

LOW MOLECULAR WEIGHT POLYMERIC SOOT DISPERSANT

FIELD OF THE DISCLOSURE

[1] The present disclosure relates to lubricant additives and lubricating oil compositions containing the same. More particularly, the present disclosure relates to low molecular weight polymeric dispersants that can improve wear and/or soot dispersion when used as lubricant additives.

BACKGROUND

[2] Internal combustion engines can produce soot as a result of incomplete combustion. Soot formation is generally more prevalent in diesel engines compared to gasoline engines due to the differences in how fuel is injected and ignited. Accumulation of soot can lead to number of issues such as increasing engine wear leading to engine failure. Thus, improving dispersancy of suspended soot or sludge that forms during the operation or use of the lubricant in engines is critically important for sustained engine operation.

SUMMARY OF THE INVENTION

[3] In one aspect, this disclosure is related to a polymeric dispersant composition, wherein the polymeric dispersant can be represented by the following generalized structure:



, wherein A is liquid hydrocarbon polymer and B is independently alkyl polyarene or alkyl arene, n is 1 to 15; and wherein the liquid hydrocarbon polymer has a number average molecular weight (Mn) from about 1,500 to about 16,000.

[4] In another aspect, this disclosure is related to a lubricating oil composition comprising: a major amount of a base oil of lubricating viscosity; and a polymeric dispersant represented by the following generalized structure:

$A-B_n$, wherein A is liquid hydrocarbon polymer and B is independently alkyl polyarene or alkyl arene, n is 1 to 15; and wherein the liquid hydrocarbon polymer has a number average molecular weight (Mn) from about 1,500 to about 16,000.

[5] In yet another aspect, this disclosure is related to a method for improving wear or soot dispersion in an internal combustion engine, the method comprising lubricating the engine with a lubricating oil composition comprising: a major amount of base oil; and a polymeric dispersant represented by the following generalized structure:

$A-B_n$, wherein A is liquid hydrocarbon polymer and B is independently alkyl polyarene or alkyl arene, n is 1 to 15; and wherein the liquid hydrocarbon polymer has a number average molecular weight (Mn) from about 1,500 to about 16,000.

DETAILED DESCRIPTION

Definitions

[6] The following terms will be used throughout the specification and will have the following meanings unless otherwise indicated.

[7] The term “a major amount” of a base oil refers to where the amount of the base oil is at least 40 wt. % of the lubricating oil composition. In some embodiments, “a major amount” of a

base oil refers to an amount of the base oil more than 50 wt. %, more than 60 wt. %, more than 70 wt. %, more than 80 wt. %, or more than 90 wt. % of the lubricating oil composition.

[8] The term "Total Base Number" or "TBN" refers to the level of alkalinity in an oil sample, which indicates the ability of the composition to continue to neutralize corrosive acids, in accordance with ASTM Standard No. D2896 or equivalent procedure. The test measures the change in electrical conductivity, and the results are expressed as mgKOH/g (the equivalent number of milligrams of KOH needed to neutralize 1 gram of a product). Therefore, a high TBN reflects strongly overbased products and, as a result, a higher base reserve for neutralizing acids.

[9] "HOB" refers to high overbased with a TBN above 250 on an actives basis and "LOB" refers to low overbased with a TBN below 100 on an actives basis.

[10] The term "liquid polymer" and/or related terms such as "liquid hydrocarbon polymer" refers to a polymer that is liquid under ambient temperature and pressure. In some embodiments, the liquid polymers of the present disclosure exhibit KV100 of less than 3000 cSt and can be chemically grafted (e.g., radical initiation, acylating agent, etc.). Specific examples of liquid hydrocarbon polymers include "liquid olefin copolymer" which refers to an olefin copolymer that is liquid under ambient temperature and pressure.

[11] This disclosure relates to a low molecular weight polymeric dispersants and lubricating oil compositions containing the same. The low molecular weight polymeric dispersant can be used as a lubricant additive to impart one or more performance benefits to a lubricating oil composition.

Polymeric Dispersant

[12] The low molecular weight polymeric dispersant can be used as a lubricant additive to provide protection against wear and/or improve soot dispersion in an internal combustion engine.

[13] In some embodiments, the polymeric dispersant composition can be represented by the following generalized structure:



wherein A is liquid hydrocarbon polymer and B is independently alkyl polyarene or alkyl arene, n is 1 to 15; and wherein the liquid hydrocarbon polymer has a number average molecular weight (M_n) from about 1,500 to about 16,000.

[14] The low molecular weight polymeric dispersant of this disclosure may be synthesized or obtained by any compatible means. For example, one compatible synthetic approach involves a grafting reaction whereby a low molecular weight polymer is reacted with a vinyl arene in the presence of a free radical initiator.

[15] In some embodiments, the low molecular weight polymeric dispersant is the reaction product of (a) liquid hydrocarbon polymer having a number average molecular weight (M_n) from about 1,500 and about 16,000; and (b) vinyl arene. The M_n of the liquid hydrocarbon polymer can be measured by any compatible method such as gel permeation chromatography.

Liquid Hydrocarbon Polymer

[16] The liquid hydrocarbon polymer of this disclosure is characterized by low molecular weight, particularly when compared to olefin copolymers conventionally used as viscosity index improvers. The number average (M_n) molecular weight of the liquid hydrocarbon polymer is from about 1,500 to about 16,000 such as from about 1,500 to about 15,500, about 1,500 to about 15,000, about 1,500 to about 14,500, about 1,500 to about 14,000, about 1,500 to about 13,500, about 1,500 to about 13,000, about 1,500 to about 12,500, about 1,500 to about 12,000, about 1,500 to about 11,500, about 1,500 to about 11,000, about 1,500 to about 10,500, about 1,500 to about

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[17] Suitable examples of liquid hydrocarbon polymers include, but are not limited to, ethylene-based olefin copolymers such as ethylene-propylene copolymers. Copolymers herein can include blends or reacted products of ethylene and one or more C3 to C28 alpha-olefins, and additionally optionally other dienes or polyenes and thus may herein also include terpolymers, and other higher forms.

