

TITLE

Alkylphenol Detergents

BACKGROUND OF THE INVENTION

5 **[0001]** The disclosed technology relates to hydrocarbyl- (e.g. alkyl-) phenol detergents and their salts having oligomers of branched olefins, including branched polyenes, such as terpenes. Such compounds and their salts are useful as lubricant additives.

10 **[0002]** Phenol-based detergents are known. Among these are phenates based on phenolic monomers, linked with sulfur bridges or alkylene bridges such as methylene linkages derived from formaldehyde. The phenolic monomers themselves are typically substituted with an aliphatic hydrocarbyl group to provide a measure of oil solubility. The hydrocarbyl groups may be alkyl groups, and, historically, dodecylphenol (or propylene tetramer-substituted phenol) has been widely used. An
15 early reference to basic sulfurized polyvalent metal phenates is U.S. Patent 2,680,96, Walker et al., June 1, 1954; see also U.S. Patent 3,372, 1 16, Meinhardt, March 6, 1968.

20 **[0003]** Recently, however, certain alkylphenols and products prepared from them have come under increased scrutiny due to their association as potential endocrine disruptive materials. In particular, alkylphenol detergents which are based on phenols alkylated with oligomers of propylene, specifically propylene tetramer (or tetrapropenyl), may contain residual alkyl phenol species. There is interest, therefore, in developing alkyl-substituted phenol detergents, for uses in lubricants, fuels, and as industrial additives, which contain a reduced or eliminated amount of dodecylphenol component and other substituted phenols having propylene oligomer substituents
25 of 10 to 15 carbon atoms. Nevertheless, it is desirable that the products should have similar oil-solubility parameters as phenates prepared from C10-15 propylene oligomers.

30 **[0004]** There have been several efforts to prepare phenate detergents that do not contain C_n alkyl phenols derived from oligomers of propylene. U.S. Patent 7,435,709, Stonebraker et al., October 14, 2008, discloses a linear alkylphenol derived detergent substantially free of endocrine disruptive chemicals. It comprises a

salt of a reaction product of (1) an olefin having at least 10 carbon atoms, where greater than 90 mole % of the olefin is a linear C20-C30 n-alpha olefin, and wherein less than 10 mole % of the olefin is a linear olefin of less than 20 carbon atoms, and less than 5 mole % of the olefin a branched chain olefin of 18 carbons or less, and (2)
5 a hydroxyaromatic compound

[0005] U.S. Application 2011/0190185, Siquin et al, August 4, 2011, discloses an overbased salt of an oligomerized alkylhydroxyaromatic compound. The alkyl group is derived from an olefin mixture comprising propylene oligomers having an initial boiling point of at least about 195 °C and a final boiling point of greater
10 than 325 °C. The propylene oligomers may contain a distribution of carbon atoms that comprise at least about 50 weight percent of C 14 to C20 carbon atoms.

[0006] U.S. Application 2011/0124539, Siquin et al, May 26, 2011, discloses an overbased, sulfurized salt of an alkylated hydroxyaromatic compound. The alkyl substituent is a residue of at least one isomerized α -olefin having from 15 to
15 about 99 wt. % branching. The hydroxyaromatic compound may be phenol, cresols, xylenols, or mixtures thereof.

[0007] U.S. Application 2011/0118160, Campbell et al., May 19, 2011, discloses an alkylated hydroxyaromatic compound substantially free of endocrine disruptive chemicals. An alkylated hydroxyaromatic compound is prepared by reacting
20 a hydroxyaromatic compound with at least one branched olefinic propylene oligomer having from about 20 to about 80 carbon atoms. Suitable hydroxyaromatic compounds include phenol, catechol, resorcinol, hydroquinone, pyrogallol, cresol, and the like.

[0008] U.S. Application 2010/0029529, Campbell et al., February 4, 2010, discloses an overbased salt of an oligomerized alkylhydroxyaromatic compound. The alkyl group is derived from an olefin mixture comprising propylene oligomers having an initial boiling point of at least about 195 °C and a final boiling point of no more
25 than about 325 °C. Suitable hydroxyaromatic compounds include phenol, catechol, resorcinol, hydroquinone, pyrogallol, cresol, and the like.

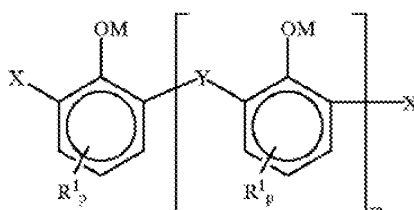
[0009] U.S. Application 2008/0269351, Campbell et al., October 30, 2008, discloses an alkylated hydroxyaromatic compound substantially free of endocrine
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disruptive chemicals, prepared by reacting a hydroxyaromatic compound with a branched olefinic oligomer having from about 20 to about 80 carbon atoms.

[0010] U.S. Application 2017/0211008, Walker et al., July 27, 2017, discloses metal salts and overbased metal salts of an oligomerized alkylphenol compound. The alkyl group is derived from oligomers of an olefin compound containing 3 to 8 carbon atoms, and wherein the polyolefin-derived alkyl group comprises at least 30 mol per-

[0011] WO/PCT application 2013/059173, Cook et al., discloses an overbased salt of an oligomerized alkylhydroxyaromatic compound. The alkyl group is a combination of very short hydrocarbyl group (i.e. 1 to 8 carbon atoms) and a long hydrocarbyl group (at least about 25 carbon atoms). Suitable compounds include those made from a mixture of para-cresol and polyisobutylene-substituted phenol.

[0012] Other general technology includes that of U.S. Patent 6,310,009, Carrick et al., October 30, 2001, which discloses salts of the general structure



where R^1 may be an alkyl group of 1 to 60 carbon atoms, e.g., 9 to 18 carbon atoms. It is understood that R^1 will normally comprise a mixture of various chain lengths, so that the foregoing numbers will normally represent an average number of carbon atoms in the R^1 groups (number average).

SUMMARY OF THE INVENTION

[0013] The disclosed technology, may solve at least one problem of providing a phenolic material with appropriate oil solubility, providing anti-wear performance, frictional performance, providing oxidation performance, viscosity performance, and detergency (characteristic of moderate chain length alkyl groups). In one embodiment the disclosed technology may also solve the problem of containing C12 alkyl phenol moieties i.e., the disclosed technology may be free from or substantially free

from C12 alkyl phenol moieties typically formed from oligomerisation or polymerisation of propylene.

[0014] One aspect of the disclosed technology relates to an alkylphenol detergent composition comprising at least one phenol moiety having a hydrocarbyl group attached thereto. The hydrocarbyl group can include at least one oligomer having monomers equivalent, in some embodiments, to 5 to 10 carbon atom branched olefins, and in some embodiments, more particularly to 5 to 10 carbon atom branched polyenes. In embodiments, the monomers making up the oligomers can be equivalent to isoprene. The oligomer itself can be equivalent to a terpene, and more particularly can be equivalent to any of (2E,5E,7E,10E)-3,6,10-trimethyldodeca-2,5,7,10-tetraene; (3E,7E,10E)-2,7,10-trimethyldodeca-1,3,7,10-tetraene; (E)-2,9-dimethyl-5-(prop-1-ene-2-yl)deca-1,3,8-triene; (3E,6E,10E)-2,6,10-trimethyldodeca-1,3,6,10-tetraene; (E)-7,11-dimethyl-3-methylenedodeca-1,6,10-triene; (6E,10E)-7,11,15-trimethyl-3-methylenehexadeca-1,6,10,14-tetraene; (3E,6E,10E)-3,7,11,15-tetramethylhexadeca-1,3,6,10,1-pentaene; (6E,10E,14E)-7,11,14-trimethyl-3-methylenehexadeca-1,6,10,14-tetraene; (3E,9E,13E)-2,10,13-trimethyl-6-(prop-1-en-2-yl)pentadeca-1,3,9,13-tetraene.

[0015] The oligomer can also be equivalent to a hydrogenated (partial or complete) form of a terpene, such as, for example, any of 3,7,11-trimethyldodec-1-ene; 2,6,10-trimethyldodec-2-ene; (E)-3,7,11-trimethyldodec-2-ene; 2,6-dimethyl-10-methylenedodecane; (E)-2,6,10-trimethyldodec-6-ene; (E)-3,7,11-trimethyldodec-3-ene; (E)-2,6,10-trimethyldodec-5-ene; 3,7,11-trimethyldodeca-1,10-diene

[0016] In embodiments, the hydrocarbyl unit of the alkylphenol detergent can contain from 15 to 60 carbon atoms.

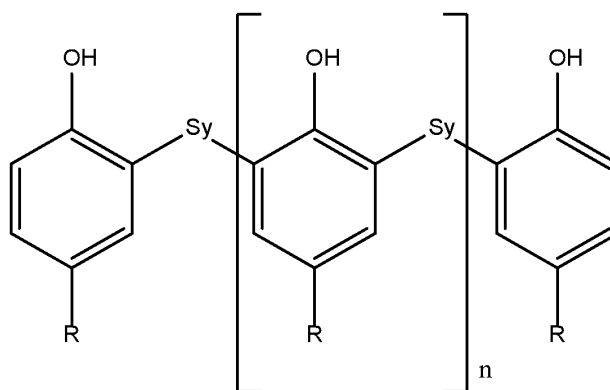
[0017] The alkylphenol detergent can include alkylphenol moiety equivalent to any of 4-(3,7,11-trimethyldodecan-2-yl)phenol; 4-(2,6,10-trimethyldodecan-2-yl)phenol; 4-(3,7,11-trimethyldodec-10-en-2-yl)phenol; 4-(2,6,10-trimethyldodec-11-en-2-yl)phenol.

