# POLYALPHAOLEFIN PHENOLS WITH HIGH PARA-POSITION SELECTIVITY

## TECHNICAL FIELD

**[0001]** The present disclosure generally relates to lubricating oil compositions and sulfurized additives therefor provided from polyalphaolefin-substituted phenols and salts thereof having high para-position selectivity and/or reactivity on the aromatic ring.

## BACKGROUND

**[0002]** Metal salts of sulfurized alkyl phenols, otherwise known as alkyl phenates, tend to be useful lubricating oil additives. These additives may function, for example, as detergents, friction modifiers, and/or dispersants while providing an alkalinity base to aid in the neutralization of acids generated during automotive operation, when used in a lubricant in an automotive application. Unsulfurized variants of some alkyl phenates or phenols (for instance, tetrapropylene phenols or phenates having C12 alkyl substitution) have reduced utility and tend to be less desired in the lubricant for many reasons. As such, additive manufacturers seek to minimize levels of such unsulfurized alkyl phenates and/or alkyl phenols in their additives.

**[0003]** Current solutions, however, have one or more shortcomings when seeking to minimize levels of unsulfurized alkyl phenate/phenol variants when the additives are also overbased. Varying the alkyl substitution may be one potential option, but alternative alkyl substitution on the phenol moiety is also problematic in the context of overbased lubricant detergents. Desired lubricant additives prefer alkyl substitution at the para-position of the aromatic ring because, among other reasons, such substitution permits efficient sulfurization and functionality as an overbased detergent. However, many suitable alkyl substituents from other olefins preferentially alkylate at the ortho-position, which is undesired in the context of lubricant additives.

## SUMMARY AND TERMS

**[0004]** In accordance with one example, a sulfurized alkyl phenate comprising a polyalphaolefin substituted bridged hydroxyaromatic compound or salt thereof is described herein. In approaches, the polyalphaolefin is derived from C6 to C14 monomers forming dimers,

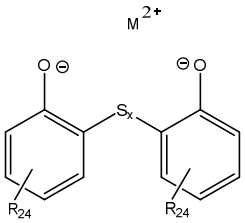
trimers, tetramers, pentamers, copolymers thereof, copolymer variants thereof, or combinations thereof.

**[0005]** In other examples, the sulfurized alkyl phenate of the previous paragraph may be combined with one or more optional features or examples in any combination. These optional features or examples may include one or more of the following: wherein about 40 mol percent or greater of the polyalphaolefin includes a carbon atom configured to form a tertiary carbocation; and/or wherein at least one alkyl group adjacent the tertiary carbocation is an alkyl group having 1, 2, or 3 carbon atoms, preferably having 2 carbon atoms, and most preferably having 1 carbon atom; and/or wherein the carbon atom configured to form a tertiary carbocation is positioned to react with the hydroxyaromatic compound at the para-position; and/or wherein the polyalphaolefin is obtained from C6 to C12 monomers forming dimers, trimers, tetramers, pentamers, or combinations thereof, preferably C8 to C10 monomers forming dimers, trimers, tetramers, pentamers, or combinations thereof; and/or wherein about 50 mol percent or greater of the polyalphaolefin includes a carbon atom configured to form a tertiary carbocation, preferably about 60 mol percent or greater, more preferably about 75 mol percent or greater, more preferably about 85 mol percent or greater, and most preferably about 90 mol percent or greater; and/or wherein the polyalphaolefin contains vinylidene olefins, trisubstituted olefins, or mixtures thereof; and/or wherein the polyalphaolefin contains greater than about 40 mol percent, greater than about 50 mol percent, greater than about 75 mol percent, or greater than about 90 mol percent of vinylidene olefins; and/or wherein the polyalphaolefin is a trisubstituted olefin and includes about 40 weight percent or more of the dimer, preferably, about 50 weight percent or more of the dimer, and more preferably about 70 weight percent or more of the dimer; and/or wherein the polyalphaolefin includes about 40 weight percent or less of the trimer; and/or about 20 weight percent or less of the tetramer; and/or about 5 weight percent or less of the pentamer; and/or wherein the polyalphaolefin contains predominately vinylidene olefins, trisubstituted olefins, or mixtures thereof and includes about 40 weight percent or more of the C3 or shorter alkyl group adjacent the tertiary carbocation, preferably about 50 weight percent or more, and more preferably about 75 weight percent or more; and/or wherein the polyalphaolefin includes double bonds having a vinylidene structure and/or a tri-substituted structure; and/or wherein the polyalphaolefin includes about 40 mol percent or more of a vinylidene olefin, a tri-substituted olefin, or combinations thereof, preferably about 60 mol

percent or more, more preferably about 75 mol percent or more, even more preferably about 85 mol percent or more, and most preferably about 90 mol percent or more.