[18] In some embodiments, the ethylene content of the copolymer is in the range of 10 to 80 percent by weight, such as 10 to 75 percent, 10 to 70 percent, 10 to 65 percent, 10 to 60 percent 10 to 50 percent, 10 to 45 percent, 10 to 40 percent, 10 to 35 percent, 10 to 30 percent 10 to 25 percent 10 to 20 percent, 10 to 15 percent, 15 to 80 percent, 15 to 75 percent, 15 to 70 percent, 15 to 65 percent, 15 to 60 percent, 15 to 55 percent, 15 to 50 percent, 15 to 45 percent, 15 to 40 percent, 15 to 35 percent, 15 to 30 percent, 15 to 25 percent, 15 to 20 percent, 20 to 80 percent, 20

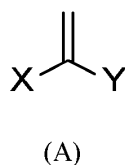
to 75 percent, 20 to 70 percent, 20 to 65 percent, 20 to 60 percent, 20 to 55 percent, 20 to 50 percent, 20 to 45 percent, 20 to 40 percent, 20 to 35 percent, 20 to 30 percent, 20 to 25 percent, 25 to 80 percent, 25 to 75 percent, 25 to 70 percent, 25 to 65 percent, 25 to 60 percent, 25 to 55 percent, 25 to 50 percent, 25 to 45 percent, 25 to 40 percent, 25 to 35 percent, 25 to 30 percent, 30 to 80 percent, 30 to 75 percent, 30 to 70 percent, 30 to 65 percent, 30 to 60 percent, 30 to 55 percent, 30 to 50 percent, 30 to 45 percent, 30 to 40 percent, 30 to 35 percent, 35 to 80 percent, 35 to 75 percent, 35 to 70 percent, 35 to 65 percent, 35 to 60 percent, 35 to 55 percent, 35 to 50 percent, 35 to 45 percent, 35 to 40 percent, 40 to 80 percent, 40 to 75 percent, 40 to 70 percent, 40 to 65 percent, 40 to 60 percent, 40 to 55 percent, 40 to 50 percent, 40 to 45 percent, 45 to 80 percent, 45 to 75 percent, 45 to 70 percent, 45 to 65 percent, 45 to 60 percent, 45 to 55 percent, 45 to 50 percent, 50 to 80 percent, 50 to 75 percent, 50 to 70 percent, 50 to 65 percent, 50 to 60 percent, 50 to 55 percent, 55 to 80 percent, 55 to 75 percent, 55 to 70 percent, 55 to 65 percent, 55 to 60 percent, 60 to 80 percent, 60 to 75 percent, 60 to 70 percent, 60 to 65 percent, 65 to 80 percent, 65 to 75 percent, 65 to 70 percent, 70 to 80 percent, 70 to 75 percent, or 75 to 80 percent.

[19] In some embodiments, the ethylene-based copolymer is an ethylene-propylene copolymer. The propylene content of the ethylene-propylene copolymer is in the range of 20 to 90 percent by weight, such as 20 to 85 percent, 20 to 80 percent, 20 to 75 percent, 20 to 70 percent, 20 to 65 percent, 20 to 60 percent, 20 to 50 percent, 20 to 45 percent, 20 to 40 percent, 20 to 35 percent, 20 to 30 percent, 20 to 25 percent, 25 to 90 percent, 25 to 85 percent, 25 to 80 percent, 25 to 75 percent, 25 to 70 percent, 25 to 65 percent, 25 to 60 percent, 25 to 55 percent, 25 to 50 percent, 25 to 45 percent, 25 to 40 percent, 25 to 35 percent, 25 to 30 percent, 30 to 90 percent, 30 to 85 percent, 30 to 80 percent, 30 to 75 percent, 30 to 70 percent, 30 to 65 percent, 30 to 60 percent, 30 to 55 percent, 30 to 50 percent, 30 to 45 percent, 30 to 40 percent, 30 to 35 percent, 35 to 90 percent, 35

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Vinyl Arene

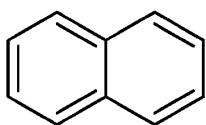
[20] The vinyl arene of this disclosure can be represented by the following generalized structure (A):



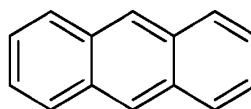
wherein X is an aromatic group and Y is a hydrogen atom or a methyl group.

[21] Polyaromatic arenes are characterized by two or more aromatic rings. Arenes can also include one or more heteroatoms such nitrogen, boron, and the like. Non-limiting examples of

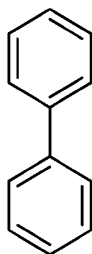
polyaromatic arenes include naphthalene (I), anthracene (II), biphenyl (III), triphenylmethane (IV), carbazole (V), and the like.



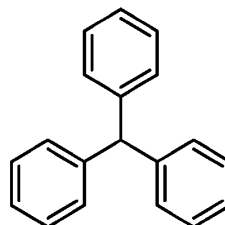
(I)



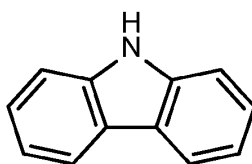
(II)



(III)

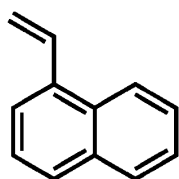


(IV)

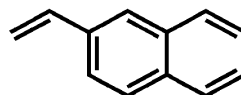


(V)

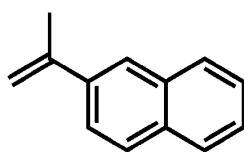
[22] Specific examples of vinyl polyaromatic arenes include 1-vinylnaphthalene (VI), 2-vinylnaphthalene (VII), 2-(1-methylethenyl)naphthalene (VIII), 9-vinylanthracene (IX), 4-vinylbiphenyl (X), 4-benzhydrylstyrene (XI), 9-vinylcarbazole (XII), and 9-(1-methylethenyl)-9H-carbazole (XIII).



