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(54) LUBRICANT COMPOSITION SUITABLE FOR USE IN GASOLINE DIRECT INJECTION ENGINES

(57) Use in a turbo-charged gasoline direct injection (GDI) engine of a lubricant composition to reduce engine wear. The lubricant composition includes a major amount of oil of lubricating viscosity, and a minor amount of at least one highly grafted, multi-functional olefin copolymer made by reacting an acylating agent with an olefin copolymer having a number average molecular weight greater than about 1,000 in the presence of a free radical initiator to provide an acylated olefin copolymer having a degree of grafting (DOG) of the acylating agent on the olefin copolymer of at least 0.5 wt.%, and reacting the acylated olefin copolymer with an amine to provide a highly grafted, multi-functional olefin copolymer. The highly grafted, multi-functional olefin copolymer is effective to reduce engine wear in the turbo-charged GDI engine to below engine wear provided by a lubricant composition devoid of the highly grated, multi-functional olefin copolymer.

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Description

TECHNICAL FIELD:

[0001] The disclosure relates to lubricant compositions for turbo charged gasoline direct injection (GDI) engines and in particular to lubricant compositions that provide reduced wear in turbo charged GDI engines.

BACKGROUND AND SUMMARY:

[0002] For the purposes of this disclosure, the following definitions of terms are provided in order to clarify the meanings of certain terms as used herein.

[0003] The terms "oil composition," "lubrication composition," "lubricating oil composition," "lubricating oil," "lubricant composition," "lubricating composition," "fully formulated lubricant composition," "lubricant," "crankcase oil," "crankcase lubricant," "engine oil," "engine lubricant," "motor oil," and "motor lubricant" are considered synonymous, fully interchangeable terminology referring to the finished lubrication product comprising a major amount of a base oil plus a minor amount of an additive composition.

[0004] As used herein, the terms "additive package," "additive concentrate," "additive composition," "engine oil additive package," "engine oil additive concentrate," "crankcase additive package," "crankcase additive concentrate," "motor oil additive package," "motor oil concentrate," are considered synonymous, fully interchangeable terminology referring the portion of the lubricating composition excluding the major amount of base oil stock mixture. The additive package may or may not include the viscosity index improver or pour point depressant.

[0005] As used herein, the term "hydrocarbyl substituent" or "hydrocarbyl group" is used in its ordinary sense, which is well-known to those skilled in the art. Specifically, it refers to a group having a carbon atom directly attached to the remainder of the molecule and having predominantly hydrocarbon character. Examples of hydrocarbyl groups include:

(a) hydrocarbon substituents, that is, aliphatic (e.g., alkyl or alkenyl), alicyclic (e.g., cycloalkyl, cycloalkenyl) substituents, and aromatic-, aliphatic-, and alicyclic-substituted aromatic substituents, as well as cyclic substituents wherein the ring is completed through another portion of the molecule (e.g., two substituents together form an alicyclic moiety);
(b) substituted hydrocarbon substituents, that is, substituents containing non-hydrocarbon groups which, in the context of this disclosure, do not alter the predominantly hydrocarbon substituent (e.g., halo (especially chloro and fluoro), hydroxy, alkoxy, mercapto, alkylmercapto, nitro, nitroso, amino, alkylamino, and sulfoxy); and
(c) hetero substituents, that is, substituents which, while having a predominantly hydrocarbon character, in the context of this disclosure, contain other than carbon in a ring or chain otherwise composed of carbon atoms. Heteroatoms may include sulfur, oxygen, and nitrogen, and encompass substituents such as pyridyl, furyl, thienyl, and imidazolyl. In general, no more than two, for example, no more than one, non-hydrocarbon substituent will be present for every ten carbon atoms in the hydrocarbyl group; typically, there will be no non-hydrocarbon substituents in the hydrocarbyl group.

[0006] As used herein, the term "percent by weight", unless expressly stated otherwise, means the percentage the recited component represents to the weight of the entire composition.

[0007] The terms "soluble," "oil-soluble," or "dispersible" used herein may, but does not necessarily, indicate that the compounds or additives are soluble, dissolvable, miscible, or capable of being suspended in the oil in all proportions. The foregoing terms do mean, however, that they are, for instance, soluble, suspendable, dissolvable, or stably dispersible in oil to an extent sufficient to exert their intended effect in the environment in which the oil is employed. Moreover, the additional incorporation of other additives may also permit incorporation of higher levels of a particular additive, if desired.

[0008] The term "TBN" as employed herein is used to denote the Total Base Number in mg KOH/g as measured by the method of ASTM D2896 or ASTM D4739.

[0009] The term "alkyl" as employed herein refers to straight, branched, cyclic, and/or substituted saturated chain moieties of from about 1 to about 100 carbon atoms.

[0010] The term "alkenyl" as employed herein refers to straight, branched, cyclic, and/or substituted unsaturated chain moieties of from about 3 to about 10 carbon atoms.

[0011] The term "aryl" as employed herein refers to single and multi-ring aromatic compounds that may include alkyl, alkenyl, alkylaryl, amino, hydroxyl, alkoxy, halo substituents, and/or heteroatoms including, but not limited to, nitrogen, oxygen, and sulfur.

[0012] The term "chain stretch" means cam chain wear as evidenced by a reduction in the metal to metal contact areas of the chain and sprocket in an engine.

[0013] The term "polymer" is used generically to encompass ethylene copolymers, terpolymers or interpolymers. Such materials may contain amounts of other olefinic monomers so long as the basic characteristics of the polymers are not materially changed.

[0014] Turbo-charged gasoline direct injection (GDI) engines are designed to provide improved fuel economy without sacrificing engine performance. While such GDI engines typically achieve outstanding performance and improved fuel economy, such engines generate soot at increased levels than in conventional engines. The soot accumulates in the lubricant and tends to increase engine wear. Evidence of engine wear may be evident by excessive cam chain "stretch." Cam chain stretch is a term in the art used by automobile manufacturers to quantify the amount of wear exhibited by the cam chain. The cam chain does not actually stretch, but wear of the metal contacting parts causes the chain to loosen so that the timing of the engine is affected. Accordingly, there is a need for lubricant compositions which are effective to reduce engine wear in turbo-charged GDI engines.

[0015] In accordance an embodiment, the disclosure provides a use in a turbo-charged gasoline direct injection (GDI) engine of a lubricant composition to reduce engine wear. The lubricant composition includes a major amount of oil of lubricating viscosity, and a minor amount of at least one highly grafted, multi-functional olefin copolymer made by reacting an acylating agent with an olefin copolymer having a number average molecular weight greater than about 1,000 in the presence of a free radical initiator to provide an acylated olefin copolymer having a degree of grafting (DOG) of the acylating agent on the olefin copolymer of at least 0.5 wt.%, and reacting the acylated olefin copolymer with an amine to provide a highly grafted, multi-functional olefin copolymer. The highly grafted, multi-functional olefin copolymer is effective to reduce engine wear in the turbo-charged GDI engine to below engine wear provided by a lubricant composition devoid of the highly grated, multi-functional olefin copolymer.

[0016] Accordingly, a primary advantage of the exemplary embodiments may reduced engine wear as exhibited by a reduced iron content of the lubricant and/or reduced cam chain stretch.

DETAILED DESCRIPTION OF EXEMPLARY EMBODIMENTS:

[0017] As described in more detail below, a lubricating oil for a turbo-charged GDI engine may be synergistically improved by the addition of a particular highly grafted, multi-functional olefin copolymer. More particularly, a lubricating oil containing a conventional dispersant/inhibitor (DI) package may be significantly improved for use in turbo-charged GDI engines by incorporating the highly grafted olefin copolymer as a dispersant/viscosity index improver. Such lubricating oil compositions, as described more fully herein, may be particularly useful for lubricating internal combustion gasoline engines that generate soot in excess of the amount of soot generated by a conventional gasoline engine.

[0018] The lubricant composition described herein may be suitable for any engine lubricant irrespective of the sulfur, phosphorus, or sulfated ash (ASTM D-874) content. The sulfur content of the engine oil lubricant may be about 1 wt% or less, or about 0.8 wt% or less, or about 0.5 wt% or less, or about 0.3 wt% or less. In one embodiment the sulfur content may be in the range of about 0.001 wt% to about 0.5 wt%, or about 0.01 wt% to about 0.3 wt%. The phosphorus content may be about 0.2 wt% or less, or about 0.1 wt% or less, or about 0.085 wt% or less, or about 0.08 wt% or less, or even about 0.06 wt% or less, about 0.055 wt% or less, or about 0.05 wt% or less. In one embodiment the phosphorus content may be about 50 ppm to about 1000 ppm, or about 325 ppm to about 850 ppm. The total sulfated ash content may be about 2 wt% or less, or about 1.5 wt% or less, or about 1.1 wt% or less, or about 1 wt% or less, or about 0.8 wt% or less, or about 0.5 wt% or less. In one embodiment the sulfated ash content may be about 0.05 wt% to about 0.9 wt%, or about 0.1 wt% or about 0.2 wt% to about 0.45 wt%. In another embodiment, the sulfur content may be about 0.4 wt% or less, the phosphorus content may be about 0.08 wt% or less, and the sulfated ash is about 1 wt% or less. In yet another embodiment the sulfur content may be about 0.3 wt% or less, the phosphorus content is about 0.05 wt% or less, and the sulfated ash may be about 0.8 wt% or less.

[0019] In one embodiment the lubricating composition is an engine oil, wherein the lubricating composition may have (i) a sulfur content of about 0.5 wt% or less, (ii) a phosphorus content of about 0.1 wt% or less, and (iii) a sulfated ash content of about 1.5 wt% or less.

[0020] The base oil used in the lubricating oil compositions herein may be selected from any of the base oils in Groups I-V as specified in the American Petroleum Institute (API) Base Oil Interchangeability Guidelines. The five base oil groups are as follows:

Table 1

Base oil Category	Sulfur (%)		Saturates (%)	Viscosity Index
Group I	> 0.03	and/or	<90	80 to 120
Group II	≤0.03	and	≥90	80 to 120
Group III	≤0.03	and	≥90	≥120

(continued)

Base oil Category	Sulfur (%)		Saturates (%)	Viscosity Index
Group IV	All polyalphaolefins (PAOs)			
Group V	All others not included in Groups I, II, III, or IV			

[0021] Groups I, II, and III are mineral oil process stocks. Group IV base oils contain true synthetic molecular species, which are produced by polymerization of olefinically unsaturated hydrocarbons. Many Group V base oils are also true synthetic products and may include diesters, polyol esters, polyalkylene glycols, alkylated aromatics, polyphosphate esters, polyvinyl ethers, and/or polyphenyl ethers, and the like, but may also be naturally occurring oils, such as vegetable oils. It should be noted that although Group III base oils are derived from mineral oil, the rigorous processing that these fluids undergo causes their physical properties to be very similar to some true synthetics, such as PAOs. Therefore, oils derived from Group III base oils may be referred to as synthetic fluids in the industry.

