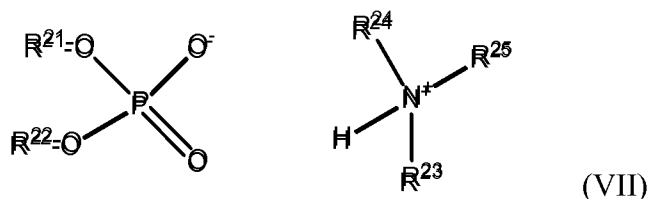
[0043] Demulsifiers are known in the art and include but are not limited to derivatives of propylene oxide, ethylene oxide, polyoxyalkylene alcohols, alkyl amines, amino alcohols, diamines or polyamines reacted sequentially with ethylene oxide or substituted ethylene oxides or mixtures thereof. Examples of demulsifiers
30 include polyethylene glycols, polyethylene oxides, polypropylene oxides, (ethylene oxide-propylene oxide) polymers, including block copolymers of ethylene oxide and propylene oxide, and mixtures thereof. In some embodiments the demulsifiers is a

polyether. Demulsifiers may be present in the composition from 0.002 to 0.012 pbw.

[0044] Pour point depressants are known in the art and include but are not limited to esters of maleic anhydride-styrene copolymers, polymethacrylates; polyacrylates; polyacrylamides; condensation products of haloparaffin waxes and aromatic compounds; vinyl carboxylate polymers; and terpolymers of dialkyl fumarates, vinyl esters of fatty acids, ethylene-vinyl acetate copolymers, alkyl phenol formaldehyde condensation resins, alkyl vinyl ethers and mixtures thereof.

[0045] The compositions of the invention may also include a rust inhibitor. Suitable rust inhibitors include hydrocarbyl amine salts of alkylphosphoric acid, hydrocarbyl amine salts of dialkyldithiophosphoric acid, hydrocarbyl amine salts of hydrocarbyl arenesulphonic acid, fatty carboxylic acids or esters thereof, an ester of a nitrogen-containing carboxylic acid, an ammonium sulfonate, an imidazoline, mono-thio phosphate salts or esters, or any combination thereof; or mixtures thereof.

[0046] Suitable hydrocarbyl amine salts of alkylphosphoric acid of the invention are represented by the following formulas:

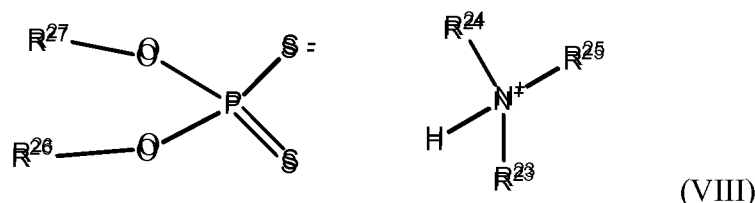


wherein R^{21} and R^{22} are independently hydrogen, alkyl chains or hydrocarbyl, and in some embodiments at least one of R^{21} and R^{22} are hydrocarbyl. R^{21} and R^{22} contain about 4 to about 30, about 8 to about 25, or even about 8 or 10 to about 20, or even from 13 to about 19 carbon atoms. R^{23} , R^{24} and R^{25} are independently hydrogen, alkyl branched or linear alkyl chains with about 1 to about 30, in other embodiments about 4 to about 24, or even from about 6 to about 20, and in some embodiments about 8 or 10 to about 16 carbon atoms. R^{23} , R^{24} and R^{25} are independently hydrogen, alkyl branched or linear alkyl chains, and in some embodiments at least one, or even two of R^{23} , R^{24} and R^{25} are hydrogen, and further where at least one of R^{23} , R^{24} and R^{25} is a hydrocarbyl group containing at least 8 carbon atoms.

[0047] Examples of alkyl groups suitable for R^{23} , R^{24} and R^{25} include but are not limited to butyl, sec butyl, isobutyl, tert-butyl, pentyl, n-hexyl, sec-hexyl, n-octyl, 2-ethyl, hexyl, ethyl-hexyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, octadecenyl, nonadecyl, eicosyl or mixtures thereof.

[0048] In one embodiment the hydrocarbyl amine salt of an alkylphosphoric acid is the reaction product of a C_{14} to C_{18} alkylated phosphoric acid with Primene 81R (produced and sold by Rohm & Haas) which is a mixture of C_{11} to C_{14} tertiary alkyl primary amines.