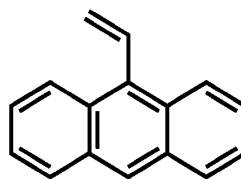
(VI)



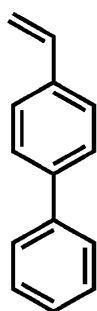
(VII)



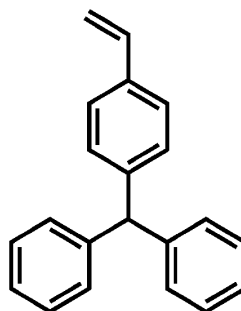
(VIII)



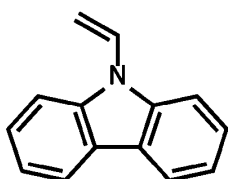
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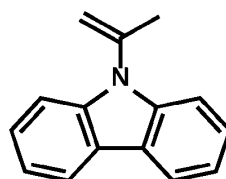
(X)



(XI)



(XII)



(XIII)

Free Radical Initiator

[23] The grafting reaction can be catalyzed by a free radical initiator. Examples of free radical initiator include peroxides, hydroperoxides, peresters, and also azo compounds and preferably those which have a boiling point greater than 100°C and decompose thermally within the grafting temperature range to provide free radicals. Representatives of these free-radical initiators are peroxides (diacyl peroxides such as benzoyl peroxide, dialkyl peroxides such as 1,1-bis(tert-butylperoxy)cyclohexane, 1,1-bis(tert-butylperoxy)-3,3,5-trimethylcyclohexane, 2,2-bis(tert-butylperoxy)butane, dicumylperoxide, tert-butylcumylperoxide, bis(tert-butylperoxyisopropyl)benzene, di-tert-butylperoxide (DTBP), di-tert-amylperoxide, 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane, 2,5-dimethyl-2,5-di(tert-butylperoxy)-hexyne), hydroperoxides, peroxyesters such as tert-butyl peroxy benzoate, tert-butylperoxy acetate, O,O-tert-butyl-O-(2-ethylhexyl)monoperoxy carbonate, peroxyketals such as n-butyl 4,4-di-(tert-butylperoxy)valerate and the like. The initiator is used in an amount of from about 0.005% and about 1% by weight based on the weight of the reaction mixture solution. The grafting is preferably carried out in an inert atmosphere, such as under nitrogen blanketing. The resulting polymer intermediate is characterized by having acylating groups, typified by a carboxylic acid or acid chloride, within its structure. The initiator is typically used in an amount of from about 0.005% and about 1% by weight based on the weight of the reaction mixture solution.

[24] A more detailed discussion of free radical initiators can be found in Reactive Modifiers for Polymers Softcover reprint of the original 1st ed. 1997 Edition. by S. Al-Malaika (Editor), the relevant parts of which are hereby incorporated by reference.

Other Additives

[25] Optionally, the lubricating oil composition may further comprise an additive that can impart or improve any desirable property of the lubricating oil composition. Any additive known to a person of ordinary skill in the art may be used in the lubricating oil compositions disclosed herein. Some suitable additives have been described in Mortier et al., "Chemistry and Technology of Lubricants," 2nd Edition. London, Springer, (1996); and Leslie R. Rudnick, "Lubricant Additives: Chemistry and Applications," New York, Marcel Dekker (2003), both of which are incorporated herein by reference. In some embodiments, the additive can be selected from the group consisting of antioxidants, antiwear agents, detergents, rust inhibitors, demulsifiers, friction modifiers, multi-functional additives, viscosity index improvers, pour point depressants, foam inhibitors, metal deactivators, dispersants, corrosion inhibitors, lubricity improvers, thermal stability improvers, anti-haze additives, icing inhibitors, dyes, markers, static dissipaters, biocides and combinations thereof.

[26] In general, the concentration of each of the additives in the lubricating oil composition, when used, may range from about 0.001 wt. % to about 10 wt. %, from about 0.01 wt. % to about 5 wt. %, or from about 0.1 wt. % to about 2.5 wt. %, based on the total weight of the lubricating oil composition. Further, the total amount of the additives in the lubricating oil composition may range from about 0.001 wt. % to about 20 wt. %, from about 0.01 wt. % to about 10 wt. %, or from about 0.1 wt. % to about 5 wt. %, based on the total weight of the lubricating oil composition.

Detergents

[27] The lubricating oil composition may comprise a metal detergent such as a metal salicylate, metal phenate, or metal sulfonate. The metal can be any metal suitable for making detergents.

Non-limiting examples of suitable metals include alkali metals, alkaline earth metals and transition metals. In some embodiments, the metal is Ca, Mg, Ba, K, Na, Li or the like.

[28] Generally, the amount of the detergent is from about 0.001 wt. % to about 10 wt. %, from about 0.05 wt. % to about 3 wt. %, or from about 0.1 wt. % to about 1 wt. %, based on the total weight of the lubricating oil composition.

[29] Optionally, the lubricating oil composition may comprise additional detergents generally known in the art. Some suitable detergents have been described in Mortier et al., "Chemistry and Technology of Lubricants," 2nd Edition, London, Springer, Chapter 3, pages 75-85 (1996); and Leslie R. Rudnick, "Lubricant Additives: Chemistry and Applications," New York, Marcel Dekker, Chapter 4, pages 113-136 (2003), both of which are incorporated herein by reference. Examples of these detergents include phenates, salicylates, phosphonates, and the like.

[30] In some embodiments the detergent comprises at least one high overbased (TBN above 250 on an actives basis).

[31] Overbased metal detergents are generally produced by carbonating a mixture of hydrocarbons, detergent acid, for example: sulfonic acid, alkylhydroxybenzoate etc., metal oxide or hydroxides (for example calcium oxide or calcium hydroxide) and promoters such as xylene, methanol and water. For example, for preparing an overbased calcium sulfonate, in carbonation, the calcium oxide or hydroxide reacts with the gaseous carbon dioxide to form calcium carbonate. The sulfonic acid is neutralized with an excess of CaO or Ca(OH)₂, to form the sulfonate.

[32] Generally speaking, overbased detergents may be low overbased (LOB), e.g., an overbased salt having a TBN below 100 on an actives basis. In one aspect, the TBN of a low overbased salt may be from about 10 to about 100. In another aspect, the TBN of a low overbased salt may be from about 10 to about 80. Overbased detergents may be medium overbased (MOB),

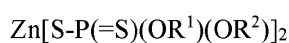
e.g., an overbased salt having a TBN from about 100 to about 250 on an actives basis. In one aspect, the TBN of a medium overbased salt may be from about 100 to about 200. In another aspect, the TBN of a medium overbased salt may be from about 125 to about 175. Overbased detergents may be high overbased (HOB), e.g., an overbased salt having a TBN above 250 on an actives basis. In one aspect, the TBN of a high overbased salt may be from about 250 to about 800 on an actives basis.

