

ANTINOXIDANT SLUDGE CONTROL ADDITIVES

This is a continuation-in-part of U.S. Serial No. 551,076 filed October 31, 1995, which is based on PM 94CL 033.

FIELD OF THE INVENTION

The present invention relates to control of sludge formation in lubes.

BACKGROUND OF THE INVENTION

Oxides of nitrogen, also referred to as NO_x, are by-products of the operation of internal combustion engines. These oxides are emitted, for example, as exhaust gas from the combustion of hydrocarbon fuels. They react even at relatively low temperatures (e.g., 70° - 120°C) with components of motor oils, such as additives, to form sludge and contribute to lube oil degradation. It would be advantageous to develop additives, lube oil formulations, and methods that can address lube oil degradation and minimize sludge formation particularly in the presence of NO_x. Applicants' invention addresses these needs.

SUMMARY OF THE INVENTION

The present invention provides for a method for mitigating sludge formation in engine oils by adding to an engine oil of lubricating viscosity an effective, minor amount of a molecule having at least one head portion enriched in NO_x reactive carbon-carbon unsaturation and at least one oil soluble aliphatic and aromatic hydrocarbon tail portion having an absence of carbon-carbon unsaturation of suitable chain length in an optimum ratio of head to tail sufficient to reduce NO_x-induced sludge formation in the engine oil. Preferred examples of such molecules include polyethylene propylene copolymer- and polyisobutylene-grafted hydroquinone polyalkylthiophenes,

fullerene-grafted lube oil basestock, ethylene propylene polymer-grafted phenol and ethylene butylene polymer-grafted phenol.

The present invention also provides for lube oil compositions and additive concentrates for mitigating sludge formation containing the foregoing molecules.

The present invention may suitably comprise, consist or consist essentially of the elements or steps disclosed herein and may be practiced in the absence of an element or step not specifically disclosed.

DETAILED DESCRIPTION OF THE INVENTION

The present invention provides for methods for controlling sludge (i.e., insolubles) formation, particularly that induced by NO_x , in lube oils and the lube degradation resulting from the combustion of hydrocarbonaceous fuels using NO_x -reactive sludge control additives (also referred to herein as "antioxidant additives"), and provides for formulated lube oil compositions and additive concentrates containing these additives. Examples of such fuels include those typically used for internal combustion engines such as crankcase lubricating fuels for spark-ignited and compression-ignited internal combustion engines, such as automobile, truck, marine diesel and railroad diesel engines and such as, for example, in U.S. Patent 5,558,802. Nitrous oxides and reactive intermediates of their reactions (" NO_x ") are produced in internal combustion engines from a variety of sources such as blowby gases and thermal degradation of organonitrates. As used herein the term " NO_x -reactive" includes reactivity to nitrous oxides and to the products of reactive organonitrate species such as sludge precursors. The most typical oxide of nitrogen is NO_2 , however, other reactive nitrogen oxides may also be present and the present invention also may be effectively carried out in the presence of such oxides.

Lube oils and additives typically present therein degrade in the engine in the presence of NO_x , oxygen and heat to form sludge precursors and sludge. Applicants have discovered novel additives and methods for reducing the occurrence of such degradation chemistry. These additives can be used to preserve the lifetime of current additives by preferentially reacting with NO_x . Thus Applicants' invention provides a method for mitigating sludge formation associated with certain currently available additives by rendering them resistant to degradation into insolubles, i.e., sludge. The invention is also useful in the design of new additives suitable for use to minimize sludge formation. Applicants' method of controlling sludge formation in lube oils is based on the discovery of the existence of a class of molecules that have in an optimum relationship of both carbon-carbon unsaturated NO_x -reactive portions and oil soluble aromatic, preferably aliphatic, hydrocarbyl portions having a chain length sufficient to maintain solubility of the NO_x -reactive and NO_x -reacted molecule in a lube oil. The method also may be employed, for example, to render current additives resistant to sludge formation.