[0022] The base oil used in the disclosed lubricating oil composition may be a mineral oil, animal oil, vegetable oil, synthetic oil, or mixtures thereof. Suitable oils may be derived from hydrocracking, hydrogenation, hydrofinishing, unrefined, refined, and re-refined oils, and mixtures thereof.

[0023] Unrefined oils are those derived from a natural, mineral, or synthetic source without or with little further purification treatment. Refined oils are similar to the unrefined oils except that they have been treated in one or more purification steps, which may result in the improvement of one or more properties. Examples of suitable purification techniques are solvent extraction, secondary distillation, acid or base extraction, filtration, percolation, and the like. Oils refined to the quality of an edible may or may not be useful. Edible oils may also be called white oils. In some embodiments, lubricant compositions are free of edible or white oils.

[0024] Re-refined oils are also known as reclaimed or reprocessed oils. These oils are obtained similarly to refined oils using the same or similar processes. Often these oils are additionally processed by techniques directed to removal of spent additives and oil breakdown products.

[0025] Mineral oils may include oils obtained by drilling or from plants and animals or any mixtures thereof. For example such oils may include, but are not limited to, castor oil, lard oil, olive oil, peanut oil, corn oil, soybean oil, and linseed oil, as well as mineral lubricating oils, such as liquid petroleum oils and solvent-treated or acid-treated mineral lubricating oils of the paraffinic, naphthenic or mixed paraffinic-naphthenic types. Such oils may be partially or fully hydrogenated, if desired. Oils derived from coal or shale may also be useful.

[0026] Useful synthetic lubricating oils may include hydrocarbon oils such as polymerized, oligomerized, or interpolymerized olefins (e.g., polybutylenes, polypropylenes, propyleneisobutylene copolymers); poly(1-hexenes), poly(1-octenes), trimers or oligomers of 1-decene, e.g., poly(1-decenes), such materials being often referred to as α-olefins, and mixtures thereof; alkyl-benzenes (e.g. dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di-(2-ethylhexyl)-benzenes); polyphenyls (e.g., biphenyls, terphenyls, alkylated polyphenyls); diphenyl alkanes, alkylated diphenyl alkanes, alkylated diphenyl ethers and alkylated diphenyl sulfides and the derivatives, analogs and homologs thereof or mixtures thereof. Polyalphaolefins are typically hydrogenated materials.

[0027] Other synthetic lubricating oils include polyol esters, diesters, liquid esters of phosphorus-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, and the diethyl ester of decane phosphonic acid), or polymeric tetrahydrofurans. Synthetic oils may be produced by Fischer-Tropsch reactions and typically may be hydroisomerized Fischer-Tropsch hydrocarbons or waxes. In one embodiment oils may be prepared by a Fischer-Tropsch gas-to-liquid synthetic procedure as well as other gas-to-liquid oils.

[0028] The amount of the oil of lubricating viscosity present may be the balance remaining after subtracting from 100 wt% the sum of the amount of the performance additives inclusive of viscosity index improver(s) and/or pour point depressant(s) and/or other top treat additives. For example, the oil of lubricating viscosity that may be present in a finished fluid may be a major amount, such as greater than about 50 wt%, greater than about 60 wt%, greater than about 70 wt%, greater than about 80 wt%, greater than about 85 wt%, or greater than about 90 wt%. The dissolved pelletized copolymer intermediate possessing carboxylic acid acylating functions subsequently reacted with an amine compound.

[0029] In another embodiment, the highly grafted, multi-functional olefin copolymer product may be added to lubricating compositions in an amount sufficient to reduce engine wear, particularly cam chain wear in a turbo-charged GDI engine.

[0030] As described more fully in U.S. Patent No. 7,253,231, the highly grafted, multi-functional olefin copolymer is provided as the reaction product of a previously dehydrated copolymer substrate that is derived from a polymer of ethylene and one or more C_3 to C_{23} alpha-olefins. The copolymer is acylated with an acylating agent and is further reacted with an amine to provide the multi-functional product. The foregoing multi-functional product may be used in lubrication compositions to provide one or more functions including as a viscosity index (VI) modifier, dispersant, film formation improver, deposit controller, as well engine wear reduction.

[0031] The polymer substrate starting material for multi-functional olefin copolymer is derived from copolymers of ethylene and one or more C_3 to C_{23} alpha-olefins. Copolymers of ethylene and propylene are suitably used to make the copolymer. "Copolymers" herein may include without limitation blends or reacted products of ethylene and one or more C_3 to C_{23} alpha-olefins, and additionally optionally other dienes or polyenes. Thus, "copolymers" herein also includes terpolymers, and other higher forms. Other alpha-olefins suitable in place of propylene to form the copolymer or to be used in combination with ethylene and propylene to form a terpolymer include 1-butene, 1-pentene, 1-hexene, 1-octene and styrene; .alpha,ω-diolefins such as 1,5-hexadiene, 1,6-heptadiene, 1,7-octadiene; branched chain alpha-olefins such as 4-methylbutene-1,5-methylpentene-1 and 6-methylheptene-1; and mixtures thereof.

[0032] Methods for making the copolymers described above are described, e.g., in U.S. Pat. Nos. 4,863,623, 5,075,383, and 6,107,257, which descriptions are incorporated herein by reference. The polymer substrate also may be commercially obtained having the properties indicated herein.

[0033] More complex polymer substrates, often designated as interpolymers, also may be used as the olefin polymer starting material, which may be prepared using a third component. The third component generally used to prepare an interpolymer substrate is a polyene monomer selected from nonconjugated dienes and trienes. The-non-conjugated diene component is one having from 5 to 14 carbon atoms in the chain. For example, the diene monomer may be characterized by the presence of a vinyl group in its structure and can include cyclic and bicyclo compounds. Representative dienes include 1,4-hexadiene, 1,4-cyclohexadiene, dicyclopentadiene, 5-ethylidene-2-norbornene, vinylnorbornene, 5-methylene-2-norborene, 1,5-heptadiene, and 1,6-octadiene. A mixture of more than one diene may be used in the preparation of the interpolymer. A suitable nonconjugated diene for preparing a terpolymer or interpolymer substrate is 1,4-hexadiene.

[0034] The triene component may have at least two nonconjugated double bonds, and up to about 30 carbon atoms in the chain. Typical trienes that may be used to prepare the interpolymer of the disclosure are 1-isopropylidene-3α,4,7,7α -tetrahydroindene, 1-isopropylidenedicyclopentadiene, dihydro-isodicyclopentadiene, and 2-(2-methylene-4methyl-3-pentenyl)[2.2.1]bicyclo-5-heptene.

[0035] Ethylene-propylene or higher alpha-olefin copolymers may consist of from about 15 to 80 mole percent ethylene and from about 85 to 20 mole percent C_3 to C_{23} alpha-olefin with the mole ratios in one embodiment being from about 35 to 75 mole percent ethylene and from about 65 to 25 mole percent of a C_3 to C_{23} alpha-olefin, with the proportions in another embodiment being from 50 to 70 mole percent ethylene and 50 to 30 mole percent C_3 to C_{23} alpha-olefin, and the proportions in yet another embodiment being from 55 to 65 mole percent ethylene and 45 to 35 mole percent C_3 to C_{23} alpha-olefin.

[0036] Terpolymer variations of the foregoing polymers may contain from about 0 to 10 mole percent of a nonconjugated diene or triene. Other termonomer levels are less than 1 mole percent.

[0037] The starting polymer that is acylated is desirably an oil-soluble, linear or branched polymer having a number average molecular weight from about 1,000 to 500,000, and for example a number average molecular weight of 50,000 to 250,000, as determined by gel permeation chromatography and universal calibration standardization.

[0038] The polymerization reaction used to form an ethylene olefin copolymer may be conducted in the presence of a conventional Ziegler-Natta or metallocene catalyst system. The polymerization medium is not specific and may include solution, slurry, or gas phase processes, as known to those skilled in the art. When solution polymerization is employed, the solvent may be any suitable inert hydrocarbon solvent that is liquid under reaction conditions for polymerization of alpha-olefins; examples of satisfactory hydrocarbon solvents include straight chain paraffins having from 5 to 8 carbon atoms, with hexane being preferred. Aromatic hydrocarbons, for example, aromatic hydrocarbon having a single benzene nucleus, such as benzene, toluene and the like; and saturated cyclic hydrocarbons having boiling point ranges approximating those of the straight chain paraffinic hydrocarbons and aromatic hydrocarbons described above are particularly suitable. The solvent selected may be a mixture of one or more of the foregoing hydrocarbons. When slurry polymerization is employed, the liquid phase for polymerization is preferably liquid propylene. It is desirable that the polymerization medium be free of substances that will interfere with the catalyst components.

[0039] The polymer described above, i.e., the olefin polymer component, may be conveniently obtained in the form of ground or pelletized polymer. The olefin polymer may also be supplied as either a pre-mixed bale or a pre-mixed friable chopped agglomerate form.

[0040] In one embodiment, ground polymer bales or other forms of the olefin copolymer are fed to an extruder, e.g., a single or twin screw extruder, or a Banbury or other mixer having the capability of heating and effecting the desired level of mechanical work (agitation) on the polymer substrate for the dehydration step. A nitrogen blanket can be maintained at the feed section of the extruder to minimize the introduction of air.

[0041] The olefin copolymer is initially heated before being admixed with any other reactants in the extruder or other mixer with venting to eliminate moisture content in the feed material. The dried olefin copolymer is in one embodiment then fed into another extruder section or separate extruder in series for conducting the grafting reaction.

[0042] A graft monomer is next grafted onto the polymer backbone of the polymer olefin copolymer to form an acylated ethylene-alphaolefin polymer.

[0043] Suitable graft monomers include ethylenically unsaturated carboxylic acid materials, such as unsaturated dicarboxylic acid anhydrides and their corresponding acids. Examples of these graft monomers are set forth, for example, in U.S. Pat. No. 5,837,773, which descriptions are incorporated herein by reference. Carboxylic reactants which are suitable for grafting onto the ethylene-alphaolefin interpolymers contain at least one ethylenic bond and at least one carboxylic acid or its anhydride groups or a polar group which is convertible into said carboxyl groups by oxidation or hydrolysis. The carboxylic reactants are selected from the group consisting of acrylic, methacrylic, cinnamic, crotonic, maleic, fumaric and itaconic reactants or a mixture of two or more of these. In the case of unsaturated ethylene copolymers or terpolymers, itaconic acid or its anhydride is useful due to its reduced tendency to form a cross-linked structure during the free-radical grafting process.

[0044] The ethylenically unsaturated carboxylic acid materials typically may provide one or two carboxylic groups per mole of reactant to the grafted copolymer. That is, methyl methacrylate may provide one carboxylic group per molecule to the grafted copolymer while maleic anhydride may provide two carboxylic groups per molecule to the grafted copolymer.