[0018] The alkylphenol detergent can be a sulfur-bridged phenate detergent, a sulfur-free alkylene-bridged phenate detergent, a salicylate detergent, or mixtures thereof. The alkylphenol detergent can include one or more alkali metals, one or

more alkaline earth metals, or mixtures thereof. The alkylphenol detergent composition can be overbased, and in embodiments, have a metal ratio of at least 1.5, at least 5, or at least 7.

[0019] In an embodiment, the alkylphenol detergent can be an overbased sulfur-coupled phenate detergent with a metal ratio of at least 1.5.

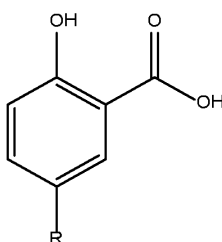
[0020] In an embodiment, the alkylphenol detergent composition can be a sulfur-bridged phenate represented by the structure



wherein each R is an aliphatic hydrocarbyl group equivalent to an oligomer of isoprene, higher branched olefins, or mixtures thereof, that contains 15 to 60 carbon atoms; each y can be 1 to 4; and n = 0 to 8, or 1 to 6, or 1 to 4, or 2 to 4.

[0021] In an embodiment, the alkylphenol detergent can be a neutral or overbased salt of alkylsalicylic acid.

[0022] In an embodiment, the alkylphenol detergent can be an alkylsalicylate represented by the structure



where R is an aliphatic hydrocarbyl group equivalent to an oligomer of isoprene, higher branched olefins, or mixtures thereof, and wherein the hydrocarbyl group contains 15 to 60 carbon atoms.

[0023] Another aspect of the technology relates to a lubricating composition having (a) an oil of lubricating viscosity and (b) the alkylphenol detergent composition as described herein. In embodiments, lubricating composition can be substantially free to free of an alkylphenol-containing detergent wherein the alkylphenol is derived from oligomers of propene. The lubricating composition can also include other additives, such as, for example, other detergents besides the instant alkylphenol detergent, zinc dialkyldithiophosphate, dispersants, antiwear agents, extreme pressure agents, corrosion inhibitors, etc.

[0024] A further aspect of the technology relates to methods of lubricating a mechanical device, for example, by supplying to the device the lubricating composition described herein containing the alkylphenol detergent. The mechanical device can be, for example, an internal combustion engine, an automotive driveline device, such as a transmission or an axle, or an off-highway vehicle. The technology could also be employed in industrial applications, such as industrial hydraulics.

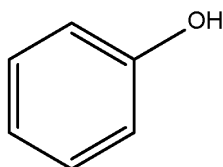
DETAILED DESCRIPTION OF THE INVENTION

[0025] Various preferred features and embodiments will be described below by way of non-limiting illustration.

[0026] The disclosed technology includes an alkylphenol detergent composition (or just alkylphenol for short), a lubricating composition containing the alkylphenol, a method for lubricating a mechanical device with a lubricating composition containing the alkylphenol, and a use of the alkylphenol, all of which will be more particularly described herein.

[0027] One aspect of the disclosed technology is an alkylphenol detergent composition. The alkylphenol detergent will include at least one phenol moiety with at least one hydrocarbyl group attached thereto. Those of ordinary skill in the art can observe a chemical composition and readily imagine the moieties to which the composition may be derived from. As used herein, reference to the phenol moiety means that moiety of the alkylphenol detergent composition one of ordinary skill in the art could imagine would be derived from a phenol, i.e., of Formula I.

Formula I

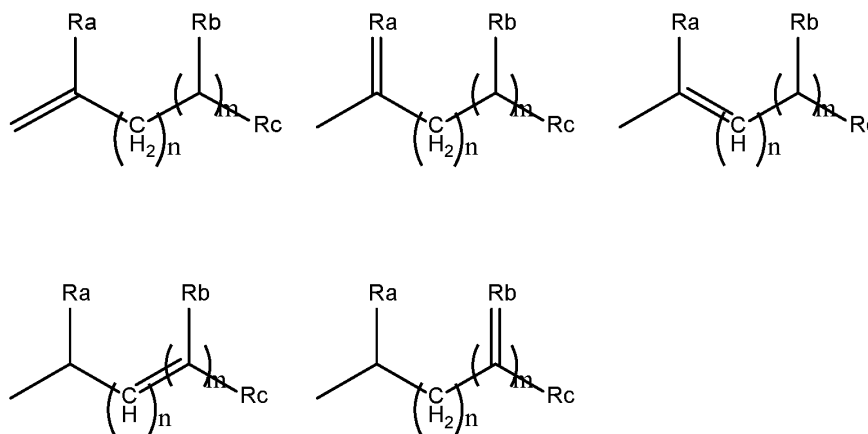


[0028] The alkylphenol will also include a hydrocarbyl group. As used herein, the term "hydrocarbyl group" is used in its ordinary sense, which is well-known to those skilled in the art. Specifically, it refers to a group having a carbon atom directly attached to the remainder of the molecule and having predominantly hydrocarbon character. Examples of hydrocarbyl groups include, for example: hydrocarbon substituents, including aliphatic, alicyclic, and aromatic substituents; 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; and hetero substituents, that is, substituents which similarly have a predominantly hydrocarbon character but contain other than carbon in a ring or chain.

[0029] While the hydrocarbyl group can include elements of non-hydrocarbyl character (i.e., nitrogen, halogens, etc.), in many embodiments the hydrocarbyl group can be of substantially, or even completely, hydrocarbon character. In some embodiments, the hydrocarbyl group can be of substantially or completely aliphatic character.

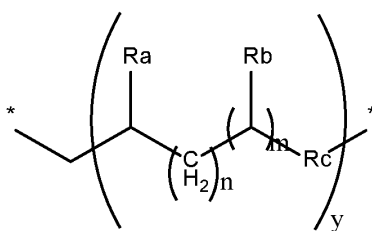
[0030] The hydrocarbyl group can comprise, consist essentially of, or consist of at least one oligomer, and the at least one oligomer itself can comprise, consist essentially of, or consist of monomers equivalent to 5 to 10 carbon atom branched olefins. By employing the terminology "equivalent to," it is recognized that the referenced compound, in this case the monomers of the oligomer, are slightly altered in their final state from their original state; for example, an oligomerized monomer *versus* the lone monomer. In other words, the hydrocarbyl group, when looked at in discreet units, contains identifiable oligomer units, and the identifiable oligomer units can be further broken down into identifiable alkyl units that, as a monomer would be considered a 5 to 10 carbon atom branched olefin.

[0031] A branched olefin, as used herein, refers to an alkyl chain having at least one double bond and at least one tertiary carbon atom. Without limiting the branched olefin, examples of such branched olefins can be represented by the following example branched olefin formulas.



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where Ra, Rb, and Rc can be H or a lower C₁ to C₅ alkyl group; n and m can be, independently, integers of 0 to 6, with the proviso that n+m is from 1 to 6; and the olefin has from 5 to 10 carbon atoms. An oligomer of such a branched olefin could be, for example, oligomers of the following formula.

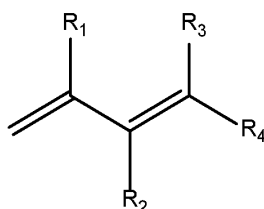


10 where Ra, Rb, Rc, m and n are as above, and y is an integer of 2 to 18, or 2 to 15, or 2 to 12.

[0032] The branched olefin can also be polyenes. That is, the hydrocarbyl group can comprise, consist essentially of, or consist of at least one oligomer, and

the at least one oligomer itself can comprise, consist essentially of, or consist of monomers equivalent to 5 to 10 carbon atom branched polyene compounds. As used herein a polyene is a poly-unsaturated alkylene compound having at least 2 double bonds (also known as a diene), and in some cases 3, 4, or 5 double bonds.

- 5 **[0033]** Branched polyene compounds can be described as alkyl chains having at least two double bonds in the chain, and at least one tertiary carbon atom. Although the polyene compound may include more than 2 double bonds, an example branched polyene compound may be a branched conjugated diene represented by the following formula,

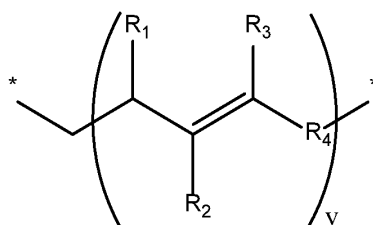


- 10 where R₁, R₂, R₃, and R₄ are independently H, or lower C₁ to C₅ alkyl groups; with the proviso that at least one of R₁, R₂, R₃, and R₄ is an alkyl group and that taken together the conjugated diene has a total of from 5 to 10 carbon atoms.

- 15 **[0034]** The at least one oligomer in the hydrocarbyl group can be oligomerized from 5 to 10 carbon atom branched olefin/polyenes, or the oligomer may be prepared in some other manner. For example, the oligomer may be formed by 1,2-monomer addition or 1,4-monomer addition. In one embodiment, oligomers of 5 to 10 carbon atom branched polyenes may formed by 1,4-addition of the monomers, followed by partial hydrogenation of the resulting material to form a mono-olefinic alkylating agent, which could then react with phenol to form the oligomeric alkyl phenol. The
- 20 hydrocarbyl group may also be derived from an alkylating agent containing a heteroatom, such as phytol or farnesol, which may be prepared from reacting monomers of a mono or polyene containing a heteroatom. For instance, Tetrahedron Vol 43. No. 19. pp. 4481 to 4486, 1987 describes the synthesis of phytol from two C₁₀ units derived from geraniol.

