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(54) Title: LUBRICATING OIL COMPOSITIONS WITH VISCOSITY AND DEPOSIT CONTROL

Fig. 6

AO Code	CE21	IE19	IE20	CE22	IE21	IE22	CE23	IE23	IE24	CE24	IE25	IE26
A							1.0	1.0	1.0	2.0	2.0	2.0
B												
C	1.0	1.0	1.0	2.0	2.0	2.0						
D												
E												
F												
G												
H												
I		1.3	2.7		1.3	2.7		1.3	2.7		1.3	2.7
E1												
E2												
E3												
E4												
Balance	RF5	RF5	RF5	RF5	RF5	RF5	RF5	RF5	RF5	RF5	RF5	RF5
TEOST 24C, deposit mg	29.5	18	22.8	30.3	27.8	9.8	19.6	23	13.6	23.4	5.8	6.2
ROT, hrs	333	425	458	496	489	556	325	415	444	458	490	506
MHT TEOST 300 °C, mg	49	21	19	26	16	9	39	22	16	14	12	9

(57) Abstract: A method for improving viscosity control, while maintaining or improving deposit control, of a lubricating oil in an engine or other mechanical component lubricated with the lubricating oil by using as the lubricating oil a formulated oil. The formulated oil has a composition including a lubricating oil base stock as a major component, and at least one polymeric aminic antioxidant, as a minor component. The at least one polymeric aminic antioxidant is the polymerization reaction product of one or more unsubstituted or hydrocarbyl-substituted diphenyl amines, one or more unsubstituted or hydrocarbyl-substituted phenyl naphthyl amines, or both one or more of unsubstituted or hydrocarbyl-substituted diphenylamine with one or more unsubstituted or hydrocarbyl-substituted phenyl naphthylamine. The lubricating oil base stock is present in an amount from 1 to 85 weight percent and the at least one polymeric aminic antioxidant is present in an amount from 0.1 to 5 weight percent.



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

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LUBRICATING OIL COMPOSITIONS WITH VISCOSITY AND DEPOSIT CONTROL**FIELD**

[0001] This disclosure relates to engine lubricating oils with viscosity control and deposit control. In particular, this disclosure relates to lubricating oils, methods for improving viscosity control and deposit control of a lubricating oil in an engine or other mechanical component lubricated with the lubricating oil, and methods for improving oxidative stability and deposit control, of a lubricating oil in an engine or other mechanical component lubricated with the lubricating oil. The lubricating oils of this disclosure are useful as passenger vehicle engine oil (PVEO) products or commercial vehicle engine oil (CVEO) products.

BACKGROUND

[0002] Lubricant oxidative stability is one of the key parameters controlling oil life, which translates in oil drain interval in practical terms. Additionally, deposit formation is an issue associated with the decomposition of the base stock molecules mostly propagated by oxidative chain reactions. There are several conventional approaches to improve the resistance to oxidation of a finished lubricant product, but most products are formulated using small molecules such as diphenylamine (DPA) or a phenolic antioxidant.

[0003] Improved oxidation stability is necessary to increase oil life and oil drain intervals, thus reducing the amount of used oil generated as a consequence of more frequent oil changes. Longer oil life and oil drain intervals are key benefits that are desirable to end customers. Traditional antioxidant packages provide standard protection leaving the main differentiation hinging on the quality of the base stock in the formulation.

[0004] What is needed is newly designed lubricants capable of controlling oxidation and oil thickening for longer periods of time as compared to conventional lubricants. Further, what is needed is newly designed lubricants that enable extended oil life in combination with desired deposit control and cleanliness performance.

SUMMARY

[0005] This disclosure relates to engine lubricating oils with viscosity control and deposit control. In particular, this disclosure relates to lubricating oils, methods for improving viscosity control and deposit control of a lubricating oil in an engine or other mechanical component lubricated with the lubricating oil, and methods for improving oxidative stability and deposit control, of a lubricating oil in an engine or other mechanical component lubricated with the lubricating oil. The lubricating oils of this disclosure are useful as passenger vehicle engine oil (PVEO) products or commercial vehicle engine oil (CVEO) products.

[0006] This disclosure also relates in part to a method for improving viscosity control, while

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maintaining or improving deposit control, of a lubricating oil in an engine or other mechanical component lubricated with the lubricating oil by using as the lubricating oil a formulated oil. The formulated oil has a composition comprising a lubricating oil base stock as a major component, and at least one polymeric aminic antioxidant, as a minor component. The at least one polymeric aminic antioxidant is the polymerization reaction product of one or more unsubstituted or hydrocarbyl-substituted diphenyl amines, one or more unsubstituted or hydrocarbyl-substituted phenyl naphthyl amines, or both one or more of unsubstituted or hydrocarbyl-substituted diphenylamine with one or more unsubstituted or hydrocarbyl-substituted phenyl naphthylamine. The lubricating oil base stock is present in an amount from about 1 to about 85 weight percent, based on the total weight of the lubricating oil. The at least one polymeric aminic antioxidant is present in an amount from about 0.1 to about 5 weight percent, based on the total weight of the lubricating oil.

[0007] This disclosure further relates in part to a method for improving viscosity control, while maintaining or improving deposit control, of a lubricating oil in an engine or other mechanical component lubricated with the lubricating oil by using as the lubricating oil a formulated oil. The formulated oil has a composition comprising a lubricating oil base stock as a major component, and at least one polymeric aminic antioxidant, as a minor component. The lubricating oil base stock comprises at least one branched polyol ester, which is obtained by reacting one or more polyhydric alcohols with one or more branched mono-carboxylic acids containing at least about 4 carbon atoms. The at least one polymeric aminic antioxidant is the polymerization reaction product of one or more unsubstituted or hydrocarbyl-substituted diphenyl amines, one or more unsubstituted or hydrocarbyl-substituted phenyl naphthyl amines, or both one or more of unsubstituted or hydrocarbyl-substituted diphenylamine with one or more unsubstituted or hydrocarbyl-substituted phenyl naphthylamine. The lubricating oil base stock is present in an amount from about 1 to about 85 weight percent, based on the total weight of the lubricating oil. The at least one polymeric aminic antioxidant is present in an amount from about 0.1 to about 5 weight percent, based on the total weight of the lubricating oil.

[0008] This disclosure yet further relates in part to a lubricating oil having a composition comprising a lubricating oil base stock as a major component, and at least one polymeric aminic antioxidant, as a minor component. The at least one polymeric aminic antioxidant is the polymerization reaction product of one or more unsubstituted or hydrocarbyl-substituted diphenyl amines, one or more unsubstituted or hydrocarbyl-substituted phenyl naphthyl amines, or both one or more of unsubstituted or hydrocarbyl-substituted diphenylamine with one or more unsubstituted or hydrocarbyl-substituted phenyl naphthylamine. The lubricating oil base stock is

present in an amount from about 1 to about 85 weight percent, based on the total weight of the lubricating oil. The at least one polymeric aminic antioxidant is present in an amount from about 0.1 to about 5 weight percent, based on the total weight of the lubricating oil.

[0009] This disclosure still further relates in part to a lubricating oil having a composition comprising a lubricating oil base stock as a major component, and at least one polymeric aminic antioxidant, as a minor component. The lubricating oil base stock comprises at least one branched polyol ester, which is obtained by reacting one or more polyhydric alcohols with one or more branched mono-carboxylic acids containing at least about 4 carbon atoms. The at least one polymeric aminic antioxidant is the polymerization reaction product of one or more unsubstituted or hydrocarbyl-substituted diphenyl amines, one or more unsubstituted or hydrocarbyl-substituted phenyl naphthyl amines, or both one or more of unsubstituted or hydrocarbyl-substituted diphenylamine with one or more unsubstituted or hydrocarbyl-substituted phenyl naphthylamine. The lubricating oil base stock is present in an amount from about 1 to about 85 weight percent, based on the total weight of the lubricating oil. The at least one polymeric aminic antioxidant is present in an amount from about 0.1 to about 5 weight percent, based on the total weight of the lubricating oil.

[0010] This disclosure also relates in part to a method for improving oxidative stability, while maintaining or improving deposit control, of a lubricating oil in an engine or other mechanical component lubricated with the lubricating oil by using as the lubricating oil a formulated oil. The formulated oil has a composition comprising a lubricating oil base stock as a major component, and at least one polymeric aminic antioxidant, as a minor component. The at least one polymeric aminic antioxidant is the polymerization reaction product of one or more unsubstituted or hydrocarbyl-substituted diphenyl amines, one or more unsubstituted or hydrocarbyl-substituted phenyl naphthyl amines, or both one or more of unsubstituted or hydrocarbyl-substituted diphenylamine with one or more unsubstituted or hydrocarbyl-substituted phenyl naphthylamine. The lubricating oil base stock is present in an amount from about 1 to about 85 weight percent, based on the total weight of the lubricating oil. The at least one polymeric aminic antioxidant is present in an amount from about 0.1 to about 5 weight percent, based on the total weight of the lubricating oil.

[0011] This disclosure further relates in part to a method for improving oxidative stability, while maintaining or improving deposit control, of a lubricating oil in an engine or other mechanical component lubricated with the lubricating oil by using as the lubricating oil a formulated oil. The formulated oil has a composition comprising a lubricating oil base stock as a major component, and at least one polymeric aminic antioxidant, as a minor component. The

lubricating oil base stock comprises at least one branched polyol ester, which is obtained by reacting one or more polyhydric alcohols with one or more branched mono-carboxylic acids containing at least about 4 carbon atoms. The at least one polymeric aminic antioxidant is the polymerization reaction product of one or more unsubstituted or hydrocarbyl-substituted diphenyl amines, one or more unsubstituted or hydrocarbyl-substituted phenyl naphthyl amines, or both one or more of unsubstituted or hydrocarbyl-substituted diphenylamine with one or more unsubstituted or hydrocarbyl-substituted phenyl naphthylamine. The lubricating oil base stock is present in an amount from about 1 to about 85 weight percent, based on the total weight of the lubricating oil. The at least one polymeric aminic antioxidant is present in an amount from about 0.1 to about 5 weight percent, based on the total weight of the lubricating oil.

[0012] It has been surprisingly found that, in accordance with this disclosure, oxidative stability is improved, and deposit control is maintained or improved, as compared to oxidative stability and deposit control achieved using a lubricating oil other than the formulated oil.

[0013] In particular, it has been surprisingly found that, for oil life assessed using the engine oil Bulk Oxidation Test (BOT) and the Oxidative Stability Test (OST) as described herein, the number of hours to 200% increase in kinematic viscosity at 40°C is increased as compared to the number of hours to 200% increase in kinematic viscosity at 40°C of a lubricating oil containing a minor amount of an antioxidant other than the polymeric aminic antioxidant.

[0014] More, in particular, it has been surprisingly found that, in deposit measurements of the lubricating oil by thermo-oxidation engine oil simulation (TEOST 33C) measured by ASTM D6335, the amount of total deposits is reduced or maintained as compared to the amount of total deposits in a lubricating oil containing a minor component other than the at least one polymeric aminic antioxidant. It has been also surprisingly found that the benefits associated with the invention are exhibited with a modified version of the MHT TEOST (ASTM D7097).

[0015] Other objects and advantages of the present disclosure will become apparent from the detailed description that follows.

BRIEF DESCRIPTION OF THE DRAWINGS

[0016] Fig. 1 shows chemical structures and nomenclature of illustrative antioxidants used in lubricating oil formulations in accordance with the Examples.

[0017] Fig. 2 shows tabulated results of Bulk Oxidation Test (BOT) performance as a function of antioxidant selection in accordance with the Examples.

[0018] Fig. 3 shows tabulated results of TEOST 33C performance as a function of antioxidant selection in accordance with the Examples.

[0019] Fig. 4 shows tabulated results of antioxidant package evaluation based on Bulk

Oxidation Test (BOT) and Oxidation Stability Test (OST) methods in accordance with the Examples.

[0020] Fig. 5 shows tabulated results of antioxidant package evaluation based on Bulk Oxidation Test (BOT), in particular, the effect of phenolic antioxidants included in the formulations, in accordance with the Examples.

[0021] Fig. 6 shows tabulated results of antioxidant packages based on Bulk Oxidation Test, TEOST 33C (ASTM D6335), and modified MHT TEOST (ASTM D7097 run at 300 °C).

DETAILED DESCRIPTION

[0022] All numerical values within the detailed description and the claims herein are modified by “about” or “approximately” the indicated value, and take into account experimental error and variations that would be expected by a person having ordinary skill in the art.

[0023] In accordance with this disclosure, in using polymeric antioxidants containing amine functional groups, oxidative stability is increased (e.g., by more than 3 times), as measured by Bulk Oxidation Test (BOT), when comparing the performance of a traditional small molecule antioxidant. It has been found that the use of phenolic antioxidant can lead to decreased oxidative stability when employed above a relatively small treat rate. Using a high level of aminic antioxidant can provide similar oxidative stability benefits, however, when used at these high treat rates, the deposit control as measured by TEOST 33C is unacceptable per industry requirements. In contrast, in accordance with this disclosure, when polymerized aminic antioxidants are used in the formulation, excellent oxidation and viscosity control are observed along with unexpected and significant improvement in deposit control.

[0024] Also, in accordance with this disclosure, a method is provided to improve oxidative stability through the lifetime of a lubricant through selection of polymerized aminic antioxidants in combination with Group V base stocks. Additionally, the deposit control characteristics as measured by TEOST 33C and modified MHT TEOST tests, track the ranking observed in oxidation control with the best candidates also show lowest deposit.

[0025] Further, in accordance with this disclosure, finished lubricants can be designed that are capable of controlling oxidation and oil thickening for long durations (e.g., 2-3 times longer) as compared to conventional lubricants. This disclosure also enables extended oil life in combination with superior deposit control and cleanliness performance through a balance of antioxidant chemistry, in light of the negative performance in oxidation control observed when employing similarly high concentrations of hindered phenol, and in light of the deposit debits observed when employing diphenylamine antioxidants at high treat rates.

[0026] Employing polymeric aminic antioxidants allows for an exponential improvement in

oxidative stability, highlighting potential synergies with traditional aminic antioxidants, which debits are observed in the presence of increasing amounts of phenolic antioxidants. In addition, when targeting the same level of oxidation performance with traditional small molecule antioxidants (e.g., diphenylamine and hindered phenol) as is seen with polymeric aminic antioxidants, there are negative performance impacts observed in the areas of high temperature deposits and decreased oxidative stability in some cases.

Branched Polyol Ester Lubricating Oil Base Stocks

[0027] Branched polyol esters comprise a useful base stock of this disclosure. The branched polyol esters are obtained by reacting one or more polyhydric alcohols, preferably the hindered polyols (such as the neopentyl polyols, e.g., neopentyl glycol, trimethylol ethane, 2-methyl-2-propyl-1,3-propanediol, trimethylol propane, pentaerythritol and dipentaerythritol) with single or mixed branched mono-carboxylic acids containing at least about 4 carbon atoms, preferably C₅ to C₃₀ branched mono-carboxylic acids including 2,2-dimethyl propionic acid (neopentanoic acid), neoheptanoic acid, neo-octanoic acid, neononanoic acid, iso-hexanoic acid, neodecanoic acid, 2-ethyl hexanoic acid (2EH), 3,5,5-trimethyl hexanoic acid (TMH), isoheptanoic acid, isooctanoic acid, isononanoic acid, isodecanoic acid, or mixtures of any of these materials. These branched polyol esters include fully converted and partially converted polyol esters.

[0028] Particularly useful polyols include, for example, neopentyl glycol, 2,2-dimethylol butane, trimethylol ethane, trimethylol propane, trimethylol butane, mono-pentaerythritol, technical grade pentaerythritol, di-pentaerythritol, tri-pentaerythritol, ethylene glycol, propylene glycol and polyalkylene glycols (e.g., polyethylene glycols, polypropylene glycols, 1,4-butanediol, sorbitol and the like, 2-methylpropanediol, polybutylene glycols, etc., and blends thereof such as a polymerized mixture of ethylene glycol and propylene glycol). The most preferred alcohols are technical grade (e.g., approximately 88% mono-, 10% di- and 1-2% tri-pentaerythritol) pentaerythritol, mono-pentaerythritol, di-pentaerythritol, neopentyl glycol and trimethylol propane.

[0029] Particularly useful branched mono-carboxylic acids include, for example, 2,2-dimethyl propionic acid (neopentanoic acid), neoheptanoic acid, neo-octanoic acid, neononanoic acid, iso-hexanoic acid, neodecanoic acid, 2-ethyl hexanoic acid (2EH), 3,5,5-trimethyl hexanoic acid (TMH), isoheptanoic acid, isooctanoic acid, isononanoic acid, isodecanoic acid, or mixtures of any of these materials. One especially preferred branched acid is 3,5,5-trimethyl hexanoic acid. The term "neo" as used herein refers to a trialkyl acetic acid, i.e., an acid which is triply substituted at the alpha carbon with alkyl groups.

[0030] Preferably, the branched polyol ester is derived from a polyhydric alcohol and a

branched mono-carboxylic acid. In particular, the branched polyol ester is obtained by reacting one or more polyhydric alcohols with one or more branched mono-carboxylic acids containing at least about 4 carbon atoms.

[0031] Preferred branched polyol esters useful in this disclosure include, for example, mono-pentaerythritol ester of branched mono-carboxylic acids, di-pentaerythritol ester of branched mono-carboxylic acids, trimethylolpropane ester of C₈-C₁₀ acids, and the like.

[0032] Other synthetic esters that can be useful in this disclosure are those which are obtained by reacting one or more polyhydric alcohols, preferably the hindered polyols (such as the neopentyl polyols, e.g., neopentyl glycol, trimethylol ethane, 2-methyl-2-propyl-1,3-propanediol, trimethylol propane, pentaerythritol and dipentaerythritol) with mono carboxylic acids containing at least about 4 carbon atoms, preferably branched C₅ to C₃₀ acids including caprylic acid, capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, arachic acid, and behenic acid, or the corresponding branched chain fatty acids or unsaturated fatty acids such as oleic acid, or mixtures of any of these materials.