**[0005a]** In one aspect, the present disclosure refers to a sulfurized alkyl phenate comprising a polyalphaolefin substituted bridged hydroxyaromatic compound or salt thereof, wherein the polyalphaolefin is derived from one or more C6 to C14 monomers forming an oligomer in the form of a dimer, a trimer, a tetramer, a pentamer or combinations thereof, or copolymers of the oligomer, copolymer variants of the oligomer, or combinations thereof; and wherein 40 mol percent or greater of the polyalphaolefin includes a carbon atom configured to form a tertiary carbocation positioned to react with the hydroxyaromatic compound at the para-position.

**[0006]** In yet other examples, a detergent composition including a sulfurized alkyl phenate having a structure of Formula IX is provided herein. In approaches, Formula IX includes

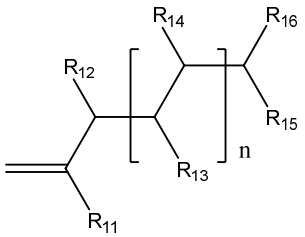



(Formula IX)

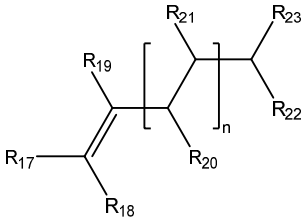
wherein each $R_{24}$ independently, is a polyalphaolefin derived from C6 to C14 monomers forming a dimer, trimer, tetramer, pentamer, copolymer, copolymer variants, or combination thereof including a residue of a tertiary carbocation forming the bond to the aromatic ring, wherein at least 50 mol percent of $R_{24}$ is bonded to the aromatic ring at the para-position; x is an integer from 1 to 4; and $M^{2+}$ is a divalent metal ion.

**[0007]** In other examples, the detergent composition of the previous paragraph may be combined with one or more optional features or examples in any combination. These optional features or examples may include one or more of the following: wherein each $R_{24}$, independently, has at least one alkyl group adjacent the tertiary carbocation having 1, 2, or 3 carbon atoms, preferably having 2 carbon atoms, and more preferably, having 1 carbon atom; and/or wherein each $R_{24}$, independently, is formed from C8 to C12 monomers forming a dimer, a trimer, a tetramer, a pentamer, or combination thereof, and preferably from C8 to C10 monomers forming a dimer, a trimer, a tetramer, a pentamer, or combination thereof; and/or wherein $R_{24}$ is derived from vinylidene olefins, trisubstituted olefins, or mixtures thereof; and/or wherein the $R_{24}$ contains about 40 mol percent or greater, about 50 mol percent or greater, about 75 mol percent or greater, or about 90 mol percent or greater of vinylidene olefins; and/or wherein the $R_{24}$ is a trisubstituted olefin and about 40 weight percent or more of $R_{24}$ is a dimer, about 50 weight percent or more of $R_{24}$ is a dimer, or about 70 weight percent or more of $R_{24}$ is a dimer; and/or wherein about 40 weight percent or less of $R_{24}$ is a trimer, about 20 weight percent or less of $R_{24}$ is a tetramer, and/or about 5 weight percent or less of $R_{24}$ is a pentamer; and/or wherein about 40 weight percent or more of the alkyl group adjacent the tertiary carbocation is the C3 or shorter alkyl group, preferably about 50 weight percent or more, and more preferably about 75

weight percent or more; and/or wherein the $R_{24}$ group is derived from a mixture of oligomers and a majority of oligomers in the mixture have the structure of Formula VI and/or Formula VII below:



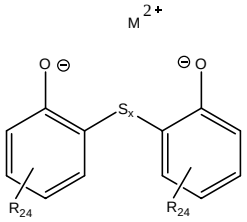

(Formula VI)




(Formula VII)

wherein $R_{11}$ is an alkyl group; each of $R_{12}$, $R_{13}$, $R_{14}$, $R_{15}$, and/or $R_{16}$, is the same or different at each occurrence, and independently represents a hydrogen or a substituted or unsubstituted hydrocarbyl group; only one of $R_{17}$, $R_{18}$ and $R_{19}$ is hydrogen and one of the remaining two of $R_{17}$, $R_{18}$ and $R_{19}$ is a substituted or unsubstituted hydrocarbyl group having 1, 2, or 3 carbons and the other of the remaining two of $R_{17}$, $R_{18}$ and $R_{19}$ is a substituted or unsubstituted hydrocarbyl group; each of $R_{20}$, $R_{21}$, $R_{22}$, and/or $R_{23}$, is the same or different at each occurrence, and independently represents a hydrogen or a substituted or unsubstituted hydrocarbyl group; each n is, independently, an integer of 0 to 3.

**[0007a]** In one aspect, the present disclosure refers to a detergent composition including a sulfurized alkyl phenate having a structure of Formula IX:




(Formula IX)

wherein

each $R_{24}$ independently, is a polyalphaolefin derived from one or more C6 to C14 monomers forming an oligomer in the form of a dimer, a trimer, a tetramer, a pentamer, or combinations thereof, or copolymers of the oligomer, copolymer variants of the oligomer, or combinations thereof including a residue of a tertiary carbocation forming the bond to the aromatic ring, wherein at least 50 mol percent of $R_{24}$ is bonded to the aromatic ring at the para-position; wherein each $R_{24}$, independently, has 40 weight percent or more of at least one alkyl group adjacent the tertiary carbocation having 1, 2, or 3 carbon atoms;

x is an integer from 1 to 4; and

$M^{2+}$ is a divalent metal ion.

**[0008]** In yet further examples, a lubricating oil composition including the sulfurized alkyl phenate or the detergent composition of any example of this Summary is provided herein combined with of one or more base oils of lubricating viscosity. In one aspect, the present disclosure refers to a lubricating oil composition including the sulfurized alkyl phenate disclosed herein and one or more base oils of lubricating viscosity. In another aspect, the present disclosure refers to a lubricating oil composition including the detergent composition disclosed herein and one or more base oils of lubricating viscosity.

**[0009]** In yet further examples, an alkyl phenol suitable for forming a sulfurized alkyl phenate detergent composition is described herein. In approaches, the alkyl phenol includes the reaction product of a hydroxyaromatic compound and a polyalphaolefin oligomer derived from C6 to C14 dimers, trimers, tetramers, pentamers, copolymers, copolymer variants, or combinations thereof.

**[00010]** In other examples of the alkyl phenol of the previous paragraph, the alkyl phenol may be combined with optional examples or features in any combination. The optional features or examples may include one or more of the following: wherein the polyalphaolefin oligomer is derived from C8 to C12 dimers, trimers, tetramers, pentamers, or combinations thereof, and preferably C8 to C10 dimers, trimers, tetramers, pentamers, or combinations thereof; and/or wherein about 40 mol percent or greater of the polyalphaolefin oligomer includes a carbon atom configured to form a tertiary carbocation and at least one of the alkyl groups

oligomer is a tetramer, and/or about 5 weight percent or less of the polyalphaolefin oligomer is a pentamer; and/or wherein about 40 weight percent or more of the alkyl group adjacent the tertiary carbocation is the C3 or shorter alkyl group, preferably about 50 weight percent or more, and more preferably about 75 weight percent or more.

**[00011]** In yet other examples, use of a polyalphaolefin as described in any example of this Summary is provided for forming a detergent compositions and/or a substituted bridged hydroxyaromatic compound or salt thereof for use in a detergent composition.

**[00012]** The following definitions of terms are provided in order to clarify the meanings of certain terms as used herein.