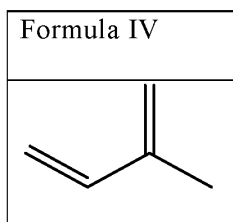
In another example, the oligomer may also be produced via biological activity, such as through the fermentation of a cell culture system that is capable of producing the desired branched olefin/polyene or a composition having the appearance of an oligomer containing monomers equivalent to 5 to 10 carbon atom branched olefin/polyene compounds. For instance, WO 2011/160081 provides a biological pathway for the production of isoprene, and the use of the so-produced isoprene to produce oligomers (also called terpenes, i.e., having a formula of $(C_5H_8)_n$, where n is 2, 3, 4, 5 or higher). The hydrocarbyl group may also be derived from an alkylating agent produced from a biological pathway, including, for instance, a biological pathway for the production of natural phytol from the crude extraction of silkworm excrement, *Morus alba* leaf, bamboo leaf, pine needle and *Ginkgo biloba* leaf, for example as taught in CN 102807471 A Dec 05, 2012. Other biological pathways are known to produce the oligomers (e.g., terpenes) themselves.

[0035] An oligomer containing monomers equivalent to 5 to 10 carbon atom branched olefins could be, for example, oligomers of the following formula



where R_1 , R_2 , R_3 , and R_4 and y are the same as defined above.

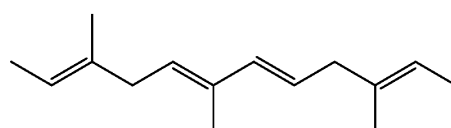
[0036] The branched polyene compound containing 5 to 10 carbon atoms may include isoprene monomers of Formula IV.



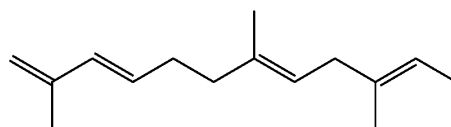
In addition to isoprene, suitable branched olefins 2-methyl-1-butene, 3-methyl-1-butene, 4-methyl-1-pentene, 2-methyl-1-pentene, 3-methyl-1-pentene, 2-methyl-1-hexene, 3-methyl-1-hexene, 5-methyl-1-hexene, 4-methyl-1-hexene, 2-methyl-1-heptene, 2,3-dimethyl-1,3-butadiene, 2,4-dimethyl-1,3-pentadiene, 3-methyl-1,3-pentadiene, and mixtures thereof.

[0037] In an embodiment, the oligomer contains units equivalent to isoprene. An isoprene oligomer containing 15 to 60 carbon atoms would contain 3 to 12 isoprene monomer units. An isoprene polymer or oligomer containing 15 to 30 carbon atoms would contain 3 or 6 isoprene monomer units.

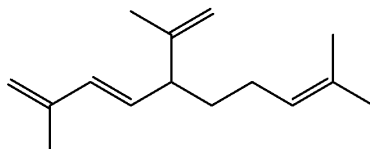
[0038] In an embodiment, the oligomer can be a trimer of isoprene, which can be envisioned in the following forms



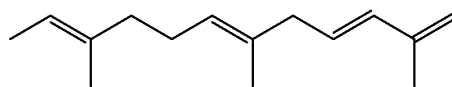
(2*E*,5*E*,7*E*,10*E*)-3,6,10-trimethyldodeca-2,5,7,10-tetraene



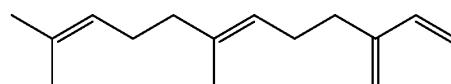
(3*E*,7*E*,10*E*)-2,7,10-trimethyldodeca-1,3,7,10-tetraene



(*E*)-2,9-dimethyl-5-(prop-1-en-2-yl)deca-1,3,8-triene

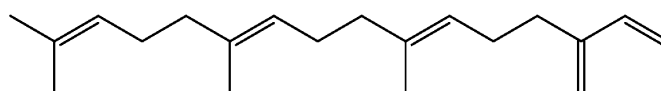
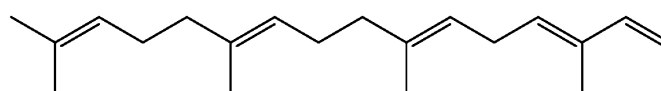
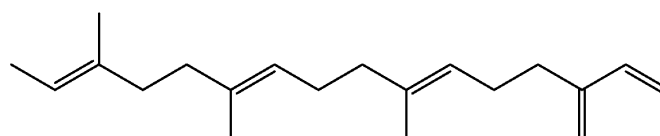
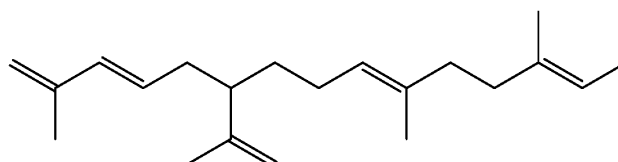


(3*E*,6*E*,10*E*)-2,6,10-trimethyldodeca-1,3,6,10-tetraene



(*E*)-7,11-dimethyl-3-methylenedodeca-1,6,10-triene

[0039] Tetramers of isoprene may also be employed in the oligomer, and can be envisioned in the following forms

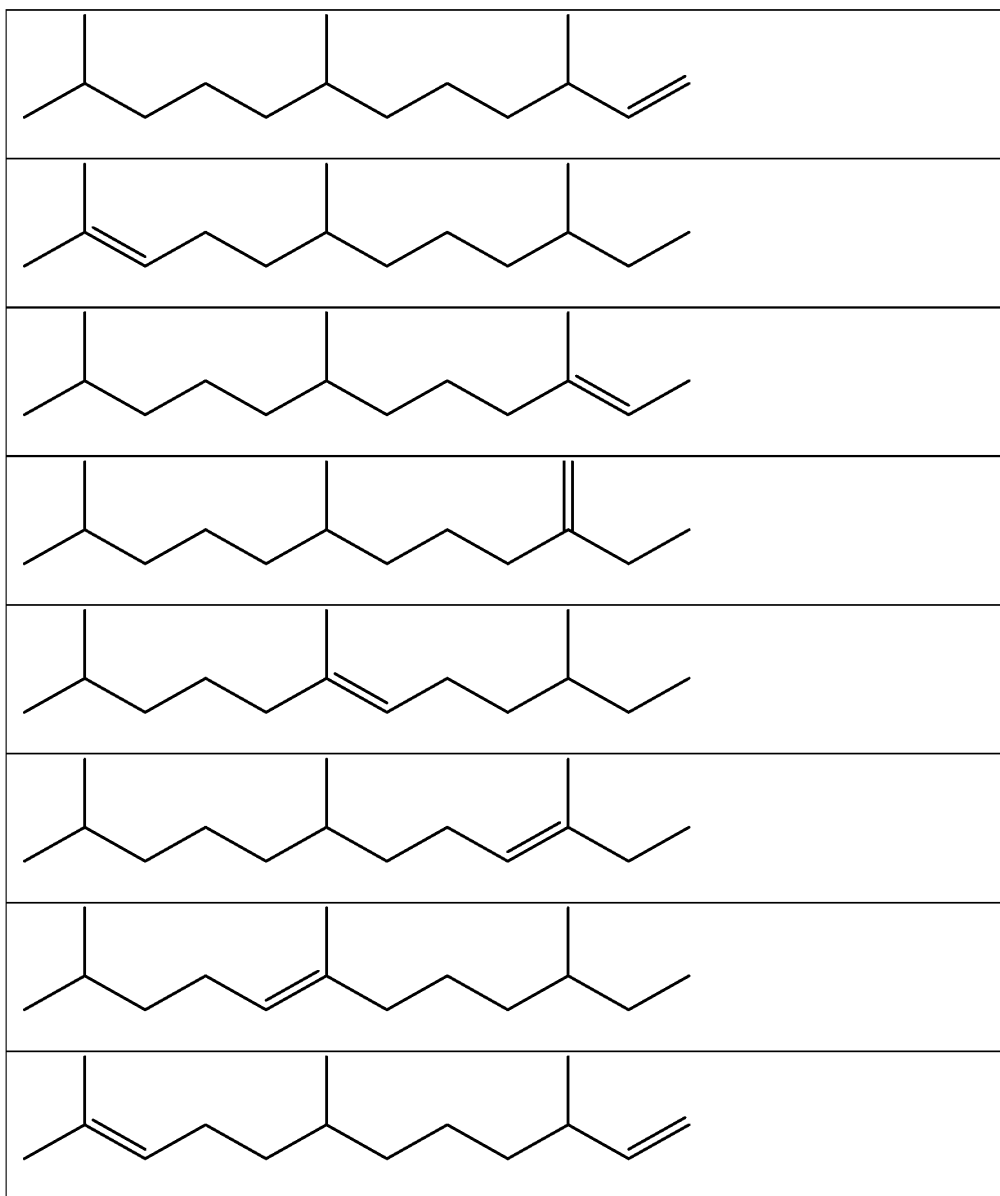
(6^E,10^E)-7,11,15-trimethyl-3-methylenhexadeca-1,6,10,14-tetraene(3^E,6^E,10^E)-3,7,11,15-tetramethylhexadeca-1,3,6,10,14-pentaene(6^E,10^E,14^E)-7,11,14-trimethyl-3-methylenhexadeca-1,6,10,14-tetraene(3^E,9^E,13^E)-2,10,13-trimethyl-6-(prop-1-en-2-yl)pentadeca-1,3,9,13-tetraene

[0040] In one embodiment, the hydrocarbyl group of the alkylphenol detergent can comprise, consist essentially of, or consist of oligomer compounds comprising, consisting essentially of, or consisting of at least 50 mol% monomers equivalent to isoprene, at least 75 mol% monomers equivalent to isoprene, or at least 90 mol% monomers equivalent to isoprene. In one embodiment, the hydrocarbyl group in the alkylphenol detergent consists of oligomers of isoprene.

