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(54) **VIBRATION RESISTANT INDUSTRIAL GEAR OILS**

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(57) **ABSTRACT**

The invention relates to industrial gear oil compositions that have been specially designed to be vibration resistant. That is the industrial gear oil compositions of the invention provide good performance and/or protection even when the equipment in which the composition is used is subjected to external vibration, including but not limited to vibration during transportation of the equipment. The industrial gear oil compositions include a combination of additives that provide surprisingly good protection against damage caused by vibration.

VIBRATION RESISTANT INDUSTRIAL GEAR OILS

[0001] The invention relates to industrial gear oil compositions that have been specially designed to be vibration resistant. That is the industrial gear oil compositions of the invention provide good performance and/or protection even when the equipment in which the composition is used is subjected to external vibration, including but not limited to vibration during transportation of the equipment. The industrial gear oil compositions include a combination of additives that provide surprisingly good protection against damage caused by vibration.

BACKGROUND OF THE INVENTION

[0002] Industrial gearboxes operating in a mill or plant environment are often subjected to vibratory stress, or vibration, originating from proximate or surrounding equipment. The sources of this vibration may be other nearby gearboxes, motors, pumps, etc. Also, industrial gearboxes may suffer from vibratory stress during transport. Backlash can also be a source of vibration for industrial gearboxes.

[0003] Many industrial gearboxes are not used in mobile equipment but rather are part of stationary devices. Such devices, including the industrial gearboxes present in the device, are generally not designed for mobility, nor the ability to withstand the forces, including vibration, that can occur with movement. However, nearly all of this equipment and/or its componentry must be transported at some point from it place of manufacture to the location where the equipment is be assembled and/or operated.

[0004] During this period of transportation, which can be length and involve railway and/or highway transport, the equipment, including the industrial gearboxes, are subjected to many forces and stresses including vibration. It is noted that this vibration is not caused by the operation of the industrial gearbox itself, rather it is external vibration which the industrial gearbox is often subjected to while it itself is in a non-operative state. That is the internal pieces of the industrial gearbox are not themselves moving, or at least are not moving per their normal operation.

[0005] Similarly, even after an industrial gearbox is installed, it is generally surrounded by other equipment that is often operating even when the industrial gearbox itself it not. This surrounding equipment can generate various forces and stresses that can act on the industrial gearbox, including vibration, like the forces described above experienced during transportation.

[0006] Thus unique environments are created, subjecting the industrial gearbox to forces and stresses, including this described external vibration, for which the industrial gearbox and the industrial gear oil composition inside the industrial gearbox, are not specifically designed. That is, industrial gearboxes and the industrial gear oil compositions inside them are generally designed with the operation and of the industrial gearbox in mind, the forces and stresses caused by that operation, and providing good protection and performance during such operation. The conditions and stresses experienced by industrial gear boxes during non-operational periods, including the vibration that can be experienced during transportation and/or from nearby operating equipment, are generally overlooked.

[0007] It has been discovered that such vibration, can cause significant wear and premature fatigue and/or failure in industrial gear boxes, even when a conventional industrial gear oil composition is present in the industrial gear boxes, and that this vibration-caused wear and premature fatigue can reduce the service life of the equipment and result in higher equipment maintenance costs and down time.

[0008] There is an ongoing need to develop industrial gear oil compositions that can not only provide acceptable performance and protection during the operation of an industrial gearbox, but also provide protection during non-operational periods where the industrial gearbox is subjected to external forces and stresses, including external vibration.

SUMMARY OF THE INVENTION

[0009] The invention provides industrial gear oil compositions designed to provide protection during non-operational periods where the industrial gearbox is subjected to external forces and stresses, including external vibration. These industrial gear oil compositions can also provide acceptable performance and protection during the operation of the industrial gearboxes in which they are used. The disclosed technology provides an industrial gear oil composition that includes an oil of lubricating viscosity, a phosphorus-containing compound, and a sulfurized fatty ester.

[0010] In some embodiments the phosphorus-containing compound is essentially free of, or even completely free of, phosphoric acid esters and/or amine salts thereof.

[0011] The invention provides for the described industrial gear oil composition where the oil of lubricating viscosity includes mineral and/or natural base oil. In some embodiments the oil of lubricating viscosity is essentially free of, or even completely free of, synthetic base oils.

[0012] The invention provides for the described industrial gear oil composition where the oil of lubricating viscosity includes synthetic base oil. In some embodiments the oil of lubricating viscosity is essentially free of, or even completely free of, mineral and/or natural base oils.

[0013] The invention provides for the described industrial gear oil composition where the phosphorus-containing compound includes an alkyl phosphite, a phosphoric acid ester, an amine salt of a phosphoric acid ester, or some combination thereof.

[0014] The invention further provides for the described industrial gear oil composition where the phosphorus-containing compound includes an alkyl phosphites or esters thereof.

[0015] The invention provides for the described industrial gear oil composition where the sulfurized fatty ester includes a sulfurized natural oil.

[0016] The invention provides for the described industrial gear oil composition where the sulfurized fatty ester includes a sulfurized rapeseed oil.

[0017] The invention provides for the described industrial gear oil composition where the sulfurized fatty ester further includes one or more additional additives. These additional additive may include sulfurized olefins (different than the sulfurized fatty ester), phosphoric acid esters, thiophosphates, thiophosphoric acid esters and/or amine salts thereof, thiadiazoles and/or substituted thiadiazole, tolyltriazoles and/or substituted triazoles, polyethers, alkenyl amines and/or polyolefin amide alkenamines, ester copolymers, carboxylic esters, dispersants, hydrocarbon polymers, or any combination thereof, including more than one of any of the additional additives.