One embodiment is a method of retarding or controlling sludge formation and lube oil degradation which comprises combining with an engine oil of lubricating viscosity an effective amount of at least one sludge mitigation compound having at least one first moiety or portion enriched in NO_x -reactive carbon-carbon unsaturation and at least one second moiety or portion deficient in NO_x -reactive carbon-carbon unsaturation and enriched in aliphatic and/or aromatic hydrocarbyl groups. The relative proportion of first and second moieties must be effective to render the molecule NO_x -reactive and lube oil soluble. Aliphatic hydrocarbyl groups are preferably essentially free of carbon-carbon unsaturation. These moieties also are, respectively, referred to herein as "head" or " NO_x -reactive head," and "tail" or "aliphatic hydrocarbyl tail" portions or "centers" or moieties for convenience. These terms are meant to indicate a localization or concentration of the particular structure or feature identified. For example, a molecule useful in the present invention will have, in combination, at least one head and tail portions, provided that the number, structure and combination are sufficient to impart NO_x -reactivity to the head portion and to impart oil solubility to the tail portion and to

the molecule as a whole both in its NO_x-reactive and NO_x-reacted forms. The dual character of the molecule as being NO_x-reactive and oil soluble are essential to the invention.

Other embodiments are formulations that contain a major portion or amount of a basestock boiling in the lube oil range and a minor portion of the sludge mitigation/control (antioxidant) additive. The effect of using the compound is to reduce propensity of NO_x in the base oil to react form insolubles, i.e., sludge. The minor portion or amount of the additive is an amount effective to mitigate or control sludge formation and lube oil degradation. Typically, this may be achieved in amounts from about 0.1 to about 10 wt%, preferably from about 0.2 to about 5 wt% of the additive compound. The formulation may optionally contain other additives such as viscosity modifiers, antioxidants, dispersants, detergents, antiwear agents, friction modifiers, corrosion inhibitors, demulsifiers, pour point depressants and antifoam agents.

It is believed that the additive can chemically immobilize NO_x by reaction of the NO_x-reactive carbon-carbon unsaturated portion(s) of the molecule with NO_x while remaining soluble in the lube oil. This result is unexpected because other additives used in lube oils typically react with NO_x to form sludge precursors and sludge rather than oil soluble species. Applicants' invention mitigates this result.

The starting materials disclosed herein may be purchased commercially or synthesized using known procedures. Fullerene grafted hydrocarbons may be prepared as known in the art. Fullerene adducts of base oils may be prepared similarly.

NO_x-reactive moieties suitable for use as head portions include reactive carbon-carbon unsaturated bonds that react with NO_x and reaction products thereof to form oxidatively stable reaction products. Other reactive carbon-carbon unsaturation includes reactive acetylenic, olefinic, conjugated dienes, aryl and heteroaromatic groups (aromatic ring containing sulfur, oxygen, nitrogen heteroatoms). A localization of such groups, particularly as exemplified by fullerenes, is extremely desirable, as such

structures have a greater NO_x trapping capacity, and hence, capability to sludge formation. Substituents and groups that do not interfere with the reactivity of the carbon-carbon unsaturation with NO_x or with of the overall solubility of the molecule in the lube oil also may be present and those that promote reactivity of the unsaturated sites with NO_x are desirable.

Hydrocarbons suitable for use as the tail portion of the antioxidant molecule can have an absence of unsaturation and are oil soluble aliphatic and aromatic hydrocarbyl groups that are essentially inert to oxidation at engine conditions. The minimum number of carbon atoms in the hydrocarbyl portion of the molecule is affected by the number and relative polarity of the NO_x-reactive centers in order to maintain oil solubility of the molecule. Thus fewer hydrocarbyl chains of reduced length are required for less polar NO_x-reactive centers. In all cases, the minimum chain length is typically at least C₄, more preferably at least C₆ up to a maximum chain length of C₁₄₀ per head group. More typically, chains containing from at least C₆ up to C₁₄₀ aliphatic and aromatic hydrocarbyl groups per NO_x-reactive head group or center are suitable, more preferably from C₁₂ to C₁₀₀, most preferably C₁₈ to C₄₅ chains per NO_x reactive moiety (head group) depending on the identity of the head group or center. For example, polythiophene requires at least one C₆, preferably C₈ aliphatic hydrocarbyl tail per thiophene moiety; phenol requires at least one C₁₈ aliphatic hydrocarbyl chain. Base oils for grafting as tail portions are suitably any lube basestock, i.e., any hydrocarbon boiling in the lube oil range, examples of which include S150N, S600N, and polymerized alpha-olefins ("PAOs"). Hydrocarbon polymers (polyolefins) can also be used as tail portions.

A NO_x-reactive center is bonded to the aliphatic hydrocarbyl center by a carbon to carbon bond.