[0045] The grafting reaction to form the acylated olefin copolymers is generally carried out with the aid of a free-radical initiator either in bulk or in solution. The grafting may be carried out in the presence of a free-radical initiator dissolved in oil. The use of a free-radical initiator dissolved in oil results in a more homogeneous distribution of acylated groups over the olefin copolymer molecules.

[0046] The free-radical initiators which may be used to graft the ethylenically unsaturated carboxylic acid material to the polymer backbone 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 azobutyronitrile, dicumyl peroxide, 2,5-dimethylhexane-2,5-bis-tertiarybutyl peroxide and 2,5-dimethylhex-3-yne-2,5-bis-tertiary-butyl peroxide. The initiator may be used in an amount ranging from about 0.005% to about 1% by weight based on the weight of the reaction mixture.

[0047] To perform the grafting reaction as a solvent-free or essentially solvent-free bulk process, the graft monomer and olefin copolymer are in one embodiment fed to an extruder, e.g., a single or twin screw extruder e.g. Werner & Pfleiderer's ZSK series, or a Banbury or other mixer, having the capability of heating and effecting the desired level of mechanical work (agitation) on the reactants for the grafting step. In one embodiment, grafting is conducted in an extruder, and particularly a twin screw extruder. A nitrogen blanket is maintained at the feed section of the extruder to minimize the introduction of air.

[0048] Grafting may also be conducted in an extruder, such as a twin-screw extruder. A nitrogen blanket is maintained at the feed section of the extruder to minimize the introduction of air. In another embodiment, the olefinic carboxylic acylating agent may be injected at one injection point, or is alternatively injected at two injection points in a zone of the extruder without significant mixing e.g. a transport zone. Such injection may result in an improved efficiency of the grafting and leads to a lower gel content.

[0049] Suitable extruders are generally known available for conducting grafting, and the prior dehydration procedure. The dehydration of the polymer substrate and subsequent grafting procedures may be performed in separate extruders set up in series. Alternatively, a single extruder having multiple treatment or reaction zones may be used to sequentially conduct the separate operations within one piece of equipment. Illustrations of suitable extruders are set forth, e.g., in U.S. Pat. No. 3,862,265 and U.S. Pat. No. 5,837,773, which descriptions are incorporated herein by reference.

[0050] In forming the acylated olefin copolymers, the olefin copolymer generally is fed to plastic processing equipment such as an extruder, intensive mixer or masticator, heated to a temperature of at least 60°, for example, 150° to 240° C., and the ethylenically unsaturated carboxylic acid reagent and free-radical initiator are separately co-fed to the molten copolymer to effect grafting. The reaction is carried out optionally with mixing conditions to effect grafting of the olefin copolymers. If molecular weight reduction and grafting are performed simultaneously, illustrative mixing conditions are described in U.S. Pat. No. 5,075,383, which are incorporated herein by reference. The processing equipment is generally purged with nitrogen to prevent oxidation of the copolymer and to aid in venting unreacted reagents and byproducts of the grafting reaction. The residence time in the processing equipment is controlled to provide for the desired degree of acylation and to allow for purification of the acylated copolymer via venting. Mineral or synthetic lubricating oil may optionally be added to the processing equipment after the venting stage to dissolve the acylated copolymer.

[0051] The grafting reaction may also be carried out in solvent-free or essentially solvent free environment. Accordingly, the grafting reaction may be performed in the absence of hydrocarbon solvents. The avoidance of hydrocarbon solvents during the grafting reaction, such as alkanes (e.g., hexane), eliminates or significantly reduces the risk and problem of undesired side reactions of such solvents during the grafting reaction which can form undesired grafted alkyl succinic anhydride by-products and impurities. Also, reduced amounts of transient unfunctionalized polymer (ungrafted polymer) are present after grafting in solventless grafting reactions, which results in a more active product. Therefore, the resulting copolymer intermediate is a more active product. A reduction is achieved in levels of undesirable grafted solvent (i.e., grafted hexyl succinic anhydride) and transient unfunctionalized (nongrafted) copolymer.

[0052] Hydrocarbon solvents that may be omitted according to certain embodiments of the present disclosure include solvents that generally are more volatile than the reactants of the grafting reaction described herein, for example, solvents having a boiling point less than about 150° C. under standard atmospheric pressure conditions (i.e., approximately 14.7 1b./in^2 absolute). The solvents that may be omitted include, for example, open-chain aliphatic compounds such as C_9 or lower alkanes, alkenes and alkynes (e.g., C_5 to C_8 alkanes such as hexane); aromatic hydrocarbons (e.g., compounds having a benzene nucleus such as benzene and toluene); alicyclic hydrocarbons such as saturated cyclic hydrocarbons (e.g., cyclohexane); ketones; or any combinations of these. In one embodiment, it is desirable to omit all solvents having boiling points approximating or lower than that of nonane under standard atmospheric conditions. Some conventional grafting reactions have been performed in the presence of considerable amounts of hydrocarbon solvent, such as approximately 15% to 60% hexane content. By comparison, in one embodiment of the present disclosure, the total amount of these types of such solvents in the grafting reaction mass does not exceed 0.5 wt. % content thereof.

[0053] The grafted copolymer intermediate exits from the die face of the extruder either immediately after grafting, or after shearing and vacuum stripping (discussed below in more detail) if performed in different sections of the same extruder or a separate extruder arranged in series with the extruder in which grafting is conducted.

[0054] The resulting copolymer intermediate comprises an acylated olefin copolymer characterized by having carboxylic acid acylating functionality randomly within its structure. The amount of carboxylic acid acylating agent (e.g., maleic anhydride) that is grafted onto the prescribed copolymer backbone (i.e., the copolymer substrate) is important. This parameter is referred to herein as the degree of grafting (DOG), further described as the mass percentage of acylating agent on the acylated copolymer. The DOG generally is in the range of 0.5 to 3.0 wt. %, particularly in the range of 1.5 to 2.5 wt. %, and more particularly in the range of 1.7 to 2.3 wt. %, of carboxylic acid acylating agent grafted on the copolymer backbone.

[0055] The DOG value of a particular additive reaction product may be determined either by infrared peak ratio analysis of acid or anhydride moiety versus copolymer alkyl functionality or by titration (Total Acid/Anhydride Number) (TAN) of the additive reaction product. The TAN value in turn can be used to estimate the degree of grafting (DOG).

[0056] The carboxylic reactant is grafted onto the prescribed copolymer backbone to provide 0.15 to 0.75 carboxylic groups per 1000 number average molecular weight units (Mn) of the copolymer backbone, desirably 0.2 to 0.5 carboxylic groups per 1000 number average molecular weight. For example, a copolymer substrate with M_n of 20,000 is grafted with 3 to 15 carboxylic groups per copolymer chain or 1.5 to 7.5 moles of maleic anhydride per mole of copolymer. A copolymer with M_n of 100,000 is grafted with 15 to 75 carboxylic groups per copolymer chain or 7.5 to 37.5 moles of maleic anhydride per copolymer chain. The minimum level of functionality is the level needed to achieve the minimum satisfactory dispersancy performance.

[0057] The molecular weight of the acylated olefin copolymer, i.e., the copolymer intermediate, may be reduced by mechanical, thermal, or chemical means, or a combination thereof. Techniques for degrading or reducing the molecular weight of such copolymers are generally known in the art. The number average molecular weight is reduced to suitable level for use in single grade or multigrade lubricating oils.

[0058] In one embodiment, the initial copolymer intermediate has an initial number average molecular weight ranging from about 1,000 to about 500,000 upon completion of the grafting reaction. In one embodiment, to prepare an additive intended for use in multigrade oils, the copolymer intermediate's number average molecular weight is reduced down to a range of about 1,000 to about 80,000.

[0059] Alternatively, grafting and reduction of the high molecular weight olefin copolymer may be done simultaneously. In another alternative, the high molecular weight olefin copolymer may be first reduced to the prescribed molecular weight before grafting. When the olefin copolymer's average molecular weight is reduced before grafting, its number average molecular weight is sufficiently reduced to a value below about 80,000, e.g., in the range of about 1,000 to 80,000.

[0060] Reduction of the molecular weight of the copolymer intermediate, or the olefin copolymer feed material during or prior to grafting, to a prescribed lower molecular weight typically is conducted in the absence of a solvent or in the presence of a base oil, using either mechanical, thermal, or chemical means, or combination of these means. Generally, the copolymer intermediate, or olefin copolymer, is heated to a molten condition at a temperature in the range of about 250° C. to about 350° C. and it is then subjected to mechanical shear, thermally or chemical induced cleavage or combination of said means, until the copolymer intermediate (or olefin copolymer) is reduced to the prescribed molecular weight. The shearing may be effected within an extruder section, such as described, e.g., in U.S. Pat. No. 5,837,773, which descriptions are incorporated herein by reference. Alternatively, mechanical shearing may be conducted by forcing the molten copolymer intermediate (or olefin copolymer) through fine orifices under pressure or by other mechanical means.

[0061] Upon completion of the grafting reaction, unreacted carboxylic reactant and free radical initiator usually are removed and separated from the copolymer intermediate before further functionalization is performed on the copolymer intermediate. The unreacted components may be eliminated from the reaction mass by vacuum stripping, e.g., the reaction mass may be heated to temperature of about 150° C. to about 450° C. under agitation with a vacuum applied for a period sufficient to remove the volatile unreacted graft monomer and free radical initiator ingredients. Vacuum stripping may be performed in an extruder section equipped with venting means.

[0062] The copolymer intermediate may be pelletized before further processing in accordance with embodiments of the disclosure herein. Pelletization of the copolymer intermediate helps to isolate the intermediate product and reduce contamination thereof until further processing is conducted thereon at a desired time.

[0063] The copolymer intermediate may be formed into pellets by a variety of process methods commonly practiced in the art of plastics processing. Such techniques include underwater pelletization, ribbon or strand pelletization or conveyor belt cooling. When the strength of the copolymer is inadequate to form into strands, the preferred method is underwater pelletization. Temperatures during pelletization should not exceed 30° C. Optionally, a surfactant can be added to the cooling water during pelletization to prevent pellet agglomeration.

[0064] The mixture of water and quenched copolymer pellets is conveyed to a dryer such as a centrifugal drier for removal of water. Pellets may be collected in a box or plastic bag at any volume for storage and shipment. Under some conditions of storage and/or shipment at ambient conditions, pellets may tend to agglomerate and stick together. The pellets may be ground by mechanical methods to provide high surface area solid pieces for easy and quick dissolution into oil.