[33] In some embodiments, the lubricating oil composition comprises low levels of sulfur containing calcium phenates (e.g., about 40 mmol or less of Ca from sulfurized phenates such as 35 mmol or less, 30 mmol or less, 25 mmol or less, 20 mmol or less, 10 mmol or less, 5 mmol or less and 0 mmol).

Anti-wear agents

[34] Optionally, the lubricating oil composition disclosed herein can comprise one or more anti-wear agents. In some embodiments, the lubricating oil composition is free or substantially free of sulfur-containing anti-wear composition.

[35] Anti-wear agents reduce wear of metal parts. Suitable anti-wear agents include dihydrocarbyl dithiophosphate metal salts such as zinc dihydrocarbyl dithiophosphates (ZDDP) of the following structure:



wherein R^1 and R^2 may be the same or different hydrocarbyl radicals having from 1 to 18 (e.g., 2 to 12) carbon atoms and including radicals such as alkyl, alkenyl, aryl, arylalkyl, alkaryl and cycloaliphatic radicals. Particularly preferred as R^1 and R^2 groups are alkyl groups having from 2 to 8 carbon atoms (e.g., the alkyl radicals may be ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-

butyl, n-pentyl, isopentyl, n-hexyl, isohexyl, 2-ethylhexyl). In order to obtain oil solubility, the average number of carbon atoms of the mixture of R^1 and R^2 on the molar basis will be at least 4.5. The zinc dihydrocarbyl dithiophosphate can therefore comprise zinc dialkyl dithiophosphates. The zinc dialkyl dithiophosphate is a primary, secondary zinc dialkyl dithiophosphate, or a combination thereof. ZDDP may be present at 3 wt. % or less (e.g., 0.1 to 1.5 wt. %, or 0.5 to 1.0 wt %) of the lubricating oil composition.

Dispersants

[36] The lubricating oil composition disclosed herein can further comprise a dispersant. Dispersants maintain in suspension materials resulting from oxidation during engine operation that are insoluble in oil, thus preventing soot or sludge flocculation and precipitation or deposition on metal parts. Dispersants useful herein include nitrogen-containing, ashless (metal-free) dispersants known to be effective to reduce formation of deposits upon use in gasoline and diesel engines. Suitable dispersants include hydrocarbyl succinimides, hydrocarbyl succinamides, mixed ester/amides of hydrocarbyl-substituted succinic acid, hydroxyesters of hydrocarbyl-substituted succinic acid, and Mannich condensation products of hydrocarbyl-substituted phenols, formaldehyde and polyamines. Also suitable are condensation products of polyamines and hydrocarbyl-substituted phenyl acids. Mixtures of these dispersants can also be used. More particularly, succinimide-based dispersants include borated succinimides, non-borated succinimides, post-treated succinimides, and the like.

[37] Basic nitrogen-containing ashless dispersants are well-known lubricating oil additives and methods for their preparation are extensively described in the patent literature. Preferred dispersants are the alkenyl succinimides and succinamides where the alkenyl-substituent is a long-

chain of preferably greater than 40 carbon atoms. These materials are readily made by reacting a hydrocarbyl-substituted dicarboxylic acid material with a molecule containing amine functionality. Examples of suitable amines are polyamines such as polyalkylene polyamines, hydroxy-substituted polyamines and polyoxyalkylene polyamines. As is known in the art, the dispersants may be post-treated (e.g., with a boronating agent, epoxide, ethylene carbonate, or a cyclic carbonate). Nitrogen-containing ashless (metal-free) dispersants are basic and contribute to the TBN of a lubricating oil composition to which they are added, without introducing additional sulfated ash. Dispersants may be present at 0.1 to 10 wt. % (e.g., 0.5 to 8, 0.7 to 7, 0.7 to 6, 0.7 to 6, 0.7 to 5, 0.7 to 4 wt. %), based on an actives level, of the lubricating oil composition. Nitrogen from the dispersants is present from greater than 0.0050 to 0.30 wt. % (e.g., greater than 0.0050 to 0.10 wt. %, 0.0050 to 0.080 wt. %, 0.0050 to 0.060 wt. %, 0.0050 to 0.050 wt. %, 0.0050 to 0.040 wt. %, 0.0050 to 0.030 wt. %) based on the weight of the dispersants in the finished oil.

Antioxidants

[38] Optionally, the lubricating oil composition disclosed herein can further comprise an additional antioxidant that can reduce or prevent the oxidation of the base oil. Any antioxidant known by a person of ordinary skill in the art may be used in the lubricating oil composition. Non-limiting examples of suitable antioxidants include amine-based antioxidants (e.g., alkyl diphenylamines, phenyl- α -naphthylamine, alkyl or aralkyl substituted phenyl- α -naphthylamine, alkylated p-phenylene diamines, tetramethyl-diaminodiphenylamine and the like), phenolic antioxidants (e.g., 2-tert-butylphenol, 4-methyl-2,6-di-tert-butylphenol, 2,4,6-tri-tert-butylphenol, 2,6-di-tert-butyl-p-cresol, 2,6-di-tert-butylphenol, 4,4'-methylenebis-(2,6-di-tert-butylphenol), 4,4'-thiobis(6-di-tert-butyl-o-cresol) and the like), sulfur-based antioxidants (e.g., dilauryl-3,3'-

thiodipropionate, sulfurized phenolic antioxidants and the like), phosphorous-based antioxidants (e.g., phosphites and the like), zinc dithiophosphate, oil-soluble copper compounds and combinations thereof. The amount of the antioxidant may vary from about 0.01 wt. % to about 10 wt. %, from about 0.05 wt. % to about 5 wt. %, or from about 0.1 wt. % to about 3 wt. %, based on the total weight of the lubricating oil composition. Some suitable antioxidants have been described in Leslie R. Rudnick, "Lubricant Additives: Chemistry and Applications," New York. Marcel Dekker, Chapter 1, pages 1-28 (2003), which is incorporated herein by reference.