[0018] In some embodiments these additional additives are free of antioxidants. In some embodiments these additional additives are free of fatty amines. In some embodiments these additional additives are free of high total base number over-based detergents. In some embodiments these additional additives are free of zinc dithiophosphates.

[0019] The invention further provides for the described industrial gear oil composition where the weight ratio of the phosphorus-containing compound to the sulfurized fatty ester in the industrial gear oil composition is from 1:10 to 10:1. In other embodiments the weight ratio is from 1:1 to 1:10, or from 1:5 to 5:1, or 1:1 to 1:5, or from 1:1 to 1:3, or even about 1:2.

[0020] The invention further provides for the described industrial gear oil composition where the weight the phosphorus-containing compound is present from 0.1 to 10 percent by weight of the overall industrial gear oil composition and the sulfurized fatty ester is present from 0.1 to 20 percent by weight of the overall industrial gear oil composition.

[0021] The invention further provides a process of making an industrial gear oil composition that includes the step of: (1) mixing (a) an oil of lubricating viscosity, (b) a phosphorus-containing compound, and (c) a sulfurized fatty ester, resulting in an industrial gear oil composition. The process can be used to prepare any of the industrial gear oil compositions described herein.

[0022] The invention further provides a method of improving the vibration resistance of an industrial gear oil composition that includes the step of: (1) adding to an industrial gear oil composition, which comprises (a) an oil of lubricating viscosity, (b) a phosphorus-containing compound, and (c) a sulfurized fatty ester, resulting in an industrial gear oil composition with improved vibration resistance. The method can utilize any of the industrial gear oil compositions described herein.

[0023] The invention further provides a use of an additive package to improve the vibration resistance of an industrial gear oil composition where the industrial gear oil composition includes (a) an oil of lubricating viscosity, and where the additive package includes (b) a phosphorus-containing compound and (c) a sulfurized fatty ester. The use can utilize any of the industrial gear oil compositions described herein.

DETAILED DESCRIPTION OF THE INVENTION

[0024] Various preferred features and embodiments will be described below by way of non-limiting illustration.

[0025] The invention provides an industrial gear oil composition that includes: (a) an oil of lubricating viscosity; (b) a phosphorus-containing compound; and (c) a sulfurized fatty ester.

The Oil of Lubricating Viscosity

[0026] The compositions of the invention include an oil of lubricating viscosity.

[0027] The oil of lubricating viscosity can be present in a major amount, for a lubricant composition, or in a concentrate forming amount, for a concentrate and/or additive composition. The industrial gear oil compositions of the invention may be either lubricant compositions or concentrate and/or additive compositions.

[0028] 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 98 percent by weight, and often greater than 80 percent by weight of the overall composition.

[0029] The oil of lubricating viscosity may include natural and synthetic oils, oil derived from hydrocracking, hydrogenation, and hydrofinishing, unrefined, refined and re-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, secondary distillation, acid or base extraction, filtration, percolation and similar processes. Re-refined oils are also known as reclaimed or reprocessed oils, and are obtained by processes similar to those used to obtain refined oils. Re-refined oils are often are processed by techniques directed to removal of spent additives and oil breakdown products.

[0030] Natural oils useful as the oil of lubricating viscosity include animal oils and 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.

[0031] 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. In some embodiments the oil of lubricating viscosity used in the invention is a synthetic oil that includes polymerized polyisobutylene, and in some embodiments the oil of lubricating viscosity used in the invention is a synthetic oil that includes polymerized polyisobutylene and a polyalphaolefin.

[0032] 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 includes 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.

[0033] 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 percent by weight, and/or <90 percent by weight saturates, viscosity index 80-120); Group II (sulfur content ≤0.03 percent by weight and ≥90 percent by weight saturates, viscosity index 80-120); Group III (sulfur content ≤0.03 percent by weight and ≥90 percent by weight saturates, viscosity index ≥120); Group IV (all polyalphaolefins, or PAO, such as PAO-2, PAO-

4, PAO-5, PAO-6, PAO-7 or PAO-8); and Group V (which encompasses "all others"). 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.

[0034] In some embodiments the lubricating oil component of the present invention includes a Group II or Group III base oil, or a combination thereof. 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.

[0035] The compositions of the present invention may include some amount of Group I base oils, and even Group IV and Group V base oils. 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 98 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.

[0036] 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.

[0037] In some embodiments the invention provides a Group II composition, that is the oil of lubricating viscosity includes Group II oil, and can even be primarily if not exclusively Group II oil.

[0038] The various described oils of lubricating viscosity may be used alone or in combinations. The oil of lubricating viscosity may be used in the described industrial gear lubricant compositions in the range of about 40 percent by weight to about 99.6 percent by weight, or from a minimum of 49.8, 70, 85, 93, 93.5 or even 97 up to a maximum of 99.6, 98.8, 98.3 or even 96.8 percent by weight. In other embodiments the oil of lubricating viscosity may be used from a minimum of 40, 65, 73, 73.5, or even 81 up to a maximum of 99.6, 99.5, 98.6, 94.1, 88.3, or even 80.8 percent by weight.

The Phosphorus-Containing Compound

[0039] The compositions of the invention include a phosphorus containing compound.