[0065] The pelletized copolymer intermediate may be supplied as an unground or ground form of the pellets. The pelletized acylated copolymer intermediate is dissolved in solvent neutral oil. The pellets generally are dissolved in the solvent at an introduction level of from about 5 wt. % to about 25 wt. %, particularly about 10 wt. % to about 15 wt. %, and more particularly about 12 wt. % to about 13 wt. %, based on the resulting solution (solute and solvent) viscosity.

[0066] The pelletized copolymer intermediate can be dissolved in the solvent neutral at temperature of, for example, about 135° C. to about 165° C. with mechanical stirring under a nitrogen blanket. The dissolving mixture may be sparged with inert gas during the dissolution for about 4 to 16 hours. Such treatment may be performed in a continuous stirred process vessel of suitable capacity.

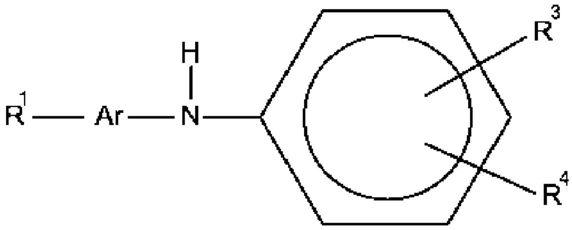
[0067] The inert sparging gas may be nitrogen. The dissolution and sparging, if used, may be prior to the subsequent amination procedure. One or more spargers are located within the vessel at locations submerged beneath the surface of the solution, preferably near the bottom of the solution, and bubble inert gas through the solution. Nitrogen sparging removes moisture from the dissolved copolymer intermediate and solvent oil. Importantly, the removal of moisture from the copolymer intermediate may act to convert any polymeric dicarboxylic diacids present back to the desired copolymeric dicarboxylic anhydride form.

[0068] For instance, where maleic anhydride is used as the grafting monomer, some portion of the pelletized copolymer intermediate may inadvertently transform to a copolymeric succinic diacid form. In general, this change is more apt to occur as a function of a longer shelf life. The conducting of nitrogen sparging during dissolution of the copolymer intermediate and prior to amination has the benefit of converting the copolymeric succinic diacid back into the desired active polymeric succinic anhydride form before the copolymer intermediate is further reacted and functionalized (e.g., aminated). Consequently, a more highly functionalized and active aminated product may be obtained in subsequent processing. The conversion of polymeric succinic diacid back into the active polymeric succinic anhydride form can be monitored by measuring the viscosity of the solution. The solution viscosity decreases significantly from an initial higher value down to a steady-state value upon conversion of all or essentially all of the polymeric succinic diacid back into the desired polymeric succinic anhydride form.

[0069] The amine may be selected from compounds such as described, e.g., in U.S. Pat. Nos. 4,863,623, 5,075,383, and 6,107,257, which descriptions are incorporated herein by reference.

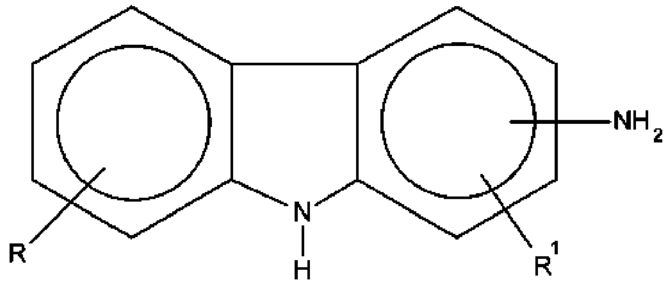
[0070] In one embodiment, the amine compound may be selected from the group consisting of:

(a) an N-arylphenylenediamine represented by the formula:

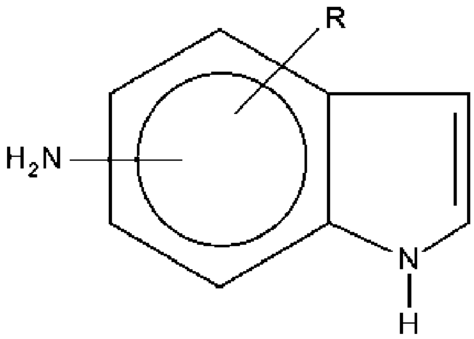


in which Ar is aromatic and R^1 is --H, --NH_2, --(--NH-Aryl)$_n$--H, --(--NH-Alkyl)$_n$--H, --NH-arylalkyl, a branched or straight chain radical having from 4 to 24 carbon atoms that can be alkyl, alkenyl, alkoxyl, aralkyl, alkaryl, hydroxyalkyl or aminoalkyl, R^2 is (--NH_2, --($NH(CH_2)_n$--)$_m$--NH_2, --$(CH_2)_n$--NH_2, -aryl-NH_2, in which n and m each has a value from 1 to 10, and R^3 is hydrogen, alkyl, alkenyl, alkoxyl, aralkyl, alkaryl having from 4 to 24 carbon atoms,

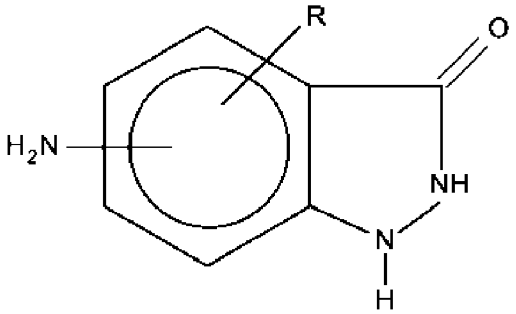
(b) an aminocarbazole represented by the formula:



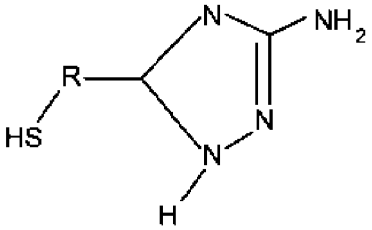
in which R and R^1 represent hydrogen or an alkyl, alkenyl, or alkoxyl radical having from 1 to 14 carbon atoms,
(c) an aminoindole represented by the formula:



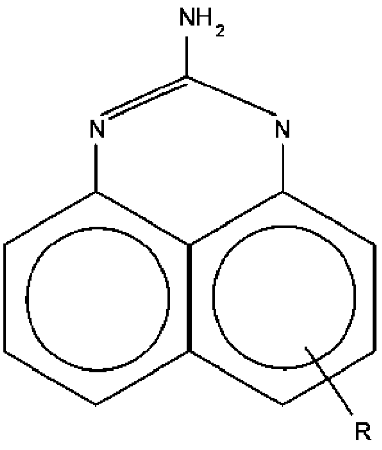
in which R represents hydrogen or an alkyl radical having from 1 to 14 carbon atoms,
(d) an amino-indazolinone represented by the formula:



in which R is hydrogen or an alkyl radical having from 1 to 14 carbon atoms,
(e) an aminomercaptotriazole represented by the formula:

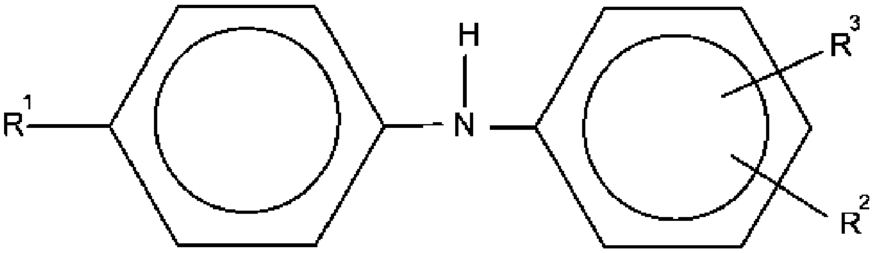


in which R can be absent or can be C_1-C_{10} linear or branched hydrocarbon selected from the group consisting of alkyl, aryl, alkaryl, or arylalkyl.
(f) an aminopyrimidine represented by the formula:



in which R represents hydrogen or an alkyl or alkoxyl radical having from 1 to 14 carbon atoms.

[0071] In one embodiment, the amine compound may be, e.g., an N-arylphenylenediamine represented by the general formula:



in which R^1 is hydrogen, --NH-aryl, --NH-arylalkyl, --NH-alkyl, or a branched or straight chain radical having from 4 to 24 carbon atoms that can be alkyl, alkenyl, alkoxyl, aralkyl, alkaryl, hydroxyalkyl or aminoalkyl; R^2 is $--NH_2$, $CH_2--(CH_2)_n--NH_2$, CH_2-aryl-NH_2, in which n has a value from 1 to 10 and R.sup.3 is hydrogen, alkyl, alkenyl, alkoxyl, aralkyl, alkaryl having from 4 to 24 carbon atoms.

[0072] Particularly useful amines in the present disclosure are the N-arylphenylenediamines, more specifically the N-phenylphenylenediamines, for example, N-phenyl-1,4-phenylenediamine, N-phenyl-1,3-phenylendiamine, and N-phenyl-1,2-phenylenediamine.

[0073] Illustrations of other useful amines include those described in U.S. Pat. Nos. 4,863,623 and 6,107,257, which are incorporated herein by reference.

[0074] It is desirable that the amines contain only one primary amine group so as to avoid coupling and/or gelling of the olefin copolymers.

[0075] The reaction between the copolymer having grafted thereon carboxylic acid acylating function and the prescribed amine compound may be conducted by heating a solution of the copolymer substrate under inert conditions and then adding the amine compound to the heated solution generally with mixing to effect the reaction. It is convenient to employ an oil solution of the copolymer substrate heated to 120° to 175° C., while maintaining the solution under a nitrogen blanket. The amine compound may be added to this solution and the reaction is effected under the noted conditions.

[0076] The amine compound may be dissolved with a surfactant and added to a mineral or synthetic lubricating oil or solvent solution containing the acylated olefin copolymer. The solution of amine and olefin copolymer may be heated with agitation under an inert gas purge at a temperature in the range of 120° to 200° C. as described in U.S. Pat. No. 5,384,371, the disclosure of which is herein incorporated by reference. The reactions may be carried out conveniently in a stirred reactor under nitrogen purge.

[0077] In one aspect, a polymeric succinic anhydride oil solution is reacted with N-phenyl-1,4-phenylenediamines, along with ethoxylated lauryl alcohol in a reactor carried out at 165° C.

[0078] Surfactants which may be used in carrying out the reaction of the acylated olefin copolymer with the polyamine(s) include but are not limited to those characterized as having (a) solubility characteristics compatible with mineral or synthetic lubricating oil, (b) boiling point and vapor pressure characteristics so as not to alter the flash point of the oil and (c) polarity suitable for solubilizing the polyamine(s).