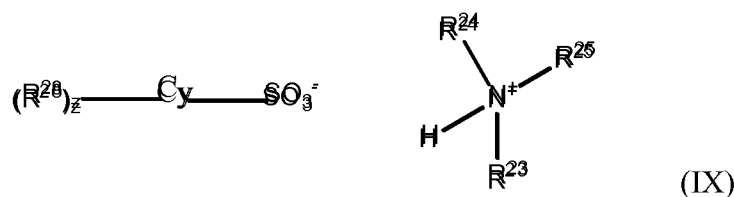
[0049] Hydrocarbyl amine salts of dialkyldithiophosphoric acid of the invention used in the rust inhibitor package are represented by the formula:



wherein R^{26} and R^{27} are independently branched or linear alkyl groups. R^{26} and R^{27} contain about 3 to about 30, or from about 4 to about 25, or from about 5 to about 20, or even from about 6 to about 19 carbon atoms. R^{23} , R^{24} and R^{25} are as described above.

[0050] Examples of hydrocarbyl amine salts of dialkyldithiophosphoric acid of the invention include but are not limited to the reaction product(s) of diheptyl or dioctyl or dinonyl dithiophosphoric acids with ethylenediamine, morpholine or Primene 81R or mixtures thereof.

[0051] Suitable hydrocarbyl amine salts of hydrocarbyl arenesulphonic acids used in the rust inhibitor package of the invention are represented by the formula:



wherein Cy is a benzene or naphthalene ring. R^{28} is a hydrocarbyl group with about 4 to about 30, or from about 6 to about 25, or from about 8 to about 20 carbon

atoms. z is independently 1, 2, 3, or 4 and in some embodiments z is 1 or 2. R^{23} , R^{24} and R^{25} are as described above.

[0052] Examples of hydrocarbyl amine salts of hydrocarbyl arenesulphonic acid of the invention include but are not limited to the ethylenediamine salt of dinonylnaphthalene sulphonic acid.

[0053] Examples of suitable fatty carboxylic acids or esters thereof include glycerol monooleate and oleic acid. An example of a suitable ester of a nitrogen-containing carboxylic acid includes oleyl sarcosine.

[0054] The rust inhibitors may be present in the range from 0.02-0.2, from 0.03 to 0.15, from 0.04 to 0.12, or from 0.05 to 0.1 pbw of the lubricating oil composition. The rust inhibitors of the invention may be used alone or in mixtures thereof.

[0055] The lubricating compositions of the invention may also include a metal deactivator. Metal deactivators are used to neutralise the catalytic effect of metal for promoting oxidation in lubricating oil. Suitable metal deactivators include but are not limited to triazoles, tolyltriazaoles, a thiadiazole, or combinations thereof, as well as derivatives thereof. Examples include derivatives of benzotriazoles, benzimidazole, 2-alkyldithiobenzimidazoles, 2-alkyldithiobenzothiazoles, 2-(N,N'-dialkyldithio-carbamoyl)benzothiazoles, 2,5-bis(alkyl-dithio)-1,3,4-thiadiazoles, 2,5-bis(N,N'-dialkyldithiocarbamoyl)-1,3,4-thiadiazoles, 2-alkyldithio-5-mercapto thiadiazoles or mixtures thereof. These additives may be used from 0.01 to 0.25 percent by weight in the overall composition.

[0056] In some embodiments the metal deactivator is a hydrocarbyl substituted benzotriazole compound. The benzotriazole compounds with hydrocarbyl substitutions include at least one of the following ring positions 1- or 2- or 4- or 5- or 6- or 7- benzotriazoles. The hydrocarbyl groups contain about 1 to about 30, preferably about 1 to about 15, more preferably about 1 to about 7 carbon atoms, and most preferably the metal deactivator is 5-methylbenzotriazole used alone or mixtures thereof.

[0057] The metal deactivators may be present in the range from 0.001 to 0.1, from 0.01 to 0.04 or from 0.015 to 0.03 pbw of the lubricating oil composition.

Metal deactivators may also be present in the composition from 0.002 or 0.004 to 0.02 pbw. The metal deactivator may be used alone or mixtures thereof.