Foam Inhibitors

[39] The lubricating oil composition disclosed herein can optionally comprise a foam inhibitor or an anti-foam that can break up foams in oils. Any foam inhibitor or anti-foam known by a person of ordinary skill in the art may be used in the lubricating oil composition. Non-limiting examples of suitable anti-foams include silicone oils or polydimethylsiloxanes, fluorosilicones, alkoxyated aliphatic acids, polyethers (e.g., polyethylene glycols), branched polyvinyl ethers, alkyl acrylate polymers, alkyl methacrylate polymers, polyalkoxyamines and combinations thereof. In some embodiments, the anti-foam comprises glycerol monostearate, polyglycol palmitate, a trialkyl monothiophosphate, an ester of sulfonated ricinoleic acid, benzoylacetone, methyl salicylate, glycerol monooleate, or glycerol dioleate. The amount of the anti-foam may vary from about 0.0005 wt. % to about 5 wt. %, from about 0.05 wt. % to about 3 wt. %, or from about 0.1 wt. % to about 1 wt. %, based on the total weight of the lubricating oil composition. Some suitable anti-foams have been described in Mortier et al., "Chemistry and Technology of Lubricants," 2nd Edition, London, Springer, Chapter 6, pages 190-193 (1996), which is incorporated herein by reference.

Molybdenum Additive

[40] In some embodiments, the lubricating oil composition comprises a molybdenum additive. Some non-limiting examples of suitable molybdenum additives include molybdenum succinimide, sulfurized oxymolybdenum dithiocarbamate, sulfurized oxymolybdenum organophosphorodithioate, oxymolybdenum monoglyceride, oxymolybdenum diethylate amide, amine-molybdenum complex compound, and sulfur-containing molybdenum complex compound.

The Oil of Lubricating Viscosity

[41] The lubricating oil compositions disclosed herein generally comprise at least one oil of lubricating viscosity. Any base oil known to a skilled artisan can be used as the oil of lubricating viscosity disclosed herein. Some base oils suitable for preparing the lubricating oil compositions have been described in Mortier et al., "Chemistry and Technology of Lubricants," 2nd Edition, London, Springer, Chapters 1 and 2 (1996); and A. Sequeria, Jr., "Lubricant Base Oil and Wax Processing," New York, Marcel Decker, Chapter 6, (1994); and D. V. Brock, Lubrication Engineering, Vol. 43, pages 184-5, (1987), all of which are incorporated herein by reference. Generally, the amount of the base oil in the lubricating oil composition may be from about 70 to about 99.5 wt. %, based on the total weight of the lubricating oil composition. In some embodiments, the amount of the base oil in the lubricating oil composition is from about 75 to about 99 wt. %, from about 80 to about 98.5 wt. %, or from about 80 to about 98 wt. %, based on the total weight of the lubricating oil composition.

[42] In certain embodiments, the base oil is or comprises any natural or synthetic lubricating base oil fraction. Some non-limiting examples of synthetic oils include oils, such as

polyalphaolefins or PAOs, prepared from the polymerization of at least one alpha-olefin, such as ethylene, or from hydrocarbon synthesis procedures using carbon monoxide and hydrogen gases, such as the Fisher-Tropsch process. In certain embodiments, the base oil comprises less than about 10 wt. % of one or more heavy fractions, based on the total weight of the base oil. A heavy fraction refers to a lube oil fraction having a viscosity of at least about 20 cSt at 100° C. In certain embodiments, the heavy fraction has a viscosity of at least about 25 cSt or at least about 30 cSt at 100° C. In further embodiments, the amount of the one or more heavy fractions in the base oil is less than about 10 wt. %, less than about 5 wt. %, less than about 2.5 wt. %, less than about 1 wt. %, or less than about 0.1 wt. %, based on the total weight of the base oil. In still further embodiments, the base oil comprises no heavy fraction.

[43] In certain embodiments, the lubricating oil compositions comprise a major amount of a base oil of lubricating viscosity. In some embodiments, the base oil has a kinematic viscosity at 100°C. from about 2.5 centistokes (cSt) to about 20 cSt, from about 4 centistokes (cSt) to about 20 cSt, or from about 5 cSt to about 16 cSt. The kinematic viscosity of the base oils or the lubricating oil compositions disclosed herein can be measured according to ASTM D 445, which is incorporated herein by reference.

[44] In other embodiments, the base oil is or comprises a base stock or blend of base stocks. In further embodiments, the base stocks are manufactured using a variety of different processes including, but not limited to, distillation, solvent refining, hydrogen processing, oligomerization, esterification, and rerefining. In some embodiments, the base stocks comprise a rerefined stock. In further embodiments, the rerefined stock shall be substantially free from materials introduced through manufacturing, contamination, or previous use.

[45] In some embodiments, the base oil comprises one or more of the base stocks in one or more of Groups I-V as specified in the American Petroleum Institute (API) Publication 1509, Fourteen Edition, December 1996 (i.e., API Base Oil Interchangeability Guidelines for Passenger Car Motor Oils and Diesel Engine Oils), which is incorporated herein by reference. The API guideline defines a base stock as a lubricant component that may be manufactured using a variety of different processes. Groups I, II and III base stocks are mineral oils, each with specific ranges of the amount of saturates, sulfur content and viscosity index. Group IV base stocks are polyalphaolefins (PAO). Group V base stocks include all other base stocks not included in Group I, II, III, or IV.

[46] In some embodiments, the base oil comprises one or more of the base stocks in Group I, II, III, IV, V or a combination thereof. In other embodiments, the base oil comprises one or more of the base stocks in Group II, III, IV or a combination thereof. In further embodiments, the base oil comprises one or more of the base stocks in Group II, III, IV or a combination thereof wherein the base oil has a kinematic viscosity from about 2.5 centistokes (cSt) to about 20 cSt, from about 4 cSt to about 20 cSt, or from about 5 cSt to about 16 cSt at 100°C.

