

**METHOD FOR IMPROVING EMULSION**  
**CHARACTERISTICS OF ENGINE OILS**

**FIELD**

**[0001]** This disclosure relates to lubricating engines using formulated lubricating oils containing a coupled block copolymer that are capable of emulsifying water contamination in a lubricating oil as well as improving thermal-oxidative stability and elastomer compatibility/manageability in an engine lubricated with the lubricating oil.

**BACKGROUND**

**[0002]** Lubricants in commercial use today are prepared from a variety of natural and synthetic base stocks admixed with various additive packages and solvents depending upon their intended application. The base stocks typically include mineral oils, poly alpha olefins (PAO), gas-to-liquid base oils (GTL), silicone oils, phosphate esters, diesters, polyol esters, and the like.

**[0003]** With the use of E85 fuels, in an internal combustion engine, the engine oil can become contaminated with water and fuel. Phase separation can occur, resulting in an aqueous layer and an oil layer. This can affect the lubrication and detergency properties of an engine oil.

**[0004]** To mitigate this issue, an engine oil should be capable of emulsifying water contamination. A new standard test method was introduced into the latest ILSAC GF-5 specification: Evaluation of the Ability of Engine Oil to Emulsify Water and Simulated Ed85 Fuel (ASTM D7563). This is a relatively new test method and there are no specific additives developed that address emulsion

characteristics in engine oils. Pour Point Depressants (commonly polymethacrylates) have found some application in controlling emulsion.

**[0005]** Therefore, there is a need for engine oil additives capable of emulsifying water contamination in an engine oil so as to enable the engine oil to pass the ILSAC GF-5 specification and ASTM D7563 test.

**[0006]** The present disclosure also provides many additional advantages, which shall become apparent as described below.

### **SUMMARY**

**[0007]** The lubricating oils of this disclosure exhibit significantly improved emulsion characteristics, as measured by ASTM D7563, in comparison with lubricating oils that do not contain a coupled block copolymer. The lubricating oils of this disclosure also exhibit improved thermal-oxidative stability and elastomer compatibility/manageability in comparison with lubricating oils that do not contain a coupled block copolymer. The coupled block copolymer used in the lubricating oils of this disclosure imparts desired emulsion characteristics to a lubricating oil contaminated with water and fuel, and also imparts desired thermo-oxidative stability and elastomer compatibility in an engine lubricated with the lubricating oil.

**[0008]** This disclosure is directed in part to a method for improving the ability of an engine lubricating oil contaminated with water and fuel to emulsify water contamination by using as the engine lubricating oil a formulated oil comprising a lubricating oil base stock as a major component and a coupled block copolymer as a minor component. The coupled block copolymer comprises: an "A" block of a functionalized hydrocarbon moiety including one or more functional end groups derived from: epoxides, amines, acids, acid

chlorides, acid anhydrides, halogens, vinyl or vinylidene double bonds, aromatic rings or thiols; and a “B” block of a functionalized polyether moiety including one or more functional end groups derived from: epoxides, amines, acids, acid chlorides, acid anhydrides, halogens, vinyl or vinylidene double bonds, aromatic rings or thiols. The end group of the polyether moiety is different than the end group of the hydrocarbon moiety, and the hydrocarbon moiety and the polyether moiety are copolymerizable therewith. In an engine lubricated with said lubricating oil, the ability of the engine lubricating oil contaminated with water and fuel to emulsify water contamination is improved as compared to the ability of an engine lubricating oil contaminated with water and fuel to emulsify water contamination using a lubricating oil containing a minor component other than the coupled block copolymer.