**[00013]** The terms “oil composition,” “lubrication composition,” “lubricating oil composition,” “lubricating oil,” “lubricant composition,” “lubricating composition,” “fully formulated lubricant composition,” and “lubricant” are considered synonymous, fully interchangeable terminology referring to the finished lubrication product comprising a major amount of a base oil plus a minor amount of an additive composition.

**[00014]** As used herein, the terms “additive package,” “additive concentrate,” and “additive composition" are considered synonymous, fully interchangeable terminology referring the portion of the lubricating oil composition excluding the major amount of base oil stock mixture.

**[00015]** The term “overbased,” unless otherwise specified, relates to metal salts, such as metal salts of sulfonates, carboxylates, salicylates, and/or phenates, wherein the amount of metal present exceeds the stoichiometric amount. Such salts may have a conversion level in excess of 100% (i.e., they may comprise more than 100% of the theoretical amount of metal needed to convert the acid to its “normal,” “neutral” salt). The expression “metal ratio,” often abbreviated as MR, is used to designate the ratio of total chemical equivalents of metal in the overbased salt to chemical equivalents of the metal in a neutral salt according to known chemical reactivity and stoichiometry. In a normal or neutral salt, the metal ratio is one and in an overbased salt, MR, is greater than one. They are commonly referred to as overbased, hyperbased, or superbased salts and may be salts of organic sulfur acids, carboxylic acids, salicylates, sulfonates, and/or phenols.

**[00016]** The term “alkaline earth metal” relates to calcium, barium, magnesium, and strontium, and the term “alkali metal” refers to lithium, sodium, potassium, rubidium, and cesium.

**[00017]** As used herein, and unless otherwise specified, the term “hydrocarbyl” or

"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 a predominantly hydrocarbon character. Each hydrocarbyl group is independently selected from hydrocarbon substituents, and substituted hydrocarbon substituents containing one or more of halo groups, hydroxyl groups, alkoxy groups, mercapto groups, nitro groups, nitroso groups, amino groups, pyridyl groups, furyl groups, imidazolyl groups, oxygen and nitrogen, and wherein no more than two non-hydrocarbon substituents are present for every ten carbon atoms in the hydrocarbyl group. In some examples, hydrocarbyl includes the term “alkyl.” The term "alkyl" as employed herein and unless otherwise specified, refers to straight, branched, cyclic, and/or substituted saturated chain moieties of from about 1 to about 100 carbon atoms. The term "alkenyl" as employed herein refers to straight, branched, cyclic, and/or substituted unsaturated chain moieties of from about 3 to about 10 carbon atoms. The term “aryl” as employed herein refers to single and multi-ring aromatic compounds that may include alkyl, alkenyl, alkylaryl, amino, hydroxyl, alkoxy, halo substituents, and/or heteroatoms including, but not limited to, nitrogen, oxygen, and sulfur.

**[00018]** As used herein, and unless otherwise specified, the term "hydrocarbylene substituent" or "hydrocarbylene group" is used in its ordinary sense, which is well-known to those skilled in the art. Specifically, it refers to a group that is directly attached at two locations of the molecule to the remainder of the molecule by a carbon atom and having predominantly hydrocarbon character. Each hydrocarbylene group is independently selected from divalent hydrocarbon substituents, and substituted divalent hydrocarbon substituents containing halo groups, alkyl groups, aryl groups, alkylaryl groups, arylalkyl groups, hydroxyl groups, alkoxy groups, mercapto groups, nitro groups, nitroso groups, amino groups, pyridyl groups, furyl groups, imidazolyl groups, oxygen and nitrogen, and wherein no more than two non-hydrocarbon substituents is present for every ten carbon atoms in the hydrocarbylene group.

**[00019]** As used herein, the term "percent by weight", unless expressly stated otherwise, means the percentage the recited component represents to the weight of the entire composition.

**[00020]** The terms “soluble,” "oil-soluble," or "dispersible" used herein may, but does not necessarily, indicate that the compounds or additives are soluble, dissolvable, miscible, or capable of being suspended in the oil in all proportions. The foregoing terms do mean, however,

that they are, for instance, soluble, suspendable, dissolvable, or stably dispersible in oil to an extent sufficient to exert their intended effect in the environment in which the oil is employed. Moreover, the additional incorporation of other additives may also permit incorporation of higher levels of a particular additive, if desired.