[0040] The phosphorus containing compound can include a hydrocarbyl phosphite, a phosphoric acid ester, an amine salt of a phosphoric acid ester, or any combination thereof. In some embodiments the phosphorus containing compound includes a hydrocarbyl phosphite, an ester thereof, or a combination thereof. In some embodiments the phosphorus containing compound includes a hydrocarbyl phosphite.

[0041] In some embodiments the hydrocarbyl phosphite is an alkyl phosphite. By alkyl it is meant an alkyl group containing only carbon and hydrogen atoms, however either saturated or unsaturated alkyl groups are contemplated, or even mixtures thereof. In some embodiments the phosphorus containing compound includes an alkyl phosphite that has a fully saturated alkyl group. In some embodiments the phosphorus containing compound includes an alkyl phosphite that has an alkyl group with some unsaturation, for example, one double bond between carbon atoms. Such unsaturated alkyl groups may also be referred to as alkenyl groups, but are included within the term "alkyl group" as used herein unless otherwise noted.

[0042] In some embodiments the phosphorus containing compound includes an alkyl phosphite, a phosphoric acid ester, an amine salt of a phosphoric acid ester, or any combination thereof. In some embodiments the phosphorus containing compound includes an alkyl phosphite, an ester thereof, or a combination thereof. In some embodiments the phosphorus containing compound includes an alkyl phosphite.

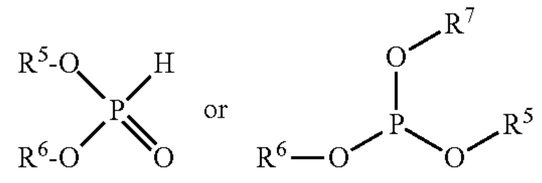
[0043] In some embodiments the phosphorus containing compound includes an alkenyl phosphite, a phosphoric acid ester, an amine salt of a phosphoric acid ester, or any combination thereof. In some embodiments the phosphorus containing compound includes an alkenyl phosphite, an ester thereof, or a combination thereof. In some embodiments the phosphorus containing compound includes an alkenyl phosphite.

[0044] In some embodiments the phosphorus containing compound includes dialkyl hydrogen phosphites.

[0045] In some embodiments the phosphorus-containing compound is essentially free of, or even completely free of, phosphoric acid esters and/or amine salts thereof.

[0046] In some embodiments the phosphorus-containing compound may be described as a fatty phosphite. Suitable phosphites include those having at least one hydrocarbyl group with 4 or more, or 8 or more, or 12 or more, carbon atoms. Typical ranges for the number of carbon atoms on the hydrocarbyl group include 8 to 30, or 10 to 24, or 12 to 22, or 14 to 20, or 16 to 18. The phosphite may be a mono-hydrocarbyl substituted phosphite, a di-hydrocarbyl substituted phosphite, or a tri-hydrocarbyl substituted phosphite. In one embodiment the phosphite is sulphur-free i.e., the phosphite is not a thiophosphite.

[0047] The phosphite having at least one hydrocarbyl group with 4 or more carbon atoms may be represented by the formulae:



wherein at least one of R^5, R^6 and R^7 may be a hydrocarbyl group containing at least 4 carbon atoms and the other may be hydrogen or a hydrocarbyl group. In one embodiment R^5, R^6 and R^7 are all hydrocarbyl groups. The hydrocarbyl groups may be alkyl, cycloalkyl, aryl, acyclic or mixtures thereof. In the formula with all three groups R^5, R^6 and R^7, the compound may be a tri-hydrocarbyl substituted phosphite i.e., R^5, R^6 and R^7 are all hydrocarbyl groups and in some embodiments may be alkyl groups

[0048] The alkyl groups may be linear or branched, typically linear, and saturated or unsaturated, typically saturated. Examples of alkyl groups for R^5, R^6 and R^7 include octyl, 2-ethylhexyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tet-

radecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, octadecenyl, nonadecyl, eicosyl or mixtures thereof.

[0049] In some embodiments the fatty phosphite component of the invention, and/or the composition overall is essentially free of, or even completely free of phosphoric acid ester and/or amine salts thereof.

[0050] In some embodiments the fatty phosphite comprises an alkenyl phosphite or esters thereof, for example esters of dimethyl hydrogen phosphite. The dimethyl hydrogen phosphite may be esterified, and in some embodiments transesterified, by reaction with an alcohol, for example oleyl alcohol.

[0051] The fatty phosphite may be present in the overall industrial gear lubricant composition from 0.3 to 10 percent by weight, or in other embodiments from a minimum level of 0.3, 0.7, or even 1.2 up to a maximum level of 10, 5, 2.5, 2.0, 1.7, 1.5, or even 1.2 percent by weight.

The Sulfurized Fatty Ester

[0052] The compositions of the invention include a sulfurized fatty ester.

[0053] These sulfurized fatty esters may include mixtures of sulfurized fatty esters with sulfurized olefins and/or polysulfides. The sulfurized olefins and polysulfides may be derived from isobutylene, butylene, propylene, ethylene, or some combination thereof. In some examples the sulfurized fatty ester is a sulfurized olefin derived from any of the natural oils or synthetic oils described above, or even some combination thereof. For example the sulfurized fatty ester may be derived from vegetable oil.