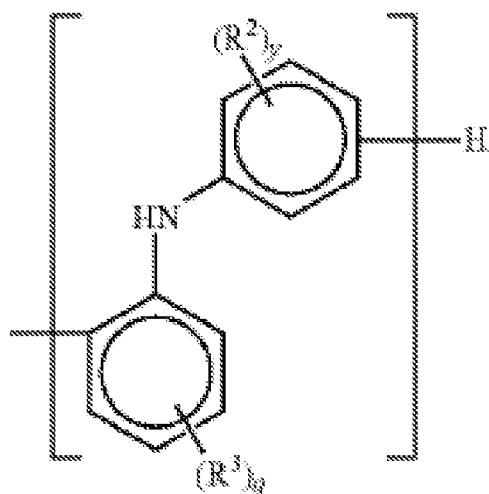
[0033] Other ester base oils useful in this disclosure include adipate esters. The dialkyl adipate ester is derived from adipic acid and a branched alkyl alcohol.

[0034] Mixtures of branched polyol ester base stocks with other lubricating oil base stocks (e.g., Groups I, II, III, IV and V base stocks) may be useful in the lubricating oil formulations of this disclosure.

[0035] The branched polyol ester can be present in an amount of from about 1 to about 50 weight percent, or from about 5 to about 45 weight percent, or from about 10 to about 40 weight percent, or from about 15 to about 35 weight percent, or from about 20 to about 30 weight percent, based on the total weight of the formulated oil.

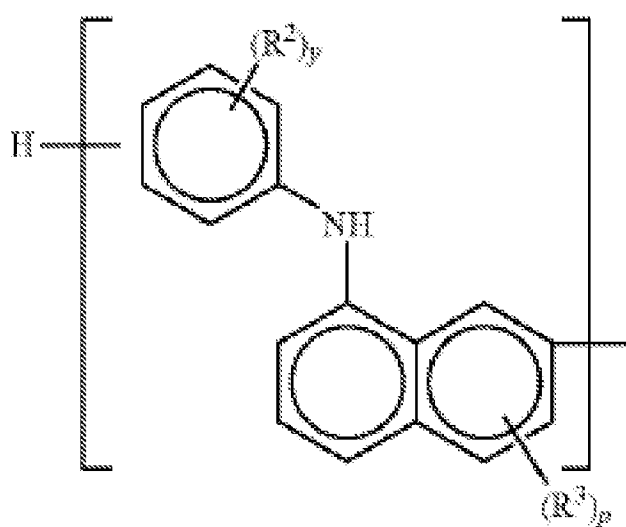
Polymeric Aminic Antioxidants

[0036] Polymeric aminic antioxidants are the polymerization reaction products of one or more unsubstituted or hydrocarbyl-substituted diphenyl amines, one or more unsubstituted or hydrocarbyl-substituted phenyl naphthyl amines or both one or more of unsubstituted or hydrocarbyl-substituted diphenylamine with one or more unsubstituted or hydrocarbyl-substituted phenyl naphthylamine. A representative schematic is presented below:



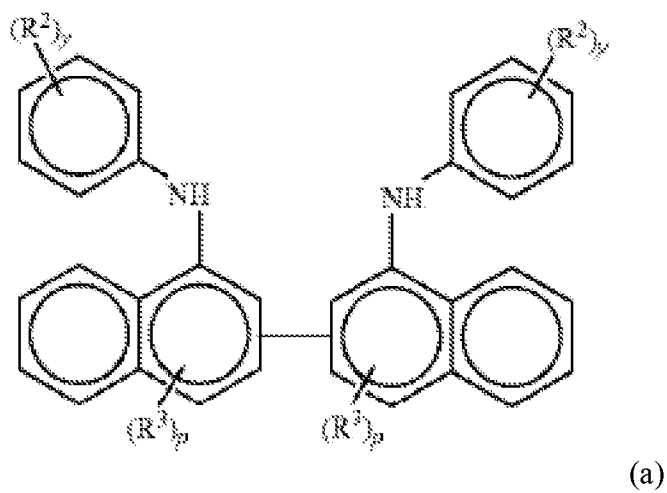
(A)

and/or

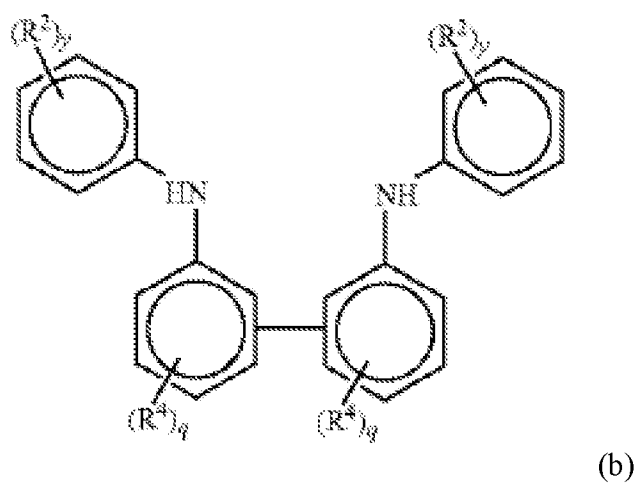


(B)

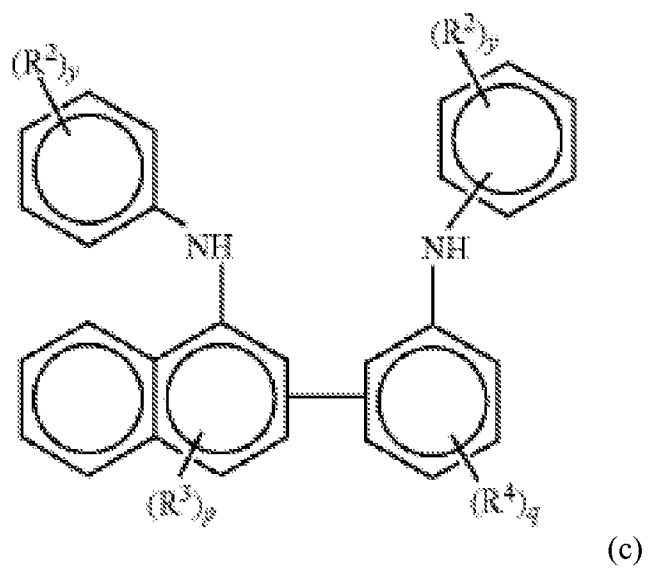
wherein (A) and (B) each range from zero to 10, preferably zero to 5, more preferably zero to 3, most preferably 1 to 3, provided (A)+(B) is at least 2; R^2 is a styrene or C1 to C30 alkyl, R^3 is a styrene or C1 to C30 alkyl, q and y individually range from 0 to up to the valence of the aryl group to which the respective R groups are attached; for example:



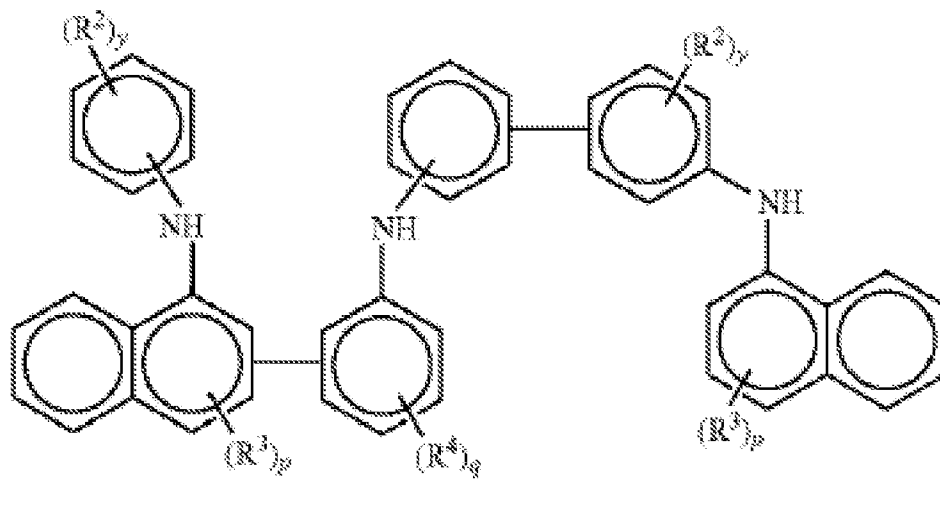
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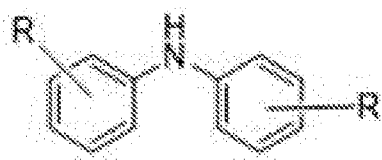
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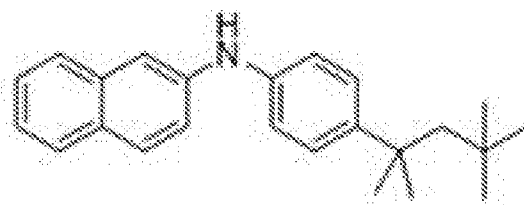
wherein R^2 is a styrene or C1 to C30 alkyl, R^3 is a styrene or C1 to C30 alkyl, R^4 is a styrene or C1 to C30 alkyl, preferably R^2 is a C1 to C30 alkyl, R^3 is a C1 to C30 alkyl, R^4 is a C1 to C30 alkyl, more preferably R^2 is a C4 to C10 alkyl, R^3 is a C4 to C10 alkyl and R^4 is a C4 to C10 alkyl, p, q and y individually range from 0 to up to the valence of the aryl group to which the respective R groups are attached, preferably at least one of p, q and y range from 1 to up to the valence of the aryl group to which the respective R group(s) are attached, more preferably p, q and y each individually range from at least 1 to up to the valence of the aryl group to which the respective R groups are attached.

[0037] In a preferred embodiment, the at least one polymeric aminic antioxidant is the polymerization reaction product formed by any combination of (A) and (B) above including, but not limited to, (A)(A), (A)(B), (B)(B), (A)(A)(B), (A)(A)(A), (A)(B)(A), (B)(B)(B), (B)(B)(A), (A)(A)(A)(A), (A)(A)(B)(B), (A)(A)(A)(B), (B)(B)(B)(B), (B)(B)(B)(A), (A)(A)(A)(A)(A), (A)(B)(A)(B)(A), (A)(B)(B)(B)(A), and the like.

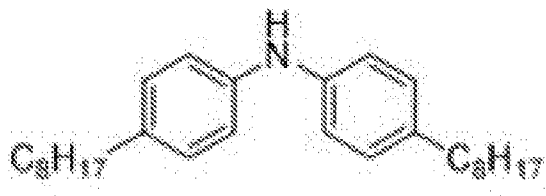
[0038] In another preferred embodiment, the at least one polymeric aminic antioxidant is the polymerization reaction product formed by any combination of:



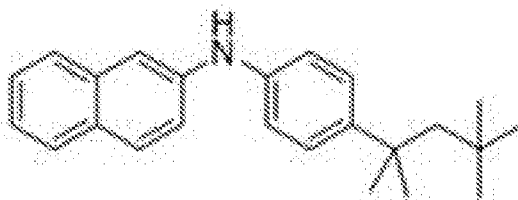
wherein R is H, C_4H_9 , C_8H_{17} , or C_9H_{19} ; and/or



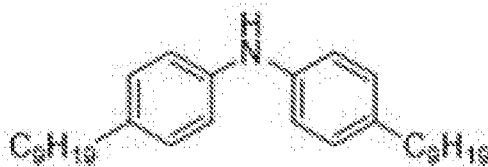
[0039] In a further preferred embodiment, the at least one polymeric aminic antioxidant is the polymerization reaction product formed by any combination of:



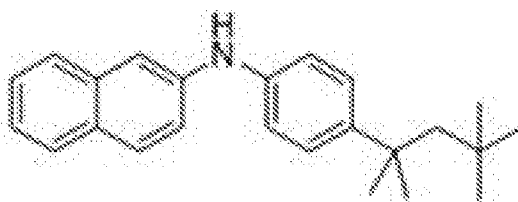
and/or



[0040] In yet a further preferred embodiment, the at least one polymeric aminic antioxidant is the polymerization reaction product formed by any combination of:



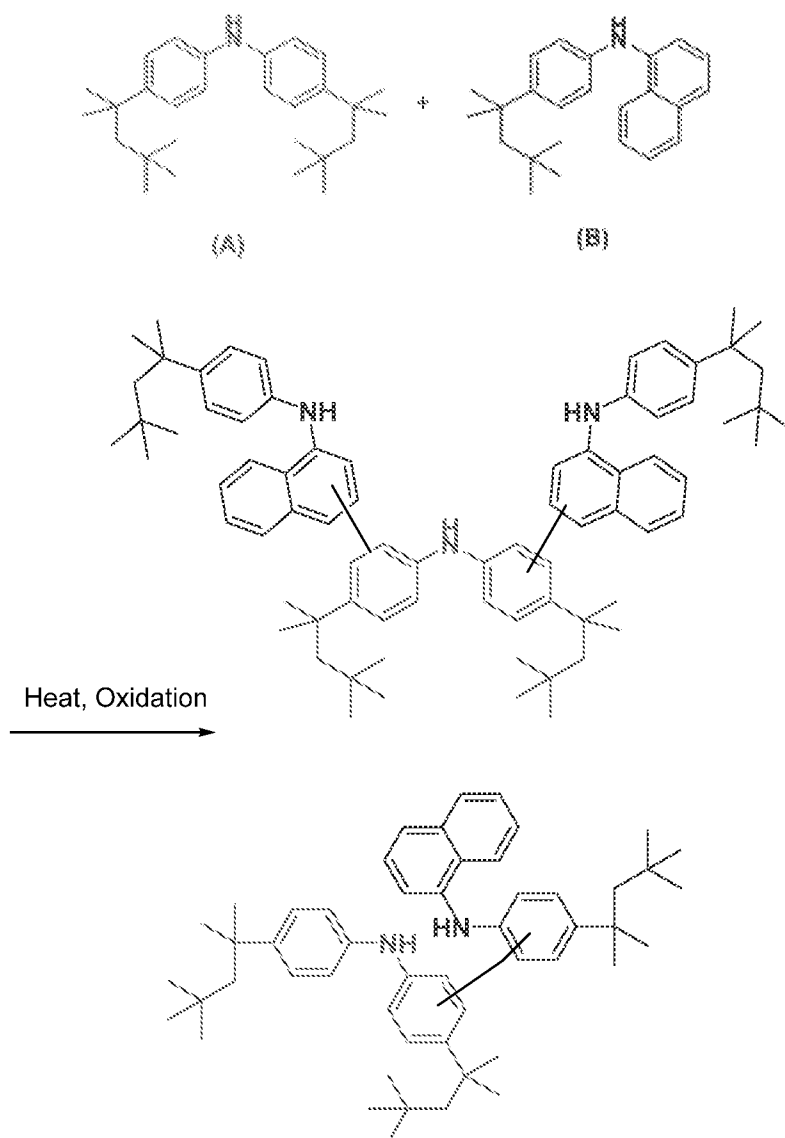
and/or



[0041] Other more extensive oligomers are within the scope of this disclosure, but materials of formulae (a), (b), (c) and (d) are preferred.

[0042] The polymeric aminic antioxidant may contain nonpolymerized aryl amine antioxidant starting materials as a result of the preparation procedure. Additional monomeric amine antioxidants may be added to the lubricant to impart desired properties. Examples of monomeric amine antioxidants include but are not limited to diphenyl amine, alkylated diphenyl amines, styrenated diphenyl amines, phenyl-N-naphthyl amine, alkylated phenyl-N-naphthyl amines, styrenated phenyl-N-naphthyl amines, phenothiazine, alkylated phenothiazine, and styrenated phenothiazine. Other antioxidants such as hindered phenols and zinc dithiophosphates can also be added to the lubricant in addition to the polymerized amine antioxidant.

[0043] The polymeric aminic antioxidants useful in this disclosure can be prepared by conventional polymerization reactions. See, for example, U.S. Patent Nos. 6,426,324 and 8,623,795. An illustrative polymerization reaction for preparing preferred polymeric aminic antioxidants useful in this disclosure is set forth below. The product of the reaction can yield more than the two oligomers shown below, for example, any combination of (A) and (B) below including, but not limited to, (A)(A), (A)(B), (B)(B), (A)(A)(B), (A)(A)(A), (A)(B)(A), (B)(B)(B), (B)(B)(A), (A)(A)(A)(A), (A)(A)(B)(B), (A)(A)(A)(B), (B)(B)(B)(B), (B)(B)(B)(A), (A)(A)(A)(A)(A), (A)(B)(A)(B)(A), (A)(B)(B)(B)(A), and the like.



[0044] The polymeric aminic antioxidant is present in an amount in the range 0.1 to 10 wt % (active ingredient), preferably 0.1 to 5 wt % (active ingredient), or 0.1 to 4 wt % (active ingredient), or 0.1 to 2.5 wt % (active ingredient) or 0.1 to 1.5 wt % (active ingredient), or 1.5 to 4 wt % (active ingredient), of polymerized aminic antioxidant exclusive of any unpolymerized aryl amine which may be present or any added antioxidants.

Other Lubricating Oil Base Stocks

[0045] A wide range of lubricating base oils is known in the art. Lubricating base oils that are useful in the present disclosure are both natural oils, and synthetic oils, and unconventional oils (or mixtures thereof) can be used unrefined, refined, or rerefined (the latter is also known as reclaimed or reprocessed oil). Unrefined oils are those obtained directly from a natural or synthetic source and used without added purification. These include shale oil obtained directly from retorting operations, petroleum oil obtained directly from primary distillation, and ester oil obtained directly from an esterification process. Refined oils are similar to the oils discussed for unrefined oils except refined oils are subjected to one or more purification steps to improve at least one lubricating oil property. One skilled in the art is familiar with many purification processes. These processes include solvent extraction, secondary distillation, acid extraction, base extraction, filtration, and percolation. Rerefined oils are obtained by processes analogous to refined oils but using an oil that has been previously used as a feed stock.