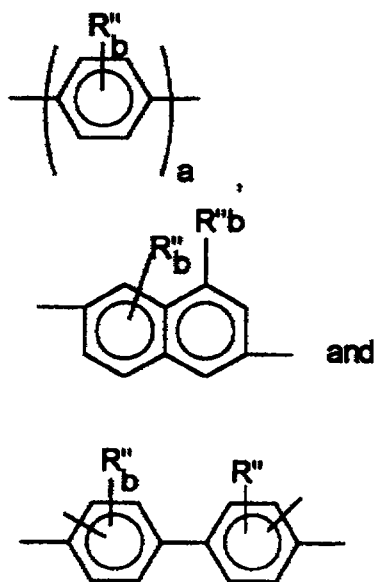
After grafting of the head and tail groups, the resulting antioxidant molecule must contain sites of unsaturation in the head portion(s) capable of reacting with or immobilizing NO_x to form oxidatively stable, non-oxidizable moieties and

suitable hydrocarbyl tail portion(s) to maintain the oil solubility of the molecule at the conditions present in engines.

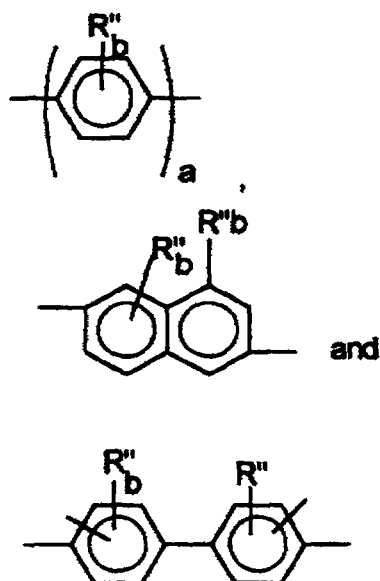
A lower limit also exists on the characteristics of the head group, because sites or head groups having a lower concentration of NO_x-reactive carbon-carbon unsaturation (e.g., monoalkenes and monoalkynes) will immobilize less NO_x per weight or volume of oil. In practical terms an upper limit exists on the number, length and structure of the aliphatic and aromatic hydrocarbyl center(s) which is related to the number, size and structure of the NO_x reactive center(s) and vice versa. Dilution of the activity of the NO_x-reactive center(s) is undesirable, as is dilution of the solubility promoting effect of the aliphatic hydrocarbyl center(s).

The actual combination of head and tail groups may be varied within the parameters established herein. Examples of suitable combinations include C₆₀ or C₇₀ grafted to a C₃₀ to C₄₅ aliphatic hydrocarbyl lube oil basestock, ethylene-propylene copolymer ("EP") bound to hydroquinone, ethylene-propylene copolymer bound to phenol ethylene-butene copolymer ("EB"), poly n-butenes, polythiophene (and other unsaturated, heteroatom containing cyclic moieties) bound to C₈ to C₄₅ alkylhydrocarbons.

Preferably, these sludge mitigation compounds include a major amount of lubricating oil containing an effective amount of at least one compound selected from the group consisting of (A) at least one alkyl substituted hydroxyaromatic compound formed by alkylation of at least one polymer selected from the group consisting of (i) unsaturated ethylene alpha olefin copolymer, (ii) poly(alpha olefin) homopolymer and copolymer, (iii) polybutenes, (iv) polybutadiene polymers and copolymers, wherein said ethylene alpha olefin copolymer contains from about 20 to about 70% ethylene and at least 15% of the polymer chains contain terminal ethyleneidene unsaturation, and wherein said polybutadiene polymers and copolymers contain one or more unsaturation sites prior to said alkylation, and wherein said polymers are alkylated with compounds of the formula H-Ar-(OH)_n where Ar is selected from the group consisting of



wherein a is 1 or 2, R'' is independently a halogen radical or hydrocarbyl radical containing from 1 to about 10 carbon atoms, and b is independently an integer from 0 to 2 and c is an integer from 0 to 2, and (B) a compound formed by alkylation of any of said polymers (i)-(iv) with a compound selected from the group consisting of (v) fullerenes, acetylenes, thiophenes, conjugated dienes, aryls aromatics and heterocyclic aromatics. More preferably, the ethylene alpha olefin copolymer will have an ethyleneidene content of from about 50 to about 100. Also more preferably, the hydroxyaromatic compounds include an effective amount of at least one alkyl substituted hydroxyaromatic compound formed by alkylation of at least one polymer selected from the group consisting of (i) unsaturated ethylene alpha olefin copolymer, (ii) poly(alpha olefin) homopolymer and copolymer, (iii) polybutenes, (iv) polybutadiene polymers and copolymers, wherein said ethylene alpha olefin copolymer contains from about 20 to about 70% ethylene and at least 15% of the polymers chains contain terminal ethyleneidene unsaturation, and wherein said polybutadiene polymers and copolymers contain one or more unsaturation sites prior to said alkylation, and wherein said polymers are alkylated with compounds of the formula $H-Ar-(OH)_c$, where Ar is selected from the group consisting of