[47] The base oil may be selected from the group consisting of natural oils of lubricating viscosity, synthetic oils of lubricating viscosity and mixtures thereof. In some embodiments, the base oil includes base stocks obtained by isomerization of synthetic wax and slack wax, as well as hydrocrackate base stocks produced by hydrocracking (rather than solvent extracting) the aromatic and polar components of the crude. In other embodiments, the base oil of lubricating viscosity includes natural oils, such as animal oils, vegetable oils, mineral oils (e.g., liquid petroleum oils and solvent treated or acid-treated mineral oils of the paraffinic, naphthenic or mixed paraffinic-naphthenic types), oils derived from coal or shale, and combinations thereof. Some non-limiting examples of animal oils include bone oil, lanolin, fish oil, lard oil, dolphin oil, seal oil, shark oil,

tallow oil, and whale oil. Some non-limiting examples of vegetable oils include castor oil, olive oil, peanut oil, rapeseed oil, corn oil, sesame oil, cottonseed oil, soybean oil, sunflower oil, safflower oil, hemp oil, linseed oil, tung oil, oiticica oil, jojoba oil, and meadow foam oil. Such oils may be partially or fully hydrogenated.

[48] In some embodiments, the synthetic oils of lubricating viscosity include hydrocarbon oils and halo-substituted hydrocarbon oils such as polymerized and inter-polymerized olefins, alkylbenzenes, polyphenyls, alkylated diphenyl ethers, alkylated diphenyl sulfides, as well as their derivatives, analogues and homologues thereof, and the like. In other embodiments, the synthetic oils include alkylene oxide polymers, interpolymers, copolymers and derivatives thereof wherein the terminal hydroxyl groups can be modified by esterification, etherification, and the like. In further embodiments, the synthetic oils include the esters of dicarboxylic acids with a variety of alcohols. In certain embodiments, the synthetic oils include esters made from C₅ to C₁₂ monocarboxylic acids and polyols and polyol ethers. In further embodiments, the synthetic oils include tri-alkyl phosphate ester oils, such as tri-n-butyl phosphate and tri-iso-butyl phosphate.

[49] In some embodiments, the synthetic oils of lubricating viscosity include silicon-based oils (such as the polyakyl-, polyaryl-, polyalkoxy-, polyaryloxy-siloxane oils and silicate oils). In other embodiments, the synthetic oils include liquid esters of phosphorus-containing acids, polymeric tetrahydrofurans, polyalphaolefins, and the like.

[50] Base oil derived from the hydroisomerization of wax may also be used, either alone or in combination with the aforesaid natural and/or synthetic base oil. Such wax isomerate oil is produced by the hydroisomerization of natural or synthetic waxes or mixtures thereof over a hydroisomerization catalyst.

[51] In further embodiments, the base oil comprises a poly-alpha-olefin (PAO). In general, the poly-alpha-olefins may be derived from an alpha-olefin having from about 2 to about 30, from about 4 to about 20, or from about 6 to about 16 carbon atoms. Non-limiting examples of suitable poly-alpha-olefins include those derived from octene, decene, mixtures thereof, and the like. These poly-alpha-olefins may have a viscosity from about 2 to about 15, from about 3 to about 12, or from about 4 to about 8 centistokes at 100°C. In some instances, the poly-alpha-olefins may be used together with other base oils such as mineral oils.

[52] In further embodiments, the base oil comprises a polyalkylene glycol or a polyalkylene glycol derivative, where the terminal hydroxyl groups of the polyalkylene glycol may be modified by esterification, etherification, acetylation and the like. Non-limiting examples of suitable polyalkylene glycols include polyethylene glycol, polypropylene glycol, polyisopropylene glycol, and combinations thereof. Non-limiting examples of suitable polyalkylene glycol derivatives include ethers of polyalkylene glycols (e.g., methyl ether of polyisopropylene glycol, diphenyl ether of polyethylene glycol, diethyl ether of polypropylene glycol, etc.), mono- and polycarboxylic esters of polyalkylene glycols, and combinations thereof. In some instances, the polyalkylene glycol or polyalkylene glycol derivative may be used together with other base oils such as poly-alpha-olefins and mineral oils.

[53] In further embodiments, the base oil comprises any of the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, alkyl succinic acids, alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkyl malonic acids, alkenyl malonic acids, and the like) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, propylene glycol, and the like). Non-limiting examples of these esters include dibutyl

adipate, di(2-ethylhexyl) sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, and the like.

[54] In further embodiments, the base oil comprises a hydrocarbon prepared by the Fischer-Tropsch process. The Fischer-Tropsch process prepares hydrocarbons from gases containing hydrogen and carbon monoxide using a Fischer-Tropsch catalyst. These hydrocarbons may require further processing in order to be useful as base oils. For example, the hydrocarbons may be dewaxed, hydroisomerized, and/or hydrocracked using processes known to a person of ordinary skill in the art.

[55] In further embodiments, the base oil comprises an unrefined oil, a refined oil, a rerefined oil, or a mixture thereof. Unrefined oils are those obtained directly from a natural or synthetic source without further purification treatment. Non-limiting examples of unrefined oils include shale oils obtained directly from retorting operations, petroleum oils obtained directly from primary distillation, and ester oils obtained directly from an esterification process and used without further treatment. Refined oils are similar to the unrefined oils except the former have been further treated by one or more purification processes to improve one or more properties. Many such purification processes are known to those skilled in the art such as solvent extraction, secondary distillation, acid or base extraction, filtration, percolation, and the like. Rerefined oils are obtained by applying to refined oils processes similar to those used to obtain refined oils. Such rerefined oils are also known as reclaimed or reprocessed oils and often are additionally treated by processes directed to removal of spent additives and oil breakdown products.

[56] The following examples are presented to exemplify embodiments but are not intended to limit the application to the specific embodiments set forth. Unless indicated to the contrary, all

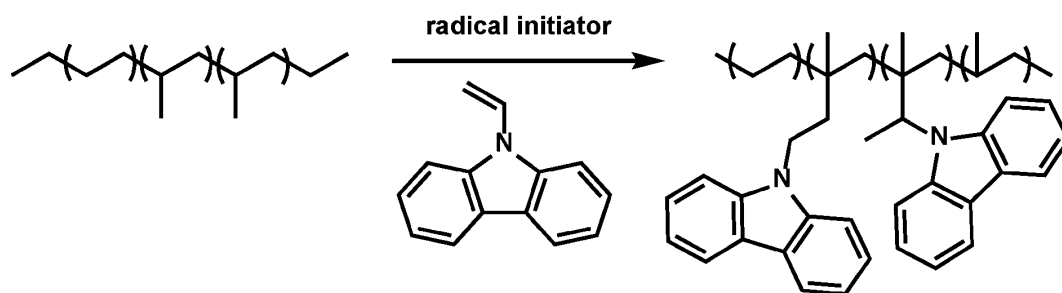
parts and percentages are by weight. All numerical values are approximate. When numerical ranges are given, it should be understood that embodiments outside the stated ranges may still fall within the scope of the application. Specific details described in each example should not be construed as necessary features.