[0079] A suitable class of such surfactants includes the reaction products of aliphatic and aromatic hydroxy compounds with ethylene oxide, propylene oxide or mixtures thereof. Such surfactants are commonly known as aliphatic or phenolic alkoxylates. Useful surfactants can include those surfactants that contain a functional group, e.g., --OH, capable of reacting with the acylated olefin copolymer. Ethoxylated lauryl alcohol ($C_{12}H_{25}(OCH_2CH_2)_nOH$) is also useful herein. Ethoxylated lauryl alcohol is identified under CAS no. 9002-92-0. The ethoxylated lauryl alcohol is a processing aid and viscosity stabilizer for the final multifunctional viscosity modifier product. The ethoxylated lauryl alcohol facilitates the amine charge into the reaction mixture. It is a reaction agent ensuring that no acylated functionality is left unreacted. Any unreacted acylated functionality may cause undesirable viscosity drift in finished lubrication formulations. The surfactant also modifies the viscoelastic response in the multifunctional viscosity modifier product allowing improved handling at low temperature (70 to 90° C.).

[0080] The quantity of surfactant used depends in part on its ability to solubilize the amine. Typically, concentrations of 5 to 40 wt. % amine are employed. The surfactant may also be added separately, instead of or in addition to the concentrates discussed above, such that the total amount of surfactant in the finished additive is 10 wt. % or less.

[0081] The highly grafted, multi-functional olefin copolymers of the present disclosure may be incorporated into lubricating oil in any convenient way. Thus, the highly grafted, multi-functional olefin copolymers may be added directly to the lubricating oil by dispersing or dissolving the same in the lubricating oil at the desired level of concentration. Such blending into the lubricating oil may occur at room temperature or elevated temperatures. Alternatively, the highly grafted, multi-functional olefin copolymers can be blended with a suitable oil-soluble solvent/diluent (such as benzene, xylene, toluene, lubricating base oils and petroleum distillates) to form a concentrate, and then blending the concentrate with a lubricating oil to obtain the final formulation. Such additive concentrates will typically contain (on an active ingredient (A.I.) basis) from about 3 to about 45 wt. %, and preferably from about 10 to about 35 wt. %, highly grafted, multi-functional olefin copolymer additive, and typically from about 20 to 90 wt %, preferably from about 40 to 60 wt %, base oil based on the concentrate weight.

[0082] Several of the amine reactants have the tendency to form highly colored oxidation products, comprising members of the class of staining amine antioxidants. Unreacted amine which is left in the oil solution after the amination reaction may give rise to undesirable and/or unstable color in the oil solution. The acylated olefin copolymer also may be color stabilized after the amination reaction, such as by reacting the acylated olefin copolymer with a C_7 to C_{12} alkyl aldehyde (e.g., nonyl aldehyde). For example, the reaction may proceed when the alkyl aldehyde agent is added in an amount of about 0.2 to about 0.6 wt. % under similar temperature and pressure conditions as used in the amination reaction for about 2 to about 6 hours.

[0083] To increase the purity of the aminated, color stabilized acylated olefin copolymer product, it may be filtered by either bag or cartridge filtration or both in series.

[0084] As indicated above, the copolymer intermediate may be prepared in the absence of solvent. Also, the copolymer intermediate may be received in pelletized or bale form as a starting material for performing the additional functionalization(s), viz. amination and color stabilization, on the grafted copolymer intermediate. The copolymer intermediate need not be received directly from the die face of an extruder or similar grafting reaction vessel, but instead the copolymer intermediate has been vacuum stripped of unreacted reactants and pelletized before these further functionalizations are performed on it. Therefore, the pelletized copolymer intermediate contains less contaminants than a product that has been grafted in the presence of a solvent (which can lead to side reaction products) and/or aminated immediately after the grafting reaction as part of a continuous process flow arrangement (which leaves unreacted components as impurities in the reaction mass).

[0085] In addition, the use of inert gas sparging on the copolymer intermediate dissolved in neutral oil prior to amination has the benefit of converting polymeric succinic diacid present back into the desired active polymeric succinic anhydride form before the copolymer intermediate is further reacted and functionalized (e.g, aminated).

[0086] Also, since unreacted graft monomer, e.g., maleic anhydride is effectively removed after the grafting step during vacuum stripping that precedes pelletizing and dissolution, amination proceeds more efficiently. That is, the presence of unreacted graft monomers are undesirable during the amination step as they may compete with the grafted copolymer (polymer intermediate) in reactions with the amine, reducing the level of functionalization achieved.

[0087] Therefore, the multi-functional reaction end product of embodiments of the present disclosure may contain fewer impurities (i.e., unreacted reactants, side reaction products and by-products) and may be more active for a given amount thereof. In one embodiment, the additive reaction product may contain less than 0.1 wt. % total impurities comprising unreacted reactants, side reaction products and reaction by-products. The remainder may be composed of active grafted, multifunctionalized olefin copolymer either entirely, or substantially in combination with some minor amount of beneficial or inert additive introduced during processing, such as an antioxidant or colorant, which does not significantly reduce or impair the activity of the product compound.

[0088] The highly grafted, multi-functional olefin copolymer product compounds of the present disclosure optionally may be post-treated so as to impart additional properties necessary or desired for a specific lubricant application. Post-treatment techniques are well known in the art and include boronation, phosphorylation, glycolation, ethylene-carbonation, and maleination.

[0089] Suitable treat rates of the highly grafted, multi-functional olefin copolymer product compounds including process oil (i.e., not neat) would be from about 0.25 wt% to about 20 wt% in a finished lubricant. Further suitable treat rates may be from about 1 wt% to about 15 wt% or from about 1.5 wt% to about 10 wt% in a finished lubricant.

[0090] Lubricating oil formulations for gasoline engines as described herein may conventionally contain additional additives that will supply the characteristics that are required in the formulations. Among these types of additives are included additional viscosity index improvers, antioxidants, corrosion inhibitors, detergents, dispersants, pour point depressants, antiwear agents, antifoaming agents, demulsifiers and friction modifiers. These additives are provided in what is commonly called a dispersant/inhibitor (DI) package.

Antiwear Agents

[0091] The lubricating oil compositions herein also may optionally contain one or more antiwear agents. Examples of suitable antiwear agents include, but are not limited to, a metal thiophosphate; a metal dialkyldithiophosphate; a phosphoric acid ester or salt thereof; a phosphate ester(s); a phosphite; a phosphorus-containing carboxylic ester, ether, or amide; a sulfurized olefin; thiocarbamate-containing compounds including, thiocarbamate esters, alkylene-coupled thiocarbamates, and bis(S-alkyldithio-carbamyl)disulfides; and mixtures thereof. The phosphorus containing antiwear agents are more fully described in European Patent 612 839. The metal in the dialkyl dithio phosphate salts may be an alkali metal, alkaline earth metal, aluminum, lead, tin, molybdenum, manganese, nickel, copper, titanium, or zinc. A useful antiwear agent may be zinc dialkylthiophosphate.

[0092] Further examples of suitable antiwear agents include titanium compounds, tartrates, tartrimides, oil soluble amine salts of phosphorus compounds, sulfurized olefins, phosphites (such as dibutyl phosphite), phosphonates, thiocarbamate-containing compounds, such as thiocarbamate esters, thiocarbamate amides, thiocarbamic ethers, alkylene-coupled thiocarbamates, and bis(S-alkyldithiocarbamyl) disulfides. The tartrate or tartrimide may contain alkyl-ester groups, where the sum of carbon atoms on the alkyl groups may be at least 8. The antiwear agent may in one embodiment include a citrate.

[0093] The antiwear agent may be present in ranges including about 0 wt% to about 15 wt%, or about 0.01 wt% to about 10 wt%, or about 0.05 wt% to about 5 wt%, or about 0.1 wt% to about 3 wt% of the lubricating composition.

Boron-Containing Compounds

[0094] The lubricating oil compositions herein may optionally contain one or more boron-containing compounds.

[0095] Examples of boron-containing compounds include borate esters, borated fatty amines, borated epoxides, borated detergents, and borated dispersants, such as borated succinimide dispersants, as disclosed in U.S. Patent No. 5,883,057.

[0096] The boron-containing compound, if present, can be used in an amount sufficient to provide up to about 8 wt%, about 0.01 wt% to about 7 wt%, about 0.05 wt% to about 5 wt%, or about 0.1 wt% to about 3 wt% of the lubricating composition.

Detergents

[0097] The lubricant composition may optionally further comprise one or more neutral, low based, or overbased detergents, and mixtures thereof. Suitable detergent substrates include phenates, sulfur containing phenates, sulfonates, calixarates, salixarates, salicylates, carboxylic acids, phosphorus acids, mono- and/or di-thiophosphoric acids, alkyl phenols, sulfur coupled alkyl phenol compounds, or methylene bridged phenols. Suitable detergents and their methods of preparation are described in greater detail in numerous patent publications, including US 7,732,390 and references cited therein. The detergent substrate may be salted with an alkali or alkaline earth metal such as, but not limited to, calcium, magnesium, potassium, sodium, lithium, barium, or mixtures thereof. In some embodiments, the detergent is free of barium. A suitable detergent may include alkali or alkaline earth metal salts of petroleum sulfonic acids and long chain mono- or di-alkylarylsulfonic acids with the aryl group being benzyl, tolyl, and xylyl. Examples of suitable detergents include, but are not limited to, calcium phenates, calcium sulfur containing phenates, calcium sulfonates, calcium calixarates, calcium salixarates, calcium salicylates, calcium carboxylic acids, calcium phosphorus acids, calcium mono- and/or di-thiophosphoric acids, calcium alkyl phenols, calcium sulfur coupled alkyl phenol compounds, calcium methylene bridged phenols, magnesium phenates, magnesium sulfur containing phenates, magnesium sulfonates, magnesium calixarates, magnesium salixarates, magnesium salicylates, magnesium carboxylic acids, magnesium phosphorus acids, magnesium mono- and/or di-thiophosphoric acids, magnesium alkyl phenols, magnesium sulfur coupled alkyl phenol compounds, magnesium methylene bridged phenols, sodium phenates, sodium sulfur containing phenates, sodium sulfonates, sodium calixarates, sodium salixarates, sodium salicylates, sodium carboxylic acids, sodium phosphorus acids, sodium mono- and/or di-thiophosphoric acids, sodium alkyl phenols, sodium sulfur coupled alkyl phenol compounds, or sodium methylene bridged phenols.

[0098] Overbased detergent additives are well known in the art and may be alkali or alkaline earth metal overbased detergent additives. Such detergent additives may be prepared by reacting a metal oxide or metal hydroxide with a substrate and carbon dioxide gas. The substrate is typically an acid, for example, an acid such as an aliphatic substituted sulfonic acid, an aliphatic substituted carboxylic acid, or an aliphatic substituted phenol.

[0099] The terminology "overbased" relates to metal salts, such as metal salts of sulfonates, carboxylates, and phenates, wherein the amount of metal present exceeds the stoichiometric amount. Such salts may have a conversion level in excess of 100% (i.e., they may comprise more than 100% of the theoretical amount of metal needed to convert the acid to its "normal," "neutral" salt). The expression "metal ratio," often abbreviated as MR, is used to designate the ratio of total chemical equivalents of metal in the overbased salt to chemical equivalents of the metal in a neutral salt according to known chemical reactivity and stoichiometry. In a normal or neutral salt, the metal ratio is one and in an overbased salt, MR, is greater than one. They are commonly referred to as overbased, hyperbased, or superbased salts and may be salts of organic sulfur acids, carboxylic acids, or phenols.