wherein a is 1 or 2, R'' is independently a halogen radical or hydrocarbyl radical containing from 1 to about 10 carbon atoms, and b is independently an integer from 0 to 2 and c is an integer from 0 to 2 is added to said lubricating oil.

More preferably alkyl substituted hydroxyaromatic compounds may be selected from the group consisting of a phenol or hydroquinone alkylation product substituted with a poly(α olefin) polymer preferably selected from the group consisting of ethene butene, poly n -butene, polyisobutene, ethene propene, and mixtures thereof. Ethene butene phenol is a more preferred alkyl substituted hydroxyaromatic compound. When the hydroxyaromatic compound is a phenol, the percent of ortho and para groups varies from 100% ortho to 100% para and mixtures thereof, but preferably 100% para. The polymers desirably have an M_n of from about 300 to 100,000, preferably, 800 to about 2,000. For ethene butene the more preferred range of M_n is from about 800 to about 5,000, most preferably 800 to about 2,000.

For use as a lubricant additive the molecule will be soluble (i.e., soluble or stably dispersible) in the lube oil both before and on reaction with NO_x and compatible with other additives present over the range of operating conditions at which the lube is used.

Sludge reduction of at least two times, preferably at least ten times, that of untreated basestock can be achieved.

The following examples illustrate the invention:

A. Sample Procedures for Synthesis of Antioxidant Molecules

Example 1: Free-radical Grafting of Fullerenes to Poly(alphaolefins) "PAO"

100 g of PAO (Mobil SHF 61) was mixed with 1 g of C_{60} in a 500 ml round bottom flask equipped with condenser and a nitrogen bubbler. The solution was heated at 160°C and 0.8 ml of t-butyl peroxide was added dropwise under nitrogen. The reddish-brown solution was allowed to stir at that temperature for 1 hour. After cooling to room temperature, the solution was mixed with 100 ml of heptane and filtered. The solvent was evaporated on rotary evaporator.

The product was characterized by the Gel Permeation Chromatography (GPC). In the C_{60} grafted PAO, a new peak corresponding to approximately 2 and 3 molecules of PAO are attached to C_{60} molecule were observed along with the peaks due to PAO.

Example 2: Alkylation of Ethylene Propylene copolymer with Phenol

In a 250 ml round-bottom flask were charged 4.3 g of phenol and 50 ml of heptane. To this was added 6 g of Amberlyst-15 and the mixture was heated to 90°C. Added to this was 20 g of an EP polymer (mw = 870) and the solution was maintained at 90°C for another 8 hours. The reaction mixture was then filtered, the filtrate evaporated, and the resultant product redissolved in heptane. The heptane solution was filtered and the filtrate evaporated under vacuum to obtain the product.

IR spectra of the product revealed new peak appearing at 3612 cm^{-1} (indicating a change in the nature of the hydroxyl groups on the aromatic ring that would indicate the presence of a substituent) and disappearance of the double bond peaks of the EP polymer at 3065 , 1645 and 885 cm^{-1} (indicating the loss of the polymer unsaturation). This indicates that the phenol was alkylated.

Example 3: Alkylation of Ethylene Propylene Copolymer with Hydroquinone

In a 250 ml round-bottom flask were charged 6.32 g (0.0575 moles) of hydroquinone (mw = 110) and 50 ml of heptane. To this was added 10 g of Amberlyst-15 and the mixture was heated to 90°C . Added to this was 50 g of an EP polymer (mw = 870) and the solution was maintained at 90°C for another 2 hours. The reaction mixture was then filtered, the filtrate evaporated, and the resultant product redissolved in heptane. The heptane solution was itself filtered and the filtrate evaporated under vacuum to obtain the product.