**[0009]** This disclosure is also directed in part to a method for improving thermo-oxidative stability and elastomer compatibility in an engine lubricated with a lubricating oil by using as the lubricating oil a formulated oil comprising a lubricating oil base stock as a major component and a coupled block copolymer as a minor component. The coupled block copolymer comprises: an “A” block of a functionalized hydrocarbon moiety including one or more functional end groups derived from: epoxides, amines, acids, acid chlorides, acid anhydrides, halogens, vinyl or vinylidene double bonds, aromatic rings or thiols; and a “B” block of a functionalized polyether moiety including one or more functional end groups derived from: epoxides, amines, acids, acid chlorides, acid anhydrides, halogens, vinyl or vinylidene double bonds, aromatic rings or thiols. The end group of the polyether moiety is different than the end group of the hydrocarbon moiety, and the hydrocarbon moiety and the polyether moiety are copolymerizable therewith. In an engine lubricated with said lubricating oil, thermo-oxidative stability and elastomer compatibility are improved as compared to thermo-oxidative stability and elastomer compatibility achieved

using a lubricating oil containing a minor component other than the coupled block copolymer.

**[0010]** This disclosure is further directed in part to a lubricating engine oil comprising a lubricating oil base stock as a major component and a coupled block copolymer as a minor component. The coupled block copolymer comprises: an “A” block of a functionalized hydrocarbon moiety including one or more functional end groups derived from: epoxides, amines, acids, acid chlorides, acid anhydrides, halogens, vinyl or vinylidene double bonds, aromatic rings or thiols; and a “B” block of a functionalized polyether moiety including one or more functional end groups derived from: epoxides, amines, acids, acid chlorides, acid anhydrides, halogens, vinyl or vinylidene double bonds, aromatic rings or thiols. The end group of the polyether moiety is different than the end group of the hydrocarbon moiety, and wherein the hydrocarbon moiety and the polyether moiety are copolymerizable therewith. In an engine lubricated with said lubricating oil, the ability of the engine lubricating oil contaminated with water and fuel to emulsify water contamination is improved as compared to the ability of an engine lubricating oil contaminated with water and fuel to emulsify water contamination using a lubricating oil containing a minor component other than the coupled block copolymer.

**[0011]** This disclosure is yet further directed in part to a lubricating engine oil comprising a lubricating oil base stock as a major component and a coupled block copolymer as a minor component. The coupled block copolymer comprises: an “A” block of a functionalized hydrocarbon moiety including one or more functional end groups derived from: epoxides, amines, acids, acid chlorides, acid anhydrides, halogens, vinyl or vinylidene double bonds, aromatic rings or thiols; and a “B” block of a functionalized polyether moiety including one or more functional end groups derived from: epoxides, amines, acids, acid chlorides, acid anhydrides, halogens, vinyl or vinylidene double bonds, aromatic

rings or thiols. The end group of the polyether moiety is different than the end group of the hydrocarbon moiety, and wherein the hydrocarbon moiety and the polyether moiety are copolymerizable therewith. In an engine lubricated with said lubricating oil, thermo-oxidative stability and elastomer compatibility are improved as compared to thermo-oxidative stability and elastomer compatibility achieved using a lubricating oil containing a minor component other than the coupled block copolymer.

**[0012]** It has been surprisingly found that the lubricating oils containing a coupled block copolymer in accordance with this disclosure improve the ability of the engine lubricating oil contaminated with water and fuel to emulsify water contamination as compared to the ability of an engine lubricating oil contaminated with water and fuel to emulsify water contamination using a lubricating oil containing a minor component other than the coupled block copolymer. In addition, it has been surprisingly found in an engine lubricated with the lubricating oil of this disclosure, thermo-oxidative stability and elastomer compatibility are improved as compared to thermo-oxidative stability and elastomer compatibility achieved using a lubricating oil containing a minor component other than the coupled block copolymer.

**[0013]** Further objects, features and advantages of the present disclosure will be understood by reference to the following drawings and detailed description.

#### **BRIEF DESCRIPTION OF THE DRAWINGS**

**[0014]** Fig. 1 graphically shows the results of the ASTM D7563 E85 emulsion testing. One test was conducted at 0°C and the other test conducted at 25°C as shown in the Examples.

**[0015]** Fig. 2 graphically shows the results of Pressure Differential Scanning Calorimetry (PDSC) at 210°C and 100 psi air. This test measures enthalpy change over time as shown in the Examples. The point at which a significant exotherm occurs is considered the induction time. A greater resistance to oxidation induction is desirable.