[0054] Examples of suitable sulfurized fatty esters include sulfurized animal or vegetable fat and/or oil such as beef tallow, lard, fish oil, rapeseed oil, or soybean oil. Additional examples include sulfurized unsaturated fatty acid esters, where the esters are obtained by reacting an unsaturated fatty acid with one or more various alcohols. Examples of useful unsaturated fatty acids on which the sulfurized fatty esters described may be based include oleic acid, linoleic acid, and fatty acids extracted from the above-described animal or vegetable fat and oil. Specific examples of useful sulfurized fatty esters include sulfurized methyl oleate, sulfurized rice bran fatty acid octyl, sulfurized rapeseed oil, and a mixture thereof.

[0055] In some embodiments the sulfurized fatty ester includes a sulfurized natural oil. In some embodiments the sulfurized fatty ester includes a sulfurized animal and/or vegetable oil. In some embodiments the sulfurized fatty ester includes a sulfurized vegetable oil. In some embodiments the sulfurized fatty ester includes a sulfurized unsaturated oil. In some embodiments the sulfurized fatty ester includes a sulfurized unsaturated natural oil. In some embodiments the sulfurized fatty ester includes a sulfurized unsaturated vegetable oil.

[0056] In some embodiments the sulfurized fatty ester described above further includes one or more sulfurized olefins and/or polysulfides.

[0057] In some embodiments the sulfurized fatty ester includes a sulfurized rapeseed oil.

Additional Additives

[0058] The compositions of the invention may further include one or more additional additives, for example the composition of the invention may include an industrial gear additive package. In other words, the compositions of the invention are designed to be industrial gear lubricants, or additive packages for making the same. The present invention does not relate to automotive gear lubricants or other lubricating compositions.

[0059] Any combination of conventional additive packages designed for industrial gear application may be used. The invention inherently assumes such additive packages are essentially free of the phosphorus containing compounds and sulfurized fatty esters described above, or at least do not contain the type of the phosphorus containing compounds and sulfurized fatty esters specified by the particular embodiment of the invention.

[0060] The additional additives which may be present in the industrial gear oil compositions of the invention include: a demulsifier, a pour point depressant, an antioxidant, a dispersant, a metal deactivator (such as a copper deactivator), an antiwear agent, an extreme pressure agent, a viscosity modifier, or some mixture thereof. In some embodiments the additives may each be present in the range from 50, 75, 100 or even 150 ppm up to 5, 4, 3, 2 or even 1.5 percent by weight, or from 75 ppm to 0.5 percent by weight, from 100 ppm to 0.4 percent by weight, or from 150 ppm to 0.3 percent by weight, where the percent by weight values are with regards to the overall lubricating oil composition. However it is noted that some additives, including viscosity modifying polymers, which may alternatively be considered 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. Each of the described additional additives may be used alone or as mixtures thereof.

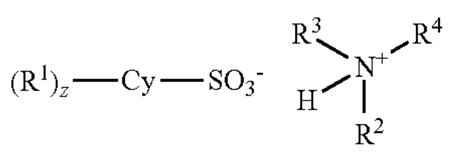
[0061] Antifoams, also known as foam inhibitors, are known in the art and include but are not limited to organic silicones and non-silicon foam inhibitors. Examples of organic silicones include dimethyl silicone and polysiloxanes. Examples of non-silicon foam inhibitors include but are not limited to 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 or 0.004 pbw or even 0.001 to 0.003 pbw.

[0062] 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 include polyethylene glycols, polyethylene oxides, polypropylene oxides, (ethylene oxide-propylene oxide) polymers and mixtures thereof. In some embodiments the demulsifiers are polyethers. Demulsifiers may be present in the composition from 0.002 to 0.2 pbw.

[0063] 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.

[0064] The compositions of the invention may also include a rust inhibitor, other than some of the additives described above. Suitable rust inhibitors include 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, monothio phosphate salts or esters, or any combination thereof; or mixtures thereof. Examples of hydrocarbyl amine salts of dialkyldithiophosphoric acid of the invention include but are not limited to those described above, as well as the reaction product(s) of diheptyl or dioctyl or dinonyl dithiophosphoric acids with ethylenediamine, morpholine or Primene™ 81R or mixtures thereof. Suitable hydrocarbyl amine salts of hydrocarbyl arenesulphonic acids used in the rust inhibitor package of the invention are represented by the formula:



(V)

wherein Cy is a benzene or naphthalene ring. R^1 is a hydrocarbyl group with about 4 to about 30, preferably about 6 to about 25, more preferably about 8 to about 20 carbon atoms. z is independently 1, 2, 3, or 4 and most preferably z is 1 or 2. R^2, R^3 and R^4 are the same as described above. Examples of hydrocarbyl amine salts of hydrocarbyl arenesulphonic acid of the invention include but are not limited to the ethylenediamine salt of dinonylnaphthalene sulfonic acid. 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. The rust inhibitors may be present in the range from 0.02 to 0.2, from 0.03 to 0.15, from 0.04 to 0.12, or from 0.05 to 0.1 percent by weight of the lubricating oil composition. The rust inhibitors of the invention may be used alone or in mixtures thereof.

[0065] The 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, tolyltriazoles, a thiadiazole, or combinations thereof, as well as derivatives thereof. Examples include derivatives of benzotriazoles other than those described above, 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. 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. The metal deactivators may be present in the range from 0.001 to 0.5, 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.