IR spectra of the product revealed new peaks appearing at 3620 and 1400 cm^{-1} (indicating a change in the nature of the hydroxyl groups on the aromatic ring that would indicate the presence of a substituent) and disappearance of the double bond peaks of the EP polymer at 3065 , 1645 and 885 cm^{-1} (indicating the loss of the polymer unsaturation). This indicates that the dihydroxyaromatic was alkylated.

B. General Procedure for Bench Tests

Bench tests were conducted to measure the impact of the sludge control additives described in this invention on sludge formation in lubricating oils. In the sludge simulation test NO_2 gas, delivered into the lube oil at a predetermined fixed rate, or a model organonitrate compound was contacted with the identified lubricant containing the sludge control additive of the present invention. The lube oil was allowed to react with NO_2 or the organonitrate compound, in the presence of 1 g of myrcene, a diene. The reaction was

carried out at temperatures of 95°C to simulate Sequence VE sump or of 150°C to simulate Sequence IIE sump, each for 2 hrs.

Example 1: VE Sump Simulation

Samples were removed from the reaction mixture and analyzed by infrared spectroscopy to follow the change in sludge formation as a function of time in the presence of NO₂. At the end of the test the reaction mixture was filtered and the total amount of sludge produced was weighed. The following three samples were tested:

Sample Contents

- A Basestock + NO₂ + myrcene (Comparative Example)
- B 20% Basestock grafted with C₆₀ in a 5:1 ratio + A
- C C₆₀ (ungrafted) + A (Comparative Example)

The results are shown in Table I below.

TABLE - I Sludge weight in grams

<u>BASESTOCK</u>	<u>A</u>	<u>B</u>	<u>C</u>
PAO	2.12	0.41	1.44
S150N	2.45	0.35	4.01

The results indicate that only B produced significant decreases in sludge formation.

Example 2: Sequence III E Sump Simulation

Each of the five tests listed below was conducted using the model sludge precursor, $C_8H_{17}NO_3$ under identical conditions in the presence of 100/mmol $C_8H_{17}NO_3$ /kg of lube. Samples were removed for infrared spectral analysis and at the end of the test the lube solutions were filtered and the total sludge weighed. The results are shown in Table II.

TABLE - II Sludge weight in grams/100g of lube

<u>SAMPLE</u>	<u>SLUDGE Wt (g)</u>
S150N + myrcene (Comparative Example)	2.12
S150N + 20% S150N grafted C_{60} + myrcene	0.90
S1250N + C_{60} (ungrafted) + myrcene (Comparative Example)	1.70

The results indicate that only the lube oils containing the antioxidant molecules produced significant decreases in sludge formation.

Example 3: VE Sump Simulation

A test was run using poly(C_6 -thiophene) and poly(C_8 -thiophene) as antioxidant comparison, but in which the formation of organic nitrate and nitro species and the buildup of a carbonyl species also were measured periodically using infra-red spectroscopy. Samples were taken periodically from the reaction mixture and analyzed using FTIR to follow the composition change. The total amount of the sludge was collected, rinsed with pentane, dried and weighed at the end of each test. The NO_x performance data compared with the base case and are shown below in Table IV.

TABLE IV

<u>SAMPLE</u>	<u>SLUDGE WT (g)</u>	<u>RNO₂</u>	<u>RONO₂</u>	<u>fC=O</u>	<u>MYRCENE DECAY</u>
Base case S150N	1.81	11.8	2.7	2.5	-99%
Base case S150N + 0.8 wt% Poly(C ₆ - thiophene)	1.12	13.9	3.1	3.2	-98%
Base case S150N + 0.8 wt% Poly(C ₈ - thiophene)	0.32	18.4	3.7	3.5	-48%

The presence of the antioxidant additives had a beneficial effect on sludge mitigation.

Example 4: VE Sump Simulation

EP-bound phenol as well as EP-bound hydroquinone were evaluated in the NO_x test discussed above. The performance data compared to the Base Case and are shown in Table V.