[0041] In some embodiments, the oligomer can be hydrogenated forms, either partial or complete, of what the oligomer of the alkylene units would otherwise appear as. Hydrogenation may be performed, for example, by any hydrogenating agent known to a skilled artisan. For example, a saturated oligomer of polyene compounds can be prepared by hydrogenating at least a portion of the double bonds in the oligomer in the presence of a hydrogenation reagent, such as hydrogen in the presence of a catalyst, or by treatment with hydrazine in the presence of a catalyst.

[0042] In some embodiments, at least a portion of the C=C bonds of the oligomer is reduced to the corresponding C—C bonds by hydrogenation. In some embodiments, all of the C=C bonds of the oligomer are reduced to the corresponding C—

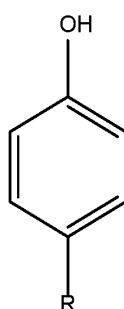
C bonds by hydrogenation. In an embodiment, the oligomer can include a hydrogenated form of oligomer in the form of any of the following structures:



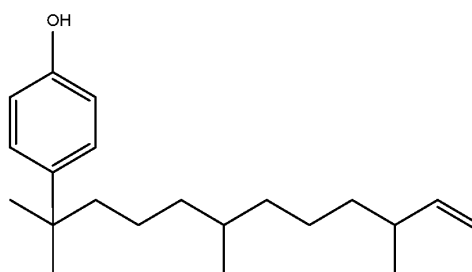
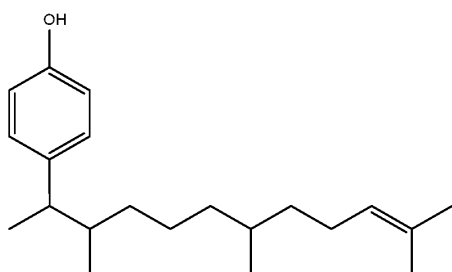
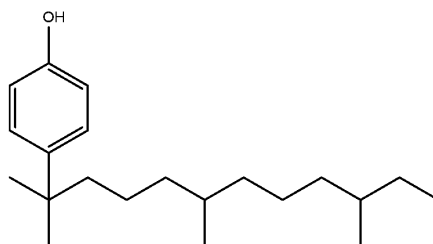
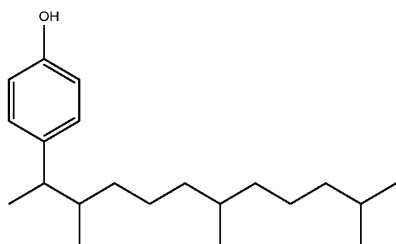
- [0043]** Whether prepared from the oligomerization of discrete units or otherwise, one of ordinary skill in the art will recognize the presence of the oligomers and monomers therein equivalent to 5 to 10 carbon atom branched polyenes within the hydrocarbyl group.

[0044] The hydrocarbyl group can contain from 10 to 200 carbon atoms, or in some examples 12 to 100 carbon atoms, or even 15 to 80 carbon atoms. In some embodiments, the hydrocarbyl group can have 15 to 60 carbon atoms, or in some cases 15 to 30 or 45 carbon atoms, or 20 to 30 carbon atoms.

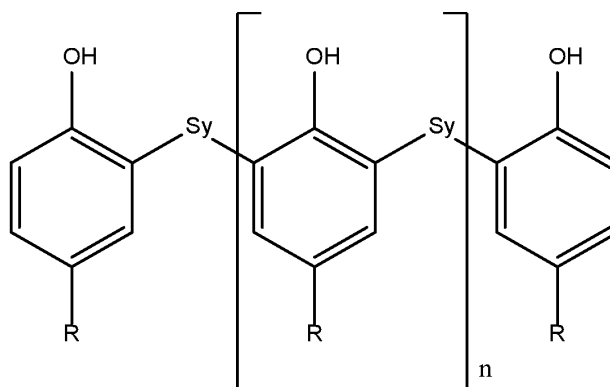
- 5 [0045] The alkylphenol detergent, including the phenol moiety and the hydrocarbyl group, may include the structure represented by the following formula.



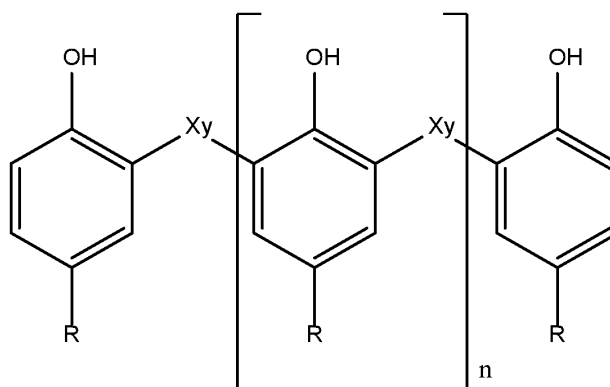
where R represents the hydrocarbyl group described above. For example, the alkylphenol can include the structure shown in the following formulas.



[0046] In certain embodiments, the alkylphenol-containing detergent may be a sulfur-bridged phenate detergent, a sulfur-free alkylene-bridged phenate detergent, or mixtures thereof. Detergents of this type are ionic (usually metal) salts of bridged phenolic compounds. The bridged phenolic compound material may be represented by the structure:



or more generally

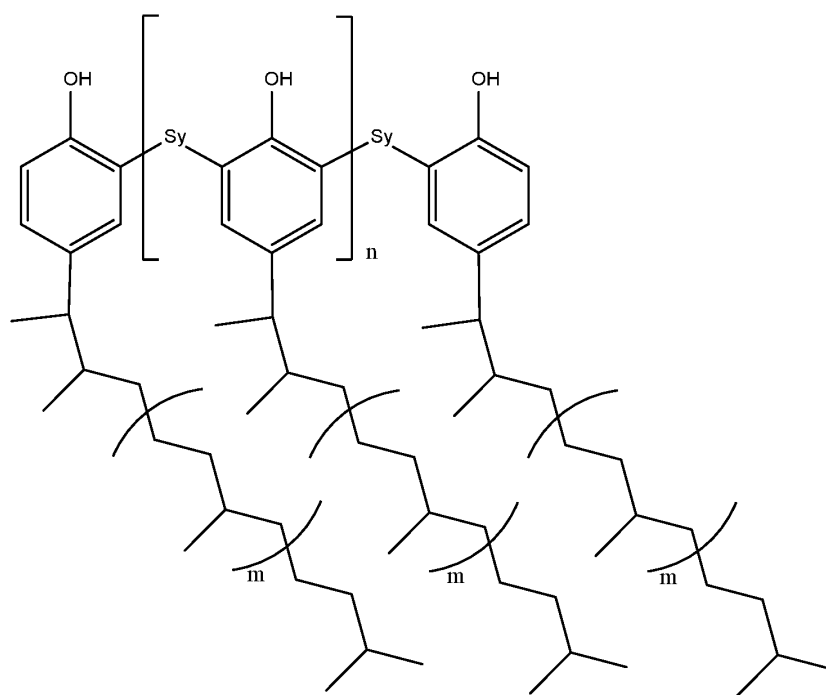


or isomers thereof, wherein each R represents the hydrocarbyl group described above having substantially or completely aliphatic character and 15 to 60, or in some cases 15 to 30 carbon atoms; aliphatic hydrocarbyl groups containing 30 to 200 or 35 to 80 carbon atoms; methyl groups; and mixtures thereof, each y can be 1 to 4.

[0047] The average number of carbon atoms in all the R groups, combined, may be 15 to 100 (or 20 to 50, or 24 to 36 or 14 to 20 or 18 to 36). Where the bridging group may be listed as "X", each X may independently be a carbon-containing bridge, or an alkylene group, or a methylene group, or a bridge of 1 or more sulfur atoms represented by S_y , where y may be 1 to 4, especially 1 or 2. In these structures, n

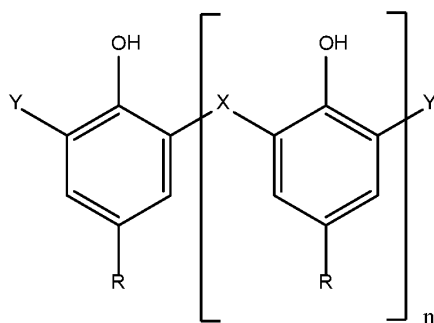
may, in certain embodiments, be 0 to 8, or 1 to 6, or 1 to 4, or 2 to 4. That is, the bridged material may, in these embodiments, contain 2 to 10 bridged phenolic groups, or 3 to 7, or 3 to 5, or 4 such groups. Since n may be zero, it may be evident that throughout this specification, the expression "oligomeric" may be interpreted to include dimeric species. Accordingly, sometimes the expression "dimeric or oligomeric" may be used to express this concept, which may include, as above, as an example, 0 to 8 interior units bracketed by $[]_n$ or 2 to 10 units overall.

[0048] In one embodiment, the sulfur-bridged alkylphenol-containing detergent may be an oligomer of p-(isoprene)phenol. A sulfur-bridged oligomer of oligo(isoprene)phenol may be represented by the structure



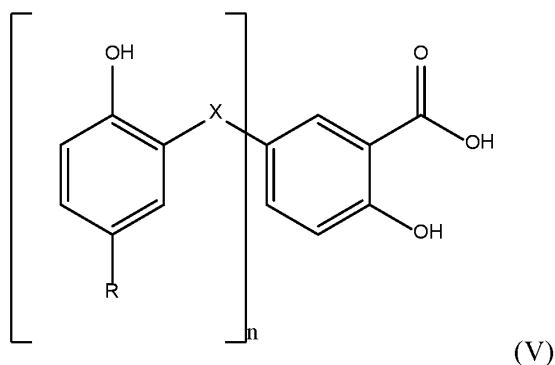
where $n = 0$ to 4, and $m = 1$ to 4 and each y can be 1 to 4.