[0066] Antioxidants may also be present including (i) an alkylated diphenylamine, and (ii) a substituted hydrocarbyl mono-sulfide. In some embodiments the alkylated diphenylamines of the invention are bis-nonylated diphenylamine and bis-octylated diphenylamine. 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. The antioxidant package may also include sterically hindered phenols. Examples of suitable hydrocarbyl groups for the sterically hindered phenols include but are not limited to 2-ethylhexyl or n-butyl ester, dodecyl or mixtures thereof. Examples of methylene-bridged sterically hindered phenols include but are not limited to 4,4'-methylene-bis(6-tert-butyl o-cresol), 4,4'-methylene-bis(2-tert-amyl-o-cresol), 2,2'-methylene-bis(4-methyl-6-tert-butylphenol), 4,4'-methylene-bis(2,6-di-tertbutylphenol) or mixtures thereof.

[0067] In some embodiments the additional additives present include a nitrogen-containing dispersant, for example a hydrocarbyl substituted nitrogen containing additive. Suitable hydrocarbyl substituted nitrogen containing additives include ashless dispersants and polymeric dispersants. Ashless dispersants are so-named because, as supplied, they do not contain metal and thus do not normally contribute to sulfated ash when added to a lubricant. However they may, of course, interact with ambient metals once they are added to a lubricant which includes metal-containing species. Ashless dispersants are characterized by a polar group attached to a relatively high molecular weight hydrocarbon chain. Examples of such materials include succinimide dispersants, Mannich dispersants, and borated derivatives thereof.

[0068] In some embodiments the additional additives present include a sulfur-containing compound other than the sulfurized fatty ester described above. Such sulfur-containing compounds may include sulfurized olefins and polysulfides. The sulfurized olefin or polysulfides may be derived from isobutylene, butylene, propylene, ethylene, or some combination thereof.

[0069] In some embodiments the additional additives present include one or more phosphorous amine salts (different from the phosphorous containing compound described above), but in amounts such that the resulting industrial gear lubricant compositions, contains no more than 1.0 percent by weight of such materials, or even no more than 0.75 or 0.6 percent by weight. In other embodiments the resulting industrial gear lubricant compositions, are essentially free of or even completely free of such phosphorous amine salts.

[0070] In some embodiments the additional additive component includes one or more antiwear additives and/or extreme pressure agents, one or more rust and/or corrosion inhibitors, one or more foam inhibitors, one or more demulsifiers, or any combination thereof. In other embodiments the additional additives, and/or the resulting industrial gear lubricant compositions, are essentially free of or even completely free of phosphorous amine salts, dispersants, or both.

[0071] In some embodiments the additional additives, and/or the resulting industrial gear lubricant compositions, include a demulsifier, a corrosion inhibitor, a friction modifier, or combination of two or more thereof. In some embodiments the corrosion inhibitor includes a tolyltriazole. In still other embodiments the additional additive component, and/or the resulting industrial gear lubricant compositions, include one or more sulfurized olefins or polysulfides; one or more phosphorus amine salts; one or more thiophosphate esters, one or more thiadiazoles, tolyltriazoles, polyethers, and/or

alkenyl amines; one or more ester copolymers; one or more carboxylic esters; one or more succinimide dispersants, or any combination thereof.

[0072] In some embodiments the compositions of the invention further include (d), one or more additional additives, that may include one or more sulfurized olefins, phosphoric acid esters, thiophosphates, thiophosphoric acid esters and/or amine salts thereof, thiadiazoles and/or substituted thiadiazole, tolyltriazoles and/or substituted triazoles, polyethers, alkyl and/or alkenyl amines and/or polyolefin amide alkenamines, ester copolymers, carboxylic esters, dispersants, hydrocarbon polymers, or any combination thereof.

[0073] Dispersants suitable for use in the compositions of the invention are not overly limited and may include borated dispersants, non-borated dispersants, succinimide dispersants (including borated and non-borated succinimide dispersants), Mannich dispersants, and the like.

[0074] In some embodiments the compositions of the invention are free of antioxidants. In some embodiments the compositions of the invention are free of fatty amines. In some embodiments the compositions of the invention are free of high TBN overbased detergents (where high TBN can mean having a TBN of >100, >50, >20 or even >10). In some embodiments the compositions of the invention are free of zinc dithiophosphates.

INDUSTRIAL APPLICATION

[0075] As noted above the invention includes both industrial gear lubricant compositions and industrial gear additive concentrate compositions that may be used to make industrial gear lubricant compositions.

[0076] In the industrial gear lubricants of the invention: component (a), the oil of lubricating viscosity, may be present from 49.8 to 99.6, or from 70 to 99.6, or from 85 to 99.6, or from 93 to 99.6, or from 93 to 98.8, or from 93.5 to 98.3 or even at about 96.8 percent by weight; component (b), the phosphorus containing compound, may be present from 0.3 to 10, or from 0.3 to 5, or from 0.3 to 2, or from 0.7 to 2, or from 0.7 to 1.5, or even at about 1.2 percent by weight; and component (c), the sulfurized fatty ester, may be present from 0.1 to 20, or from 0.1 to 10, or from 0.1 to 5, or from 0.5 to 5, or from 1 to 5, or from 1 to 4, or from 1 to 3, or even about 2 percent by weight.

[0077] In other embodiments of the invention, when one or more additional additives are present, component (a), the oil of lubricating viscosity, may be present from 40 to 99.6, or from 40 to 99.5, or from 65 to 99.5, or from 73 to 98.6, or from 73 to 94.1, or from 73 to 94.1, or from 73.5 to 88.3, or even at about 80.8 percent by weight; component (b), the phosphorus containing compound, may be present from 0.3 to 10, or from 0.3 to 5, or from 0.3 to 2, or from 0.7 to 2, or from 0.7 to 1.5, or even at about 1.2 percent by weight; component (c), the sulfurized fatty ester, may be present from 0.1 to 20, or from 0.1 to 10, or from 0.1 to 5, or from 0.5 to 5, or from 1 to 5, or from 1 to 4, or from 1 to 3, or even about 2 percent by weight; and component (d), the one or more additional additives, may be present from 0 or 0.1 to 50, or from 0 or 0.1 to 30, or from 0.1 to 20, or from 1 to 20, or from 5 to 20, or from 10 to 20, or even about 16 percent by weight.