[0046] Groups I, II, III, IV and V are broad base oil stock categories developed and defined by the American Petroleum Institute (API Publication 1509; www.API.org) to create guidelines for lubricant base oils. Group I base stocks have a viscosity index of between about 80 to 120 and contain greater than about 0.03% sulfur and/or less than about 90% saturates. Group II base stocks have a viscosity index of between about 80 to 120, and contain less than or equal to about 0.03% sulfur and greater than or equal to about 90% saturates. Group III stocks have a viscosity index greater than about 120 and contain less than or equal to about 0.03 % sulfur and greater than about 90% saturates. Group IV includes polyalphaolefins (PAO). Group V base stock includes base stocks not included in Groups I-IV. The table below summarizes properties of each of these five groups.

	Base Oil Properties		
	Saturates	Sulfur	Viscosity Index
Group I	<90 and/or	>0.03% and	≥80 and <120
Group II	≥90 and	≤0.03% and	≥80 and <120
Group III	≥90 and	≤0.03% and	≥120
Group IV	Polyalphaolefins (PAO)		
Group V	All other base oil stocks not included in Groups I, II, III or IV		

[0047] Natural oils include animal oils, vegetable oils (castor oil and lard oil, for example), and mineral oils. Animal and vegetable oils possessing favorable thermal oxidative stability can be used. Of the natural oils, mineral oils are preferred. Mineral oils vary widely as to their crude source, for example, as to whether they are paraffinic, naphthenic, or mixed paraffinic-

naphthenic. Oils derived from coal or shale are also useful. Natural oils vary also as to the method used for their production and purification, for example, their distillation range and whether they are straight run or cracked, hydrotreated, or solvent extracted.

[0048] Group II and/or Group III hydroprocessed or hydrocracked base stocks, including synthetic oils such as polyalphaolefins, alkyl aromatics and synthetic esters are also well known base stock oils.

[0049] Synthetic oils include hydrocarbon oil. Hydrocarbon oils include oils such as polymerized and interpolymerized olefins (polybutylenes, polypropylenes, propylene isobutylene copolymers, ethylene-olefin copolymers, and ethylene-alphaolefin copolymers, for example). Polyalphaolefin (PAO) oil base stocks are commonly used synthetic hydrocarbon oil. By way of example, PAOs derived from C₈, C₁₀, C₁₂, C₁₄ olefins or mixtures thereof may be utilized. See U.S. Patent Nos. 4,956,122; 4,827,064; and 4,827,073.

[0050] The number average molecular weights of the PAOs, which are known materials and generally available on a major commercial scale from suppliers such as ExxonMobil Chemical Company, Chevron Phillips Chemical Company, BP, and others, typically vary from about 250 to about 3,000, although PAO's may be made in viscosities up to about 150 cSt (100°C). The PAOs are typically comprised of relatively low molecular weight hydrogenated polymers or oligomers of alphaolefins which include, but are not limited to, C₂ to about C₃₂ alphaolefins with the C₈ to about C₁₆ alphaolefins, such as 1-hexene, 1-octene, 1-decene, 1-dodecene and the like, being preferred. The preferred polyalphaolefins are poly-1-hexene, poly-1-octene, poly-1-decene and poly-1-dodecene and mixtures thereof and mixed olefin-derived polyolefins. However, the dimers of higher olefins in the range of C₁₄ to C₁₈ may be used to provide low viscosity base stocks of acceptably low volatility. Depending on the viscosity grade and the starting oligomer, the PAOs may be predominantly trimers and tetramers of the starting olefins, with minor amounts of the higher oligomers, having a viscosity range of 1.5 to 12 cSt. PAO fluids of particular use may include 3.0 cSt, 3.4 cSt, and/or 3.6 cSt and combinations thereof. Bi-modal mixtures of PAO fluids having a viscosity range of 1.5 to 150 cSt may be used if desired.

[0051] The PAO fluids may be conveniently made by the polymerization of an alphaolefin in the presence of a polymerization catalyst such as the Friedel-Crafts catalysts including, for example, aluminum trichloride, boron trifluoride or complexes of boron trifluoride with water, alcohols such as ethanol, propanol or butanol, carboxylic acids or esters such as ethyl acetate or ethyl propionate. For example the methods disclosed by U.S. Patent Nos. 4,149,178 or 3,382,291 may be conveniently used herein. Other descriptions of PAO synthesis are found in the following U.S. Patent Nos. 3,742,082; 3,769,363; 3,876,720; 4,239,930; 4,367,352; 4,413,156;

4,434,408; 4,910,355; 4,956,122; and 5,068,487. The dimers of the C₁₄ to C₁₈ olefins are described in U.S. Patent No. 4,218,330.

[0052] The alkylated naphthalene can be used as base oil or base oil component and can be any hydrocarbyl molecule that contains at least about 5% of its weight derived from a naphthenoid moiety, or its derivatives. These alkylated naphthalenes include alkyl naphthalenes, alkyl naphthols, and the like. The naphthenoid group can be mono-alkylated, dialkylated, polyalkylated, and the like. The naphthenoid group can be mono- or poly-functionalized. The naphthenoid group can also be derived from natural (petroleum) sources, provided at least about 5% of the molecule is comprised of the naphthenoid moiety. Viscosities at 100°C of approximately 3 cSt to about 50 cSt are preferred, with viscosities of approximately 3.4 cSt to about 20 cSt often being more preferred for the naphthylene component. In one embodiment, an alkyl naphthalene where the alkyl group is primarily comprised of 1-hexadecene is used. Other alkylates of naphthalene can be advantageously used. Naphthalene or methyl naphthalene, for example, can be alkylated with olefins such as octene, decene, dodecene, tetradecene or higher, mixtures of similar olefins, and the like.

[0053] Alkylated naphthalenes of the present disclosure may be produced by well-known Friedel-Crafts alkylation of aromatic compounds. See Friedel-Crafts and Related Reactions, Olah, G. A. (ed.), Inter-science Publishers, New York, 1963. For example, an aromatic compound, such as naphthalene, is alkylated by an olefin, alkyl halide or alcohol in the presence of a Friedel-Crafts catalyst. See Friedel-Crafts and Related Reactions, Vol. 2, part 1, chapters 14, 17, and 18, See Olah, G. A. (ed.), Inter-science Publishers, New York, 1964. Many homogeneous or heterogeneous, solid catalysts are known to one skilled in the art. The choice of catalyst depends on the reactivity of the starting materials and product quality requirements. For example, strong acids such as AlCl₃, BF₃, or HF may be used. In some cases, milder catalysts such as FeCl₃ or SnCl₄ are preferred. Newer alkylation technology uses zeolites or solid super acids.

[0054] Mixtures of alkylated naphthalene base stocks with other lubricating oil base stocks (e.g., Groups I, II, III, IV and V base stocks) may be useful in the lubricating oil formulations of this disclosure.

[0055] The alkylated naphthalene can be present in an amount of from about 30 to about 99.8 weight percent, or from about 35 to about 95 weight percent, or from about 40 to about 90 weight percent, or from about 45 to about 85 weight percent, or from about 50 to about 80 weight percent, or from about 55 to about 75 weight percent, or from about 60 to about 70 weight percent, based on the total weight of the formulated oil.

[0056] Other useful lubricant oil base stocks include wax isomerate base stocks and base oils, comprising hydroisomerized waxy stocks (e.g. waxy stocks such as gas oils, slack waxes, fuels hydrocracker bottoms, etc.), hydroisomerized Fischer-Tropsch waxes, Gas-to-Liquids (GTL) base stocks and base oils, and other wax isomerate hydroisomerized base stocks and base oils, or mixtures thereof Fischer-Tropsch waxes, the high boiling point residues of Fischer-Tropsch synthesis, are highly paraffinic hydrocarbons with very low sulfur content. The hydroprocessing used for the production of such base stocks may use an amorphous hydrocracking/hydroisomerization catalyst, such as one of the specialized lube hydrocracking (LHDC) catalysts or a crystalline hydrocracking/hydroisomerization catalyst, preferably a zeolitic catalyst. For example, one useful catalyst is ZSM-48 as described in U.S. Patent No. 5,075,269, the disclosure of which is incorporated herein by reference in its entirety. Processes for making hydrocracked/hydroisomerized distillates and hydrocracked/hydroisomerized waxes are described, for example, in U.S. Patent Nos. 2,817,693; 4,975,177; 4,921,594 and 4,897,178 as well as in British Patent Nos. 1,429,494; 1,350,257; 1,440,230 and 1,390,359. Each of the aforementioned patents is incorporated herein in their entirety. Particularly favorable processes are described in European Patent Application Nos. 464546 and 464547, also incorporated herein by reference. Processes using Fischer-Tropsch wax feeds are described in U.S. Patent Nos. 4,594,172 and 4,943,672, the disclosures of which are incorporated herein by reference in their entirety.

[0057] Gas-to-Liquids (GTL) base oils, Fischer-Tropsch wax derived base oils, and other wax-derived hydroisomerized (wax isomerate) base oils be advantageously used in the instant disclosure, and may have useful kinematic viscosities at 100°C of about 3 cSt to about 50 cSt, preferably about 3 cSt to about 30 cSt, more preferably about 3.5 cSt to about 25 cSt, as exemplified by GTL 4 with kinematic viscosity of about 4.0 cSt at 100°C and a viscosity index of about 141. These Gas-to-Liquids (GTL) base oils, Fischer-Tropsch wax derived base oils, and other wax-derived hydroisomerized base oils may have useful pour points of about -20°C or lower, and under some conditions may have advantageous pour points of about -25°C or lower, with useful pour points of about -30°C to about -40°C or lower. Useful compositions of Gas-to-Liquids (GTL) base oils, Fischer-Tropsch wax derived base oils, and wax-derived hydroisomerized base oils are recited in U.S. Patent Nos. 6,080,301; 6,090,989, and 6,165,949 for example, and are incorporated herein in their entirety by reference.

[0058] The hydrocarbyl aromatics can be used as base oil or base oil component and can be any hydrocarbyl molecule that contains at least about 5% of its weight derived from an aromatic moiety such as a benzenoid moiety or naphthenoid moiety, or their derivatives. These

hydrocarbyl aromatics include alkyl benzenes, alkyl naphthalenes, alkyl diphenyl oxides, alkyl naphthols, alkyl diphenyl sulfides, alkylated bis-phenol A, alkylated thiodiphenol, and the like. The aromatic can be mono-alkylated, dialkylated, polyalkylated, and the like. The aromatic can be mono- or poly-functionalized. The hydrocarbyl groups can also be comprised of mixtures of alkyl groups, alkenyl groups, alkynyl, cycloalkyl groups, cycloalkenyl groups and other related hydrocarbyl groups. The hydrocarbyl groups can range from about C₆ up to about C₆₀ with a range of about C₈ to about C₂₀ often being preferred. A mixture of hydrocarbyl groups is often preferred, and up to about three such substituents may be present. The hydrocarbyl group can optionally contain sulfur, oxygen, and/or nitrogen containing substituents. The aromatic group can also be derived from natural (petroleum) sources, provided at least about 5% of the molecule is comprised of an above-type aromatic moiety. Viscosities at 100°C of approximately 3 cSt to about 50 cSt are preferred, with viscosities of approximately 3.4 cSt to about 20 cSt often being more preferred for the hydrocarbyl aromatic component. In one embodiment, an alkyl naphthalene where the alkyl group is primarily comprised of 1-hexadecene is used. Other alkylates of aromatics can be advantageously used. Naphthalene or methyl naphthalene, for example, can be alkylated with olefins such as octene, decene, dodecene, tetradecene or higher, mixtures of similar olefins, and the like. Useful concentrations of hydrocarbyl aromatic in a lubricant oil composition can be about 2% to about 25%, preferably about 4% to about 20%, and more preferably about 4% to about 15%, depending on the application.

[0059] Alkylated aromatics such as the hydrocarbyl aromatics of the present disclosure may be produced by well-known Friedel-Crafts alkylation of aromatic compounds. See Friedel-Crafts and Related Reactions, Olah, G. A. (ed.), Inter-science Publishers, New York, 1963. For example, an aromatic compound, such as benzene or naphthalene, is alkylated by an olefin, alkyl halide or alcohol in the presence of a Friedel-Crafts catalyst. See Friedel-Crafts and Related Reactions, Vol. 2, part 1, chapters 14, 17, and 18, See Olah, G. A. (ed.), Inter-science Publishers, New York, 1964. Many homogeneous or heterogeneous, solid catalysts are known to one skilled in the art. The choice of catalyst depends on the reactivity of the starting materials and product quality requirements. For example, strong acids such as AlCl₃, BF₃, or HF may be used. In some cases, milder catalysts such as FeCl₃ or SnCl₄ are preferred. Newer alkylation technology uses zeolites or solid super acids.

[0060] Other useful fluids of lubricating viscosity include non-conventional or unconventional base stocks that have been processed, preferably catalytically, or synthesized to provide high performance lubrication characteristics.

[0061] Non-conventional or unconventional base stocks/base oils include one or more of a

mixture of base stock(s) derived from one or more Gas-to-Liquids (GTL) materials, as well as isomerate/isodewaxate base stock(s) derived from natural wax or waxy feeds, mineral and or non-mineral oil waxy feed stocks such as slack waxes, natural waxes, and waxy stocks such as gas oils, waxy fuels hydrocracker bottoms, waxy raffinate, hydrocrackate, thermal crackates, or other mineral, mineral oil, or even non-petroleum oil derived waxy materials such as waxy materials received from coal liquefaction or shale oil, and mixtures of such base stocks.

[0062] GTL materials are materials that are derived via one or more synthesis, combination, transformation, rearrangement, and/or degradation/deconstructive processes from gaseous carbon-containing compounds, hydrogen-containing compounds and/or elements as feed stocks such as hydrogen, carbon dioxide, carbon monoxide, water, methane, ethane, ethylene, acetylene, propane, propylene, propyne, butane, butylenes, and butynes. GTL base stocks and/or base oils are GTL materials of lubricating viscosity that are generally derived from hydrocarbons; for example, waxy synthesized hydrocarbons, that are themselves derived from simpler gaseous carbon-containing compounds, hydrogen-containing compounds and/or elements as feed stocks. GTL base stock(s) and/or base oil(s) include oils boiling in the lube oil boiling range (1) separated/fractionated from synthesized GTL materials such as, for example, by distillation and subsequently subjected to a final wax processing step which involves either or both of a catalytic dewaxing process, or a solvent dewaxing process, to produce lube oils of reduced/low pour point; (2) synthesized wax isomerates, comprising, for example, hydrodewaxed or hydroisomerized cat and/or solvent dewaxed synthesized wax or waxy hydrocarbons; (3) hydrodewaxed or hydroisomerized cat and/or solvent dewaxed Fischer-Tropsch (F-T) material (i.e., hydrocarbons, waxy hydrocarbons, waxes and possible analogous oxygenates); preferably hydrodewaxed or hydroisomerized/followed by cat and/or solvent dewaxing dewaxed F-T waxy hydrocarbons, or hydrodewaxed or hydroisomerized/followed by cat (or solvent) dewaxing dewaxed, F-T waxes, or mixtures thereof.

[0063] GTL base stock(s) and/or base oil(s) derived from GTL materials, especially, hydrodewaxed or hydroisomerized/followed by cat and/or solvent dewaxed wax or waxy feed, preferably F-T material derived base stock(s) and/or base oil(s), are characterized typically as having kinematic viscosities at 100°C of from about 2 mm²/s to about 50 mm²/s (ASTM D445). They are further characterized typically as having pour points of -5°C to about -40°C or lower (ASTM D97). They are also characterized typically as having viscosity indices of about 80 to about 140 or greater (ASTM D2270).

[0064] In addition, the GTL base stock(s) and/or base oil(s) are typically highly paraffinic (>90% saturates), and may contain mixtures of monocycloparaffins and multicycloparaffins in

combination with non-cyclic isoparaffins. The ratio of the naphthenic (i.e., cycloparaffin) content in such combinations varies with the catalyst and temperature used. Further, GTL base stock(s) and/or base oil(s) typically have very low sulfur and nitrogen content, generally containing less than about 10 ppm, and more typically less than about 5 ppm of each of these elements. The sulfur and nitrogen content of GTL base stock(s) and/or base oil(s) obtained from F-T material, especially F-T wax, is essentially nil. In addition, the absence of phosphorous and aromatics make this material especially suitable for the formulation of low SAP products.

[0065] The term GTL base stock and/or base oil and/or wax isomerase base stock and/or base oil is to be understood as embracing individual fractions of such materials of wide viscosity range as recovered in the production process, mixtures of two or more of such fractions, as well as mixtures of one or two or more low viscosity fractions with one, two or more higher viscosity fractions to produce a blend wherein the blend exhibits a target kinematic viscosity.

[0066] The GTL material, from which the GTL base stock(s) and/or base oil(s) is/are derived is preferably an F-T material (i.e., hydrocarbons, waxy hydrocarbons, wax).

[0067] Base oils for use in the formulated lubricating oils useful in the present disclosure are any of the variety of oils corresponding to API Group I, Group II, Group III, Group IV, and Group V oils and mixtures thereof, preferably API Group II, Group III, Group IV, and Group V oils and mixtures thereof, more preferably the Group III to Group V base oils due to their exceptional volatility, stability, viscometric and cleanliness features.

[0068] This other base oil typically is present in an amount ranging from about 0.1 to about 90 weight percent, or from about 1 to about 80 weight percent, or from about 1 to about 70 weight percent, or from about 1 to about 60 weight percent, or from about 1 to about 50 weight percent, based on the total weight of the composition. The base oil may be selected from any of the synthetic or natural oils typically used as crankcase lubricating oils for spark ignition and compression-ignited engines. The base oil conveniently has a kinematic viscosity, according to ASTM standards, of about 2.5 cSt to about 12 cSt (or mm²/s) at 100°C and preferably of about 2.5 cSt to about 9 cSt (or mm²/s) at 100°C. Mixtures of synthetic and natural base oils may be used if desired. Mixtures of Group III, IV, and V may be preferable.