[0049] In certain embodiments, the alkylene-bridged phenate detergent may be a saligenin detergent. A saligenin detergent contains a bridged-alkyl phenol compound that may be an alkylene coupled alkylphenol represented by the structure



where each R represents the hydrocarbyl group described above having 15 to 60, or in some cases 15 to 30 carbon atoms; aliphatic hydrocarbyl groups containing 30 to 200 or 35 to 80 carbon atoms; methyl groups; and mixtures thereof; where the each bridging group (X) may be independently a carbon-containing bridge, or a hydrocarbylether linkage (such as $-\text{CH}_2\text{-O-CH}_2-$), or an alkylene group, or a methylene group; each Y may be independently $-\text{CHO}$ or $-\text{CH}_2\text{OH}$; wherein the $-\text{CHO}$ groups comprise at least about 10 mole percent of the X and Y groups; and n may be an integer from 1 to 10.

[0050] In certain embodiments, the alkylene-bridged phenate detergent may be a salixarate detergent. A salixarate detergent contains a bridged-alkyl phenol compound that may be an alkylene coupled alkylphenol that may be further bridged or coupled to salicylic acid. The bridged phenol of a salixarate may be represented by the structure (V)



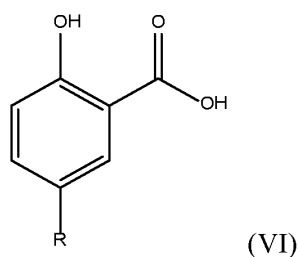
where R represents the hydrocarbyl group described above having substantially or completely aliphatic character and 15 to 60, or in some cases 15 to 30 carbon atoms; aliphatic hydrocarbyl groups containing 30 to 200 or 35 to 80 carbon atoms; methyl

groups; and mixtures thereof; where the each bridging group (X) may be independently a carbon-containing bridge, or an alkylene group, or a methylene group; and n may be an integer from 1 to 10.

[0051] The bridged alkylphenol detergents may be neutral or overbased or superbased. Such overbased detergents are generally single phase, homogeneous Newtonian systems characterized by a metal and/or ammonium content in excess of that which would be present for neutralization according to the stoichiometry of the metal or ammonium and the particular acidic organic compound reacted with the metal or ammonium compound. The overbased materials are typically prepared by reacting an acidic material (typically an inorganic acid or lower carboxylic acid such as carbon dioxide) with a mixture of bridged alkylphenol compounds (referred to as a substrate), a stoichiometric excess of a metal base, typically in a reaction medium of an one inert, organic solvent (e.g., mineral oil, naphtha, toluene, xylene) for the acidic organic substrate. Typically also a small amount of promoter such as a phenol or alcohol is present, and in some cases a small amount of water. The acidic organic substrate will normally have a sufficient number of carbon atoms to provide a degree of solubility in oil.

[0052] In certain embodiments, the overbased bridged-phenol detergent may be a metal-containing detergent, an amine or ammonium containing detergent, or mixtures thereof. In one embodiment, the overbased metal-containing detergent may be zinc, sodium, calcium or magnesium salts of a phenate, sulfur containing phenate, salixarate or saligenin. In one embodiment, the overbased detergent comprises a salt of an alkylamine or quaternary ammonium compound. Overbased salixarates, phenates and saligenins typically have a total base number (TBN) (by ASTM D3896) of 120 to 600 mg KOH/g.

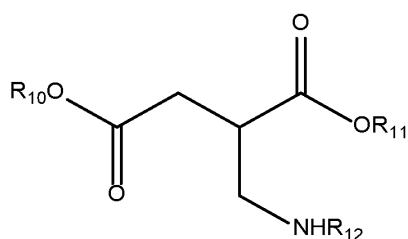
[0053] In certain embodiments, the alkylphenol detergent composition may be an alkylsalicylate or salicylate detergent. A salicylate detergent may be a neutral or overbased metal salt of alkylsalicylic acid. Alkylsalicylic acid may be represented by the formula (VI)



where R represents the hydrocarbyl group described above having substantially or completely aliphatic character and 15 to 60, or in some cases 15 to 30 carbon atoms; aliphatic hydrocarbyl groups containing 30 to 200 or 35 to 80 carbon atoms; methyl groups; and mixtures thereof.

[0054] The alkylsalicylate may be a neutral or nearly neutral salt of alkylsalicylic acid; by nearly neutral, it is meant that there is an excess of base of no more than 15 mol percent, i.e. if the salt is metal-containing, the metal ratio is 1.15 or less. In one embodiment, the neutral salt of the alkylsalicylic acid may be an amine or ammonium salt, a metal salt, or mixtures thereof.

[0055] Amines suitable for use in the preparation of the neutral amine salted alkylsalicylate are not overly limited and may include any alkyl amine, di- or tri-alkyl amine, though generally are fatty acid amines derived from fatty carboxylic acids. The alkyl group present in the amine may contain from 10 to 30 carbon atoms, or from 12 to 18 carbon atoms, and may be linear or branched. In some embodiments, the alkyl group may be linear and unsaturated. Typical amines include 2-ethylexylamine, pentadecylamine, octadecylamine, cetylamine, oleylamine, decylamine, dodecylamine, dimethyldodecylamine, tridecylamine, heptadecylamine, octadecylamine, stearylamine, and any combination thereof. In some embodiments, the fatty acid derived amine salt of an alkylsalicylic acid may be a salt of oleylamine. In certain embodiments, the amine may be a gamma-aminoester compound; aminoesters of this type may be derived from Michael addition of a primary amine to an alkyl diester of itaconic acid represented by the formula



where R_{10} and R_{11} are hydrocarbyl groups containing 2 to 30 carbon atoms, and R_{12} is a hydrocarbyl group containing 4 to 50 carbon atoms. In some embodiments, R_{12} of the aminoester compound is an alkyl group that has at least one hydrocarbyl group substituted at the 1-, or 2-position of the alkyl group. In one embodiment, the aminoester is dibutyl 2-(((2-ethylhexyl)-amino)methyl)succinate.

[0056] In certain embodiments, the neutral salt of the alkylsalicylic acid may be a quaternary ammonium salt, also referred to as a quaternary nitrogen compound. Quaternary nitrogen compounds are characterized in that the nitrogen atom is four-coordinate; this results in a cationic species that is not protic, i.e. an acidic proton is not released under basic conditions. Quaternary nitrogen compounds may be characterized as falling into two large groups, four coordinate tetrahydrocarbylammonium compounds, for example tetrabutylammonium, and three coordinate aromatic compounds, for example N-hydrocarbylpyridinium.

[0057] The alkylphenol-containing detergents, be they phenates, saligenins, salixrates, or salicylates, may be metal-containing detergents. Metal-containing detergents may be neutral, or very nearly neutral, or overbased. An overbased detergent contains a stoichiometric excess of a metal base for the acidic organic substrate. This is also referred to as metal ratio. The term "metal ratio" is the ratio of the total equivalents of the metal to the equivalents of the acidic organic compound. A neutral metal salt has a metal ratio of one. A salt having 4.5 times as much metal as present in a normal salt will have metal excess of 3.5 equivalents, or a ratio of 4.5. The term "metal ratio" is also explained in standard textbook entitled "Chemistry and Technology of Lubricants", Third Edition, Edited by R. M. Mortier and S. T. Orszulik, Copyright 2010, page 219, sub-heading 7.25.

[0058] In one embodiment the overbased metal-containing alkylphenol detergent may be calcium or magnesium overbased detergent. In one embodiment, the

overbased detergent may comprise a calcium alkylphenol detergent with a metal ratio of at least 1.5, at least 3, at least 5, or at least 7. In certain embodiments, the overbased calcium alkylphenol detergent may have a metal ratio of 1.5 to 25, 2.5 to 20 or 5 to 16.

5 **[0059]** Alternatively, the alkylphenol detergent may be described as having TBN. Overbased phenates and salicylates typically have a total base number of 120 to 600 mg KOH/g, or 150 to 550 mg KOH/g, or 180 to 350 mg KOH/g. The amount of the alkylphenol-containing detergent present in a lubricant composition may be defined as the amount necessary to deliver an amount, or range of amounts, of TBN
10 to the lubricant composition. In certain embodiments, the alkylphenol-containing detergent may be present in a lubricant composition in amount to deliver 0.5 to 10 TBN to the composition, or 1 to 7 TBN, or 1.5 to 5 TBN to the composition.

[0060] Overbased detergents may also be defined as the ratio of the neutral detergent salt, also referred to as detergent soap, and the detergent ash. The overbased
15 detergent may have a weight ratio of ash to soap of 3:1 to 1:8, or 1.5:1 to 1 to 4.1, or 1.3:1 to 1:3.4.

[0061] The product of the disclosed technology may beneficially be used as an additive in a lubricant. The amount of the alkylphenol detergent in a lubricant may be 0.1 to 8 percent by weight, on an oil-free basis, but including the calcium carbonate
20 and other salts present in an overbased composition. When present as an overbased detergent, the amount may typically be in the range of 0.1 to 25 weight percent, or 0.2 to 28, or 0.3 to 20, or 0.5 to 15 percent. The higher amounts are typical of marine diesel cylinder lubricants, e.g., 1 or 3 or 5 percent up to 25, 20, or 15 percent. Amounts used in gasoline or heavy-duty diesel engines (not marine) will typically be in lower
25 ranges, such as 0.1 to 10 percent or 0.5 to 5 or 1 to 3 percent by weight. When used as a substantially neutral or non-overbased salt, its amount may typically be correspondingly less for each of the engine types, e.g., 0.1 to 10 percent or 0.2 to 8 or 0.3 to 6 percent.