**[00021]** The term "TBN" as employed herein is used to denote the Total Base Number in mg KOH/g as measured by the method of ASTM D2896.

**[00022]** The term “lime” as employed herein refers to, for example, calcium hydroxide, calcium oxide, and the like compounds, also known as slaked lime or hydrated lime.

**[00023]** The molecular weight for any example herein may be determined with a gel permeation chromatography (GPC) instrument obtained from Waters or the like instrument and the data processed with Waters Empower Software or the like software. The GPC instrument may be equipped with a Waters Separations Module and Waters Refractive Index detector (or the like optional equipment). The GPC operating conditions may include a guard column, 4 Agilent PLgel columns (length of 300×7.5 mm; particle size of 5 μ, and pore size ranging from 100-10000 Å) with the column temperature at about 40 °C. Un-stabilized HPLC grade tetrahydrofuran (THF) may be used as solvent, at a flow rate of 1.0 mL/min. The GPC instrument may be calibrated with commercially available polystyrene (PS) standards having a narrow molecular weight distribution ranging from 500 – 380,000 g/mol. The calibration curve can be extrapolated for samples having a mass less than 500 g/mol. Samples and PS standards can be in dissolved in THF and prepared at concentration of 0.1 to 0.5 wt. % and used without filtration. GPC measurements are also described in US 5,266,223, which is incorporated herein by reference. The GPC method additionally provides molecular weight distribution information; *see, for example,* W. W. Yau, J. J. Kirkland and D. D. Bly, “Modern Size Exclusion Liquid Chromatography”, John Wiley and Sons, New York, 1979, also incorporated herein by reference.

**[00024]** Additional details and advantages of the disclosure will be set forth in part in the description that follows, and/or may be learned by practice of the disclosure. The details and advantages of the disclosure may be realized and attained by means of the elements and combinations particularly pointed out in the appended claims. It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are not restrictive of the disclosure, as claimed.

## CLAIMS

1. A sulfurized alkyl phenate comprising a polyalphaolefin substituted bridged hydroxyaromatic compound or salt thereof, wherein the polyalphaolefin is derived from one or more C6 to C14 monomers forming an oligomer in the form of a dimer, a trimer, a tetramer, a pentamer or combinations thereof, or copolymers of the oligomer, copolymer variants of the oligomer, or combinations thereof; and wherein 40 mol percent or greater of the polyalphaolefin includes a carbon atom configured to form a tertiary carbocation positioned to react with the hydroxyaromatic compound at the para-position.

2. The sulfurized alkyl phenate of claim 1, wherein at least one alkyl group adjacent the tertiary carbocation is an alkyl group having 1, 2, or 3 carbon atoms.

3. The sulfurized alkyl phenate of claim 1, wherein the polyalphaolefin is obtained from one or more C8 to C12 monomers forming the oligomer in the form of the dimer, the trimer, the tetramer, the pentamer, or combinations thereof.

4. The sulfurized alkyl phenate of claim 1, wherein 50 mol percent or greater of the polyalphaolefin includes a carbon atom configured to form a tertiary carbocation.

5. The sulfurized alkyl phenate of claim 1, wherein the polyalphaolefin contains vinylidene olefins, trisubstituted olefins, or mixtures thereof.

6. The sulfurized alkyl phenate of claim 5, wherein the polyalphaolefin contains greater than 40 mol percent of the vinylidene olefins, the trisubstituted olefins, or mixtures thereof.

7. The sulfurized alkyl phenate of claim 5, wherein the polyalphaolefin is a trisubstituted olefin and includes 40 weight percent or more of the dimer.

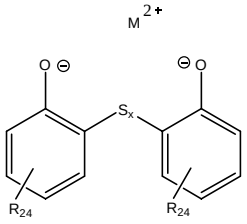
8. The sulfurized alkyl phenate of claim 7, wherein the polyalphaolefin includes 40 weight percent or less of the trimer; and/or 20 weight percent or less of the tetramer; and/or 5 weight percent or less of the pentamer.