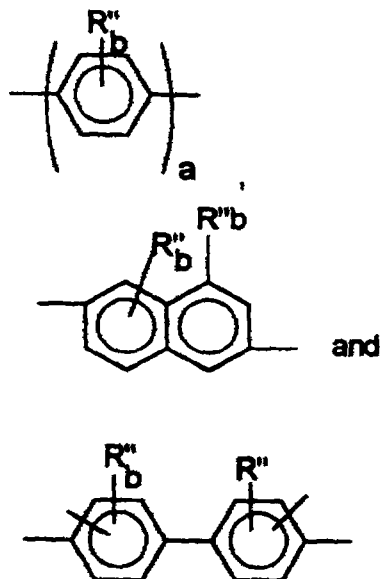
TABLE V

<u>SAMPLE</u>	<u>SLUDGE Wt (g)</u>
Base case (S150N)	1.81
EP-phenol	0.83
EP-hydroquinone	0.54

The sludge mitigation in the presence of the antioxidant additives is evident.

**CLAIMS:**

1. A lubricating oil for mitigating sludge formation in engine oils comprising: a major amount of a lubricating oil in admixture with an effective amount of at least one compound selected from the group consisting of (A) at least one alkyl substituted hydroxyaromatic compound formed by alkylation of at least one polymer selected from the group consisting of (i) unsaturated ethylene alpha olefin copolymer, (ii) poly(alpha olefin) homopolymer and copolymer, (iii) polybutenes, (iv) polybutadiene polymers and copolymers, wherein said ethylene alpha olefin copolymer contains from about 20 to about 70% ethylene and at least 15% of the polymer chains contain terminal ethyleneidene unsaturation, and wherein said polybutadiene polymers and copolymers contain one or more unsaturation sites prior to said alkylation, and wherein said polymers are alkylated with compounds of the formula $H-Ar-(OH)_c$, where Ar is selected from the group consisting of

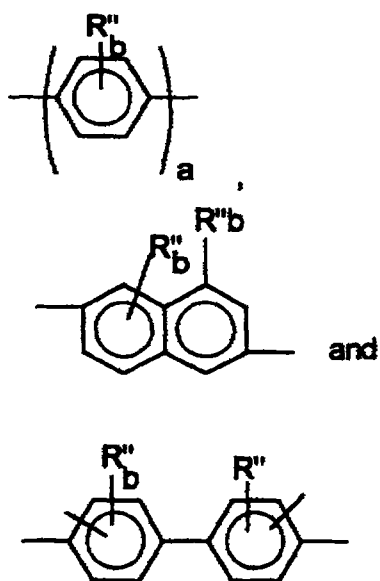


wherein a is 1 or 2, R'' is independently a halogen radical or hydrocarbyl radical containing from 1 to about 10 carbon atoms, and b is independently an integer from 0 to 2 and c is an integer from 0 to 2, and (B) a compound formed by alkylation of any of said polymers (i)-(iv) with a compound selected from the group consisting of (v)



fullerenes, acetylenes, thiophenes, conjugated dienes, aryls aromatics and heterocyclic aromatics.

2. The lubricating composition of claim 1 wherein an effective amount of at least one alkyl substituted hydroxyaromatic compound formed by alkylation of at least one polymer selected from the group consisting of (i) unsaturated ethylene alpha olefin copolymer, (ii) poly(alpha olefin) homopolymer and copolymer, (iii) polybutenes, (iv) polybutadiene polymers and copolymers, wherein said ethylene alpha olefin copolymer contains from about 20 to about 70% ethylene and at least 15% of the polymers chains contain terminal ethyleinedene unsaturation, and wherein said polybutadiene polymers and copolymers contain one or more unsaturation sites prior to said alkylation, and wherein said polymers are alkylated with compounds of the formula $H-Ar-(OH)_c$ where Ar is selected from the group consisting of



wherein a is 1 or 2, R'' is independently a halogen radical or hydrocarbyl radical containing from 1 to about 10 carbon atoms, and b is independently an integer from 0 to 2 and c is an integer from 0 to 2 is added to said lubricating oil.



3. The lubricating oil of claim 1 wherein the alkyl substituted hydroxyaromatic compound is selected from the group consisting of a phenol or hydroquinone alkylation product substituted with a polymer selected from the group consisting of ethene butene, poly n-butene, polyisobutene, and ethene propene, benzoquinone and anisol and mixtures thereof.

4. The lubricating oil of claim 1 wherein the alkyl substituted hydroxyaromatic compound is ethene butene phenol.

5. The lubricating oil of claim 2 wherein the polymers have an Mn of from about 300 to about 100,000.

6. The lubricating oil of claim 3 wherein the polymers have an Mn of 800 to about 2,000.

7. The lubricating oil of claim 3 wherein when the polymer is an ethene butene polymer the Mn is from about 800 to about 5,000.