[0058] Antioxidants other than those described above may also be present including a substituted hydrocarbyl mono-sulfide. In some embodiments the substituted hydrocarbyl monosulfides include n-dodecyl-2-hydroxyethyl sulfide, 1-(tert-dodecylthio)-2-propanol, or combinations thereof. In some embodiments the substituted hydrocarbyl monosulfide is 1-(tert-dodecylthio)-2-propanol.

[0059] Dispersants may also be present including: (i) a polyetheramine; (ii) a borated succinimide dispersant; (iii) a non-borated succinimide dispersant; (iv) a Mannich reaction product of a dialkylamine, an aldehyde and a hydrocarbyl substituted phenol; or any combination thereof. In some embodiments the dispersant component is present from 0.05 to 0.5 pbw of the overall composition.

[0060] The invention further provides for all of the compositions, methods, and uses described herein, where the specified lubricant includes a demulsifier, where the specified lubricant includes a combination of a demulsifier and a sulfurized olefin, where the specified lubricant includes a highly sulfurized olefin such as a sulfurized olefin containing at least 20% by weight sulfur, where the specified lubricant is essentially free or to even completely free of non-highly sulfurized olefins such as a sulfurized olefin containing less than 20% by weight sulfur, where the specified lubricant includes a combination of a substituted triazole and a substituted thiadiazole, where the specified lubricant is essentially free of or even completely free of metal dialkyl dithiophosphates, where the specified lubricant is essentially free of or even completely free of overbased metal-containing detergents, where the specified lubricant is essentially free of or even completely free of zinc, or any combination thereof.

Industrial Application

[0061] The invention provides a process for the preparation of lubricating oil compositions. The lubricating oil compositions are prepared by the steps comprising: a) mixing and/or dissolving in one another the components described above that includes the combination of an oil of lubricating viscosity, the substituted triazole and optionally one more addition additives. The materials are mixed until the additives are substantially or wholly dissolved, in some embodiments at elevated

temperatures in the range 40°C to 110°C, or 50°C to 95°C, or even 55°C to 85°C; and for a period of time in the range 30 seconds to 24 hours, 2 minutes to 8 hours, or 5 minutes to 4 hours; and at pressures in the range 700 mm of Hg to 2000 mm of Hg, 750 mm of Hg to 900 mm of Hg, or 755 mm of Hg to 800 mm of Hg.

5 **[0062]** The order of addition of the additives is not overly limited. The optional additives may be mixed in at the same time as the other components or at a later time using any of the mixing procedures described above.

10 **[0063]** In some embodiments a portion of oil or similar diluent is present with the components and the components are mixed into the oil. In other embodiments a minimal amount of oil or diluent is present, other than that amount inherently present in the additive from their means of production and preparation and additional base oil is added after the component have been mixed. In any event the described processes results in lubricating compositions.

15 **[0064]** In some embodiments the lubricating oil compositions may be prepared from a concentrate comprising the steps of: a) mixing all of the components described above with minimal oil and/or diluent present, other than optionally some relatively small amount to allow for reasonable handling properties. The resulting concentrate may then be used in the preparation of a lubricating composition by mixing the concentrate with an effective amount of base oil or mixtures thereof resulting in a finished fluid. Optional additives may be added to the concentrate or to the resulting final fluid. These optional additives include any of those described above. In some embodiments these optional additives include a foam inhibitor, a demulsifier, a viscosity modifier, a pour point depressant, or mixtures thereof, and may be added such that they are present in the overall compositions in the range about 0, 0.01, 0.1 or even 0.25 or up to about 13, 10, 8 or even 6 pbw.

25 **[0065]** In some embodiments the compositions of the invention have an ISO viscosity grade from 100 to 1000, or from 100 to 460, or even from 100 or 150 to 320. In some embodiments the compositions of this invention are not grease compositions or engine oil compositions. Rather these compositions can be industrial gear oils, wind turbine lubricants, bearing lubricants, and the like, and in some embodiments even automotive gear oils.

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Specific Embodiment

[0066] The invention will be further illustrated by the following examples, which set forth particularly advantageous embodiments. While the examples are provided to illustrate the invention, they are not intended to limit it.

5 [0067] The example sets below are designed to evaluate and compare the following additives: Antioxidant A, an alkylated phenol; and Antioxidant B, an alkaryl amine.