Other Additives

[0069] The formulated lubricating oil useful in the present disclosure may additionally contain one or more of the other commonly used lubricating oil performance additives including but not limited to other antioxidants, dispersants, detergents, antiwear additives, corrosion inhibitors, rust inhibitors, metal deactivators, extreme pressure additives, anti-seizure agents, wax modifiers, viscosity index improvers, viscosity modifiers, fluid-loss additives, seal compatibility

agents, friction modifiers, lubricity agents, anti-staining agents, chromophoric agents, defoamants, demulsifiers, emulsifiers, densifiers, wetting agents, gelling agents, tackiness agents, colorants, and others. For a review of many commonly used additives, see Klamann in *Lubricants and Related Products*, Verlag Chemie, Deerfield Beach, FL; ISBN 0-89573-177-0. Reference is also made to "Lubricant Additives" by M. W. Ranney, published by Noyes Data Corporation of Parkridge, NJ (1973); see also U.S. Patent No. 7,704,930, the disclosure of which is incorporated herein in its entirety. These additives are commonly delivered with varying amounts of diluent oil, that may range from 5 weight percent to 50 weight percent.

Other Antioxidants

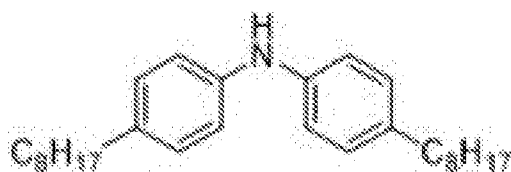
[0070] Other antioxidants may be used in combination with the polymeric aminic antioxidants. Antioxidants retard the oxidative degradation of base oils during service. Such degradation may result in deposits on metal surfaces, the presence of sludge, or a viscosity increase in the lubricant. One skilled in the art knows a wide variety of oxidation inhibitors that are useful in lubricating oil compositions. See, Klamann in *Lubricants and Related Products*, op cite, and U.S. Patent Nos. 4,798,684 and 5,084,197, for example.

[0071] Monomeric amine antioxidants are unsubstituted or hydrocarbon-substituted diphenyl amines, unsubstituted or hydrocarbyl-substituted phenyl naphthyl amines and unsubstituted or hydrocarbyl-substituted phenothiazines wherein the hydrocarbyl-substituted group is styrene or a C1 to C30 alkyl group, preferably a C1 to C10 alkyl group, more preferably a C4 to C10 alkyl group. Other monomeric aryl amines have been described in the patent literature.

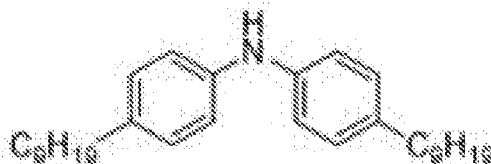
[0072] Useful antioxidants include amine antioxidants, preferably aromatic amine antioxidants. Other useful antioxidants include phenolic antioxidants (e.g., hindered phenolic antioxidants). Aromatic amine antioxidants may be used alone or in combination with phenolic antioxidants. Typical examples of amine antioxidants include: alkylated and non-alkylated aromatic amines such as aromatic monoamines of the formula $R^8R^9R^{10}N$ where R^8 is an aliphatic, aromatic or substituted aromatic group, R^9 is an aromatic or a substituted aromatic group, and R^{10} is H, alkyl, aryl or $R^{11}S(O)_xR^{12}$ where R^{11} is an alkylene, alkenylene, or aralkylene group, R^{12} is a higher alkyl group, or an alkenyl, aryl, or alkaryl group, and x is 0, 1 or 2. The aliphatic group R^8 may contain from 1 to 20 carbon atoms, and preferably contains from 6 to 12 carbon atoms. The aliphatic group is an aliphatic group. Preferably, both R^8 and R^9 are aromatic or substituted aromatic groups, and the aromatic group may be a fused ring aromatic group such as naphthyl. Aromatic groups R^8 and R^9 may be joined together with other groups such as S.

[0073] Typical aromatic amine antioxidants have alkyl substituent groups of at least 6 carbon atoms. Examples of aliphatic groups include hexyl, heptyl, octyl, nonyl, and decyl. Generally, the aliphatic groups will not contain more than 14 carbon atoms. The general types of amine antioxidants useful in the present compositions include diphenylamines, phenyl naphthylamines, phenothiazines, imidodibenzyls and diphenyl phenylene diamines. Mixtures of two or more aromatic amines are also useful. Particular examples of aromatic amine antioxidants useful in the present disclosure include: p,p'-dioctyldiphenylamine; t-octylphenyl-alpha-naphthylamine; phenyl-alpha-naphthylamine; and p-octylphenyl-alpha-naphthylamine.

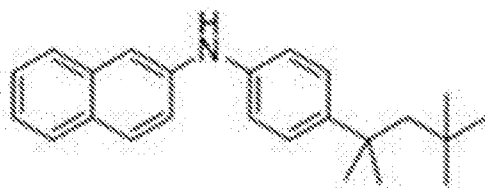
[0074] Illustrative aromatic amine antioxidants that may be used in combination with the polymeric aminic antioxidants include, for example, the following:



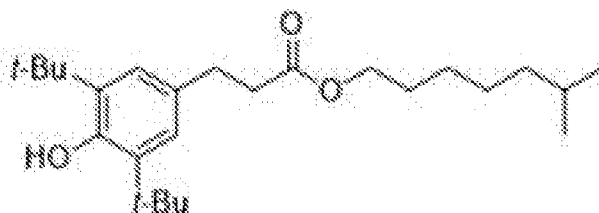
and



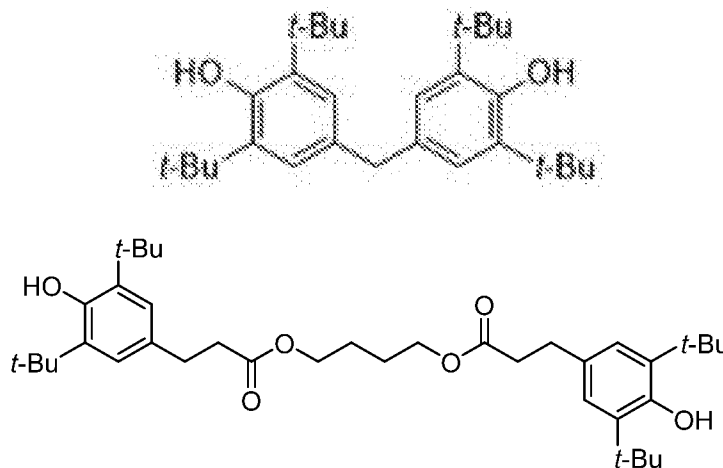
and



[0075] Illustrative phenolic antioxidants that may be used in combination with the polymeric aminic antioxidants include, for example, the following:



and



[0076] The arylamines antioxidants may be used individually or in combination. Such additives may be used in an amount of 0.01 to 5 weight percent, preferably 0.01 to 1.5 weight percent, more preferably zero to less than 1.5 weight percent, more preferably zero to less than 1 weight percent.

[0077] The phenolic antioxidants may be used individually or in combination. The phenolic antioxidants may provide potential benefits in other performance aspects. Such additives may be used in an amount of 0.01 to 1 weight percent, preferably 0.01 to 0.75 weight percent, more preferably zero to less than 0.5 weight percent. Higher amounts of phenolic antioxidants could result in decreased oxidative stability and deposit control.

Dispersants

[0078] During engine operation, oil-insoluble oxidation byproducts are produced. Dispersants help keep these byproducts in solution, thus diminishing their deposition on metal surfaces. Dispersants used in the formulation of the lubricating oil may be ashless or ash-forming in nature. Preferably, the dispersant is ashless. So called ashless dispersants are organic materials that form substantially no ash upon combustion. For example, non-metal-containing or borated metal-free dispersants are considered ashless. In contrast, metal-containing detergents discussed above form ash upon combustion.

[0079] Suitable dispersants typically contain a polar group attached to a relatively high molecular weight hydrocarbon chain. The polar group typically contains at least one element of nitrogen, oxygen, or phosphorus. Typical hydrocarbon chains contain 50 to 400 carbon atoms.

[0080] A particularly useful class of dispersants are the (poly)alkenylsuccinic derivatives, typically produced by the reaction of a long chain hydrocarbyl substituted succinic compound, usually a hydrocarbyl substituted succinic anhydride, with a polyhydroxy or polyamino compound. The long chain hydrocarbyl group constituting the oleophilic portion of the molecule which confers solubility in the oil, is normally a polyisobutylene group. Many examples of this type of dispersant

are well known commercially and in the literature. Exemplary U.S. patents describing such dispersants are U.S. Patent Nos. 3,172,892; 3,2145,707; 3,219,666; 3,316,177; 3,341,542; 3,444,170; 3,454,607; 3,541,012; 3,630,904; 3,632,511; 3,787,374 and 4,234,435. Other types of dispersant are described in U.S. Patent Nos. 3,036,003; 3,200,107; 3,254,025; 3,275,554; 3,438,757; 3,454,555; 3,565,804; 3,413,347; 3,697,574; 3,725,277; 3,725,480; 3,726,882; 4,454,059; 3,329,658; 3,449,250; 3,519,565; 3,666,730; 3,687,849; 3,702,300; 4,100,082; 5,705,458. A further description of dispersants may be found, for example, in European Patent Application No. 471 071, to which reference is made for this purpose.

[0081] Hydrocarbyl-substituted succinic acid and hydrocarbyl-substituted succinic anhydride derivatives are useful dispersants. In particular, succinimide, succinate esters, or succinate ester amides prepared by the reaction of a hydrocarbon-substituted succinic acid compound preferably having at least 50 carbon atoms in the hydrocarbon substituent, with at least one equivalent of an alkylene amine are particularly useful.

[0082] Succinimides are formed by the condensation reaction between hydrocarbyl substituted succinic anhydrides and amines. Molar ratios can vary depending on the polyamine. For example, the molar ratio of hydrocarbyl substituted succinic anhydride to TEPA can vary from about 1:1 to about 5:1. Representative examples are shown in U.S. Patent Nos. 3,087,936; 3,172,892; 3,219,666; 3,272,746; 3,322,670; and 3,652,616, 3,948,800; and Canada Patent No. 1,094,044.

[0083] Succinate esters are formed by the condensation reaction between hydrocarbyl substituted succinic anhydrides and alcohols or polyols. Molar ratios can vary depending on the alcohol or polyol used. For example, the condensation product of a hydrocarbyl substituted succinic anhydride and pentaerythritol is a useful dispersant.

[0084] Succinate ester amides are formed by condensation reaction between hydrocarbyl substituted succinic anhydrides and alkanol amines. For example, suitable alkanol amines include ethoxylated polyalkylpolyamines, propoxylated polyalkylpolyamines and polyalkenylpolyamines such as polyethylene polyamines. One example is propoxylated hexamethylenediamine. Representative examples are shown in U.S. Patent No. 4,426,305.

[0085] The molecular weight of the hydrocarbyl substituted succinic anhydrides used in the preceding paragraphs will typically range between 800 and 2,500 or more. The above products can be post-reacted with various reagents such as sulfur, oxygen, formaldehyde, carboxylic acids such as oleic acid. The above products can also be post reacted with boron compounds such as boric acid, borate esters or highly borated dispersants, to form borated dispersants generally having from about 0.1 to about 5 moles of boron per mole of dispersant reaction product.

[0086] Mannich base dispersants are made from the reaction of alkylphenols, formaldehyde, and amines. See U.S. Patent No. 4,767,551, which is incorporated herein by reference. Process aids and catalysts, such as oleic acid and sulfonic acids, can also be part of the reaction mixture. Molecular weights of the alkylphenols range from 800 to 2,500. Representative examples are shown in U.S. Patent Nos. 3,697,574; 3,703,536; 3,704,308; 3,751,365; 3,756,953; 3,798,165; and 3,803,039.

[0087] Typical high molecular weight aliphatic acid modified Mannich condensation products useful in this disclosure can be prepared from high molecular weight alkyl-substituted hydroxyaromatics or HNR₂ group-containing reactants.

[0088] Hydrocarbyl substituted amine ashless dispersant additives are well known to one skilled in the art; see, for example, U.S. Patent Nos. 3,275,554; 3,438,757; 3,565,804; 3,755,433, 3,822,209, and 5,084,197.

[0089] Preferred dispersants include borated and non-borated succinimides, including those derivatives from mono-succinimides, bis-succinimides, and/or mixtures of mono- and bis-succinimides, wherein the hydrocarbyl succinimide is derived from a hydrocarbylene group such as polyisobutylene having a Mn of from about 500 to about 5000, or from about 1000 to about 3000, or about 1000 to about 2000, or a mixture of such hydrocarbylene groups, often with high terminal vinylic groups. Other preferred dispersants include succinic acid-esters and amides, alkylphenol-polyamine-coupled Mannich adducts, their capped derivatives, and other related components.

[0090] Polymethacrylate or polyacrylate derivatives are another class of dispersants. These dispersants are typically prepared by reacting a nitrogen containing monomer and a methacrylic or acrylic acid esters containing 5 -25 carbon atoms in the ester group. Representative examples are shown in U.S. Patent Nos. 2, 100, 993, and 6,323,164. Polymethacrylate and polyacrylate dispersants are normally used as multifunctional viscosity modifiers. The lower molecular weight versions can be used as lubricant dispersants or fuel detergents.

[0091] Illustrative preferred dispersants useful in this disclosure include those derived from polyalkenyl-substituted mono- or dicarboxylic acid, anhydride or ester, which dispersant has a polyalkenyl moiety with a number average molecular weight of at least 900 and from greater than 1.3 to 1.7, preferably from greater than 1.3 to 1.6, most preferably from greater than 1.3 to 1.5, functional groups (mono- or dicarboxylic acid producing moieties) per polyalkenyl moiety (a medium functionality dispersant). Functionality (F) can be determined according to the following formula:

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

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

[0092] The polyalkenyl moiety of the dispersant may have a number average molecular weight of at least 900, suitably at least 1500, preferably between 1800 and 3000, such as between 2000 and 2800, more preferably from about 2100 to 2500, and most preferably from about 2200 to about 2400. The molecular weight of a dispersant is generally expressed in terms of the molecular weight of the polyalkenyl moiety. This is because the precise molecular weight range of the dispersant depends on numerous parameters including the type of polymer used to derive the dispersant, the number of functional groups, and the type of nucleophilic group employed.

[0093] Polymer molecular weight, specifically M_n , can be determined by various known techniques. One convenient method is gel permeation chromatography (GPC), which additionally provides molecular weight distribution information (see W. W. Yau, J. J. Kirkland and D. D. Bly, "Modern Size Exclusion Liquid Chromatography", John Wiley and Sons, New York, 1979). Another useful method for determining molecular weight, particularly for lower molecular weight polymers, is vapor pressure osmometry (e.g., ASTM D3592).

[0094] The polyalkenyl moiety in a dispersant preferably has a narrow molecular weight distribution (MWD), also referred to as polydispersity, as determined by the ratio of weight average molecular weight (M_w) to number average molecular weight (M_n). Polymers having a M_w/M_n of less than 2.2, preferably less than 2.0, are most desirable. Suitable polymers have a polydispersity of from about 1.5 to 2.1, preferably from about 1.6 to about 1.8.

[0095] Suitable polyalkenes employed in the formation of the dispersants include homopolymers, interpolymers or lower molecular weight hydrocarbons. One family of such polymers comprise polymers of ethylene and/or at least one C_3 to C_{26} alpha-olefin having the formula $H_2C = CHR^1$ wherein R^1 is a straight or branched chain alkyl radical comprising 1 to 26 carbon atoms and wherein the polymer contains carbon-to-carbon unsaturation, and a high degree of terminal ethenylidene unsaturation. Preferably, such polymers comprise interpolymers of ethylene and at least one alpha-olefin of the above formula, wherein R^1 is alkyl of from 1 to 18 carbon atoms, and more preferably is alkyl of from 1 to 8 carbon atoms, and more preferably still of from 1 to 2 carbon atoms.

[0096] Another useful class of polymers is polymers prepared by cationic polymerization of monomers such as isobutene and styrene. Common polymers from this class include

polyisobutenes obtained by polymerization of a C₄ refinery stream having a butene content of 35 to 75% by wt., and an isobutene content of 30 to 60% by wt. A preferred source of monomer for making poly-n-butenes is petroleum feed streams such as Raffinate II. These feed stocks are disclosed in the art such as in U.S. Pat. No. 4,952,739. A preferred embodiment utilizes polyisobutylene prepared from a pure isobutylene stream or a Raffinate I stream to prepare reactive isobutylene polymers with terminal vinylidene olefins. Polyisobutene polymers that may be employed are generally based on a polymer chain of from 1500 to 3000.

[0097] The dispersant(s) are preferably non-polymeric (e.g., mono- or bis-succinimides). Such dispersants can be prepared by conventional processes such as disclosed in U.S. Patent Application Publication No. 2008/0020950, the disclosure of which is incorporated herein by reference.

[0098] The dispersant(s) can be borated by conventional means, as generally disclosed in U.S. Patent Nos. 3,087,936, 3,254,025 and 5,430,105.