8. The lubricating oil of claim 1 wherein when the hydroxyaromatic compound is a phenol, the phenol has a percent of ortho and para groups of from 100% ortho to 100% para.

9. The lubrication oil of claim 1 wherein the ethylene alpha olefin copolymer has an ethyleneidene content of from about 30 to about 100 mole percent.

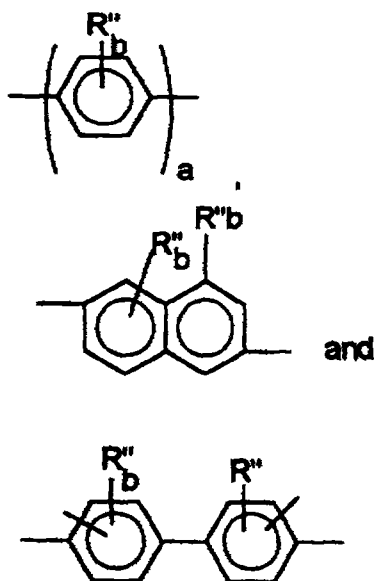
10. The lubricating oil of claim 1 further comprising detergents, dispersants, anti-wear agents, viscosity modifiers, antioxidants, surfactants and pour point depressants.



11. A method for mitigating sludge formation in engine oils, comprising:

dissolving in an engine lubricating oil an effective minor amount of a sludge mitigation compound having at least one head portion enriched in NO_x reactive carbon-carbon unsaturation and at least one oil soluble aliphatic hydrocarbyl tail portion having an absence of carbon-carbon unsaturation of suitable chain length in ratio of head to tail portion sufficient to mitigate sludge formation in the engine oil.

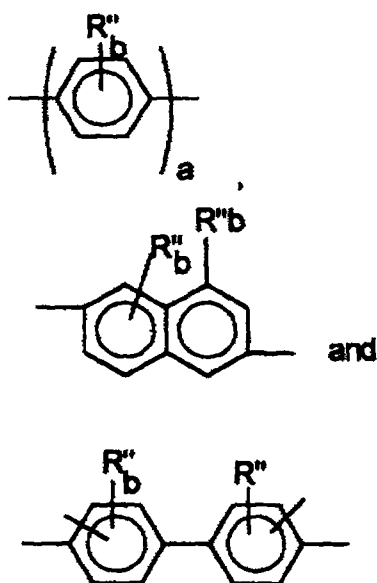
12. The method of claim 11 wherein sludge mitigation compound is at least one compound selected from the group consisting of (A) at least one alkyl substituted hydroxyaromatic compound formed by alkylation of at least one polymer selected from the group consisting of (i) unsaturated ethylene alpha olefin copolymer, (ii) poly(alpha olefin) homopolymer and copolymer, (iii) polybutenes, (iv) polybutadiene polymers and copolymers, wherein said ethylene alpha olefin copolymer contains from about 20 to about 70% ethylene and at least 15% of the polymer chains contain terminal ethyleneidene unsaturation, and wherein said polybutadiene polymers and copolymers contain one or more unsaturation sites prior to said alkylation, and wherein said polymers are alkylated with compounds of the formula H-Ar-(OH)_c , where Ar is selected from the group consisting of





wherein a is 1 or 2, R" is independently a halogen radical or hydrocarbyl radical containing from 1 to about 10 carbon atoms, and b is independently an integer from 0 to 2 and c is an integer from 0 to 2, and (B) a compound formed by alkylation of any of said polymers (i)-(iv) with a compound selected from the group consisting of (v) fullerenes, acetylenes, thiophenes, conjugated dienes, aryls aromatics and heterocyclic aromatics.

13. The method of claim 12 wherein an effective amount of at least one alkyl substituted hydroxyaromatic compound formed by alkylation of at least one polymer selected from the group consisting of (i) unsaturated ethylene alpha olefin copolymer, (ii) poly(alpha olefin) homopolymer and copolymer, (iii) polybutenes, (iv) polybutadiene polymers and copolymers, wherein said ethylene alpha olefin copolymer contains from about 20 to about 70% ethylene and at least 15% of the polymers chains contain terminal ethyleinedene unsaturation, and wherein said polybutadiene polymers and copolymers contain one or more unsaturation sites prior to said alkylation, and wherein said polymers are alkylated with compounds of the formula H-Ar-(OH)_c where Ar is selected from the group consisting of





wherein a is 1 or 2, R" is independently a halogen radical or hydrocarbyl radical containing from 1 to about 10 carbon atoms, and b is independently an integer from 0 to 2 and c is an integer from 0 to 2 is added to said lubricating oil.