[0068] To evaluate the additives, the examples in the example sets below are tested to evaluate their seal compatibility. Using NBR 902 seals the samples are
10 tested for approval under the Flender-Siemens specification (F-S) for wind turbines, which involves 1000 hours of testing at 130°C for each sample. Under this specification, ideally the fluid must give results including a hardness change of not more than 5 points (-5 to +5), a percent volume change from a 2% decrease to a 5% increase (-2% to +5%), a percent tensile decrease of no more than 60% (-60% max)
15 and a percent elongation decrease of no more than 60% (-60% max). These specifications, in particular the Flender-Siemens specification, are very hard to meet, and a relative improvement in performance over a conventional comparative example, even if not a clean pass, would still be considered to be a significant improvement. In fact, a sample that meets the specification expect for having a
20 hardness change up to +7, a volume change up to +6%, or a elongation change of down to -65% is still considered to have met the a specification and passed the test, so long as only one of these areas is outside the normal pass range. This secondary allowance for one of the ratings allows for a passing result even if the sample did not show a “clean pass” with all ratings inside the ideal ranges.

25 [0069] However, as is evident from the results, it is important to consider relative performance of the examples rather than just the pass fail result. When considering the Flender-Siemens specification (F-S) results of the example sets and comparing the relative performance it can be helpful to consider the degree to which a sample passed or failed. The following key can be used for this purpose with the
30 best result at the top of the table and the worst result at the bottom:

Result Key for Relative Performance Comparisons

Degree Rating	Description of the Rating
A PASS	Clean Pass, no ratings outside the ideal ranges.
B PASS	Pass, one rating outside the ideal range but within the secondary allowance, discussed in the description of the test method above.
F1	1 st Degree Fail, the sample failed for having two ratings outside the ideal ranges but both within the secondary allowances.
F2	2 nd Degree Fail, the sample failed for having one rating outside both the ideal range and the secondary allowances for that rating.
F3	3 rd Degree Fail, the sample failed for having one rating outside both the ideal range and the secondary allowances for that rating and also having another rating outside the ideal ranges but within the secondary allowances.
F4	4 th Degree Fail, the sample failed for having two ratings outside the both ideal range and the secondary allowances for those ratings.
F5	5 th Degree Fail, the sample failed for having two ratings outside both the ideal range and the secondary allowances for those ratings and also having a third rating outside the ideal ranges but within the secondary allowances.
F6	6 th Degree Fail, the sample failed for having three ratings outside the both ideal range and the secondary allowances for those ratings and also having a third rating outside the ideal ranges but within the secondary allowances.

Example Set 1

- 5 [0070] A set of examples is prepared in a Group I (GI) base oil. Each of the examples contains the same conventional additives package in the same amount, such that the sample is suitable for use as a lubricant in industrial gear applications. Each sample is top-treated with one of the antioxidant described above to see the impact the added materials have on the formulation's performance, specifically in regards to seal compatibility.
- 10 [0071] The conventional additive package used in each of these examples, is referred to as Additive Package A and contains a metal deactivator, a demulsifier, a rust inhibitor, a mixture of antiwear and extreme pressure agents, an antifoam agent, a detergent, and a corrosion inhibitor. None of the additives in Additive Package A meet the requirements for the antioxidant component of the invention.
- 15 [0072] The samples are tested to evaluate their seal compatibility using the same test method described above. The results from the testing of Example Set 1 are summarized in the table below:

Table 1 – Summary of Results from Example Set 1

	Ex 1-1 ¹	Ex 1-2	Ex 1-3	Ex 1-4	Ex 1-5 ¹	Ex 1-6	Ex 1-7 ¹	Ex 1-8	Ex 1-9 ¹	Ex 1-10	Ex 1-11	Ex 1-12
<i>Ex Type</i>	<i>comp</i>	<i>comp</i>	<i>comp</i>	<i>comp</i>	<i>comp</i>	<i>comp</i>	<i>comp</i>	<i>inv</i>	<i>comp</i>	<i>inv</i>	<i>inv</i>	<i>inv</i>
Base Oil ²	GI	GI	GI	GI	GI	GI	GI	GI	GI	GI	GI	GI
Add Pack	A	A	A	A	A	A	A	A	A	A	A	A
Antioxidant A		0.2		0.2		0.5		0.5		1.0		1.0
Antioxidant B			0.2	0.2			0.5	0.5			1.0	1.0
F-S Spec	<i>F4</i>	<i>F3</i>	<i>F1</i>	<i>F1</i>	<i>F4</i>	<i>F4</i>	<i>F3</i>	<i>B PASS</i>	<i>F4</i>	<i>A PASS</i>	<i>A PASS</i>	<i>A PASS</i>
Hardness Δ	8	7	7	6	9	8	8	6	8	5	4	4
%Vol Δ	2	2	2	2	2	3	3	3	2	3	3	4
%Tensile Δ	-3	0	-2	-4	11	-4	-1	-1	-3	-3	-2	-4
%Elong Δ	-72	-71	-65	-68	-74	-71	-64	-59	-72	-55	-55	-58