[0099] Such dispersants may be used in an amount of about 0.01 to 20 weight percent or 0.01 to 10 weight percent, preferably about 0.5 to 8 weight percent, or more preferably 0.5 to 4 weight percent. Or such dispersants may be used in an amount of about 2 to 12 weight percent, preferably about 4 to 10 weight percent, or more preferably 6 to 9 weight percent. On an active ingredient basis, such additives may be used in an amount of about 0.06 to 14 weight percent, preferably about 0.3 to 6 weight percent. The hydrocarbon portion of the dispersant atoms can range from C₆₀ to C₁₀₀₀, or from C₇₀ to C₃₀₀, or from C₇₀ to C₂₀₀. These dispersants may contain both neutral and basic nitrogen, and mixtures of both. Dispersants can be end-capped by borates and/or cyclic carbonates. Nitrogen content in the finished oil can vary from about 200 ppm by weight to about 2000 ppm by weight, preferably from about 200 ppm by weight to about 1200 ppm by weight. Basic nitrogen can vary from about 100 ppm by weight to about 1000 ppm by weight, preferably from about 100 ppm by weight to about 600 ppm by weight.

[00100] Dispersants as described herein are beneficially useful with the compositions of this disclosure and substitute for some or all of the surfactants of this disclosure. Further, in one embodiment, preparation of the compositions of this disclosure using one or more dispersants is achieved by combining ingredients of this disclosure, plus optional base stocks and lubricant additives, in a mixture at a temperature above the melting point of such ingredients, particularly that of the one or more M-carboxylates (M = H, metal, two or more metals, mixtures thereof).

[00101] As used herein, the dispersant concentrations are given on an "as delivered" basis. Typically, the active dispersant is delivered with a process oil. The "as delivered" dispersant typically contains from about 20 weight percent to about 80 weight percent, or from about 40

weight percent to about 60 weight percent, of active dispersant in the “as delivered” dispersant product.

Detergents

[00102] Illustrative detergents useful in this disclosure include, for example, alkali metal detergents, alkaline earth metal detergents, or mixtures of one or more alkali metal detergents and one or more alkaline earth metal detergents. A typical detergent is an anionic material that contains a long chain hydrophobic portion of the molecule and a smaller anionic or oleophobic hydrophilic portion of the molecule. The anionic portion of the detergent is typically derived from an organic acid such as a sulfur-containing acid, carboxylic acid (e.g., salicylic acid), phosphorus-containing acid, phenol, or mixtures thereof. The counterion is typically an alkaline earth or alkali metal. The detergent can be overbased as described herein.

[00103] The detergent is preferably a metal salt of an organic or inorganic acid, a metal salt of a phenol, or mixtures thereof. The metal is preferably selected from an alkali metal, an alkaline earth metal, and mixtures thereof. The organic or inorganic acid is selected from an aliphatic organic or inorganic acid, a cycloaliphatic organic or inorganic acid, an aromatic organic or inorganic acid, and mixtures thereof.

[00104] The metal is preferably selected from an alkali metal, an alkaline earth metal, and mixtures thereof. More preferably, the metal is selected from calcium (Ca), magnesium (Mg), and mixtures thereof.

[00105] The organic acid or inorganic acid is preferably selected from a sulfur-containing acid, a carboxylic acid, a phosphorus-containing acid, and mixtures thereof.

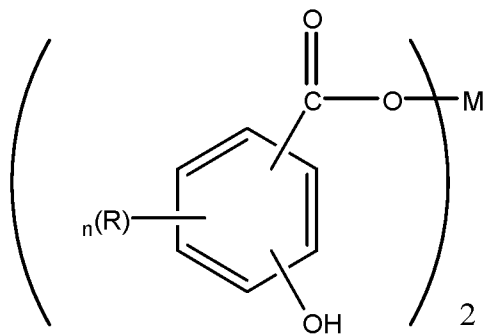
[00106] Preferably, the metal salt of an organic or inorganic acid or the metal salt of a phenol comprises calcium phenate, calcium sulfonate, calcium salicylate, magnesium phenate, magnesium sulfonate, magnesium salicylate, an overbased detergent, and mixtures thereof.

[00107] Salts that contain a substantially stoichiometric amount of the metal are described as neutral salts and have a total base number (TBN, as measured by ASTM D2896) of from 0 to 80. Many compositions are overbased, containing large amounts of a metal base that is achieved by reacting an excess of a metal compound (a metal hydroxide or oxide, for example) with an acidic gas (such as carbon dioxide). Useful detergents can be neutral, mildly overbased, or highly overbased. These detergents can be used in mixtures of neutral, overbased, highly overbased calcium salicylate, sulfonates, phenates and/or magnesium salicylate, sulfonates, phenates. The TBN ranges can vary from low, medium to high TBN products, including as low as 0 to as high as 600. Preferably the TBN delivered by the detergent is between 1 and 20. More preferably between 1 and 12. Mixtures of low, medium, high TBN can be used, along with mixtures of calcium and

magnesium metal based detergents, and including sulfonates, phenates, salicylates, and carboxylates. A detergent mixture with a metal ratio of 1, in conjunction of a detergent with a metal ratio of 2, and as high as a detergent with a metal ratio of 5, can be used. Borated detergents can also be used.

[00108] Alkaline earth phenates are another useful class of detergent. These detergents can be made by reacting alkaline earth metal hydroxide or oxide (CaO, Ca(OH)₂, BaO, Ba(OH)₂, MgO, Mg(OH)₂, for example) with an alkyl phenol or sulfurized alkylphenol. Useful alkyl groups include straight chain or branched C₁-C₃₀ alkyl groups, preferably, C₄-C₂₀ or mixtures thereof. Examples of suitable phenols include isobutylphenol, 2-ethylhexylphenol, nonylphenol, dodecyl phenol, and the like. It should be noted that starting alkylphenols may contain more than one alkyl substituent that are each independently straight chain or branched and can be used from 0.5 to 6 weight percent. When a non-sulfurized alkylphenol is used, the sulfurized product may be obtained by methods well known in the art. These methods include heating a mixture of alkylphenol and sulfurizing agent (including elemental sulfur, sulfur halides such as sulfur dichloride, and the like) and then reacting the sulfurized phenol with an alkaline earth metal base.

[00109] In accordance with this disclosure, metal salts of carboxylic acids are preferred detergents. These carboxylic acid detergents may be prepared by reacting a basic metal compound with at least one carboxylic acid and removing free water from the reaction product. These compounds may be overbased to produce the desired TBN level. Detergents made from salicylic acid are one preferred class of detergents derived from carboxylic acids. Useful salicylates include long chain alkyl salicylates. One useful family of compositions is of the formula



where R is an alkyl group having 1 to about 30 carbon atoms, n is an integer from 1 to 4, and M is an alkaline earth metal. Preferred R groups are alkyl chains of at least C₁₁, preferably C₁₃ or greater. R may be optionally substituted with substituents that do not interfere with the detergent's function. M is preferably, calcium, magnesium, barium, or mixtures thereof. More preferably, M is calcium.

[00110] Hydrocarbyl-substituted salicylic acids may be prepared from phenols by the Kolbe reaction (see U.S. Patent No. 3,595,791). The metal salts of the hydrocarbyl-substituted salicylic

acids may be prepared by double decomposition of a metal salt in a polar solvent such as water or alcohol.

[00111] Alkaline earth metal phosphates are also used as detergents and are known in the art.

[00112] Detergents may be simple detergents or what is known as hybrid or complex detergents. The latter detergents can provide the properties of two detergents without the need to blend separate materials. See U.S. Patent No. 6,034,039.

[00113] Preferred detergents include calcium sulfonates, magnesium sulfonates, calcium salicylates, magnesium salicylates, calcium phenates, magnesium phenates, and other related components (including borated detergents), and mixtures thereof. Preferred mixtures of detergents include magnesium sulfonate and calcium salicylate, magnesium sulfonate and calcium sulfonate, magnesium sulfonate and calcium phenate, calcium phenate and calcium salicylate, calcium phenate and calcium sulfonate, calcium phenate and magnesium salicylate, calcium phenate and magnesium phenate. Overbased detergents are also preferred.

[00114] The detergent concentration in the lubricating oils of this disclosure can range from about 0.5 to about 6.0 weight percent, preferably about 0.6 to 5.0 weight percent, and more preferably from about 0.8 weight percent to about 4.0 weight percent, based on the total weight of the lubricating oil.

[00115] As used herein, the detergent concentrations are given on an “as delivered” basis. Typically, the active detergent is delivered with a process oil. The “as delivered” detergent typically contains from about 20 weight percent to about 100 weight percent, or from about 40 weight percent to about 60 weight percent, of active detergent in the “as delivered” detergent product.

Viscosity Modifiers

[00116] Viscosity modifiers (also known as viscosity index improvers (VI improvers), and viscosity improvers) can be included in the lubricant compositions of this disclosure.

[00117] Viscosity modifiers provide lubricants with high and low temperature operability. These additives impart shear stability at elevated temperatures and acceptable viscosity at low temperatures.

[00118] Suitable viscosity modifiers include high molecular weight hydrocarbons, polyesters and viscosity modifier dispersants that function as both a viscosity modifier and a dispersant. Typical molecular weights of these polymers are between about 10,000 to 1,500,000, more typically about 20,000 to 1,200,000, and even more typically between about 50,000 and 1,000,000.

[00119] Examples of suitable viscosity modifiers are linear or star-shaped polymers and copolymers of methacrylate, butadiene, olefins, or alkylated styrenes. Polyisobutylene is a

commonly used viscosity modifier. Another suitable viscosity modifier is polymethacrylate (copolymers of various chain length alkyl methacrylates, for example), some formulations of which also serve as pour point depressants. Other suitable viscosity modifiers include copolymers of ethylene and propylene, hydrogenated block copolymers of styrene and isoprene, and polyacrylates (copolymers of various chain length acrylates, for example). Specific examples include styrene-isoprene or styrene-butadiene based polymers of 50,000 to 200,000 molecular weight.

[00120] Olefin copolymers are commercially available from Chevron Oronite Company LLC under the trade designation “PARATONE®” (such as “PARATONE® 8921” and “PARATONE® 8941”); from Afton Chemical Corporation under the trade designation “HiTEC®” (such as “HiTEC® 5850B”); and from The Lubrizol Corporation under the trade designation “Lubrizol® 7067C”. Hydrogenated polyisoprene star polymers are commercially available from Infineum International Limited, e.g., under the trade designation “SV200” and “SV600”. Hydrogenated diene-styrene block copolymers are commercially available from Infineum International Limited, e.g., under the trade designation “SV 50”.

[00121] The polymethacrylate or polyacrylate polymers can be linear polymers which are available from Evnoik Industries under the trade designation “Viscoplex®” (e.g., Viscoplex 6-954) or star polymers which are available from Lubrizol Corporation under the trade designation Asteric™ (e.g., Lubrizol 87708 and Lubrizol 87725).

[00122] Illustrative vinyl aromatic-containing polymers useful in this disclosure may be derived predominantly from vinyl aromatic hydrocarbon monomer. Illustrative vinyl aromatic-containing copolymers useful in this disclosure may be represented by the following general formula:



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

[00123] In an embodiment of this disclosure, the viscosity modifiers may be used in an amount of less than about 10 weight percent, preferably less than about 7 weight percent, more preferably less than about 4 weight percent, and in certain instances, may be used at less than 2 weight percent, preferably less than about 1 weight percent, and more preferably less than about 0.5 weight percent, based on the total weight of the formulated oil or lubricating engine oil. Viscosity modifiers are typically added as concentrates, in large amounts of diluent oil.

[00124] As used herein, the viscosity modifier concentrations are given on an “as delivered” basis. Typically, the active polymer is delivered with a diluent oil. The “as delivered” viscosity modifier typically contains from 20 weight percent to 75 weight percent of an active polymer for

polymethacrylate or polyacrylate polymers, or from 8 weight percent to 20 weight percent of an active polymer for olefin copolymers, hydrogenated polyisoprene star polymers, or hydrogenated diene-styrene block copolymers, in the “as delivered” polymer concentrate.

Pour Point Depressants (PPDs)

[00125] Conventional pour point depressants (also known as lube oil flow improvers) may be added to the compositions of the present disclosure if desired. These pour point depressant may be added to lubricating compositions of the present disclosure to lower the minimum temperature at which the fluid will flow or can be poured. Examples of suitable pour point depressants include polymethacrylates, polyacrylates, polyarylamides, condensation products of haloparaffin waxes and aromatic compounds, vinyl carboxylate polymers, and terpolymers of dialkylfumarates, vinyl esters of fatty acids and allyl vinyl ethers. U.S. Patent Nos. 1,815,022; 2,015,748; 2,191,498; 2,387,501; 2,655, 479; 2,666,746; 2,721,877; 2,721,878; and 3,250,715 describe useful pour point depressants and/or the preparation thereof. Such additives may be used in an amount of about 0.01 to 5 weight percent, preferably about 0.01 to 1.5 weight percent.

Seal Compatibility Agents

[00126] Seal compatibility agents help to swell elastomeric seals by causing a chemical reaction in the fluid or physical change in the elastomer. Suitable seal compatibility agents for lubricating oils include organic phosphates, aromatic esters, aromatic hydrocarbons, esters (butylbenzyl phthalate, for example), and polybutenyl succinic anhydride. Such additives may be used in an amount of about 0.01 to 3 weight percent, preferably about 0.01 to 2 weight percent.

Antifoam Agents

[00127] Anti-foam agents may advantageously be added to lubricant compositions. These agents retard the formation of stable foams. Silicones and organic polymers are typical anti-foam agents. For example, polysiloxanes, such as silicon oil or polydimethyl siloxane, provide antifoam properties. Anti-foam agents are commercially available and may be used in conventional minor amounts along with other additives such as demulsifiers; usually the amount of these additives combined is less than 1 weight percent and often less than 0.1 weight percent.

Inhibitors and Antirust Additives

[00128] Antirust additives (or corrosion inhibitors) are additives that protect lubricated metal surfaces against chemical attack by water or other contaminants. A wide variety of these are commercially available.

[00129] One type of antirust additive is a polar compound that wets the metal surface preferentially, protecting it with a film of oil. Another type of antirust additive absorbs water by incorporating it in a water-in-oil emulsion so that only the oil touches the metal surface. Yet

another type of antirust additive chemically adheres to the metal to produce a non-reactive surface. Examples of suitable additives include zinc dithiophosphates, metal phenolates, basic metal sulfonates, fatty acids and amines. Such additives may be used in an amount of about 0.01 to 5 weight percent, preferably about 0.01 to 1.5 weight percent.

Friction Modifiers

[00130] A friction modifier is any material or materials that can alter the coefficient of friction of a surface lubricated by any lubricant or fluid containing such material(s). Friction modifiers, also known as friction reducers, or lubricity agents or oiliness agents, and other such agents that change the ability of base oils, formulated lubricant compositions, or functional fluids, to modify the coefficient of friction of a lubricated surface may be effectively used in combination with the base oils or lubricant compositions of the present disclosure if desired. Friction modifiers that lower the coefficient of friction are particularly advantageous in combination with the base oils and lube compositions of this disclosure.

[00131] Illustrative friction modifiers may include, for example, organometallic compounds or materials, or mixtures thereof. Illustrative organometallic friction modifiers useful in the lubricating engine oil formulations of this disclosure include, for example, molybdenum amine, molybdenum diamine, an organotungstenate, a molybdenum dithiocarbamate, molybdenum dithiophosphates, molybdenum amine complexes, molybdenum carboxylates, and the like, and mixtures thereof. Similar tungsten based compounds may be preferable.

[00132] Other illustrative friction modifiers useful in the lubricating engine oil formulations of this disclosure include, for example, alkoxylated fatty acid esters, alkanolamides, polyol fatty acid esters, borated glycerol fatty acid esters, fatty alcohol ethers, and mixtures thereof.

[00133] Illustrative alkoxylated fatty acid esters include, for example, polyoxyethylene stearate, fatty acid polyglycol ester, and the like. These can include polyoxypropylene stearate, polyoxybutylene stearate, polyoxyethylene isostearate, polyoxypropylene isostearate, polyoxyethylene palmitate, and the like.

[00134] Illustrative alkanolamides include, for example, lauric acid diethylalkanolamide, palmitic acid diethylalkanolamide, and the like. These can include oleic acid diethylalkanolamide, stearic acid diethylalkanolamide, oleic acid diethylalkanolamide, polyethoxylated hydrocarbylamides, polypropoxylated hydrocarbylamides, and the like.

[00135] Illustrative polyol fatty acid esters include, for example, glycerol mono-oleate, saturated mono-, di-, and tri-glyceride esters, glycerol mono-stearate, and the like. These can include polyol esters, hydroxyl-containing polyol esters, and the like.

[00136] Illustrative borated glycerol fatty acid esters include, for example, borated glycerol mono-oleate, borated saturated mono-, di-, and tri-glyceride esters, borated glycerol mono-sterate, and the like. In addition to glycerol polyols, these can include trimethylolpropane, pentaerythritol, sorbitan, and the like. These esters can be polyol monocarboxylate esters, polyol dicarboxylate esters, and on occasion polyoltricarboxylate esters. Preferred can be the glycerol mono-oleates, glycerol dioleates, glycerol trioleates, glycerol monostearates, glycerol distearates, and glycerol tristearates and the corresponding glycerol monopalmitates, glycerol dipalmitates, and glycerol tripalmitates, and the respective isostearates, linoleates, and the like. On occasion the glycerol esters can be preferred as well as mixtures containing any of these. Ethoxylated, propoxylated, butoxylated fatty acid esters of polyols, especially using glycerol as underlying polyol can be preferred.

[00137] Illustrative fatty alcohol ethers include, for example, stearyl ether, myristyl ether, and the like. Alcohols, including those that have carbon numbers from C₃ to C₅₀, can be ethoxylated, propoxylated, or butoxylated to form the corresponding fatty alkyl ethers. The underlying alcohol portion can preferably be stearyl, myristyl, C₁₁ – C₁₃ hydrocarbon, oleyl, isosteryl, and the like.

[00138] The lubricating oils of this disclosure exhibit desired properties, e.g., wear control, in the presence or absence of a friction modifier.