9. The sulfurized alkyl phenate of claim 1, wherein the polyalphaolefin contains predominately vinylidene olefins, trisubstituted olefins, or mixtures thereof and includes 40 weight percent or more of the C3 or shorter alkyl group adjacent the tertiary carbocation.

10. The sulfurized alkyl phenate of claim 1, wherein the polyalphaolefin includes double bonds having a vinylidene structure and/or a tri-substituted structure.

11. The sulfurized alkyl phenate of claim 1, wherein the polyalphaolefin includes 40 mol percent or more of a vinylidene olefin, a tri-substituted olefin, or combinations thereof.

12. A detergent composition including a sulfurized alkyl phenate having a structure of Formula IX:




(Formula IX)

wherein

each $R_{24}$ independently, is a polyalphaolefin derived from one or more C6 to C14 monomers forming an oligomer in the form of a dimer, a trimer, a tetramer, a pentamer, or combinations thereof, or copolymers of the oligomer, copolymer variants of the oligomer, or combinations thereof including a residue of a tertiary carbocation forming the bond to the aromatic ring, wherein at least 50 mol percent of $R_{24}$ is bonded to the aromatic ring at the para-position; wherein each $R_{24}$, independently, has 40 weight percent or more of at least one alkyl group adjacent the tertiary carbocation having 1, 2, or 3 carbon atoms;

x is an integer from 1 to 4; and

$M^{2+}$ is a divalent metal ion.

13. The detergent composition of claim 12, wherein each $R_{24}$, independently, is formed from one or more C8 to C12 monomers forming the oligomer in the form of the dimer, the trimer, the tetramer, the pentamer, or combination thereof.

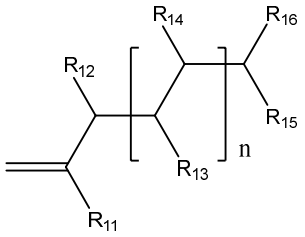
14. The detergent composition of claim 12, wherein $R_{24}$ is derived from vinylidene olefins, trisubstituted olefins, or mixtures thereof.

15. The detergent composition of claim 14, wherein the $R_{24}$ contains 40 mol percent or greater of the vinylidene olefins, the trisubstituted olefins, or mixtures thereof.

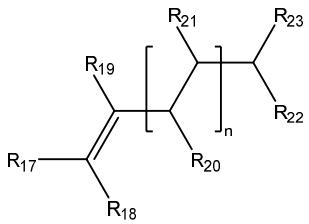
16. The detergent composition of claim 14, wherein the $R_{24}$ is a trisubstituted olefin and 40 weight percent or more of $R_{24}$ is a dimer.

17. The detergent composition of claim 16, wherein 40 weight percent or less of $R_{24}$ is a trimer, 20 weight percent or less of $R_{24}$ is a tetramer, and/or 5 weight percent or less of $R_{24}$ is a pentamer.

18. The detergent composition of claim 12, wherein the $R_{24}$ group is derived from a mixture of oligomers and a majority of oligomers in the mixture have the structure of Formula VI and/or Formula VII below:




(Formula VI)




(Formula VII)

wherein

$R_{11}$ is an alkyl group;

each of $R_{12}$, $R_{13}$, $R_{14}$, $R_{15}$, and/or $R_{16}$, is the same or different at each occurrence, and independently represents a hydrogen or a substituted or unsubstituted hydrocarbyl group;

only one of $R_{17}$, $R_{18}$ and $R_{19}$ is hydrogen and one of the remaining two of $R_{17}$, $R_{18}$ and $R_{19}$ is a substituted or unsubstituted hydrocarbyl group having 1, 2, or 3 carbons and the other of the

remaining two of $R_{17}$, $R_{18}$ and $R_{19}$ is a substituted or unsubstituted hydrocarbyl group;

each of $R_{20}$, $R_{21}$, $R_{22}$, and/or $R_{23}$, is the same or different at each occurrence, and independently represents a hydrogen or a substituted or unsubstituted hydrocarbyl group;

each n is, independently, an integer of 0 to 3.

19. A lubricating oil composition including the sulfurized alkyl phenate of claim 1 and one or more base oils of lubricating viscosity.

20. A lubricating oil composition including the detergent composition of claim 12 and one or more base oils of lubricating viscosity.