1 – Examples 1-1, 1-5 and 1-9 are repeats of the baselines which was re-tested for each set of samples at different treat levels. These examples provide good baseline comparisons while also showing the repeatability of the test.

5 2 – The base oil used in these examples is an API Group I base oil.

[0073] The results show that the inventive examples provide improved seal compatibility in Group I based formulations over the comparative examples.

Example Set 2

10 [0074] A set of examples is prepared in a Group II (GII) base oil. Each of the examples contains the same conventional additives package described above in Example Set 1. The samples are tested to evaluate their seal compatibility using the same test methods described above. The results from the testing of Example Set 2 are summarized in the table below:

15 *Table 2 – Summary of Results from Example Set 2*

	Ex 2-1 ¹	Ex 2-2	Ex 2-3	Ex 2-4	Ex 2-5 ¹	Ex 2-6	Ex 2-7 ¹	Ex 2-8
<i>Ex Type</i>	<i>comp</i>	<i>comp</i>	<i>comp</i>	<i>inv</i>	<i>comp</i>	<i>inv</i>	<i>inv</i>	<i>inv</i>
Base Oil ²	GII	GII	GII	GII	GII	GII	GII	GII
Add Pack	A	A	A	A	A	A	A	A
Antioxidant A		0.5		0.5		1.0		1.0
Antioxidant B			0.5	0.5			1.0	1.0
F-S Spec	<i>F4</i>	<i>F4</i>	<i>F3</i>	<i>F3</i>	<i>F4</i>	<i>F4</i>	<i>F3</i>	<i>F3</i>
Hardness Δ	8	8	7	6	8	8	6	6
%Vol Δ	2	2	2	3	2	2	4	4
%Tensile Δ	11	6	8	2	6	5	3	2
%Elong Δ	-74	-79	-71	-76	-76	-76	-67	-67

1 – Examples 2-1 and 2-5 are repeats of the baselines which was re-tested for each set of samples at different treat levels. These examples provide good baseline comparisons while also showing the repeatability of the test.

20 2 – The base oil used in these examples is an API Group II base oil.

[0075] The results show that the inventive examples provide improved seal compatibility in Group II based formulations. However, as is evident from the results, here it is important to consider relative performance of the examples rather than just the pass fail result.

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[0076] While the invention has been explained, it is to be understood that various modifications thereof will become apparent to those skilled in the art upon reading the specification. Therefore, it is to be understood that the invention disclosed herein is intended to cover such modifications as fall within the scope of the appended claims.

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[0077] In this specification the terms "hydrocarbyl substituent" or "hydrocarbyl group," as used herein are used in their ordinary sense, which is well-known to those skilled in the art. Specifically, they refer to a group primarily composed of carbon and hydrogen atoms that is attached to the remainder of the molecule through a carbon atom and does not exclude the presence of other atoms or groups in a proportion insufficient to detract from the molecule having a predominantly hydrocarbon character. In general, no more than two, preferably no more than one, non-hydrocarbon substituent will be present for every ten carbon atoms in the hydrocarbyl group; typically, there will be no non-hydrocarbon substituents in the hydrocarbyl group. A more detailed definition of the terms "hydrocarbyl substituent" or "hydrocarbyl group," is described in US Patent 6,583,092.