[00139] Useful concentrations of friction modifiers may range from 0.01 weight percent to 5 weight percent, or about 0.1 weight percent to about 2.5 weight percent, or about 0.1 weight percent to about 1.5 weight percent, or about 0.1 weight percent to about 1 weight percent. Concentrations of molybdenum-containing materials are often described in terms of Mo metal concentration. Advantageous concentrations of Mo may range from 25 ppm to 700 ppm or more, and often with a preferred range of 50-200 ppm. Friction modifiers of all types may be used alone or in mixtures with the materials of this disclosure. Often mixtures of two or more friction modifiers, or mixtures of friction modifier(s) with alternate surface active material(s), are also desirable.

Antiwear Additives

[00140] A metal alkylthiophosphate and more particularly a metal dialkyl dithio phosphate in which the metal constituent is zinc, or zinc dialkyl dithio phosphate (ZDDP) can be a useful component of the lubricating oils of this disclosure. ZDDP can be derived from primary alcohols, secondary alcohols or mixtures thereof. ZDDP compounds generally are of the formula



where R¹ and R² are C₁-C₁₈ alkyl groups, preferably C₂-C₁₂ alkyl groups. These alkyl groups may be straight chain or branched. Alcohols used in the ZDDP can be propanol, 2-propanol, butanol, secondary butanol, pentanols, hexanols such as 4-methyl-2-pentanol, n-hexanol, n-octanol, 2-ethyl

hexanol, alkylated phenols, and the like. Mixtures of secondary alcohols or of primary and secondary alcohol can be preferred. Alkyl aryl groups may also be used.

[00141] Preferable zinc dithiophosphates which are commercially available include secondary zinc dithiophosphates such as those available from for example, The Lubrizol Corporation under the trade designations “LZ 677A”, “LZ 1095” and “LZ 1371”, from for example Chevron Oronite under the trade designation “OLOA 262” and from for example Afton Chemical under the trade designation “HITEC 7169”.

[00142] The ZDDP is typically used in amounts of from about 0.3 weight percent to about 1.5 weight percent, preferably from about 0.4 weight percent to about 1.2 weight percent, more preferably from about 0.5 weight percent to about 1.0 weight percent, and even more preferably from about 0.6 weight percent to about 0.8 weight percent, based on the total weight of the lubricating oil, although more or less can often be used advantageously. Preferably, the ZDDP is a secondary ZDDP and present in an amount of from about 0.6 to 1.0 weight percent of the total weight of the lubricating oil.

[00143] The types and quantities of performance additives used in combination with the instant disclosure in lubricant compositions are not limited by the examples shown herein as illustrations.

[00144] When lubricating oil compositions contain one or more of the additives discussed above, the additive(s) are blended into the composition in an amount sufficient for it to perform its intended function. Typical amounts of such additives useful in the present disclosure are shown in Table 1 below.

[00145] It is noted that many of the additives are shipped from the additive manufacturer as a concentrate, containing one or more additives together, with a certain amount of base oil diluents. Accordingly, the weight amounts in the table below, as well as other amounts mentioned herein, are directed to the amount of active ingredient (that is the non-diluent portion of the ingredient). The weight percent (wt%) indicated below is based on the total weight of the lubricating oil composition.

TABLE 1

Typical Amounts of Other Lubricating Oil Components

Compound	Approximate wt% (Useful)	Approximate wt% (Preferred)
Antiwear	0.1-2	0.5-1
Dispersant	0.1-20	0.1-8
Detergent	0.1-20	0.1-8
Antioxidant	0.1-10	0.1-5
Friction Modifier	0.01-5	0.01-1.5
Pour Point Depressant (PPD)	0.0-5	0.01-1.5
Anti-foam Agent	0.001-3	0.001-0.15
Viscosity Index Improver (pure polymer basis)	0.0-8	0.1-6
Inhibitor and Antirust	0.01-5	0.01-1.5

[00146] The foregoing additives are all commercially available materials. These additives may be added independently but are usually precombined in packages which can be obtained from suppliers of lubricant oil additives. Additive packages with a variety of ingredients, proportions and characteristics are available and selection of the appropriate package will take the requisite use of the ultimate composition into account.

[00147] The following non-limiting examples are provided to illustrate the disclosure.

EXAMPLES

[00148] Several engine oil candidates were formulated as shown in Figs. 2-6. All of the ingredients used in the candidate formulated oils were commercially available. The chemical structures and nomenclature of illustrative antioxidants used in the candidate formulated oils are shown in Fig. 1. The difference amongst the polymeric antioxidant (AO) materials is related to the degree of oligomerization achieved. The Group V base stocks used in this study are labeled in Figs. 2-6 as follows for ease of reference. (E1) refers to TMP ester with alkyl carbon chain length of 7. (E2) refers to TMP ester with linear alkyl carbon chain length of 9. (E3) refers to TMP ester with branched alkyl carbon chain length of 9. (E4) refers to a pentaerythritol ester (i.e. Nycobase 1040X).

[00149] The candidates shown in Tables 2-5 are fully formulated lubricants where the balance of the formulation is generically referred to as Reference Fluid 1, 2, 3 or 4. The reference fluids contain typical base stocks combined with dispersants, detergents, antiwear additives, friction modifiers, and the like. Four different base formulations were used through the data presented

herein, RF1, RF2, RF3, RF4 and RF5 which are similar in nature with slight differences in either the base oil composition or the treat rate of some additives optimized for other performance aspects. RF1, RF2, RF3, RF4 and RF5 are approximately 60%, or 65%, or 70%, or 75%, or 80%, or 85%, or 90%, of a combination of base stocks. The combination of additives amount to 10%, or 15%, or 20%, or 25%, or 30%, or 35%, or 40%.

[00150] Oil life was assessed using two oxidation tests, the Bulk Oxidation Test (BOT) and the Oxidation Stability Test (OST).

[00151] In the BOT, an aliquot of the candidate formulated oil (100 gm), was placed in a vessel maintained at a fix temperature of 165°C, with air bubbling in the oil at a 500 cc/min +/- 25 cc/min. The vessel was loaded with 3.5 mg of a catalyst to deliver 45 ppm of metal ions to accelerate the oxidation. The kinematic viscosity at 40°C (KV40) was monitored over time, and the candidate was considered "oxidized" when the KV40 increased over 200% as compared to the starting measurement.

[00152] In the OST, a vial was loaded with 10 mL of sample, and 50 ppm of Fe in an oil soluble form. There was a head pressure of air of 50 psi and air was bubbled in the vial at 125 ml/min. The test was run maintaining the temperature at 170°C and, at a pre-determined interval, a small aliquot of the sample was taken out to measure the viscosity at 40°C. The measurement of the viscosity at 40°C was similar to ASTM D445 and the results comparable. Once the viscosity increases over 200% compared to the initial viscosity, the oil was considered condemned.

[00153] Fig. 2 shows tabulated results of BOT performance as a function of antioxidant selection. In this group of candidates, a good result in the BOT is defined as greater than 200 hours to break, or greater than 250 hours to break, or greater than 300 hours to break, or greater than 350 hours to break, or greater than 400 hours to break. The balance of the material considered in this section is either lumped in RF1 or RF2. Fig. 2 shows tabulated results obtained in the BOT where the CE 1 and CE 7 break at 161 and 215 hours respectively. When the formulation employs polymeric aminic antioxidant G in combination with higher amounts of Group V base stock (E3), the fluid can last over 500 hours in the BOT (IE 1). Leaving out the large amount of E3 while still using polymeric AO G at 3.3% treat rate of active ingredient, the performance is still good (319 hours – IE 2) but not as outstanding as observed in IE 1. The comparison between IE 1 and IE 2 highlights the synergetic effect of using both a polymeric AO and a high amount of an oxidative stable ester such as (E3). The candidate formulation blended with just 10% polyol ester (E4) does not reach the 200 hours mark in this test (CE 6), therefore confirming that the polymeric aminic antioxidant is responsible for the improved performance

and not the diluent oil that is used to deliver the additive. Using a high amount of Polymeric AO I (IE 3), excellent performance (347 hours) are observed consistently with the data obtained in IE 2. Similar excellent performance in this test is observed when using a high treat rate of traditional diphenyl amines and hindered phenol antioxidants (IE 4).

[00154] In additional testing, deposit formation of each product was compared using a thermo-oxidation engine oil simulation (TEOST 33C) measured by ASTM D6335.

[00155] Fig. 3 shows tabulated results of TEOST 33C performance as a function of antioxidant selection. A good result in the TEOST test is defined as less than 30 mg, or less than 25 mg, or less than 20 mg, or less than 15 mg, or less than 10 mg. The deposit control as measured by TEOST 33C shows that the oils formulated to last longer in the BOT also provide the lowest deposit rating. Particularly, the polymeric aminic antioxidant provides results of about 12 mg (IE 1 and IE 2) for a reduction of about 50% deposit, as compared to the reference fluid formulated with the conventional aminic/phenolic antioxidant package (CE 1). A parallel performance ranking is evident comparing the BOT performance of these three candidates where IE 1 and IE 2 broke after 512 and 319 hours respectively, while CE 1 broke after only 161 hours. Additionally, when using 4% of either AO D (CE 9) or AO C (CE 10), the deposit was 32.5 and 43.3 mg respectively. However, when using about 3% of Polymeric AO G (IE 1 and IE 2), or when using 4% of Polymeric AO I (IE 3), the deposit was 11.5, 11.8 and 7.9 mg. IE 1, IE 2 and IE 6 also had very strong performance in the BOT. Using a high treat rate of AO D (IE 4), the deposit control was to be considered acceptable (25.6 mg), while excellent BOT performance was obtained as well (464 hours). Based on the results discussed so far, there was no need to further compare TEOST 33C data versus BOT performance. For example, looking at CE 9, CE 10, CE 11 and IE 6, the expectation is that they would all have excellent BOT performance, and that the main difference will be only related to deposit control as measured by TEOST 33C.

[00156] Considering that industry requirements set the passing limit at 30 mg, the choice of the right antioxidant is critical to pass the test. This is an unexpected result given that one could expect more degradation from a polymer/oligomer that could lead to more deposit formation. Interestingly, when using a small amount of Polymeric AO G without any additional antioxidant, the deposit drops below 10 mg (IE 5). In this instance, the deposit control was the relevant performance being assessed. BOT was directionally worse as compared to the other Inventive Examples, but it was to be expected given the overall low treat rate of antioxidants. Further, a direct comparison of CE 11 and IE 6, highlights the directional debit brought by using a large amount of a small antioxidant molecule such as AO D that provided a deposit of 32.4 mg when

using 5% of this material (CE 11). By dropping the amount of AO D, while introducing 1.6% of polymeric AO I, the deposit was reduced by 50% (IE 6).

[00157] Fig. 4 shows tabulated results of antioxidant package evaluation based on both the BOT and the OST methods. A good result in the BOT is defined as greater than 200 hours to break, or greater than 250 hours to break, or greater than 300 hours to break, or greater than 350 hours to break, or greater than 400 hours to break. A good result in the OST test is defined as greater than 70 hours to break, or greater than 50 hours to break, or greater than 40 hours to break. In Fig. 4, the candidates were blended using Reference Fluid 3 (RF 3) as the balance of the material. The oxidative stability of several candidate formulations was evaluated by varying the amount and type of the antioxidant (AO) including in the matrix AO A, AO C, AO E, AO F, poly AO G and poly AO H. Increasing amounts of polymeric aminic antioxidants lead to better performance, however the hours to break did not exceed the 380 mark in the BOT (compare IE 7 vs. IE 8, CE 13 vs. CE 14, CE 15 vs. CE 16 and CE 17 vs. IE 9).

[00158] The OST, a different oxidation method, provided very similar response to what observed in BOT, thus providing an alternative and consistent option for additional evaluation. All the formulations in Fig. 4 contain a similar amount of phenolic antioxidant, which seems to affect the performance negatively. This is likely the reason why CE 13-17 do not exceed the 230 hours mark in the BOT.

[00159] Fig. 5 shows tabulated results of antioxidant package evaluation based on BOT, in particular looking at the negative effect of phenolic antioxidants when included in the formulations in high concentration (CE 20). In Fig. 5, the candidates were blended using Reference Fluid 4 (RF 4) as the balance of the material, and a good result in the BOT is defined as greater than 200 hours to break, or greater than 250 hours to break, or greater than 300 hours to break, or greater than 350 hours to break, or greater than 400 hours to break. Based on the findings in Figs. 2-4, the performance of several finished lubricants formulated without phenolic antioxidants were evaluated, and they all lasted well over 400 hours (IE 10-18). As a control, the last candidate, CE 20 in Fig. 5 contained the highest amount of phenolic antioxidant (AO E) evaluated in this study, and it provided the lowest oxidative stability in the family, going from formulations capable of lasting for almost 800 hours (IE 17) to a product lasting 165 hours (CE 20) which is lower than what measured with CE 7 (Fig. 2 - 215 hours) and similar to CE 1 (Fig. 2 - 161 hours). Remarkably, the candidates prepared with 5% of poly AO H (IE 14) did not break before 600 hours, which is at least 3 times better than the results obtained with CE 7 and about 4 times better than what observed with CE 1.

[00160] In additional testing, deposit formation of several products were compared using a modified thermo-oxidation engine oil simulation (MHT TEOST measured by ASTM D7097). The only difference compared to the standard ASTM D7097 method was the operating temperature that being changed from 285 °C to 300 °C.

[00161] Fig. 6 shows tabulated results of TEOST 33C performance as a function of antioxidant selection. Each candidate was also compared using the BOT and the modified MHT TEOST. A good result in the modified MHT TEOST test is defined as less than 35 mg, or less than 25 mg, or less than 20 mg, or less than 15 mg, or less than 10 mg. As it was shown in the previous tables, the deposit control as measured by TEOST 33C showed that the oils formulated to last longer in the BOT also provided the lowest deposit rating. Increasing levels of polymeric antioxidants such as “I” offers significant benefits when used in combination with either a traditional diphenyl amine like “C”. Particularly, the polymeric aminic antioxidant provides a deposit reduction in the modified MHT TEOST ranging from 49 mg in CE21, to 31 and 19 mg respectively in IE19 and IE20. Similar deposit reductions were observed in this test looking at CE22 (26 mg) versus IE21 (15 mg) and IE22 (9 mg). The deposit reduction was even more significant when looking at the combination of Polymeric AO “I” in combination with traditional DPA “A”. For example, the deposits in the modified MHT TEOST as measured in CE23 was 39 mg, which went down to 22 mg and 16 mg in IE23 and IE24 respectively. When the RF5 is blended using 2% of DPA “A”, CE24 showed good deposit control to begin with (14 mg), but the addition of Polymeric AO “I” provided a further improvement as shown in IE25 (12 mg) and IE26 (5 mg). The results seen with Polymeric AO “I” can be expected to be replicated with any other Polymeric AOs considered in the study and others of similar molecular structure.

[00162] It has been found that by employing a polymeric aminic antioxidant in lubricating oil formulations, viscosity control is improved exponentially in the finished formulations designed for engine oil applications. Also, it was found that the polymeric aminic antioxidants are compatible with other aminic antioxidants. It was further observed that phenolic antioxidants did not provide significant benefits at the standard treat rates, and moreover phenolic antioxidants clearly bring debits when used in higher concentrations.

PCT and EP Clauses:

[00163] 1. A method for improving viscosity control, while maintaining or improving deposit control, of a lubricating oil in an engine or other mechanical component lubricated with the lubricating oil by using as the lubricating oil a formulated oil, said formulated oil having a composition comprising a lubricating oil base stock as a major component; and at least one polymeric aminic antioxidant, as a minor component; wherein the at least one polymeric aminic

antioxidant is the polymerization reaction product of one or more unsubstituted or hydrocarbyl-substituted diphenyl amines, one or more unsubstituted or hydrocarbyl-substituted phenyl naphthyl amines, or both one or more of unsubstituted or hydrocarbyl-substituted diphenylamine with one or more unsubstituted or hydrocarbyl-substituted phenyl naphthylamine; wherein the lubricating oil base stock is present in an amount from 1 to 85 weight percent, based on the total weight of the lubricating oil; and wherein the at least one polymeric aminic antioxidant is present in an amount from 0.1 to 5 weight percent, based on the total weight of the lubricating oil.

[00164] 2. The method of clause 1 wherein, in an engine oil Bulk Oxidation Test, the number of hours to 200% increase in kinematic viscosity at 40°C is increased as compared to the number of hours to 200% increase in kinematic viscosity at 40°C of a lubricating oil containing a minor amount of an antioxidant other than the polymeric aminic antioxidant; or wherein, in deposit measurements of the lubricating oil by thermo-oxidation engine oil simulation (TEOST 33C) measured by ASTM D6335, the amount of total deposits is reduced or maintained as compared to the amount of total deposits in a lubricating oil containing a minor component other than the at least one polymeric aminic antioxidant; or wherein, in deposit measurements of the lubricating oil by thermo-oxidation engine oil simulation (MHT TEOST) measured by ASTM D7097, the amount of total deposits is reduced or maintained as compared to the amount of total deposits in a lubricating oil containing a minor component other than the at least one polymeric aminic antioxidant.

[00165] 3. The method of clauses 1 and 2 wherein the lubricating oil base stock comprises at least one branched polyol ester, which is obtained by reacting one or more polyhydric alcohols with one or more branched mono-carboxylic acids containing at least 4 carbon atoms.

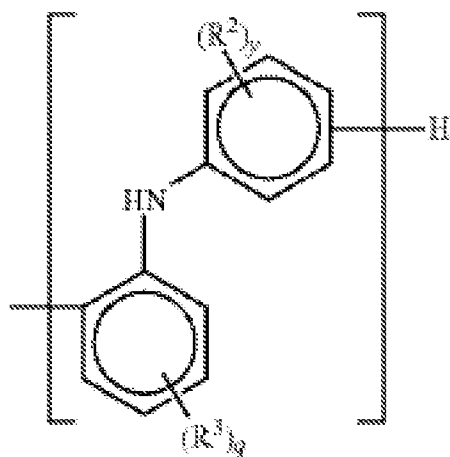
[00166] 4. The method of clauses 1-3 wherein the one or more polyhydric alcohols are selected from the group consisting of trimethylol propane, pentaerythritol, neopentyl glycol, trimethylol ethane, 2-methyl-2-propyl-1,3-propanediol, and dipentaerythritol; and wherein the one or more branched mono-carboxylic acids containing at least 4 carbon atoms are selected from the group consisting of 3,5,5-trimethyl hexanoic acid (TMH), 2,2-dimethyl propionic acid (neopentanoic acid), neoheptanoic acid, neo-octanoic acid, neononanoic acid, iso-hexanoic acid, neodecanoic acid, 2-ethyl hexanoic acid (2EH), isoheptanoic acid, isooctanoic acid, isononanoic acid, and isodecanoic acid.