[0062] In certain embodiments, the amount of the alkylphenol detergent in a
30 lubricant may be measured as the amount of alkylphenol-containing soap that is provided to the lubricant composition, irrespective of any overbasing. In one embodi-

ment, the lubricant composition may contain 0.05 weight percent to 1.5 weight percent alkylphenol-containing soap, or 0.1 weight percent to 0.9 weight percent alkylphenol-containing soap. In one embodiment, the alkylphenol-containing soap provides 20 percent by weight to 100 percent by weight of the total detergent soap in the lubricating composition. In one embodiment the alkylphenol-containing soap provides 30 percent by weight to 80 percent by weight of the total detergent soap, or 40 percent by weight to 75 percent by weight of the total detergent soap of the lubricating composition.

[0063] A lubricant composition may contain alkylphenol-containing detergents different from that of the disclosed technology. In one embodiment, the lubricant composition of the disclosed technology comprises the alkylphenol detergent of the disclosed technology in an amount 0.1 to 25 weight percent, or 0.2 to 23, or 0.3 to 20, or 0.5 to 15 weight percent, and is free of or substantially free of an alkylphenol-containing detergent derived from alkylphenol which is derived from oligomers of propylene, especially tetrapropenyl. "Substantially free of" in this case means no more than 0.01 weight percent or an amount considered to arise through contamination or other unintentional means. In some embodiments, the lubricant composition can include the alkylphenol detergent at from about 0.01 to about 2 wt%, or from about 0.1 to about 1.75 wt%, or about 0.2 to about 1.5 wt% of the lubricating composition.

Oil of Lubricating Viscosity

[0064] Another aspect of the technology is a lubricant containing the alkylphenol detergent composition. The lubricating composition includes an oil of lubricating viscosity. Such oils include natural and synthetic oils, oil derived from hydrocracking, hydrogenation, and hydrofinishing, unrefined, refined, re-refined oils or mixtures thereof. A more detailed description of unrefined, refined and re-refined oils is provided in International Publication WO2008/147704, paragraphs [0054] to [0056] (a similar disclosure is provided in US Patent Application 2010/197536, see [0072] to [0073]). A more detailed description of natural and synthetic lubricating oils is described in paragraphs [0058] to [0059] respectively of WO2008/147704 (a similar disclosure is provided in US Patent Application 2010/197536, see [0075] to [0076]). Synthetic oils may also be produced by Fischer-Tropsch reactions and typically may be hydroisomerized Fischer-Tropsch hydrocarbons or waxes. In one embodiment

oils may be prepared by a Fischer-Tropsch gas-to-liquid synthetic procedure as well as other gas-to-liquid oils.

[0065] Oils of lubricating viscosity may also be defined as specified in the American Petroleum Institute (API) Base Oil Interchangeability Guidelines (2011).

5 The five base oil groups are as follows: Group I (sulfur content >0.03 wt %, and/or <90 wt % saturates, viscosity index 80 to less than 120); Group II (sulfur content ≤ 0.03 wt %, and ≥ 90 wt % saturates, viscosity index 80 to less than 120); Group III (sulfur content ≤ 0.03 wt %, and ≥ 90 wt % saturates, viscosity index ≥ 120); Group IV (all polyalphaolefins (PAOs)); and Group V (all others not included in Groups I, II, III, or
10 IV). The oil of lubricating viscosity may also be a Group II+ base oil, which is an unofficial API category that refers to a Group II base oil having a viscosity index greater than or equal to 110 and less than 120, as described in SAE publication "Design Practice: Passenger Car Automatic Transmissions," fourth Edition, AE-29, 2012, page 12-9, as well as in US 8,216,448, column 1 line 57. The oil of lubricating viscosity
15 may also be a Group III+ base oil, which, again, is an unofficial API category that refers to a Group III base oil having a viscosity index of greater than 130, for example 130 to 133 or even greater than 135, such as 135-145. Gas to liquid ("GTL") oils are sometimes considered Group III+ base oils.

[0066] The oil of lubricating viscosity may be an API Group IV oil, or mixtures thereof, i.e., a polyalphaolefin. The polyalphaolefin may be prepared by metallocene catalyzed processes or from a non-metallocene process. The oil of lubricating viscosity may also comprise an API Group I, Group II, Group III, Group IV, Group V oil or mixtures thereof. Often the oil of lubricating viscosity is an API Group I, Group II, Group II+, Group III, Group IV oil or mixtures thereof. Alternatively the oil of lubricating viscosity is often an API Group II, Group II+, Group III or Group IV oil or mixtures thereof. Alternatively the oil of lubricating viscosity is often an API Group II, Group II+, Group III oil or mixtures thereof.

[0067] The oil of lubricating viscosity, or base oil, will overall have a kinematic viscosity at 100 °C of 2 to 10 cSt or, in some embodiments 2.25 to 9 or 2.5 to 6 or 7 or
30 8 cSt, as measured by ASTM D445. Kinematic viscosities for the base oil at 100 °C of from about 3.5 to 6 or from 6 to 8 cSt are also suitable.

[0068] The amount of the oil of lubricating viscosity present is typically the balance remaining after subtracting from 100 wt % the sum of the amount of the performance additives in the composition. Illustrative amounts may include 50 to 99 percent by weight, or 60 to 98, or 70 to 95, or 80 to 94, or 85 to 93 percent.

5 **[0069]** The lubricating composition may be in the form of a concentrate and/or a fully formulated lubricant. If the lubricating composition of the invention is in the form of a concentrate (which may be combined with additional oil to form, in whole or in part, a finished lubricant), the ratio of the of components of the invention to the oil of lubricating viscosity and/or to diluent oil include the ranges of 1:99 to 99:1 by
10 weight, or 80:20 to 10:90 by weight.

[0070] A lubricating composition may be prepared by adding the product of the process described herein to an oil of lubricating viscosity, optionally in the presence of other performance additives (as described herein below).

[0071] The other performance additives can include at least one of metal de-
15 activators, viscosity modifiers (other than the soot dispersing additive of the present invention), detergents, friction modifiers, antiwear agents, corrosion inhibitors, dispersants (other than those of the present invention), extreme pressure agents, antioxidants, foam inhibitors, demulsifiers, pour point depressants, seal swelling agents and mixtures thereof. Typically, fully-formulated lubricating oil will contain one or more
20 of these performance additives.

[0072] In one embodiment the invention provides a lubricating composition further comprising an overbased metal-containing detergent in addition to the alkylphenol-containing detergent of the present invention. The metal of the metal-containing detergent may be zinc, sodium, calcium, barium, or magnesium. Typically the
25 metal of the metal-containing detergent may be sodium, calcium, or magnesium.

[0073] The overbased metal-containing detergent may be chosen from sulfonates, non-sulfur containing phenates, sulfur containing phenates, salixarates, salicylates, and mixtures thereof, or borated equivalents thereof. The overbased detergent may be borated with a borating agent such as boric acid.

30 **[0074]** The overbased metal-containing detergent may also include "hybrid" detergents formed with mixed surfactant systems including phenate and/or sulfonate

components, e.g. phenate/salicylates, sulfonate/phenates, sulfonate/salicylates, sulfonates/phenates/salicylates, as described; for example, in US Patents 6,429,178; 6,429,179; 6,153,565; and 6,281,179. Where, for example, a “hybrid” sulfonate/phenate detergent is employed, the “hybrid” detergent would be considered
5 equivalent to amounts of distinct phenate and sulfonate detergents introducing like amounts of phenate and sulfonate soaps, respectively.

[0075] Typically, an overbased metal-containing detergent may be a zinc, sodium, calcium or magnesium salt of a sulfonate, a phenate, sulfur containing phenate, salixarate or salicylate. Overbased sulfonates, salixarates, phenates and salicylates
10 typically have a total base number of 120 to 700 TBN.

[0076] Typically, the overbased metal-containing detergent may be a calcium or magnesium overbased detergent.

[0077] In another embodiment the lubricating composition further comprises a calcium sulfonate overbased detergent having a TBN of 120 to 700. The overbased
15 sulfonate detergent may have a metal ratio of 12 to less than 20, or 12 to 18, or 20 to 30, or 22 to 25.

[0078] Overbased sulfonates typically have a total base number of 120 to 700, or 250 to 600, or 300 to 500 (on an oil free basis). Overbased detergents are known in the art. In one embodiment the sulfonate detergent may be a predominantly linear
20 alkylbenzene sulfonate detergent having a metal ratio of at least 8 as is described in paragraphs [0026] to [0037] of US Patent Application 2005065045 (and granted as US 7,407,919). Linear alkyl benzenes may have the benzene ring attached anywhere on the linear chain, usually at the 2, 3, or 4 position, or mixtures thereof. The predominantly linear alkylbenzene sulfonate detergent may be particularly useful for
25 assisting in improving fuel economy. In one embodiment the sulfonate detergent may be a metal salt of one or more oil-soluble alkyl toluene sulfonate compounds as disclosed in paragraphs [0046] to [0053] of US Patent Application 2008/0119378.

[0079] In one embodiment the lubricating composition further comprises 0.01 wt % to 2 wt %, or 0.1 to 1 wt % of a detergent different from the alkylphenol
30 detergent of the disclosed technology, wherein the further detergent is chosen from sulfonates, non-sulfur containing phenates, sulfur containing phenates, sulfonates, salixarates, salicylates, and mixtures thereof, or borated equivalents thereof.