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[0078] Each of the documents referred to above is incorporated herein by reference. Except in the Examples, or where otherwise explicitly indicated, all numerical quantities in this description specifying amounts of materials, reaction conditions, molecular weights, number of carbon atoms, and the like, are to be understood as modified by the word "about." Unless otherwise indicated, all percent and formulation values listed herein are on a weight basis. Unless otherwise indicated, each chemical or composition referred to herein should be interpreted as being a commercial grade material which may contain the isomers, by-products, derivatives, and other such materials which are normally understood to be present in the commercial grade. However, the amount of each chemical component is presented exclusive of any solvent or diluent, which may be customarily present in

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the commercial material, unless otherwise indicated. It is to be understood that the upper and lower amount, range, and ratio limits set forth herein may be independently combined. Similarly, the ranges and amounts for each element of the invention can be used together with ranges or amounts for any of the other elements.

- 5 As used herein, the expression "consisting essentially of" permits the inclusion of substances that do not materially affect the basic and novel characteristics of the composition under consideration.

What is claimed is:

1. An industrial lubricating composition comprising an oil of lubricating viscosity and an antioxidant component comprising: (i) a phenolic antioxidant, (ii)
5 an aminic antioxidant, or (iii) a combination thereof;
wherein the antioxidant component is present in the lubricating composition at 1.0 percent by weight or higher.
2. The composition of claim 1 wherein the phenolic antioxidant is present in the
10 lubricating composition from at least 0.5 percent by weight; and
wherein the aminic antioxidant is present in the lubricating composition from at least 0.5 percent by weight.
3. The composition of any of the claims 1 to 2 wherein the phenolic antioxidant
15 comprises a substituted phenol containing at least one alkyl substituent group.
4. The composition of any of the claims 1 to 3 wherein the aminic antioxidant comprises a diarylamine.
- 20 5. The composition of any of the claims 1 to 4 wherein the oil of lubricating viscosity comprises a mineral base oil.
6. The composition of any of the claims 1 to 4 wherein the oil of lubricating viscosity comprises a synthetic base oil.
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7. The composition of any of the claims 1 to 6 further comprising: an antiwear agent, an extreme pressure agent, a friction modifier, a corrosion inhibitor, a rust inhibitor, a metal deactivator, a borated dispersant, a non-borated dispersant, detergent, an antifoam, a viscosity index improver, a viscosity modifier, an
30 antioxidant, a pour point depressant, a seal swell agent, or any combination thereof.

8. A method of lubricating an industrial gear assembly comprising supplying to said assembly a lubricating composition comprising an oil of lubricating viscosity and an antioxidant component comprising: (i) a phenolic antioxidant, (ii) an aminic antioxidant, or (iii) a combination thereof;

5 wherein the antioxidant component is present in the lubricating composition at 1.0 percent by weight or higher.

9. The method of claim 8 wherein the phenolic antioxidant is present in the lubricating composition from at least 0.5 percent by weight; and

10 wherein the aminic antioxidant. antioxidant is present in the lubricating composition from at least 0.5 percent by weight.

10. The method of any of the claims 8 to 9 wherein the phenolic antioxidant comprises a substituted phenol containing at least one alkyl substituent group.

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11. The method of any of the claims 8 to 10 wherein the aminic antioxidant comprises a diarylamine.

12. The method of any of the claims 8 to 11 wherein the oil of lubricating viscosity comprises a mineral base oil.

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13. The method of any of the claims 8 to 11 wherein the oil of lubricating viscosity comprises a synthetic base oil.

25 14. The method of any of the claims 8 to 13 wherein the lubricating composition further comprising: an antiwear agent, an extreme pressure agent, a friction modifier, a corrosion inhibitor, a rust inhibitor, a metal deactivator, a borated dispersant, a non-borated dispersant, detergent, an antifoam, a viscosity index improver, a viscosity modifier, an additional antioxidant, a pour point depressant, a seal swell agent, or any combination thereof.

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15. A method of improving the seal compatibility of an industrial gear assembly lubricant comprising adding to said lubricant composition an antioxidant component comprising: (i) a phenolic antioxidant, (ii) an aminic antioxidant, or (iii) a combination thereof;

5 wherein the antioxidant component is present in the lubricant at 1.0 percent by weight or higher.

16. The use of an antioxidant component to improve the seal compatibility of an industrial gear assembly lubricant, wherein the antioxidant component comprises: (i)
10 a phenolic antioxidant, (ii) an aminic antioxidant, or (iii) a combination thereof;

 wherein the antioxidant component is present in the lubricant at 1.0 percent by weight or higher.