[00167] 5. The method of clauses 1-4 wherein the at least one branched polyol ester is selected from the group consisting of trimethylol propane ester of 3,5,5-trimethyl hexanoic acid (TMH), trimethylol propane ester of 2,2-dimethyl propionic acid (neopentanoic acid), trimethylol propane ester of neoheptanoic acid, trimethylol propane ester of neo-octanoic acid, trimethylol

propane ester of neononanoic acid, trimethylol propane ester of iso-hexanoic acid, trimethylol propane ester of neodecanoic acid, trimethylol propane ester of 2-ethyl hexanoic acid (2EH), trimethylol propane ester of isoheptanoic acid, trimethylol propane ester of isooctanoic acid, trimethylol propane ester of isononanoic acid, and trimethylol propane ester of isodecanoic acid.

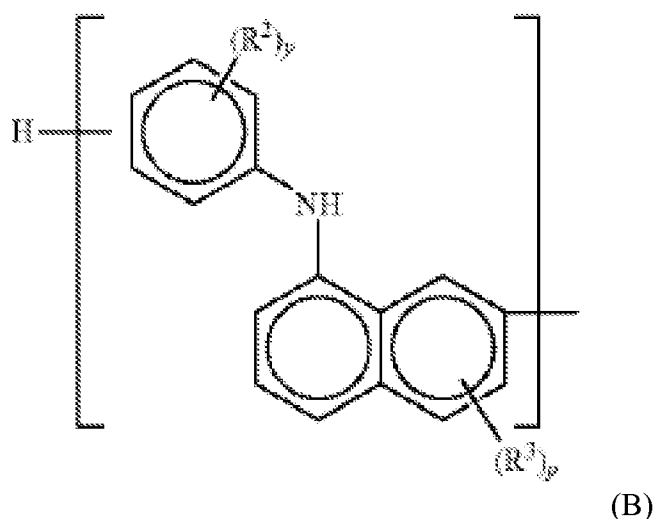
[00168] 6. The method of clauses 1-5 wherein the at least one branched polyol ester is selected from the group consisting of pentaerythritol ester of 3,5,5-trimethyl hexanoic acid (TMH), pentaerythritol ester of 2,2-dimethyl propionic acid (neopentanoic acid), pentaerythritol ester of neoheptanoic acid, pentaerythritol ester of neo-octanoic acid, pentaerythritol ester of neononanoic acid, pentaerythritol ester of iso-hexanoic acid, pentaerythritol ester of neodecanoic acid, pentaerythritol ester of 2-ethyl hexanoic acid (2EH), pentaerythritol ester of isoheptanoic acid, pentaerythritol ester of isooctanoic acid, pentaerythritol ester of isononanoic acid, and pentaerythritol ester of isodecanoic acid.

[00169] 7. The method of clauses 1-6 wherein the at least one polymeric aminic antioxidant is the polymerization reaction product of



(A)

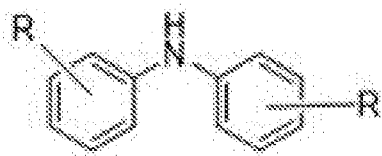
and/or



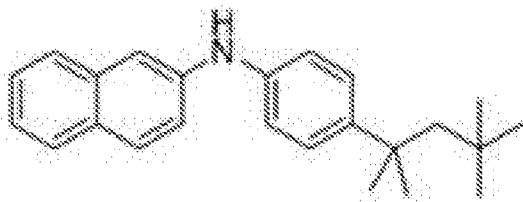
wherein (A) and (B) each range from zero to 10, provided (A)+(B) is at least 2; R^2 is a styrene or C1 to C30 alkyl, R^3 is a styrene or C1 to C30 alkyl, q and y individually range from 0 to up to the valence of the aryl group to which the respective R groups are attached.

[00170] 8. The method of clause 7 wherein the at least one polymeric aminic antioxidant is a polymerization reaction product comprising: (A)(A), (A)(B), (B)(B), (A)(A)(B), (A)(A)(A), (A)(B)(A), (B)(B)(B), (B)(B)(A), (A)(A)(A)(A), (A)(A)(B)(B), (A)(A)(A)(B), (B)(B)(B)(B), (B)(B)(B)(A), (A)(A)(A)(A)(A), (A)(B)(A)(B)(A), (A)(B)(B)(B)(A), or mixtures thereof.

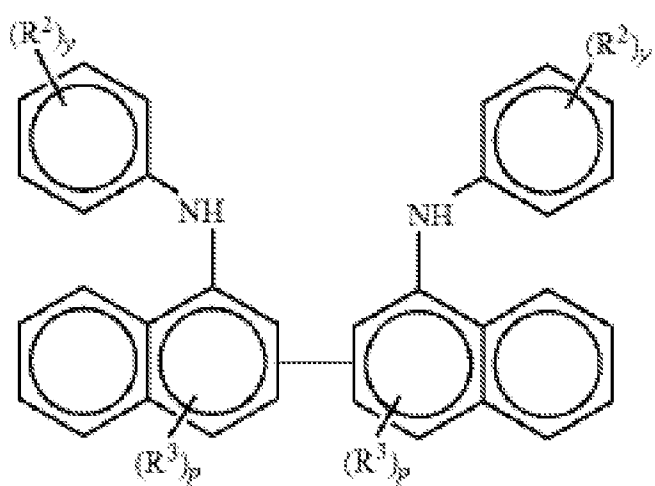
[00171] 9. The method of clauses 1-8 wherein the at least one polymeric aminic antioxidant is the polymerization reaction product formed by any combination of:



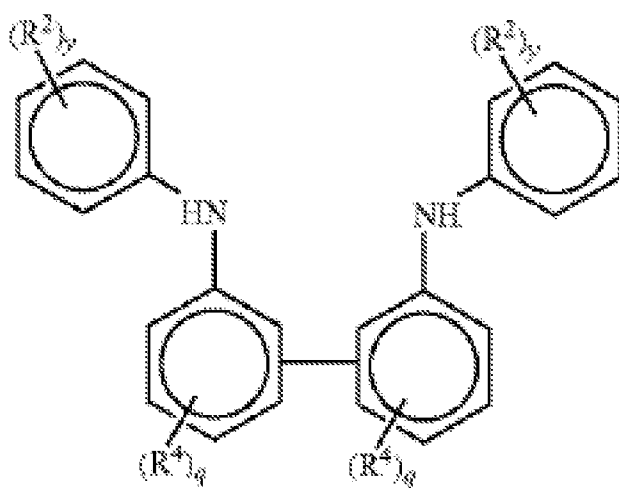
wherein R is H, C_4H_9 , C_8H_{17} , or C_9H_{19} ; and/or



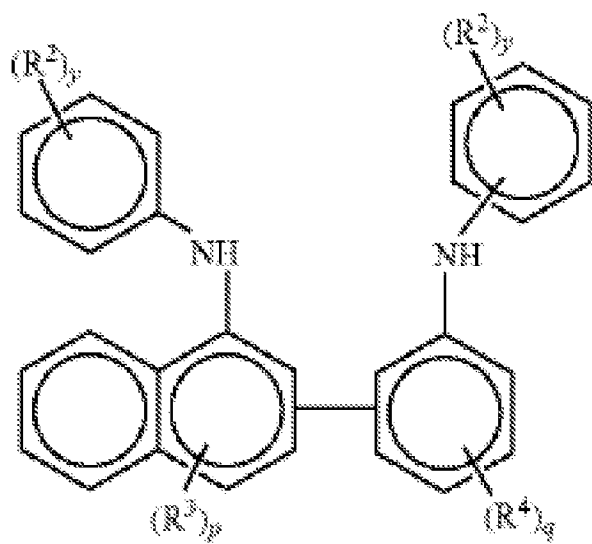
[00172] 10. The method of clauses 1-9 wherein the at least one polymeric aminic antioxidant is a polymerization reaction product selected from the group consisting of:



(a)

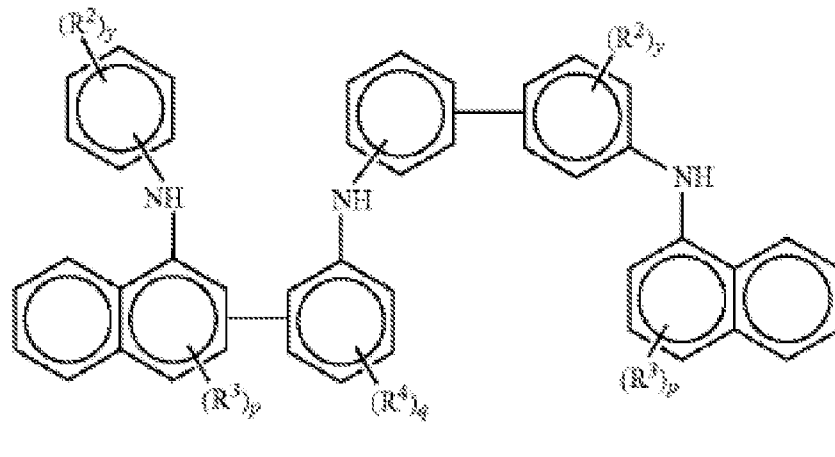


(b)



(c)

and



wherein R^2 is a styrene or C1 to C30 alkyl, R^3 is a styrene or C1 to C30 alkyl, R^4 is a styrene or C1 to C30 alkyl, p, q and y individually range from 0 to up to the valence of the aryl group to which the respective R groups are attached.

[00173] 11. The method of clauses 1-10 wherein the lubricating oil base stock is present in an amount from 5 to 45 weight percent, based on the total weight of the lubricating oil; and wherein the at least one polymeric aminic antioxidant is present in an amount from 0.1 to 2.5 weight percent, based on the total weight of the lubricating oil.

[00174] 12. The method of clauses 1-11 wherein the formulated oil further comprises one or more of a viscosity modifier, dispersant, detergent, other antioxidant, pour point depressant, corrosion inhibitor, metal deactivator, seal compatibility additive, anti-foam agent, inhibitor, and anti-rust additive.

[00175] 13. The method of clause 12 wherein the other antioxidant comprises at least one aromatic amine antioxidant, at least one phenolic antioxidant, or mixtures thereof; wherein the at least one aromatic amine antioxidant is present in an amount from 0.1 to 5 weight percent, based on the total weight of the lubricating oil; and wherein the at least one phenolic antioxidant is present in an amount from 0.1 to 1 weight percent, based on the total weight of the lubricating oil.

[00176] 14. A lubricating oil having a composition comprising a lubricating oil base stock as a major component; and at least one polymeric aminic antioxidant, as a minor component; wherein the at least one polymeric aminic antioxidant is the polymerization reaction product of one or more unsubstituted or hydrocarbyl-substituted diphenyl amines, one or more unsubstituted or hydrocarbyl-substituted phenyl naphthyl amines, or both one or more of unsubstituted or hydrocarbyl-substituted diphenylamine with one or more unsubstituted or hydrocarbyl-substituted phenyl naphthylamine; wherein the lubricating oil base stock is present in an amount from 1 to 85 weight percent, based on the total weight of the lubricating oil; and wherein the at

least one polymeric aminic antioxidant is present in an amount from 0.1 to 5 weight percent, based on the total weight of the lubricating oil.

[00177] 15. A method for improving oxidative stability, while maintaining or improving deposit control, of a lubricating oil in an engine or other mechanical component lubricated with the lubricating oil by using as the lubricating oil a formulated oil, said formulated oil having a composition comprising a lubricating oil base stock as a major component; and at least one polymeric aminic antioxidant, as a minor component; wherein the at least one polymeric aminic antioxidant is the polymerization reaction product of one or more unsubstituted or hydrocarbyl-substituted diphenyl amines, one or more unsubstituted or hydrocarbyl-substituted phenyl naphthyl amines, or both one or more of unsubstituted or hydrocarbyl-substituted diphenylamine with one or more unsubstituted or hydrocarbyl-substituted phenyl naphthylamine; wherein the lubricating oil base stock is present in an amount from 1 to 85 weight percent, based on the total weight of the lubricating oil; and wherein the at least one polymeric aminic antioxidant is present in an amount from 0.1 to 5 weight percent, based on the total weight of the lubricating oil.

[00178] All patents and patent applications, test procedures (such as ASTM methods, UL methods, and the like), and other documents cited herein are fully incorporated by reference to the extent such disclosure is not inconsistent with this disclosure and for all jurisdictions in which such incorporation is permitted.

[00179] When numerical lower limits and numerical upper limits are listed herein, ranges from any lower limit to any upper limit are contemplated. While the illustrative embodiments of the disclosure have been described with particularity, it will be understood that various other modifications will be apparent to and can be readily made by those skilled in the art without departing from the spirit and scope of the disclosure. Accordingly, it is not intended that the scope of the claims appended hereto be limited to the examples and descriptions set forth herein but rather that the claims be construed as encompassing all the features of patentable novelty which reside in the present disclosure, including all features which would be treated as equivalents thereof by those skilled in the art to which the disclosure pertains.

[00180] The present disclosure has been described above with reference to numerous embodiments and specific examples. Many variations will suggest themselves to those skilled in this art in light of the above detailed description. All such obvious variations are within the full intended scope of the appended claims.

CLAIMS:

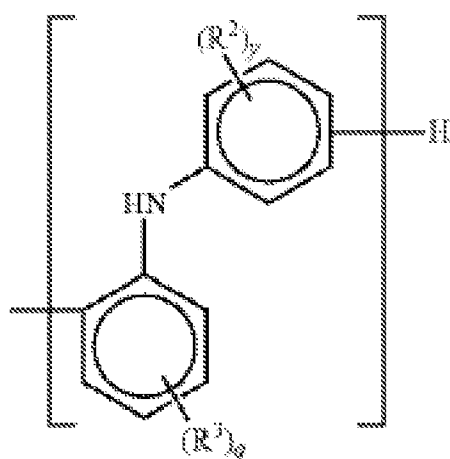
1. A method for improving viscosity control, while maintaining or improving deposit control, of a lubricating oil in an engine or other mechanical component lubricated with the lubricating oil by using as the lubricating oil a formulated oil, said formulated oil having a composition comprising a lubricating oil base stock as a major component; and at least one polymeric aminic antioxidant, as a minor component; wherein the at least one polymeric aminic antioxidant is the polymerization reaction product of one or more unsubstituted or hydrocarbyl-substituted diphenyl amines, one or more unsubstituted or hydrocarbyl-substituted phenyl naphthyl amines, or both one or more of unsubstituted or hydrocarbyl-substituted diphenylamine with one or more unsubstituted or hydrocarbyl-substituted phenyl naphthylamine; wherein the lubricating oil base stock is present in an amount from 1 to 85 weight percent, based on the total weight of the lubricating oil; and wherein the at least one polymeric aminic antioxidant is present in an amount from 0.1 to 5 weight percent, based on the total weight of the lubricating oil.
2. The method of claim 1 wherein, in an engine oil Bulk Oxidation Test, the number of hours to 200% increase in kinematic viscosity at 40°C is increased as compared to the number of hours to 200% increase in kinematic viscosity at 40°C of a lubricating oil containing a minor amount of an antioxidant other than the polymeric aminic antioxidant; or wherein, in deposit measurements of the lubricating oil by thermo-oxidation engine oil simulation (TEOST 33C) measured by ASTM D6335, the amount of total deposits is reduced or maintained as compared to the amount of total deposits in a lubricating oil containing a minor component other than the at least one polymeric aminic antioxidant; or wherein, in deposit measurements of the lubricating oil by thermo-oxidation engine oil simulation (MHT TEOST) measured by ASTM D7097, the amount of total deposits is reduced or maintained as compared to the amount of total deposits in a lubricating oil containing a minor component other than the at least one polymeric aminic antioxidant.
3. The method of claims 1 and 2 wherein the lubricating oil base stock comprises at least one branched polyol ester, which is obtained by reacting one or more polyhydric alcohols with one or more branched mono-carboxylic acids containing at least 4 carbon atoms.
4. The method of claims 1-3 wherein the one or more polyhydric alcohols are selected from the group consisting of trimethylol propane, pentaerythritol, neopentyl glycol, trimethylol ethane, 2-methyl-2-propyl-1,3-propanediol, and dipentaerythritol; and wherein the one or more branched mono-carboxylic acids containing at least 4 carbon atoms are selected from the group consisting of 3,5,5-trimethyl hexanoic acid (TMH), 2,2-dimethyl propionic acid (neopentanoic acid), neoheptanoic acid, neooctanoic acid, neononanoic acid, iso-hexanoic acid, neodecanoic acid, 2-

ethyl hexanoic acid (2EH), isoheptanoic acid, isooctanoic acid, isononanoic acid, and isodecanoic acid.

5. The method of claims 1-4 wherein the at least one branched polyol ester is selected from the group consisting of trimethylol propane ester of 3,5,5-trimethyl hexanoic acid (TMH), trimethylol propane ester of 2,2-dimethyl propionic acid (neopentanoic acid), trimethylol propane ester of neoheptanoic acid, trimethylol propane ester of neo-octanoic acid, trimethylol propane ester of neononanoic acid, trimethylol propane ester of iso-hexanoic acid, trimethylol propane ester of neodecanoic acid, trimethylol propane ester of 2-ethyl hexanoic acid (2EH), trimethylol propane ester of isoheptanoic acid, trimethylol propane ester of isooctanoic acid, trimethylol propane ester of isononanoic acid, and trimethylol propane ester of isodecanoic acid.