[0080] In one embodiment the lubricating composition further comprises a “hybrid” detergent formed with mixed surfactant systems including phenate and/or sulfonate components, e.g. phenate/salicylates, sulfonate/phenates, sulfonate/salicylates, or sulfonates/phenates/salicylates.

5 [0081] The lubricating composition in a further embodiment comprises an antioxidant, wherein the antioxidant comprises a phenolic or an aminic antioxidant or mixtures thereof. The antioxidants include diarylamines, alkylated diarylamines, hindered phenols, or mixtures thereof. When present the antioxidant is present at 0.1 wt % to 3 wt %, or 0.5 wt % to 2.75 wt %, or 1 wt % to 2.5 wt % of the lubricating
10 composition.

[0082] The diarylamine or alkylated diarylamine may be a phenyl- α -naphthylamine (PANA), an alkylated diphenylamine, or an alkylated phenyl-naphthylamine, or mixtures thereof. The alkylated diphenylamine may include di-nonylated diphenylamine, nonyl diphenylamine, octyl diphenylamine, di-octylated diphenylamine,
15 di-decylated diphenylamine, decyl diphenylamine and mixtures thereof. In one embodiment the diphenylamine may include nonyl diphenylamine, dinonyl diphenylamine, octyl diphenylamine, dioctyl diphenylamine, or mixtures thereof. In another embodiment the alkylated diphenylamine may include nonyl diphenylamine, or dinonyl diphenylamine. The alkylated diarylamine may include octyl, di-octyl, nonyl,
20 di-nonyl, decyl or di-decyl phenyl-naphthylamines.

[0083] The hindered phenol antioxidant often contains a secondary butyl and/or a tertiary butyl group as a sterically hindering group. The phenol group may be further substituted with a hydrocarbyl group (typically linear or branched alkyl) and/or a bridging group linking to a second aromatic group. Examples of suitable
25 hindered phenol antioxidants include 2,6-di-tert-butylphenol, 4-methyl-2,6-di-tert-butylphenol, 4-ethyl-2,6-di-tert-butylphenol, 4-propyl-2,6-di-tert-butylphenol or 4-butyl-2,6-di-tert-butylphenol, or 4-dodecyl-2,6-di-tert-butylphenol. In one embodiment the hindered phenol antioxidant may be an ester and may include, e.g., Irganox™ L-135 from Ciba. A more detailed description of suitable ester-containing
30 hindered phenol antioxidant chemistry is found in US Patent 6,559,105.

[0084] The lubricating composition may in a further embodiment include a dispersant, or mixtures thereof. The dispersant may be a succinimide dispersant, a

Mannich dispersant, a succinamide dispersant, a polyolefin succinic acid ester, amide, or ester-amide, or mixtures thereof. In one embodiment the dispersant may be present as a single dispersant. In one embodiment the dispersant may be present as a mixture of two or three different dispersants, wherein at least one may be a succinimide dispersant.

[0085] The succinimide dispersant may be derived from an aliphatic polyamine, or mixtures thereof. The aliphatic polyamine may be aliphatic polyamine such as an ethylenepolyamine, a propylenepolyamine, a butylenepolyamine, or mixtures thereof. In one embodiment the aliphatic polyamine may be ethylenepolyamine. In one embodiment the aliphatic polyamine may be chosen from ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylene-pentamine, pentaethylene-hexamine, polyamine still bottoms, and mixtures thereof.

[0086] In one embodiment the dispersant may be a polyolefin succinic acid ester, amide, or ester-amide. For instance, a polyolefin succinic acid ester may be a polyisobutylene succinic acid ester of pentaerythritol, or mixtures thereof. A polyolefin succinic acid ester-amide may be a polyisobutylene succinic acid reacted with an alcohol (such as pentaerythritol) and a polyamine as described above.

[0087] The dispersant may be an N-substituted long chain alkenyl succinimide. An example of an N substituted long chain alkenyl succinimide is polyisobutylene succinimide. Typically the polyisobutylene from which polyisobutylene succinic anhydride is derived has a number average molecular weight of 350 to 5000, or 550 to 3000 or 750 to 2500. Succinimide dispersants and their preparation are disclosed, for instance in US Patents 3,172,892, 3,219,666, 3,316,177, 3,340,281, 3,351,552, 3,381,022, 3,433,744, 3,444,170, 3,467,668, 3,501,405, 3,542,680, 3,576,743, 3,632,511, 4,234,435, Re 26,433, and 6,165,235, 7,238,650 and EP Patent Application 0 355 895 A.

[0088] The dispersants may also be post-treated by conventional methods by a reaction with any of a variety of agents. Among these are boron compounds (such as boric acid), urea, thiourea, dimercaptothiadiazoles, carbon disulfide, aldehydes, ketones, carboxylic acids such as terephthalic acid, hydrocarbon-substituted succinic anhydrides, maleic anhydride, nitriles, epoxides, and phosphorus compounds. In one embodiment the post-treated dispersant is borated. In one embodiment the post-

treated dispersant is reacted with dimercaptotriadiazoles. In one embodiment the post-treated dispersant is reacted with phosphoric or phosphorous acid. In one embodiment the post-treated dispersant is reacted with terephthalic acid and boric acid (as described in US Patent Application US2009/0054278.

5 **[0089]** When present, the dispersant may be present at 0.01 wt % to 20 wt %, or 0.1 wt % to 15 wt %, or 0.1 wt % to 10 wt %, or 1 wt % to 6 wt %, or 1 to 3 wt % of the lubricating composition.

10 **[0090]** The succinimide dispersant may comprise a polyisobutylene succinimide, wherein the polyisobutylene from which polyisobutylene succinimide is derived has a number average molecular weight of 350 to 5000, or 750 to 2500.

15 **[0091]** In one embodiment the friction modifier may be chosen from long chain fatty acid derivatives of amines, long chain fatty esters, or derivatives of long chain fatty epoxides; fatty imidazolines; amine salts of alkylphosphoric acids; fatty alkyl tartrates; fatty alkyl tartrides; fatty alkyl tartrides; fatty glycolates; and fatty glycolamides. The friction modifier may be present at 0 wt % to 6 wt %, or 0.01 wt % to 4 wt %, or 0.05 wt % to 2 wt %, or 0.1 wt % to 2 wt % of the lubricating composition.

20 **[0092]** As used herein the term “fatty alkyl” or “fatty” in relation to friction modifiers means a carbon chain having 10 to 22 carbon atoms, typically a straight carbon chain.

25 **[0093]** Examples of suitable friction modifiers include long chain fatty acid derivatives of amines, fatty esters, or fatty epoxides; fatty imidazolines such as condensation products of carboxylic acids and polyalkylene-polyamines; amine salts of alkylphosphoric acids; fatty alkyl tartrates; fatty alkyl tartrides; fatty alkyl tartrides; fatty phosphonates; fatty phosphites; borated phospholipids, borated fatty epoxides; glycerol esters; borated glycerol esters; fatty amines; alkoxyated fatty amines; borated alkoxyated fatty amines; hydroxyl and polyhydroxy fatty amines including tertiary hydroxy fatty amines; hydroxy alkyl amides; metal salts of fatty acids; metal salts of alkyl salicylates; fatty oxazolines; fatty ethoxyated alcohols; 30 condensation products of carboxylic acids and polyalkylene polyamines; or reaction products from fatty carboxylic acids with guanidine, aminoguanidine, urea, or thiourea and salts thereof.

[0094] Friction modifiers may also encompass materials such as sulfurised fatty compounds and olefins, molybdenum dialkyldithiophosphates, molybdenum di-thiocarbamates, sunflower oil or soybean oil monoester of a polyol and an aliphatic carboxylic acid.

5 **[0095]** In another embodiment the friction modifier may be a long chain fatty acid ester. In another embodiment the long chain fatty acid ester may be a mono-ester and in another embodiment the long chain fatty acid ester may be a triglyceride.

[0096] The lubricating composition optionally further includes at least one antiwear agent. Examples of suitable antiwear agents include titanium compounds, tar-
10 trates, tartrimides, oil soluble amine salts of phosphorus compounds, sulfurized olefins, metal dihydrocarbyldithiophosphates (such as zinc dialkyldithiophosphates), phosphites (such as dibutyl phosphite), phosphonates, thiocarbamate-containing compounds, such as thiocarbamate esters, thiocarbamate amides, thiocarbamic ethers, alkylene-coupled thiocarbamates, and bis(S-alkyldithiocarbamyl) disulfides.

15 **[0097]** The antiwear agent may in one embodiment include a tartrate, or tartrimide as disclosed in International Publication WO2006/044411 or Canadian Patent CA 1183125. The tartrate or tartrimide may contain alkyl-ester groups, where the sum of carbon atoms on the alkyl groups is at least 8. The antiwear agent may in one embodiment include a citrate as is disclosed in US Patent Application 2005/0198894.

20 **[0098]** Another class of additives includes oil-soluble titanium compounds as disclosed in US 7,727,943 and US2006/0014651. The oil-soluble titanium compounds may function as antiwear agents, friction modifiers, antioxidants, deposit control additives, or more than one of these functions. In one embodiment the oil soluble titanium compound is a titanium (IV) alkoxide. The titanium alkoxide is formed from
25 a monohydric alcohol, a polyol or mixtures thereof. The monohydric alkoxides may have 2 to 16, or 3 to 10 carbon atoms. In one embodiment, the titanium alkoxide is titanium (IV) isopropoxide. In one embodiment, the titanium alkoxide is titanium (IV) 2 ethylhexoxide. In one embodiment, the titanium compound comprises the alkoxide of a vicinal 1,2-diol or polyol. In one embodiment, the 1,2-vicinal diol
30 comprises a fatty acid mono-ester of glycerol, often the fatty acid is oleic acid.