EXAMPLES

[57] The following examples are intended for illustrative purposes only and do not limit in any way the scope.

Example 1

[58] 9-Vinylcarbazole grafted ethylene propylene copolymer was synthesized as described herein.

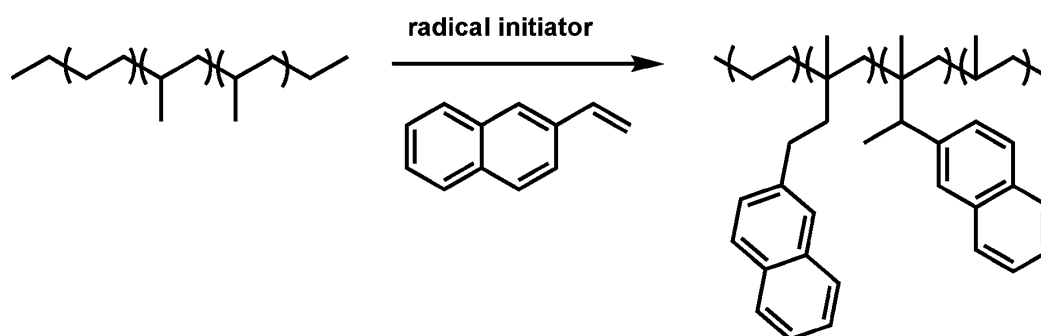


[59] Ethylene-propylene copolymer (2669.8 g, KV100 ~600 cSt) was transferred into a stirred 4-liter stainless steel reactor equipped with charging lines for 9-vinylcarbazole and 2,5-Dimethyl-2,5-di(tert-butylperoxy) hexane and nitrogen blanketed. The copolymer was heated to 155°C. Next, 9-vinylcarbazole (54.49 g in 149.6 mL acetone solution) and 2,5-dimethyl-2,5-di(tert-butylperoxy) hexane (3.65 g) were charged simultaneously into the reactor agitation zone over a 2-hour period.

[60] Upon completion of the 9-vinylcarbazole and peroxide charging, the reactor was held at temperature for an additional 30 minutes. The resulting carbazole grafted ethylene propylene copolymer has KV100 of 642.35 cSt. The reaction product was measured by gel permeation chromatography using UV detection, which confirmed the presence of carbazole groups on the polymer.

Example 2

[61] 2-Vinylnaphthalene grated ethylene-propylene copolymer was prepared as described herein.

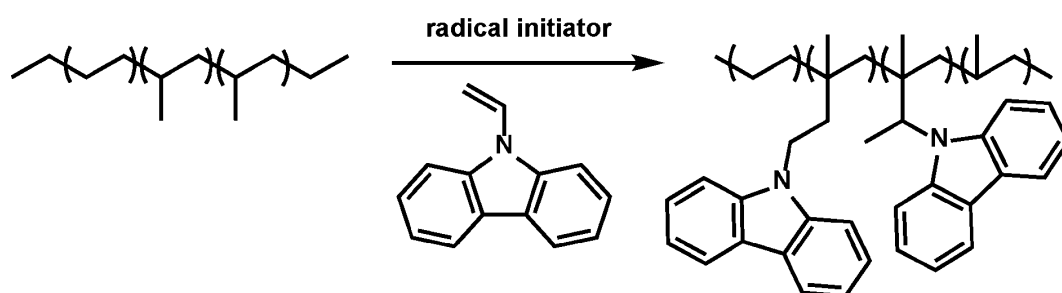


[62] Ethylene-propylene copolymer (518.7 g, KV100 ~600 cSt) was transferred into a stirred 1-liter stainless steel reactor equipped with charging lines for 2-vinylnaphthalene and di-t-amyl peroxide with nitrogen blanketed. Copolymer was heated to 170°C. 2-vinylnaphthalene (25.68 g in 84.8 mL toluene solution) and di-t-amyl peroxide (3.85 g) were charged at a constant rate simultaneously into the reactor agitation zone over a 2-hour period. Upon completion of the 2-vinylnaphthalene and peroxide charging, the reactor was held at temperature for an additional 30 minutes. The reaction was filtered, and vacuum stripped. The reaction product was measured by

gel permeation chromatography using UV detection, which confirmed the presence of naphthalene groups on the polymer.

Example 3

[63] 9-Vinylcarbazole grafted ethylene-propylene copolymer was prepared as described herein.



[64] Ethylene-propylene copolymer (504.6 g, KV100 ~2000 cSt) was transferred into a stirred 1-liter stainless steel reactor equipped with charging lines for 9-vinylcarbazole and di-t-amyl peroxide with nitrogen blanketed. Copolymer was heated to 170°C. 9-Vinylcarbazole (31.71 g in 83.39 mL toluene solution) and di-t-amyl peroxide (4.76 g) were charged at a constant rate simultaneously into the reactor agitation zone over a 2-hour period. Upon completion of the 9-vinylcarbazole and peroxide charging, the reactor was held at temperature for an additional 30 minutes. The reaction product was measured by gel permeation chromatography using UV detection, which confirmed the presence of carbazole groups on the polymer.

LUMiSizer® Sedimentation Velocity

[65] Oil samples were tested for soot handling by measuring LUMiSizer® sedimentation velocity. Each oil sample includes a baseline formulation (detergent, antioxidant, anti-wear agent, viscosity modifier, pour point depressant, and foam inhibitor) and 4 wt.% active polymeric

dispersant. The oil samples were mixed with 3 wt.% carbon black (Vulcan XC-72R) using acoustic mixer. The samples were tested in LUMiSizer® at 80°C. Extinction of transmitted light due to different rate of sedimentation related to particle size and stability of dispersion was measured. Less stable dispersions form larger particles which settle more quickly. More stable dispersions have lower sedimentation velocities. The results summarized in Table 1 below indicate that 9-vinylcarbazole or 2-vinylnaphthlene grafted polymers have significantly improved soot dispersancy compared to non-functionalized polymers.