[0078] The various ranges for the components described above can be applied to concentrate compositions by maintain the same relative ratios between components (b), (c), and (d) when present, while adjustment the amount of (a), (that is the amount of (a) will be much lower in a concentrate composition compared to a lubricant composition). In such embodiments the percent by weight values for components (b), (c), and (d) when present may be treated as parts by weight (pbw), with oil making up the balance of the concentrate composition, including anywhere from 0 or 0.1 or 0.5 or even 1 pbw up to 10, 20, 30 or even 40 or 50 pbw.

[0079] In the compositions of the invention it may be useful in some embodiments to specify the weight ratio of component (b), the phosphorus containing compound relative to component (c), the sulfurized fatty ester. In some embodiments the weight ratio of component (b) to component (c) is from 1:10 to 10:1, or from 1:1 to 1:10, or from 1:5 to 5:1, or from 1:1 to 5:1, or from 1:1 to 1:3, or from 1:1 to 1:2, or even about 3:5. These ratios may apply to the industrial gear lubricant compositions of the invention and/or to the industrial gear additive concentrate compositions of the invention.

[0080] The invention includes methods of making the industrial gear lubricant compositions and/or the industrial gear additive concentrate compositions described above. Such methods include mixing the described components together. No particular order or means of addition is believed to significantly impact the results.

[0081] The invention also includes a method of improving the vibration resistance of an industrial gearbox and/or the industrial gear oil lubricant composition used in such an industrial gearbox. The method includes the step of: (1) adding to an industrial gear oil composition, which includes (a) the oil of lubricating viscosity, the following components: (b) the phosphorus-containing compound; and (c) the sulfurized fatty ester; resulting in an industrial gear oil composition with improved vibration resistance.

[0082] The method may also involve the addition of one of the industrial gear lubricants described herein to an industrial gearbox, where the gearbox is then subjected to external vibration, resulting in an industrial gearbox with improved protection and/or resistance from any damage and/or wear caused by such external vibration, relative to the same industrial gearbox being subjected to the same external vibration where the industrial gearbox contains an industrial gear lubricant that does not contain the specified combination of additives described above.

[0083] The amount of each chemical component described is presented exclusive of any solvent or diluent oil, which may be customarily present in the commercial material, that is, on an active chemical basis, unless otherwise indicated. However, 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.

[0084] As used herein, the term "hydrocarbyl substituent" or "hydrocarbyl group" is used in its ordinary sense, which is well-known to those skilled in the art. Specifically, it refers to a group having a carbon atom directly attached to the remainder of the molecule and having predominantly hydrocarbon character. Examples of hydrocarbyl groups include:

[0085] hydrocarbon substituents, that is, aliphatic (e.g., alkyl or alkenyl), alicyclic (e.g., cycloalkyl, cycloalkenyl) substituents, and aromatic-, aliphatic-, and alicyclic-substituted aromatic substituents, as well as cyclic substituents wherein the ring is completed through another portion of the molecule (e.g., two substituents together form a ring);

[0086] substituted hydrocarbon substituents, that is, substituents containing non-hydrocarbon groups which, in the context of this invention, do not alter the predominantly hydrocarbon nature of the substituent (e.g., halo (especially chloro and fluoro), hydroxy, alkoxy, mercapto, alkylmercapto, nitro, nitroso, and sulfoxy);

[0087] hetero substituents, that is, substituents which, while having a predominantly hydrocarbon character, in the context of this invention, contain other than carbon in a ring or chain otherwise composed of carbon atoms and encompass substituents as pyridyl, furyl, thienyl and imidazolyl. Heteroatoms include sulfur, oxygen, and nitrogen. In general, no more than two, or no more than one, non-hydrocarbon substituent will be present for every ten carbon atoms in the hydrocarbyl group; alternatively, there may be no non-hydrocarbon substituents in the hydrocarbyl group.

[0088] It is known that some of the materials described above may interact in the final formulation, so that the components of the final formulation may be different from those that are initially added. For instance, metal ions (of, e.g., a detergent) can migrate to other acidic or anionic sites of other molecules. The products formed thereby, including the products formed upon employing the composition of the present invention in its intended use, may not be susceptible of easy description. Nevertheless, all such modifications and reaction products are included within the scope of the present invention; the present invention encompasses the composition prepared by admixing the components described above.

[0089] The invention may be better understood with reference to the following non-limiting examples.

EXAMPLES

[0090] A set of examples is prepared and tested in order to demonstrate the benefits of the invention.

Comparative Example 1

[0091] A reference example is prepared by mixing 1.75 percent by weight of an industrial gear oil additive package (Additive Package A) into a Group I ISO 220 base oil. The Additive Package A includes an extreme pressure agent, an combination of antiwear agents, a rust inhibitor, a metal deactivator, a antifoam agent, a demulsifier, a copper deactivator, and some diluent oil, where the extreme pressure agent includes a phosphoric acid ester and/or amine salt thereof.