[0100] Examples of suitable overbased detergents include, but are not limited to, overbased calcium phenates, overbased calcium sulfur containing phenates, overbased calcium sulfonates, overbased calcium calixarates, overbased calcium salixarates, overbased calcium salicylates, overbased calcium carboxylic acids, overbased calcium phosphorus acids, overbased calcium mono- and/or di-thiophosphoric acids, overbased calcium alkyl phenols, overbased calcium sulfur coupled alkyl phenol compounds, overbased calcium methylene bridged phenols, overbased magnesium phenates, overbased magnesium sulfur containing phenates, overbased magnesium sulfonates, overbased magnesium calixarates, overbased magnesium salixarates, overbased magnesium salicylates, overbased magnesium carboxylic acids, overbased magnesium phosphorus acids, overbased magnesium mono- and/or di-thiophosphoric acids, overbased magnesium alkyl phenols, overbased magnesium sulfur coupled alkyl phenol compounds, or overbased magnesium methylene bridged phenols.

[0101] The overbased detergent may have a metal to substrate ratio of from 1.1:1, or from 2:1, or from 4:1, or from 5:1, or from 7:1, or from 10:1.

[0102] In some embodiments, a detergent is effective at reducing or preventing rust in an engine.

[0103] The detergent may be present at about 0 wt% to about 10 wt%, or about 0.1 wt% to about 8 wt%, or about 1 wt% to about 4 wt%, or greater than about 4 wt% to about 8 wt%.

Dispersants

[0104] The lubricant composition may optionally further comprise one or more dispersants or mixtures thereof. Dispersants are often known as ashless-type dispersants because, prior to mixing in a lubricating oil composition, they do not contain ash-forming metals and they do not normally contribute any ash when added to a lubricant. Ashless type dispersants are characterized by a polar group attached to a relatively high molecular weight hydrocarbon chain. Typical ashless dispersants include N-substituted long chain alkenyl succinimides. Examples of N-substituted long chain alkenyl succinimides include polyisobutylene succinimide with number average molecular weight of the polyisobutylene substituent in the range about 350 to about 50,000, or to about 5,000, or to about 3,000. Succinimide dispersants and their preparation are disclosed, for instance in U.S. Pat. No. 7,897,696 or U.S. Pat. No. 4,234,435. The polyolefin may be prepared from polymerizable monomers containing about 2 to about 16, or about 2 to about 8, or about 2 to about 6 carbon atoms. Succinimide dispersants are typically the imide formed from a polyamine, typically a poly(ethyleneamine).

[0105] In an embodiment the present disclosure further comprises at least one polyisobutylene succinimide dispersant derived from polyisobutylene with number average molecular weight in the range about 350 to about 50,000, or to about 5000, or to about 3000. The polyisobutylene succinimide may be used alone or in combination with other dispersants.

[0106] In some embodiments, polyisobutylene, when included, may have greater than 50 mol%, greater than 60 mol%, greater than 70 mol%, greater than 80 mol%, or greater than 90 mol% content of terminal double bonds. Such PIB is also referred to as highly reactive PIB ("HR-PIB"). HR-PIB having a number average molecular weight ranging from about 800 to about 5000 is suitable for use in embodiments of the present disclosure. Conventional PIB typically has less than 50 mol%, less than 40 mol%, less than 30 mol%, less than 20 mol%, or less than 10 mol% content of terminal double bonds.

[0107] An HR-PIB having a number average molecular weight ranging from about 900 to about 3000 may be suitable. Such HR-PIB is commercially available, or can be synthesized by the polymerization of isobutene in the presence of a non-chlorinated catalyst such as boron trifluoride, as described in US Patent No. 4,152,499 to Boerzel, et al. and U.S. Patent No. 5,739,355 to Gateau, et al. When used in the aforementioned thermal ene reaction, HR-PIB may lead to higher conversion rates in the reaction, as well as lower amounts of sediment formation, due to increased reactivity. A suitable method is described in U.S. Patent No. 7,897,696.

[0108] In one embodiment the present disclosure further comprises at least one dispersant derived from polyisobutylene succinic anhydride ("PIBSA"). The PIBSA may have an average of between about 1.0 and about 2.0 succinic acid moieties per polymer.

[0109] The % actives of the alkenyl or alkyl succinic anhydride can be determined using a chromatographic technique. This method is described in column 5 and 6 in U.S. Pat. No. 5,334,321.

[0110] The percent conversion of the polyolefin is calculated from the % actives using the equation in column 5 and 6 in U.S. Pat. No. 5,334,321.

[0111] Unless stated otherwise, all percentages are in weight percent and all molecular weights are number average molecular weights.

[0112] In one embodiment, the dispersant may be derived from a polyalphaolefin (PAO) succinic anhydride.

[0113] In one embodiment, the dispersant may be derived from olefin maleic anhydride copolymer. As an example, the dispersant may be described as a poly-PIBSA.

[0114] In an embodiment, the dispersant may be derived from an anhydride which is grafted to an ethylene-propylene copolymer.

[0115] One class of suitable dispersants may be Mannich bases. Mannich bases are materials that are formed by the condensation of a higher molecular weight, alkyl substituted phenol, a polyalkylene polyamine, and an aldehyde such as formaldehyde. Mannich bases are described in more detail in U.S. Patent No. 3,634,515.

[0116] A suitable class of dispersants may be high molecular weight esters or half ester amides.

[0117] A suitable dispersant may also be post-treated by conventional methods by a reaction with any of a variety of agents. Among these are boron, urea, thiourea, dimercaptothiadiazoles, carbon disulfide, aldehydes, ketones, carboxylic acids, hydrocarbon-substituted succinic anhydrides, maleic anhydride, nitriles, epoxides, carbonates, cyclic carbonates, hindered phenolic esters, and phosphorus compounds. US 7,645,726; US 7,214,649; and US 8,048,831 are incorporated herein by reference.

In addition to the carbonate and boric acids post-treatments both the compounds may be post-treated, or further post-treatment, with a variety of post-treatments designed to improve or impart different properties. Such post-treatments include those summarized in columns 27-29 of U.S. Pat. No. 5,241,003, hereby incorporated by reference. Such treatments include, treatment with: Inorganic phosphorous acids or anhydrates (e.g., U.S. Pat. Nos. 3,403,102 and 4,648,980); Organic phosphorous compounds (e.g., U.S. Pat. No. 3,502,677); Phosphorous pentasulfides; Boron compounds as already noted above (e.g., U.S. Pat. Nos. 3,178,663 and 4,652,387); Carboxylic acid, polycarboxylic acids, anhydrides and/or acid halides (e.g., U.S. Pat. Nos. 3,708,522 and 4,948,386); Epoxides polyepoxiates or thioexpoxides (e.g., U.S. Pat. Nos. 3,859,318 and 5,026,495); Aldehyde or ketone (e.g., U.S. Pat. No. 3,458,530); Carbon disulfide (e.g., U.S. Pat. No. 3,256,185); Glycidol (e.g., U.S. Pat. No. 4,617,137); Urea, thiourea or guanidine (e.g., U.S. Pat. Nos. 3,312,619; 3,865,813; and British Patent GB 1,065,595); Organic sulfonic acid (e.g., U.S. Pat. No. 3,189,544 and British Patent GB 2,140,811); Alkenyl cyanide (e.g., U.S. Pat. Nos. 3,278,550 and 3,366,569); Diketene (e.g., U.S. Pat. No. 3,546,243); A diisocyanate (e.g., U.S. Pat. No. 3,573,205); Alkane sulfone (e.g., U.S. Pat. No. 3,749,695); 1,3-Dicarbonyl Compound (e.g., U.S. Pat. No. 4,579,675); Sulfate of alkoxylated alcohol or phenol (e.g., U.S. Pat. No. 3,954,639); Cyclic lactone (e.g., U.S. Pat. Nos. 4,617,138; 4,645,515; 4,668,246; 4,963,275; and 4,971,711); Cyclic carbonate or thiocarbonate linear monocarbonate or polycarbonate, or chloroformate (e.g., U.S. Pat. Nos. 4,612,132; 4,647,390; 4,648,886; 4,670,170); Nitrogen-containing carboxylic acid (e.g., U.S. Pat. 4,971,598 and British Patent GB 2,140,811); Hydroxy-protected chlorodicarbonyloxy compound (e.g., U.S. Pat. No. 4,614,522); Lactam, thiolactam, thiolactone or ditholactone (e.g., U.S. Pat. Nos. 4,614,603 and 4,666,460); Cyclic carbonate or thiocarbonate, linear monocarbonate or polycarbonate, or chloroformate (e.g., U.S. Pat. Nos. 4,612,132; 4,647,390; 4,646,860; and 4,670,170); Nitrogen-containing carboxylic acid (e.g., U.S. Pat. No. 4,971,598 and British Patent GB 2,440,811); Hydroxy-protected chlorodicarbonyloxy compound (e.g., U.S. Pat. No. 4,614,522); Lactam, thiolactam, thiolactone or dithiolactone (e.g., U.S. Pat. Nos. 4,614,603, and 4,666,460); Cyclic carbamate, cyclic thiocarbamate or cyclic dithiocarbamate (e.g., U.S. Pat. Nos. 4,663,062 and 4,666,459); Hydroxyaliphatic carboxylic acid (e.g., U.S. Pat. Nos. 4,482,464; 4,521,318; 4,713,189); Oxidizing agent (e.g., U.S. Pat. No. 4,379,064); Combination of phosphorus pentasulfide and a polyalkylene polyamine (e.g., U.S. Pat. No. 3,185,647); Combination of carboxylic acid or an aldehyde or ketone and sulfur or sulfur chloride (e.g., U.S. Pat. Nos. 3,390,086; 3,470,098); Combination of a hydrazine and carbon disulfide (e.g. U.S. Pat. No. 3,519,564); Combination of an aldehyde and a phenol (e.g., U.S. Pat. Nos. 3,649,229; 5,030,249; 5,039,307); Combination of an aldehyde and an O-diester of dithiophosphoric acid (e.g., U.S. Pat. No. 3,865,740); Combination of a hydroxyaliphatic carboxylic acid and a boric acid (e.g., U.S. Pat. No. 4,554,086); Combination of a hydroxyaliphatic carboxylic acid, then formaldehyde and a phenol (e.g., U.S. Pat. No. 4,636,322); Combination of a hydroxyaliphatic carboxylic acid and then an aliphatic dicarboxylic acid (e.g., U.S. Pat. No. 4,663,064); Combination of formaldehyde and a phenol and then glycolic acid (e.g., U.S. Pat. No. 4,699,724); Combination of a hydroxyaliphatic carboxylic acid or oxalic acid and then a diisocyanate (e.g. U.S. Pat. No.4,713,191); Combination of inorganic acid or anhydride of phosphorus or a partial or total sulfur analog thereof and a boron compound (e.g., U.S. Pat. No. 4,857,214); Combination of an organic diacid then an unsaturated fatty acid and then a nitrosoaromatic amine optionally followed by a boron compound and then a glycolating agent (e.g., U.S. Pat. No. 4,973,412); Combination of an aldehyde and a triazole (e.g., U.S. Pat. No. 4,963,278); Combination of an aldehyde and a triazole then a boron compound (e.g., U.S. Pat. No. 4,981,492); Combination of cyclic lactone and a boron compound (e.g., U.S. Pat. No. 4,963,275 and 4,971,711).