[0099] In one embodiment, the oil soluble titanium compound is a titanium carboxylate. In a further embodiment the titanium (IV) carboxylate is titanium neodecanoate.

[0100] The lubricating composition may in one embodiment further include a phosphorus-containing antiwear agent. Typically the phosphorus-containing antiwear agent may be a zinc dialkyldithiophosphate, phosphite, phosphate, phosphonate, and ammonium phosphate salts, or mixtures thereof. Zinc dialkyldithiophosphates are known in the art. The antiwear agent may be present at 0 wt % to 3 wt %, or 0.1 wt % to 1.5 wt %, or 0.5 wt % to 0.9 wt % of the lubricating composition. In some embodiments, the antiwear agent may be present in an amount sufficient to provide from 0 to 0.12 wt% phosphorus to the lubricating composition, or from 0.01 to 0.08 wt%, or 0.03 to 0.08 wt%, or even 0.025 to 0.06 wt% phosphorus.

[0101] Extreme Pressure (EP) agents that are soluble in the oil include sulfur- and chlorosulfur-containing EP agents, dimercaptothiadiazole or CS₂ derivatives of dispersants (typically succinimide dispersants), derivative of chlorinated hydrocarbon EP agents and phosphorus EP agents. Examples of such EP agents include chlorinated wax; sulfurized olefins (such as sulfurized isobutylene), a hydrocarbyl-substituted 2,5-dimercapto-1,3,4-thiadiazole, or oligomers thereof, organic sulfides and polysulfides such as dibenzyl disulfide, bis-(chlorobenzyl) disulfide, dibutyl tetrasulfide, sulfurized methyl ester of oleic acid, sulfurized alkylphenol, sulfurized dipentene, sulfurized terpene, and sulfurized Diels-Alder adducts; phosphosulfurized hydrocarbons such as the reaction product of phosphorus sulfide with turpentine or methyl oleate; phosphorus esters such as the dihydrocarbon and trihydrocarbon phosphites, e.g., dibutyl phosphite, diheptyl phosphite, dicyclohexyl phosphite, pentylphenyl phosphite; dipentylphenyl phosphite, tridecyl phosphite, distearyl phosphite and polypropylene substituted phenol phosphite; metal thiocarbamates such as zinc dioctyldithiocarbamate and barium heptylphenol diacid; amine salts of alkyl and dialkylphosphoric acids or derivatives including, for example, the amine salt of a reaction product of a dialkyldithiophosphoric acid with propylene oxide and subsequently followed by a further reaction with P₂O₅; and mixtures thereof (as described in US 3,197,405).

[0102] Foam inhibitors that may be useful in the lubricant compositions of the disclosed technology include polysiloxanes, copolymers of ethyl acrylate and 2-ethylhexylacrylate and optionally vinyl acetate; demulsifiers including fluorinated polysiloxanes, trialkyl phosphates, polyethylene glycols, polyethylene oxides, polypropylene oxides and (ethylene oxide-propylene oxide) polymers.

[0103] Other viscosity modifiers may include a block copolymer comprising (i) a vinyl aromatic monomer block and (ii) a conjugated diene olefin monomer block (such as a hydrogenated styrene-butadiene copolymer or a hydrogenated styrene-isoprene copolymer), a polymethacrylate, or mixtures thereof.

[0104] Pour point depressants that may be useful in the lubricant compositions of the disclosed technology include polyalphaolefins, esters of maleic anhydride-styrene copolymers, poly(meth)acrylates, polyacrylates or polyacrylamides.

[0105] Demulsifiers include trialkyl phosphates, and various polymers and copolymers of ethylene glycol, ethylene oxide, propylene oxide, or mixtures thereof.

[0106] Metal deactivators include derivatives of benzotriazoles (typically tolyltriazole), 1,2,4-triazoles, benzimidazoles, 2-alkyldithiobenzimidazoles or 2-alkyldithiobenzothiazoles. The metal deactivators may also be described as corrosion inhibitors.

[0107] Seal swell agents include sulfolene derivatives Exxon Necton-37™ (FN 1380) and Exxon Mineral Seal Oil™ (FN 3200).

[0108] In an embodiment, the lubricating composition can be employed to lubricate a mechanical device. The mechanical device can be associated with an automotive vehicle. For example, the mechanical device may be a driveline device.

[0109] Driveline devices include automatic transmissions, manual transmission, dual clutch transmissions, or an axle or differential. A driveline device lubricating composition in different embodiments may have a composition as disclosed in the following table:

Additive	Embodiments (wt %)			
	A	B	C	D
Alkylphenol Detergent	0.01 to 2	0.01 to 2	0.01 to 2	0.01 to 2
Dispersant	1 to 4	0.1 to 10, 2 to 7	0 to 5	1 to 6
Extreme Pressure Agent	3 to 6	0 to 6	0 to 3	0 to 6
Overbased Detergent	0 to 1	0.01 to 3, 0.025 to 2	0.5 to 6	0.01 to 2
Antioxidant	0 to 5	0.01 to 10 or 2	0 to 3	0 to 2
Friction Modifier	0 to 5	0.01 to 5	0.1 to 1.5	0 to 5
Viscosity Modifier	0.1 to 70	0.1 to 15	1 to 60	0.1 to 70
Any Other Performance Additive	0 to 10	0 to 8 or 10	0 to 6	0 to 10
Oil of Lubricating Viscosity	Balance to 100 %			

Footnote:

The viscosity modifier in the table above may also be considered as an alternative to an oil of lubricating viscosity.

- 5 Column A may be representative of an automotive or axle gear lubricant.
Column B may be representative of an automatic transmission lubricant.
Column C may be representative of an off-highway lubricant.
Column D may be representative of a manual transmission lubricant.

- 10 **[0110]** The mechanical device can be an internal combustion engine, such as, for example, a spark ignited internal combustion engine or a compression ignition internal combustion engine. An engine lubricant composition in different embodiments may have a composition as disclosed in the following table:

Additive	Embodiments (wt %)		
	A	B	C
Alkylphenol Detergent	0.05 to 10	0.2 to 5	0.5 to 2
Corrosion Inhibitor	0.05 to 2	0.1 to 1	0.2 to 0.5
Other Overbased Detergent	0 to 9	0.5 to 8	1 to 5
Dispersant Viscosity Modifier	0 to 5	0 to 4	0.05 to 2
Dispersant	0 to 12	0 to 8	0.5 to 6
Antioxidant	0.1 to 13	0.1 to 10	0.5 to 5
Antiwear Agent	0.1 to 15	0.1 to 10	0.3 to 5
Friction Modifier	0.01 to 6	0.05 to 4	0.1 to 2
Viscosity Modifier	0 to 10	0.5 to 8	1 to 6
Any Other Performance Additive	0 to 10	0 to 8	0 to 6
Oil of Lubricating Viscosity	Balance to 100 %		

[0111] The mechanical device may also be in a hydraulic system. A hydraulic lubricant may also comprise a formulation defined in the following table:

Hydraulic Lubricant compositions			
Additive	Embodiments (wt %)		
	A	B	C
Alkylphenol detergent as described herein	0.01 to 2.0	0.01 to 1.5	0.01 to 1.0
Antioxidant	0 to 4.0	0.02 to 3.0	0.03 to 1.5
Dispersant	0 to 2.0	0.005 to 1.5	0.01 to 1.0
Other Detergent – beside alkylphenol detergent as described herein	0 to 5.0	0.001 to 1.5	0.005 to 1.0
Anti-wear Agent	0 to 5.0	0.001 to 2	0.1 to 1.0
Friction Modifier	0 to 3.0	0.02 to 2	0.05 to 1.0
Viscosity Modifier	0 to 10.0	0.5 to 8.0	1.0 to 6.0
Any Other Performance Additive (antifoam / demulsifier/pour point depressant)	0 to 1.3	0.00075 to 0.5	0.001 to 0.4
Metal Deactivator	0 to 0.1	0.01 to 0.04	0.015 to 0.03
Rust Inhibitor	0 to 0.2	0.03 to 0.15	0.04 to 0.12
Extreme Pressure Agent	0 to 3.0	0.005 to 2	0.01 to 1.0

Oil of Lubricating Viscosity	Balance to 100 %	Balance to 100 %	Balance to 100 %
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[0112] The disclosed technology further provides a method of lubricating a circulating oil system.

[0113] The disclosed technology further provides a method of lubricating a turbine system.

[0114] The alkylphenol can be employed to lubricate any of the foregoing mechanical devices by supplying to the mechanical device the aforementioned lubricating compositions.

[0115] 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.

[0116] 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.

[0117] As used herein, the term "about" means that a value of a given quantity is within $\pm 20\%$ of the stated value. In other embodiments, the value is within $\pm 15\%$ of the stated value. In other embodiments, the value is within $\pm 10\%$ of the stated value. In other embodiments, the value is within $\pm 5\%$ of the stated value. In other embodiments, the value is within $\pm 2.5\%$ of the stated value. In other embodiments, the value is within $\pm 1\%$ of the stated value.

[0118] Additionally, as used herein, the term "substantially" means that a value of a given quantity is within $\pm 10\%$ of the stated value. In other embodiments, the value is within $\pm 5\%$ of the stated value. In other embodiments, the value is within $\pm 2.5\%$ of the stated value. In other embodiments, the value is within $\pm 1\%$ of the stated value.

[0119] 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.

[0120] 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 essential or basic and novel characteristics of the composition or method under consideration.

[0121] 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.