Comparative Example 2

[0092] A baseline example is prepared by mixing 2.0 percent by weight of an industrial gear oil additive package (Additive Package B) into a Group II ISO 220 base oil. The Additive Package B is similar to Additive Package A except it is free of the phosphoric acid ester and/or amine salt thereof extreme pressure agent present in Additive Package A.

Comparative Example 3

[0093] A comparative example is prepared by taking a portion of Comparative Example 2 and adding 4 percent by weight of a sulfurized fatty ester, in this example a sulfurized rapeseed oil.

Comparative Example 4

[0094] A comparative example is prepared by taking a portion of Comparative Example 2 and adding 2 percent by weight of alkyl phosphite, in this example a transesterified dimethyl hydrogen phosphite.

Inventive Example 5

[0095] An inventive example is prepared by taking a portion of Comparative Example 2 and adding 2 percent by weight of a sulfurized fatty ester, in this example a sulfurized rapeseed oil, and 1 percent by weight of alkyl phopshite, in this example a transesterified dimethyl hydrogen phosphite.

[0096] The formulations of these examples are summarized in the table below:

TABLE 1

Example Formulations:

	Example				
	Comp Ex 1	Comp Ex 2	Comp Ex 3	Comp Ex 4	Inv Ex 5
Group I ISO 220	98.3				
Group II ISO 220		98.0	94.0	97.0	95.0
Additive Package A	1.5				
Additive Package B		1.8	1.5	1.8	1.8
Alkyl Phosphite	0.2	0.2	0.2	1.2	1.2
Sulfurized Fatty Ester			4.0		2.0

[0097] These formulations are tested in a laboratory testing rig set-up to mimic the types of vibration industrial gears would experience in the field. The gearbox used for testing employed a small single reduction helical gear set, with each run using a new set of gears and gearbox. For each test, the gearbox was subjected to a constant high load and a constant low speed for a fixed duration, with a first test run with no vibration and then a second test run with vibration. Vibration was applied by use of a shaker attached to the shaft of the gear box and a vibration sensor placed on the gearbox was used to monitor the vibration delivered. The shaker was adjusted for each test to be harmonic with the gear mesh frequency of the test part. No temperature controls were used for the testing. After each test the gears were measured for wear by measuring the form error (that is the distance in micrometers between a given point on the tooth and the calculated means profile line) on each tooth using a PECO ND-300 profilometer. Six measurements were taken on each pinion gear tooth flank, with three traces in the profile direction (a "up and down" trace), and with three traces in the helix direction (a "right to left" trace). All 17 pinion teeth were measured for each test, giving 102 measurements per pinion.

[0098] Comparative Example 1 was tested in the laboratory rig described above to demonstrate the laboratory rig's ability to differentiate formulation performance relative to the presence of vibration. A summary of the form error measurements from this testing is provided below, where a lower form error value indicates less wear. The helix measurement average is the overall average of all the helix measurements, including all three traces taken on each gear tooth. The profile measurement average is the overall average of all the profile measurements, including all three traces taken on each gear tooth.

TABLE 2

Summary of Results for Comparative Example 1

	Comp Example 1 Without Vibration	Comp Example 1 With Vibration
Helix Measurement Avg	4.04	6.08
Profile Measurement Avg	3.35	3.54

[0099] The results show that the test procedure shows the impact of vibration on both the helix and profile of the tested gears. The test results showed higher form error values, and so higher wear when vibration was applied, especially on the helix measurements. These results show the describe test method is a useful indicator of industrial gear oil performance when subjected to external forces like vibration.

[0100] With the value of the test method established, Comparative Examples 2, 3, and 4, and Inventive Example 5 are also tested using the procedure described above. A summary of the form error measurements (in μm) from this testing is provided below, where a lower form error value indicates less wear. The helix measurement average is the overall average of all the helix measurements, including all three traces taken on each gear tooth. The helix trace 1 average is the average of the all the helix measurements taken in trace 1, where trace 1 is the closest to the gear tooth root (and therefore sees higher stress). The helix trace 2 average is the average of the all the helix measurements taken in trace 2, where trace 2 is the second closest to the gear tooth root, or the middle trace. The helix trace 3 average is the average of the all the helix measurements taken in trace 3, where trace 3 is the furthest from the gear tooth root (and so should see the lowest stress levels).

TABLE 3

Summary of Results

	Comp Example 2	Comp Example 3	Comp Example 4	Inventive Example 5
Helix Measurement Avg	4.45	4.88	4.95	3.72
Helix Trace 1 Avg	6.62	7.18	6.79	4.06
Helix Trace 2 Avg	3.82	3.75	3.91	3.36
Helix Trace 3 Avg	2.92	3.99	4.21	3.74

[0101] The results show that the inventive example provides better wear performance, and thus better vibration resistance, than the comparative examples. Comparative Example 2 is an industrial gear oil but does not contain either of the additives that provide the synergistic combination this invention focuses on. Comparative Example 3 contains a sulfurized fatty ester, but does not contain the phosphorous compound of the invention. Comparative Example 4 contains the phosphorous compound, but does not contain the sulfurized fatty ester. Only Inventive Example 5 contains the combination of the described phosphorous compound and a sulfurized fatty ester, and through this additive combination provides the best wear performance, and so the best vibration resistance in the testing. It is noted that the phosphorous compound and sulfurized fatty ester used in Inventive Example 5 are present in a total amount of 3 percent by weight, less than the 4 percent by weight of sulfurized fatty ester used in Comparative Example 3, showing the effects achieved by the invention are not merely due to higher treat rates, but are instead due to a synergy between the additives.