[0118] The TBN of a suitable dispersant may be from about 10 to about 65 on an oil-free basis, which is comparable to about 5 to about 30 TBN if measured on a dispersant sample containing about 50% diluent oil.

[0119] The dispersant, if present, can be used in an amount sufficient to provide up to about 20 wt%, based upon the final weight of the lubricating oil composition. Another amount of the dispersant that can be used may be about 0.1 wt% to about 15 wt%, or about 0.1 wt% to about 10 wt%, or about 3 wt% to about 10 wt%, or about 1 wt% to about 6 wt%, or about 7 wt% to about 12 wt%, based upon the final weight of the lubricating oil composition. In one embodiment, the lubricating oil composition utilizes a mixed dispersant system.

Friction Modifiers

[0120] The lubricating oil compositions herein also may optionally contain one or more friction modifiers. Suitable friction modifiers may comprise metal containing and metal-free friction modifiers and may include, but are not limited to, imidazolines, amides, amines, succinimides, alkoxylated amines, alkoxylated ether amines, amine oxides, amidoamines, nitriles, betaines, quaternary amines, imines, amine salts, amino guanadine, alkanolamides, phosphonates, metal-containing compounds, glycerol esters, sulfurized fatty compounds and olefins, sunflower oil other naturally occurring plant or animal oils, dicarboxylic acid esters, esters or partial esters of a polyol and one or more aliphatic or aromatic carboxylic acids, and the like.

[0121] Suitable friction modifiers may contain hydrocarbyl groups that are selected from straight chain, branched chain, or aromatic hydrocarbyl groups or mixtures thereof, and may be saturated or unsaturated. The hydrocarbyl groups may be composed of carbon and hydrogen or hetero atoms such as sulfur or oxygen. The hydrocarbyl groups may range from about 12 to about 25 carbon atoms. In some embodiments the friction modifier may be a long chain fatty acid ester. In another embodiment the long chain fatty acid ester may be a mono-ester, or a di-ester, or a (tri)glyceride. The friction modifier may be a long chain fatty amide, a long chain fatty ester, a long chain fatty epoxide derivative, or a long chain imidazoline.

[0122] Other suitable friction modifiers may include organic, ashless (metal-free), nitrogen-free organic friction modifiers. Such friction modifiers may include esters formed by reacting carboxylic acids and anhydrides with alkanols and generally include a polar terminal group (e.g. carboxyl or hydroxyl) covalently bonded to an oleophilic hydrocarbon chain. An example of an organic ashless nitrogen-free friction modifier is known generally as glycerol monooleate (GMO) which may contain mono-, di-, and triesters of oleic acid. Other suitable friction modifiers are described in U.S. Pat. No. 6,723,685, herein incorporated by reference.

[0123] Aminic friction modifiers may include amines or polyamines. Such compounds can have hydrocarbyl groups that are linear, either saturated or unsaturated, or a mixture thereof and may contain from about 12 to about 25 carbon atoms. Further examples of suitable friction modifiers include alkoxylated amines and alkoxylated ether amines. Such compounds may have hydrocarbyl groups that are linear, either saturated, unsaturated, or a mixture thereof. They may contain from about 12 to about 25 carbon atoms. Examples include ethoxylated amines and ethoxylated ether amines.

[0124] The amines and amides may be used as such or in the form of an adduct or reaction product with a boron compound such as a boric oxide, boron halide, metaborate, boric acid or a mono-, di- or tri-alkyl borate. Other suitable friction modifiers are described in U.S. Pat. No. 6,300,291, herein incorporated by reference.

[0125] A friction modifier may optionally be present in ranges such as about 0 wt% to about 10 wt%, or about 0.01 wt% to about 8 wt%, or about 0.1 wt% to about 4 wt%.

Molybdenum-containing component

[0126] The lubricating oil compositions herein also may optionally contain one or more molybdenum-containing compounds. An oil-soluble molybdenum compound may have the functional performance of an antiwear agent, an antioxidant, a friction modifier, or mixtures thereof. An oil-soluble molybdenum compound may include molybdenum dithiocarbamates, molybdenum dialkyldithiophosphates, molybdenum dithiophosphinates, amine salts of molybdenum compounds, molybdenum xanthates, molybdenum thioxanthates, molybdenum sulfides, molybdenum carboxylates, molybdenum alkoxides, a trinuclear organo-molybdenum compound, and/or mixtures thereof. The molybdenum sulfides include molybdenum disulfide. The molybdenum disulfide may be in the form of a stable dispersion. In one embodiment the oil-soluble molybdenum compound may be selected from the group consisting of molybdenum dithiocarbamates, molybdenum dialkyldithiophosphates, amine salts of molybdenum compounds, and mixtures thereof. In one embodiment the oil-soluble molybdenum compound may be a molybdenum dithiocarbamate.

[0127] Suitable examples of molybdenum compounds which may be used include commercial materials sold under the trade names such as Molyvan 822™, Molyvan™ A, Molyvan 2000™ and Molyvan 855™ from R. T. Vanderbilt Co., Ltd., and Sakura-Lube™ S-165, S-200, S-300, S-310G, S-525, S-600, S-700, and S-710 available from Adeka Corporation, and mixtures thereof. Suitable molybdenum components are described in US 5,650,381; US RE 37,363 E1; US

RE 38,929 E1; and US RE 40,595 E1, incorporated herein by reference.

[0128] Additionally, the molybdenum compound may be an acidic molybdenum compound. Included are molybdic acid, ammonium molybdate, sodium molybdate, potassium molybdate, and other alkaline metal molybdates and other molybdenum salts, e.g., hydrogen sodium molybdate, MoOCl4, MoO2Br2, Mo203Cl6, molybdenum trioxide or similar acidic molybdenum compounds. Alternatively, the compositions can be provided with molybdenum by molybdenum/sulfur complexes of basic nitrogen compounds as described, for example, in U.S. Pat. Nos. 4,263,152; 4,285,822; 4,283,295; 4,272,387; 4,265,773; 4,261,843; 4,259,195 and 4,259,194; and WO 94/06897.

[0129] Another class of suitable organo-molybdenum compounds are trinuclear molybdenum compounds, such as those of the formula Mo3SkLnQz and mixtures thereof, wherein S represents sulfur, L represents independently selected ligands having organo groups with a sufficient number of carbon atoms to render the compound soluble or dispersible in the oil, n is from 1 to 4, k varies from 4 through 7, Q is selected from the group of neutral electron donating compounds such as water, amines, alcohols, phosphines, and ethers, and z ranges from 0 to 5 and includes non-stoichiometric values. At least 21 total carbon atoms may be present among all the ligands' organo groups, such as at least 25, at least 30, or at least 35 carbon atoms. Additional suitable molybdenum compounds are described in U.S. Pat. No. 6,723,685, herein incorporated by reference.

[0130] The oil-soluble molybdenum compound may be present in an amount sufficient to provide about 0.5 ppm to about 2000 ppm, about 1 ppm to about 700 ppm, about 1 ppm to about 550 ppm, about 5 ppm to about 300 ppm, or about 20 ppm to about 250 ppm of molybdenum.

Titanium-containing compounds

[0131] Another class of additives includes oil-soluble titanium compounds. The oil-soluble titanium compounds may function as antiwear agents, friction modifiers, antioxidants, deposit control additives, or more than one of these functions. In an embodiment the oil soluble titanium compound may be a titanium (IV) alkoxide. The titanium alkoxide may be formed from a monohydric alcohol, a polyol, or mixtures thereof. The monohydric alkoxides may have 2 to 16, or 3 to 10 carbon atoms. In an embodiment, the titanium alkoxide may be titanium (IV) isopropoxide. In an embodiment, the titanium alkoxide may be titanium (IV) 2-ethylhexoxide. In an embodiment, the titanium compound may be the alkoxide of a 1,2-diol or polyol. In an embodiment, the 1,2-diol comprises a fatty acid mono-ester of glycerol, such as oleic acid. In an embodiment, the oil soluble titanium compound may be a titanium carboxylate. In an embodiment the titanium (IV) carboxylate may be titanium neodecanoate.

[0132] In an embodiment the oil soluble titanium compound may be present in the lubricating composition in an amount to provide from zero to about 1500 ppm titanium by weight or about 10 ppm to 500 ppm titanium by weight or about 25 ppm to about 150 ppm.

Viscosity Index Improvers

[0133] The lubricating oil compositions herein also may optionally contain one or more viscosity index improvers. Suitable viscosity index improvers may include polyolefins, olefin copolymers, ethylene/propylene copolymers, polyisobutenes, hydrogenated styrene-isoprene polymers, styrene/maleic ester copolymers, hydrogenated styrene/butadiene copolymers, hydrogenated isoprene polymers, alpha-olefin maleic anhydride copolymers, polymethacrylates, polyacrylates, polyalkyl styrenes, hydrogenated alkenyl aryl conjugated diene copolymers, or mixtures thereof. Viscosity index improvers may include star polymers and suitable examples are described in US Publication No. 20120101017A1.

[0134] The total amount of viscosity index improver and/or dispersant viscosity index improver may be about 0 wt% to about 20 wt%, about 0.1 wt% to about 15 wt%, about 0.1 wt% to about 12 wt%, or about 0.5 wt% to about 10 wt%, of the lubricating composition.

Other Optional Additives

[0135] Other additives may be selected to perform one or more functions required of a lubricating fluid. Further, one or more of the mentioned additives may be multi-functional and provide functions in addition to or other than the function prescribed herein.

[0136] A lubricating composition according to the present disclosure may optionally comprise other performance additives. The other performance additives may be in addition to specified additives of the present disclosure and/or may comprise one or more of metal deactivators, ashless TBN boosters, corrosion inhibitors, rust inhibitors, foam inhibitors, demulsifiers, emulsifiers, pour point depressants, seal swelling agents and mixtures thereof. Typically, fully-formulated lubricating oil will contain one or more of these performance additives.'