Table 1

	Description	Polymeric Dispersant wt%	LUMiSizer® sedimentation velocity (μm/s)
Comparative Example A	Liquid ethylene propylene copolymer (KV100 ~ 600 cSt)	4	9.2235
Example 1	Liquid ethylene propylene copolymer (KV100 ~ 600 cSt) grafted with 2wt% 9-vinyl carbazole	4	1.4575
Example 2	Liquid ethylene propylene copolymer (KV100 ~ 600 cSt) grafted with 4.8 wt% 2-vinylnaphthalene	4	1.9260
Comparative Example B	Liquid ethylene propylene copolymer (KV100 ~ 2000 cSt)	4	8.1670
Example 3	Liquid ethylene propylene copolymer (KV100 ~ 2000 cSt) grafted with 5.9 wt% 9-vinyl carbazole	4	0.4592

[66] It will be understood that various modifications may be made to the embodiments disclosed herein. Therefore, the above description should not be construed as limiting, but merely as exemplifications of embodiments of the invention. For example, the functions described above and implemented for operating are for illustration purposes only. Other arrangements and methods may be implemented by those skilled in the art without departing from the scope and spirit of this application. Moreover, those skilled in the art will envision other modifications within the scope and spirit of the claims appended hereto.

CLAIMS

1. A polymeric dispersant composition, wherein the polymeric dispersant can be represented by the following generalized structure:



wherein A is liquid hydrocarbon polymer and B is independently alkyl polyarene or alkyl arene, n is 1 to 15, and wherein the liquid hydrocarbon polymer has a number average molecular weight (M_n) from about 1,500 to about 16,000.

2. The polymeric dispersant composition of claim 1, wherein A is ethylene-propylene copolymer, ethylene-based polymer, or propylene-based polymer.

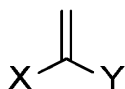
3. A polymeric dispersant composition of claim 1 prepared by reacting:

(a) a liquid hydrocarbon polymer having a number average molecular weight (M_n) from about 1,500 and about 16,000; and

(b) a vinyl arene.

4. The polymeric dispersant composition of claim 3, wherein the vinyl arene includes 2 or more aromatic rings.

5. The polymeric dispersant composition of claim 3, wherein the vinyl arene is given by the following generalized structure:



wherein X is an aromatic group and Y is hydrogen or methyl group.

6. The vinyl arene of claim 5, wherein X is naphthyl, anthracenyl, biphenyl group, triphenylmethane group, or carbazolyl.

7. The polymeric dispersant composition of claim 3, wherein vinyl arene grafted on the polymeric dispersant is 1-vinylnaphthalene, 2-vinylnaphthalene, 2-(1-methylethenyl)naphthalene, 9-vinylanthracene, 4-vinylbiphenyl, 4-benzhydrylstyrene, 9-vinylcarbazole, or 9-(1-methylethenyl)-9H-carbazole.

8. A lubricating oil composition comprising:
a major amount of a base oil of lubricating viscosity; and
a polymeric dispersant represented by the following generalized structure:



wherein A is liquid hydrocarbon polymer and B is independently alkyl polyarene or alkyl arene, n is 1 to 15; and wherein the liquid hydrocarbon polymer has a number average molecular weight (Mn) from about 1,500 to about 16,000.

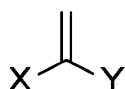
9. The lubricating oil composition of claim 8, wherein the polymeric dispersant is formed by the reaction of.

(a) a liquid hydrocarbon polymer having a number average molecular weight (M_n) between about 1,500 and about 16,000; and

(b) a vinyl arene.

10. The lubricating oil composition of claim 9, wherein the vinyl arene includes 2 or more aromatic rings.

11. The lubricating oil composition of claim 9, wherein the vinyl arene is given by the following generalized structure:



wherein X is an aromatic group and Y is hydrogen or methyl group.

12. The lubricating oil composition of claim 11, wherein X is naphthyl, anthracenyl, biphenyl group, triphenylmethane group, or carbazolyl.

13. The lubricating oil composition of claim 9, wherein vinyl arene grafted on the polymeric dispersant is 1-vinylnaphthalene, 2-vinylnaphthalene, 2-(1-methylethenyl)naphthalene, 9-vinylanthracene, 4-vinylbiphenyl, 4-benzhydrylstyrene, 9-vinylcarbazole, or 9-(1-methylethenyl)-9H-carbazole.

14. The lubricating oil composition of claim 8, wherein A is ethylene-propylene copolymer, ethylene-based polymer or propylene-based polymer.

15. A method for improving wear or soot dispersion in an internal combustion engine, the method comprising lubricating the engine with a lubricating oil composition comprising:

a major amount of base oil, and

a polymeric dispersant represented by the following generalized structure:



wherein A is liquid hydrocarbon polymer and B is independently alkyl polyarene or alkyl arene, n is 1 to 15; and wherein the liquid hydrocarbon polymer has a number average molecular weight (M_n) from about 1,500 to about 16,000.

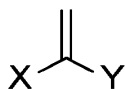
16. The method of claim 15, wherein the polymeric dispersant is formed by the reaction of

(a) a liquid hydrocarbon polymer having a number average molecular weight (M_n) between about 1,500 and about 16,000; and

(b) a vinyl arene

17. The method of claim 16, wherein the vinyl arene includes 2 or more aromatic rings.

18. The method of claim 16, wherein the vinyl arene is given by the following generalized structure:



wherein X is an aromatic group and Y is hydrogen or methyl group.

19. The method of claim 18, wherein X is naphthyl, anthracenyl, biphenyl group, triphenylmethane group, or carbazolyl.
20. The method of claim 17, wherein vinyl arene grafted on the polymeric dispersant is 1-vinylnaphthalene, 2-vinylnaphthalene, 2-(1-methylethenyl)naphthalene, 9-vinylanthracene, 4-vinylbiphenyl, 4-benzhydrylstyrene, 9-vinylcarbazole, or 9-(1-methylethenyl)-9H-carbazole.
21. The method of claim 15, wherein A is ethylene-propylene copolymer, ethylene-based polymer or propylene-based polymer.