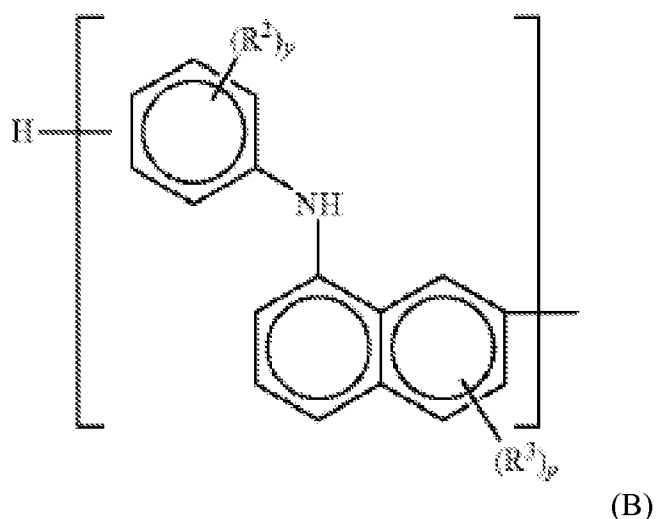
6. The method of claims 1-5 wherein the at least one branched polyol ester is selected from the group consisting of pentaerythritol ester of 3,5,5-trimethyl hexanoic acid (TMH), pentaerythritol ester of 2,2-dimethyl propionic acid (neopentanoic acid), pentaerythritol ester of neoheptanoic acid, pentaerythritol ester of neo-octanoic acid, pentaerythritol ester of neononanoic acid, pentaerythritol ester of iso-hexanoic acid, pentaerythritol ester of neodecanoic acid, pentaerythritol ester of 2-ethyl hexanoic acid (2EH), pentaerythritol ester of isoheptanoic acid, pentaerythritol ester of isooctanoic acid, pentaerythritol ester of isononanoic acid, and pentaerythritol ester of isodecanoic acid.

7. The method of claims 1-6 wherein the at least one polymeric aminic antioxidant is the polymerization reaction product of



(A)

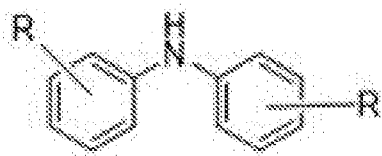
and/or



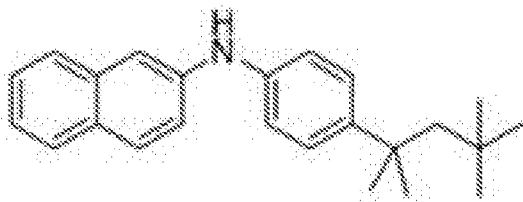
wherein (A) and (B) each range from zero to 10, provided (A)+(B) is at least 2; R^2 is a styrene or C1 to C30 alkyl, R^3 is a styrene or C1 to C30 alkyl, q and y individually range from 0 to up to the valence of the aryl group to which the respective R groups are attached.

8. The method of claim 7 wherein the at least one polymeric aminic antioxidant is a polymerization reaction product comprising: (A)(A), (A)(B), (B)(B), (A)(A)(B), (A)(A)(A), (A)(B)(A), (B)(B)(B), (B)(B)(A), (A)(A)(A)(A), (A)(A)(B)(B), (A)(A)(A)(B), (B)(B)(B)(B), (B)(B)(B)(A), (A)(A)(A)(A)(A), (A)(B)(A)(B)(A), (A)(B)(B)(B)(A), or mixtures thereof.

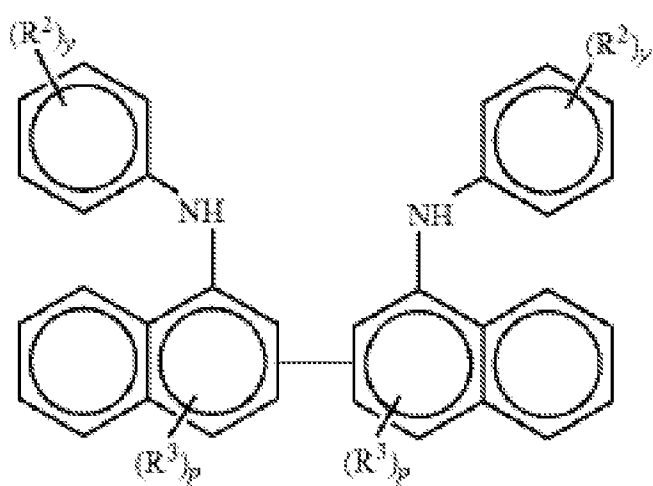
9. The method of claims 1-8 wherein the at least one polymeric aminic antioxidant is the polymerization reaction product formed by any combination of:



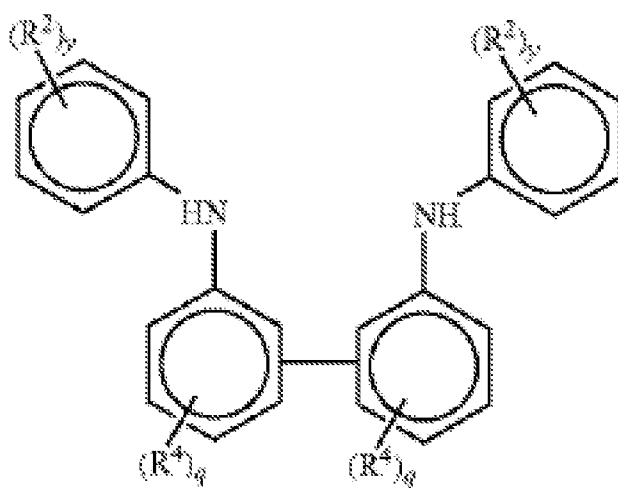
wherein R is H, C_4H_9 , C_8H_{17} , or C_9H_{19} ; and/or



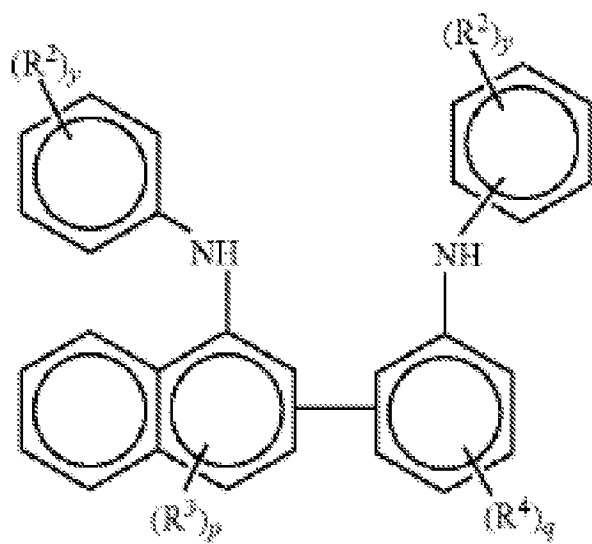
10. The method of claims 1-9 wherein the at least one polymeric aminic antioxidant is a polymerization reaction product selected from the group consisting of:



(a)

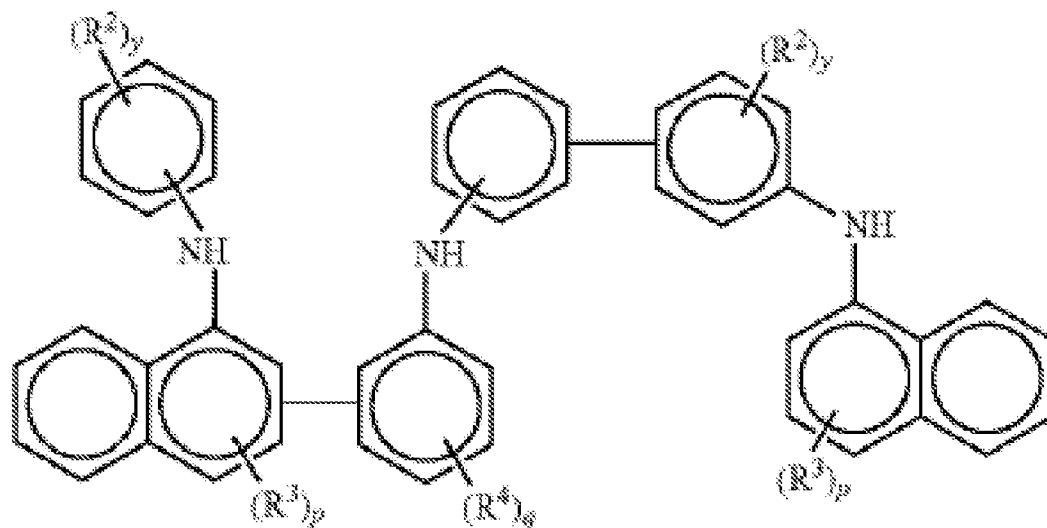


(b)



(c)

and



(d)

wherein R^2 is a styrene or C1 to C30 alkyl, R^3 is a styrene or C1 to C30 alkyl, R^4 is a styrene or C1 to C30 alkyl, p, q and y individually range from 0 to up to the valence of the aryl group to which the respective R groups are attached.

11. The method of claims 1-10 wherein the lubricating oil base stock is present in an amount from 5 to 45 weight percent, based on the total weight of the lubricating oil; and wherein the at least one polymeric aminic antioxidant is present in an amount from 0.1 to 2.5 weight percent, based on the total weight of the lubricating oil.

12. The method of claims 1-11 wherein the formulated oil further comprises one or more of a viscosity modifier, dispersant, detergent, other antioxidant, pour point depressant, corrosion inhibitor, metal deactivator, seal compatibility additive, anti-foam agent, inhibitor, and anti-rust additive.

13. The method of claim 12 wherein the other antioxidant comprises at least one aromatic amine antioxidant, at least one phenolic antioxidant, or mixtures thereof; wherein the at least one aromatic amine antioxidant is present in an amount from 0.1 to 5 weight percent, based on the total weight of the lubricating oil; and wherein the at least one phenolic antioxidant is present in an amount from 0.1 to 1 weight percent, based on the total weight of the lubricating oil.

14. A lubricating oil having a composition comprising a lubricating oil base stock as a major component; and at least one polymeric aminic antioxidant, as a minor component; wherein the at least one polymeric aminic antioxidant is the polymerization reaction product of one or more unsubstituted or hydrocarbyl-substituted diphenyl amines, one or more unsubstituted or hydrocarbyl-substituted phenyl naphthyl amines, or both one or more of unsubstituted or hydrocarbyl-substituted diphenylamine with one or more unsubstituted or hydrocarbyl-substituted phenyl naphthylamine; wherein the lubricating oil base stock is present in an amount

from 1 to 85 weight percent, based on the total weight of the lubricating oil; and wherein the at least one polymeric aminic antioxidant is present in an amount from 0.1 to 5 weight percent, based on the total weight of the lubricating oil.

15. A method for improving oxidative stability, while maintaining or improving deposit control, of a lubricating oil in an engine or other mechanical component lubricated with the lubricating oil by using as the lubricating oil a formulated oil, said formulated oil having a composition comprising a lubricating oil base stock as a major component; and at least one polymeric aminic antioxidant, as a minor component; wherein the at least one polymeric aminic antioxidant is the polymerization reaction product of one or more unsubstituted or hydrocarbyl-substituted diphenyl amines, one or more unsubstituted or hydrocarbyl-substituted phenyl naphthyl amines, or both one or more of unsubstituted or hydrocarbyl-substituted diphenylamine with one or more unsubstituted or hydrocarbyl-substituted phenyl naphthylamine; wherein the lubricating oil base stock is present in an amount from 1 to 85 weight percent, based on the total weight of the lubricating oil; and wherein the at least one polymeric aminic antioxidant is present in an amount from 0.1 to 5 weight percent, based on the total weight of the lubricating oil.

Fig. 1

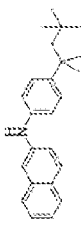
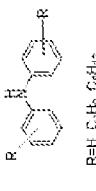
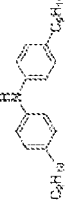
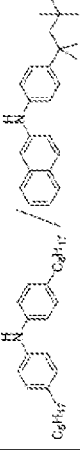
Anti Oxidants			Notes/Comments	
Name	Code	Acronym	Idealized Structure	
C8/C8 Diphenylamine	A	C8/C8 DPA		
Octylated phenyl-alpha-naphthylamine	B	PANA		
C4/C8 Diphenylamine	C	C4/C8 DPA		
C9/C9 Diphenylamine	D	C9/C9 DPA		
Hindered phenolic propionic acid ester of iso-octanol	E	Ester Phenolic AO		
4,4' methylene bis (2,6 Di-tert-butylphenol)	F	Phenolic AO		
Polymeric AO (mix of C8/C8 DPA (A) and PANA (B))	G	Poly AOs		Polymeric AO could be formed by any combination of the monomers (A) and (B); including the following examples: AA, AB, BB, AAB, AAA, ABA, BBB, BBA, AAAA, AABBB, AAAAB, BBBB, BBBB, AAAAA, ABAAA, ABBA, ABBBA
	H			
	I			

Fig. 2

AO Code	CE 1	CE 2	CE 3	CE 4	IE 1	IE 2	CE 6	IE 3	CE 7	IE 4	CE 8
A											
B											
C	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75
D										4	
E	1.38	1.38	1.38	1.38	1.38	1.38	1.38	1.38	0.75	0.75	1.38
F											
G				1	3.3	3.3					
H											
I								4			
E1		50									
E2			5								50
E3					50						
E4							10				
Balance	RF1	RF1	RF1	RF1	RF1	RF1	RF1	RF1	RF1	RF2	RF2
RF1	161	163	162	227	312	318	165	347	215	164	163

Fig. 3

AO Code	CE 1	IE 1	IE 2	CE 6	IE 3	IE 5	IE 4	CE 8	CE 9	CE 10	CE 11	IE 6
A												
B												
C	0.75	0.75	0.75	0.75	0.75		0.75	0.75		4.0		
D							4		4		5	4
E	1.38	1.38	1.38	1.38	1.38		0.75	1.38	0.5	0.5		0.75
F												
G		3.3	3.3			1						
H												
I					4							1.6
E1												
E2								50				
E3		50										
E4				10								
Balance	RF1	RF1	RF1	RF1	RF1	RF1	RF2	RF2	RF2	RF2	RF2	RF2
100% 33% deposit mg	28.5	11.5	11.3	19.5	7.9	9.4	25.4	51.4	32.5	43.3	32.4	16.6
ROT hrs	161	512	319	156	347	239	464	193	No Test	No Test	No Test	No Test

Fig. 4

AO Code	CE 12	IE 7	IE 8	CE 13	CE 14	CE 15	CE 16	CE 17	IE 9
A						0.95	0.95	0.95	0.95
B									
C	0.75	0.75	0.75						
D									
E	1.38	1.38	1.38	2.76	2.76	2.76	2.76	1.38	1.38
F								0.75	0.75
G		3.3		2		2		2	
H			5		4.5		4.5		4.5
I									
E1									
E2									
E3									
E4									
Balance	RF3	RF3	RF3	RF3	RF3	RF3	RF3	RF3	RF3
0057 bis	49	112	219	49	66	51	75	51	82
0003 bis	101	316	399	132	101	120	212	198	246

Fig. 5

AO Code	CE 18	IE 10	CE 19	IE 11	IE 12	IE 14	IE 15	IE 16	IE 17	IE 18	CE 20
A	0.95	0.95							0.95		
B											
C				0.75	0.75		0.75	0.75			
D			0.75							0.75	
E	0.75		0.75	0.75	0.75						2.76
F											
G											
H					5	5	3	1.5	5	5	
I											
E1											
E2											
E3											
E4											
Balance	RF4	RF4	RF4	RF4	RF4	RF4	RF4	RF4	RF4	RF4	RF4
BOI 015	001	070	022	002	000	003	007	000	004	004	005

Fig. 6

AO Code	CE21	IE19	IE20	CE22	IE21	IE22	CE23	IE23	IE24	CE24	IE25	IE26
A							1.0	1.0	1.0	2.0	2.0	2.0
B												
C	1.0	1.0	1.0	2.0	2.0	2.0						
D												
E												
F												
G												
H												
I		1.3	2.7		1.3	2.7		1.3	2.7		1.3	2.7
E1												
E2												
E3												
E4												
Balance	RF5	RF5	RF5	RF5	RF5	RF5	RF5	RF5	RF5	RF5	RF5	RF5
TEOST 11C, deposit mg	29.9	16	22.6	30.3	22.9	9.6	19.6	23	13.6	23.4	5.8	6.2
BOT, hrs	538	425	456	496	489	555	525	415	444	453	499	506
NHT TEOST 100 °C, mg	49	31	19	26	15	9	39	22	16	14	12	5

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2018/049841

A. CLASSIFICATION OF SUBJECT MATTER
INV. C10M169/04 C10M133/12
ADD.

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

B. FIELDS SEARCHED

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

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	paragraphs [0009], [0010], [0022]; claims; examples	13
X	WO 2012/015873 A1 (EXXONMOBIL RES & ENG CO [US]; DOUGLASS MICHAEL R [US]; JOHNSON DOUGLAS) 2 February 2012 (2012-02-02)	1-15
Y	paragraphs [0036] - [0046], [0057], [0058], [0063]; examples; tables 4,5	13
X	US 3 573 206 A (BRAID MILTON ET AL) 30 March 1971 (1971-03-30)	1-15
	column 1, line 52 - column 3, line 25 column 4, lines 6-16 column 7, lines 46-48; examples; table I	
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☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

27 November 2018

Date of mailing of the international search report

04/01/2019

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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2018/049841

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 95/16765 A2 (GOODRICH CO B F [US]) 22 June 1995 (1995-06-22) cited in the application page 23, lines 1,2; claims; examples; tables page 1, lines 5-13	1-15
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Information on patent family members

International application No

PCT/US2018/049841

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