[0102] Each of the documents referred to above is incorporated herein by reference, including any prior applications, whether or not specifically listed above, from which priority is claimed. The mention of any document is not an admission that such document qualifies as prior art or constitutes the general knowledge of the skilled person in any jurisdiction. 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." 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.

[0103] As used herein, the transitional term "comprising," which is synonymous with "including," "containing," or "characterized by," is inclusive or open-ended and does not exclude additional, un-recited elements or method steps. However, in each recitation of "comprising" herein, it is intended that the term also encompass, as alternative embodiments, the phrases "consisting essentially of" and "consisting of," where "consisting of" excludes any element or step not specified and "consisting essentially of" permits the inclusion of additional un-recited elements or steps that do not materially affect the basic and novel characteristics of the composition or method under consideration.

[0104] While certain representative embodiments and details have been shown for the purpose of illustrating the subject invention, it will be apparent to those skilled in this art that various changes and modifications can be made therein without departing from the scope of the subject invention. In this regard, the scope of the invention is to be limited only by the following claims.

1. An industrial gear oil composition comprising:
(a) an oil of lubricating viscosity;
(b) a phosphorus-containing compound; and
(c) a sulfurized fatty ester.

2. The industrial gear oil composition of claim **1** wherein the oil of lubricating viscosity comprises a mineral base oil.

3. The industrial gear oil composition of claim **1** wherein the oil of lubricating viscosity comprises a synthetic base oil.

4. The industrial gear oil composition of claim **1**, wherein the phosphorus-containing compound comprises an alkyl phosphite, a phosphoric acid ester, an amine salt of a phosphoric acid ester, or some combination thereof.

5. The industrial gear oil composition of claim **1**, wherein the phosphorus-containing compound comprises alkyl phosphites or esters thereof.

6. The industrial gear oil composition of claim **1**, wherein the sulfurized fatty ester comprises a sulfurized natural oil.

7. The industrial gear oil composition of claim **1**, wherein the sulfurized fatty ester comprises a sulfurized rapeseed oil.

8. The industrial gear oil composition of claim **1**, wherein the composition further comprises (d), one or more additional additives;

wherein component (d) comprises one or more sulfurized olefins, phosphoric acid esters, thiophosphates, thiophosphoric acid esters and/or amine salts thereof, thiadiazoles and/or substituted thiadiazole, tolyltriazoles and/or substituted triazoles, polyethers, alkenyl amines and/or polyolefin amide alkenamines, ester copolymers,

carboxylic esters, dispersants, anitfoams, hydrocarbon polymers, a sulfurized fatty ester, and or any combination thereof.

9. The industrial gear oil composition of claim **1**, wherein the weight ratio of component (b) to component (c) in the industrial gear oil composition is from 1:10 to 10:1.

10. The industrial gear oil composition of claim **1**, wherein component (b) is present from 0.1 to 10 percent by weight of the overall industrial gear oil composition; and

wherein component (c) is present from 0.1 to 20 percent by weight of the overall industrial gear oil composition.

11. A process of making an industrial gear oil composition comprising the step of: (1) mixing the following components:

(a) an oil of lubricating viscosity;

(b) a phosphorus-containing compound; and

(c) a sulfurized fatty ester;

resulting in an industrial gear oil composition.

12. The process of claim **11** wherein the oil of lubricating viscosity comprises a mineral base oil, a synthetic base oil, or a combination thereof;

wherein the phosphorus-containing compound comprises an alkyl phosphite, a phosphoric acid ester, an amine salt of a phosphoric acid ester, or some combination thereof;

wherein the sulfurized fatty ester comprises a sulfurized natural oil; and

wherein step (1) optionally further comprises mixing (d), one or more additional additives into the industrial gear oil composition;

wherein component (d) comprises one or more sulfurized olefins, phosphoric acid esters, thiophosphates, thiophosphoric acid esters and/or amine salts thereof, thiadiazoles and/or substituted thiadiazole, tolyltriazoles and/or substituted triazoles, polyethers, alkenyl amines and/or polyolefin amide alkenamines, ester copolymers, carboxylic esters, dispersants, anitfoams, hydrocarbon polymers, a sulfurized fatty ester, and or any combination thereof.

13. A method of improving the vibration resistance of an industrial gear oil composition comprising the step of: (1) adding to an industrial gear oil composition, which comprises (a) an oil of lubricating viscosity, the following components:

(b) a phosphorus-containing compound; and

(c) a sulfurized fatty ester;

resulting in an industrial gear oil composition with improved vibration resistance.

14. The method of claim **13** wherein the oil of lubricating viscosity comprises a mineral base oil, a synthetic base oil, or a combination thereof;

wherein the phosphorus-containing compound comprises an alkyl phosphite, a phosphoric acid ester, an amine salt of a phosphoric acid ester, or some combination thereof;

wherein the sulfurized fatty ester comprises a sulfurized natural oil; and

wherein step (1) optionally further comprises mixing (d), one or more additional additives into the industrial gear oil composition;

wherein component (d) comprises one or more sulfurized olefins, phosphoric acid esters, thiophosphates, thiophosphoric acid esters and/or amine salts thereof, thiadiazoles and/or substituted thiadiazole, tolyltriazoles and/or substituted triazoles, polyethers, alkenyl amines and/or polyolefin amide alkenamines, ester copolymers, carboxylic esters, dispersants, anitfoams, hydrocarbon polymers, a sulfurized fatty ester, and or any combination thereof.

15. (canceled)

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