14. The method of claim 12 wherein the alkyl substituted hydroxyaromatic compound is selected from the group consisting of a phenol or hydroquinone alkylation product substituted with a polymer selected from the group consisting of ethene butene, poly n-butene, poly isobutene, and ethene propene, benzoquinone and anisol and mixtures thereof.

15. The method of claim 12 wherein the alkyl substituted hydroxyaromatic compound is ethene butene phenol.

16. The method of claim 12 wherein the polymers have an Mn of from about 300 to about 100,000.

17. The method of claim 13 wherein when the polymer is ethene butene and the Mn is from about 800 to about 5,000.

18. The composition of claim 13 wherein when the hydroxyaromatic compound is a phenol, the phenol has a percent of ortho and para groups of from 100% ortho to 100% para.

19. The method of claim 12 wherein the ethylene alpha olefin copolymer has an ethyleneidene content of from about 30 to about 100 mole percent.

20. The method of claim 11 wherein the aliphatic hydrocarbyl tail portion is at least one C₆ aliphatic hydrocarbyl group per head portion.

21. The method of claim 11 wherein the tail portion is at least one C₁₂ to C₁₀₀ aliphatic hydrocarbyl group per head portion.



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22. The method of claim 11 wherein the additive is present in an amount of from about 0.2 to about 5 wt%.

23. The method of claim 11 wherein the tail portion is a base oil selected from the group consisting of S150N, S600N, mineral oils and the synthetic base stocks.

24. The method of claim 11 wherein the compound is selected from the group consisting of ethylene propylene copolymer-grafted hydroquinone, fullerene grafted lube oil basestock, ethylene propylene copolymer-grafted phenol.

25. The method of claim 11 wherein the head portion is selected from the group consisting of reactive acetylenic, olefinic, conjugated dienes, aryl and aromatic heterocyclic groups.

26. The method of claim 11 wherein the compound is selected from the group consisting of C_{60} grafted to a C_{30} to C_{45} aliphatic hydrocarbyl lube oil base stock and polythiophene bound to C_3 to C_{45} alkylthiophenes.

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(21) International Application Number: PCT/US96/17507 (22) International Filing Date: 30 October 1996 (30.10.96) (30) Priority Data: 08/551,076 31 October 1995 (31.10.95) US (71) Applicant (for all designated States except US): EXXON RESEARCH AND ENGINEERING COMPANY [US/US]; 180 Park Avenue, P.O. Box 390, Florham Park, NJ 07932-0390 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): PATIL, Abhimanyu, O. [US/US]; 914 Ripley Avenue, Westfield, NJ 07090 (US). FANG, Howard, L. [US/US]; 518 Glen Ridge South, Bridgewater, NJ 08807 (US). FRANCISCO, Manuel, A. [US/US]; 9 Pohatcong Terrace, Washington, NJ 07882 (US). GUTIERREZ, Antonio [US/US]; 22 Tar Heels Road, Mercerville, NJ 08619 (US). PUCKACE, James, S. [US/US]; 16 Van Hise Drive, Perrineville, NJ 08535 (US). (74) Agents: SCUORZO, Linda, M. et al.; Exxon Research and Engineering Company, P.O. Box 390, Florham Park, NJ 07932-0390 (US).		(81) Designated States: AU, CA, JP, SG US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: ANTINOXIDANT SLUDGE CONTROL ADDITIVES (57) Abstract The invention relates to a process for mitigating NO_x-induced sludge formation in engine oils by dissolving in an engine oil of lubricating viscosity an effective amount of a molecule having at least one head portion enriched in NO_x reactive carbon-carbon unsaturation and at least one oil soluble hydrocarbyl, preferably aliphatic, tail portion having an absence of carbon-carbon unsaturation of suitable chain length in an optimum ratio of head to tail sufficient to reduce NO_x-induced sludge formation in the engine oil. The invention also relates to formulated lube oil compositions containing the antioxidant additive. The molecules include polyethylene propylene copolymer- and polyisobutylene-grafted hydroquinone polyalkylthiophenes, fullerene-grafted lube oil basestock, ethylene propylene polymer-grafted phenol and ethylene butylene polymer-grafted phenol.		