[0137] Suitable metal deactivators may include derivatives of benzotriazoles (typically tolyltriazole), dimercaptothiadiazole derivatives, 1,2,4-triazoles, benzimidazoles, 2-alkyldithiobenzimidazoles, or 2-alkyldithiobenzothiazoles; foam inhibitors including copolymers of ethyl acrylate and 2-ethylhexylacrylate and optionally vinyl acetate; demulsifiers including trialkyl phosphates, polyethylene glycols, polyethylene oxides, polypropylene oxides and (ethylene oxide-propylene oxide) polymers; pour point depressants including esters of maleic anhydride-styrene, polymethacrylates, polyacrylates or polyacrylamides.

[0138] Suitable foam inhibitors include silicon-based compounds, such as siloxane.

[0139] Suitable pour point depressants may include a polymethylmethacrylates or mixtures thereof. Pour point depressants may be present in an amount sufficient to provide from about 0 wt% to about 1 wt%, about 0.01 wt% to about 0.5 wt%, or about 0.02 wt% to about 0.04 wt% based upon the final weight of the lubricating oil composition.

[0140] Suitable rust inhibitors may be a single compound or a mixture of compounds having the property of inhibiting corrosion of ferrous metal surfaces. Nonlimiting examples of rust inhibitors useful herein include oil-soluble high molecular weight organic acids, such as 2-ethylhexanoic acid, lauric acid, myristic acid, palmitic acid, oleic acid, linoleic acid, linolenic acid, behenic acid, and cerotic acid, as well as oil-soluble polycarboxylic acids including dimer and trimer acids, such as those produced from tall oil fatty acids, oleic acid, and linoleic acid. Other suitable corrosion inhibitors include long-chain alpha, omega-dicarboxylic acids in the molecular weight range of about 600 to about 3000 and alkenylsuccinic acids in which the alkenyl group contains about 10 or more carbon atoms such as, tetrapropenylsuccinic acid, tetradecenylsuccinic acid, and hexadecenylsuccinic acid. Another useful type of acidic corrosion inhibitors are the half esters of alkenyl succinic acids having about 8 to about 24 carbon atoms in the alkenyl group with alcohols such as the polyglycols. The corresponding half amides of such alkenyl succinic acids are also useful. A useful rust inhibitor is a high molecular weight organic acid. In some embodiments, an engine oil is devoid of a rust inhibitor.

[0141] The rust inhibitor, if present, can be used in an amount sufficient to provide about 0 wt% to about 5 wt%, about 0.01 wt% to about 3 wt%, about 0.1 wt% to about 2 wt%, based upon the final weight of the lubricating oil composition.

[0142] In general terms, a suitable crankcase lubricant may include additive components in the ranges listed in the following table.

Table 2

Component	**Wt. % (Suitable Embodiments)**	**Wt. % (Suitable Embodiments)**
Dispersant(s)	0.1 - 10.0	1.0 - 5.0
Antioxidant(s)	0.1 - 5.0	0.01 - 3.0
Detergent(s)	0.1 - 15.0	0.2 - 8.0
Ashless TBN booster(s)	0.0 - 1.0	0.01 - 0.5
Corrosion inhibitor(s)	0.0 - 5.0	0.0 - 2.0
Metal dihydrocarbyldithiophosphate(s)	0.1 - 6.0	0.1 - 4.0
Ash-free phosphorus compound(s)	0.0 - 6.0	0.0 - 4.0
Antifoaming agent(s)	0.0 - 5.0	0.001 - 0.15
Antiwear agent(s)	0.0 - 1.0	0.0 - 0.8
Pour point depressant(s)	0.0 - 5.0	0.01 - 1.5
Viscosity index improver(s)	0.0 - 20.0	0.25 - 10.0
Friction modifier(s)	0.01 - 5.0	0.05 - 2.0
Base oil(s)	Balance	Balance
Total	**100**	**100**

[0143] The percentages of each component above represent the weight percent of each component, based upon the weight of the final lubricating oil composition. The remainder of the lubricating oil composition consists of one or more base oils.

[0144] Additives used in formulating the compositions described herein may be blended into the base oil individually or in various sub-combinations. However, it may be suitable to blend all of the components concurrently using an additive concentrate (i.e., additives plus a diluent, such as a hydrocarbon solvent).

EXAMPLES

[0145] The following examples are illustrative, but not limiting, of the methods and compositions of the present disclosure. Other suitable modifications and adaptations of the variety of conditions and parameters normally encountered in the field, and which are obvious to those skilled in the art, are within the spirit and scope of the disclosure. All patents and publications cited herein are fully incorporated by reference herein in their entirety.

[0146] In order to determine the ability of lubricant compositions according to the disclosure to reduce engine wear, used-oil data was collected from a field test that used a 2012 Ford Explorer having a 2.0L GDI/Turbo engine.

[0147] The two lubricant compositions described below were each used in three different vehicles. Both lubricant compositions were GF-5 5W-30, whereas one of the compositions additionally contained 2 wt.% of the highly grafted, multi-functional olefin copolymer (DOCP) described herein. The results are shown in the following table.

Table 3

Oil Name	DOCP Conc., Wt %	No. Vehicles	Sample Size, n	Average ODI, mi	Average Soot, %	Average Fe, ppmw
GF-5 5W-30	0	3	17	9099	1.3	36.3
GF-5 5W-30 + DOCP	2	3	20	9039	1.3	24.8

[0148] As shown by the foregoing results, the lubricant composition containing 2 wt.% (12 wt.% active) of the highly grafted, multi-functional olefin copolymer (DOCP) exhibited significantly less iron pickup in the lubricant than the base oils devoid of the DOCP additive.

[0149] A comparison of the cam chain stretch for each of the engines is shown in the following table. The cam chain was pre-measured before the start of the test and was re-measured after 120,000 miles. The difference in length (mm) for the cam chains in each of the vehicles is shown in the following table.

Table 4

CAM CHAIN STRETCH, mm	Vehicle 1	Vehicle 2	Vehicle 3	Average	% Decrease from Baseline
GF-5 5W-30	1.75	1.30	1.83	1.63	
GF-5 5W-30 + DOCP	1.87	1.23	1.40	1.50	-7.75%

[0150] The foregoing data demonstrates that lubricant compositions containing the highly grafted, multi-functional olefin copolymer provide a significant improvement in cam chain stretch compared to the same lubricant composition devoid of the highly grafted, multi-functional olefin copolymer

[0151] Other embodiments of the present disclosure will be apparent to those skilled in the art from consideration of the specification and practice of the embodiments disclosed herein. As used throughout the specification and claims, "a" and/or "an" may refer to one or more than one. Unless otherwise indicated, all numbers expressing quantities of ingredients, properties such as molecular weight, percent, ratio, reaction conditions, and so forth used in the specification and claims are to be understood as being modified in all instances by the term "about," whether or not the term "about" is present. Accordingly, unless indicated to the contrary, the numerical parameters set forth in the specification and claims are approximations that may vary depending upon the desired properties sought to be obtained by the present disclosure. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques. Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the disclosure are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical value, however, inherently contains certain errors necessarily resulting from the standard deviation found in their respective testing measurements. It is intended that the specification and examples be considered as exemplary only, with a true scope and spirit of the disclosure being indicated by the following claims.

[0152] The foregoing embodiments are susceptible to considerable variation in practice. Accordingly, the embodiments are not intended to be limited to the specific exemplifications set forth hereinabove. Rather, the foregoing embodiments are within the spirit and scope of the appended claims, including the equivalents thereof available as a matter of law.

[0153] The patentees do not intend to dedicate any disclosed embodiments to the public, and to the extent any disclosed modifications or alterations may not literally fall within the scope of the claims, they are considered to be part hereof under the doctrine of equivalents.

Claims

1. Use in a turbo-charged gasoline direct injection (GDI) engine of a lubricant composition to reduce engine wear, the lubricant composition comprises a major amount of oil of lubricating viscosity, and a minor amount of at least one highly grafted, multi-functional olefin copolymer made by reacting an acylating agent with an olefin copolymer having a number average molecular weight greater than about 1,000 in the presence of a free radical initiator to provide an acylated olefin copolymer having a degree of grafting (DOG) of the acylating agent on the olefin copolymer of at least 0.5 wt.%, and reacting the acylated olefin copolymer with an aromatic amine or heterocyclic amine to provide a highly grafted, multi-functional olefin copolymer, wherein the highly grafted, multi-functional olefin copolymer is effective to reduce engine wear in the turbo-charged GDI engine to below engine wear provided by a lubricant composition devoid of the highly grated, multi-functional olefin copolymer.

2. The use of claim 1, wherein the olefin copolymer comprises a copolymer of ethylene and one or more C_3-C_{23} alpha olefins.

3. The use of claim 1 or claim 2, wherein the lubricating oil composition further comprises a dispersant/inhibitor package.

4. The use of claim 3, wherein the dispersant/inhibitor package comprises a dispersant, a metal-containing detergent, an antiwear agent, an antioxidant, and a friction modifier.

5. The use of claim 4, wherein the detergent is selected from the group consisting of neutral calcium sulfonate, overbased calcium sulfonate, neutral magnesium sulfonate, overbased magnesium sulfonate, neutral calcium phenate, overbased calcium phenate, neutral calcium salicylate, overbased calcium salicylate, neutral magnesium salicylate, overbased magnesium salicylate, neutral magnesium phenate, overbased magnesium phenate, and mixtures thereof.

6. The use of claim 4, wherein the dispersant comprises one or more polyalkenyl succinimide dispersants.

7. The use of claim 4, wherein the friction modifier is selected from the group consisting of non-metal containing organic friction modifiers, organometallic friction modifiers, and mixtures thereof.

8. The use of claim 7, wherein the organometallic friction modifier is selected from the group consisting of oil soluble organo-titanium, oil soluble organo-molybdenum compounds, and oil soluble organo-tungsten compounds.

9. The use of claim 7, wherein the non-metal containing friction modifier is selected from the group consisting of glycerol monooleate and nitrogen containing friction modifiers.

10. The use of any of the previous claims, wherein the acylated olefin copolymer has a degree of grafting (DOG) ranging from about 1.5 to about 2.5 wt.%.

11. The use of any of the previous claims, wherein the lubricant composition comprises from about 0.25 wt% to about 10 wt% of the highly grafted, multi-functional olefin copolymer based on a total weight of the lubricant composition.

12. The use of any of the previous claims, wherein the engine wear is exhibited by cam chain stretch.

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EUROPEAN SEARCH REPORT

Application Number
EP 15 18 2399

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X Y	US 2013/172220 A1 (RUHE JR WILLIAM RAYMOND [US]) 4 July 2013 (2013-07-04) * the whole document *	1,2, 10-12 1-12	INV. C10M159/12 C10M169/04 ADD. C10N10/08 C10N10/12 C10N30/06 C10N40/25
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	16 December 2015	Renoth, Heinz

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

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