**[0016]** Fig. 3 lists the results of elastomer compatability performance testing for four Association des Constructeurs Europeens D'Automobiles (ACEA) elastomers (i.e., Viton, Acrylate, Silicone, and Nitrile) as shown in the Examples.

### **DETAILED DESCRIPTION**

**[0017]** All numerical values within the detailed description and the claims herein are modified by “about” or “approximately” the indicated value, and take into account experimental error and variations that would be expected by a person having ordinary skill in the art.

**[0018]** This disclosure provides lubricating oils useful as engine oils and in other applications characterized by an ability to emulsify water contamination in the lubricating oil. This disclosure provides lubricating oils useful as engine oils and in other applications characterized by an excellent balance of thermo-oxidative stability and elastomer compatibility in an engine lubricated with the lubricating oil. The lubricating oils are based on high quality base stocks including a major portion of a hydrocarbon base fluid such as a PAO or GTL with a secondary base stock component which is preferably a coupled block copolymer. In the present specification and claims, the terms base oil(s) and base stock(s) are used interchangeably.

### Lubricating Oil Base Stocks

**[0019]** A wide range of lubricating oils is known in the art. Lubricating oils that are useful in the present disclosure are both natural oils and synthetic oils. Natural and synthetic oils (or mixtures thereof) can be used unrefined, refined, or rerefined (the latter is also known as reclaimed or reprocessed oil). Unrefined oils are those obtained directly from a natural or synthetic source and used without added purification. These include shale oil obtained directly from retorting operations, petroleum oil obtained directly from primary distillation, and ester oil obtained directly from an esterification process. Refined oils are similar to the oils discussed for unrefined oils except refined oils are subjected to one or more purification steps to improve the at least one lubricating oil property. One skilled in the art is familiar with many purification processes. These processes include solvent extraction, secondary distillation, acid extraction, base extraction, filtration, and percolation. Rerefined oils are obtained by processes analogous to refined oils but using an oil that has been previously used as a feed stock.

**[0020]** Groups I, II, III, IV and V are broad categories of base oil stocks developed and defined by the American Petroleum Institute (API Publication 1509; [www.API.org](http://www.API.org)) to create guidelines for lubricant base oils. Group I base stocks generally have a viscosity index of between 80 to 120 and contain greater than 0.03% sulfur and less than 90% saturates. Group II base stocks generally have a viscosity index of between 80 to 120, and contain less than or equal to 0.03% sulfur and greater than or equal to 90% saturates. Group III stock generally has a viscosity index greater than 120 and contains less than or equal to 0.03% sulfur and greater than 90% saturates. Group IV includes polyalphaolefins (PAO). Group V base stocks include base stocks not included in Groups I-IV. The table below summarizes properties of each of these five groups.

|           | Base Oil Properties                    |            |                 |
|-----------|----------------------------------------|------------|-----------------|
|           | Saturates                              | Sulfur     | Viscosity Index |
| Group I   | <90 and/or                             | >0.03% and | ≥80 and <120    |
| Group II  | ≥90 and                                | ≤0.03% and | ≥80 and <120    |
| Group III | ≥90 and                                | ≤0.03% and | ≥120            |
| Group IV  | All polyalphaolefins (PAO)             |            |                 |
| Group V   | All Stocks Not Included in Groups I-IV |            |                 |

**[0021]** Natural oils include animal oils, vegetable oils (castor oil and lard oil, for example), and mineral oils. Animal and vegetable oils possessing favorable thermal oxidative stability can be used. Of the natural oils, mineral oils are preferred. Mineral oils vary widely as to their crude source, for example, as to whether they are paraffinic, naphthenic, or mixed paraffinic-naphthenic. Oils derived from coal or shale are also useful in the present disclosure. Natural oils vary also as to the method used for their production and purification, for example, their distillation range and whether they are straight run or cracked, hydrotreated, or solvent extracted.

**[0022]** Group II and/or Group III hydroprocessed or hydrocracked base stocks, as well as synthetic oils such as polyalphaolefins, alkyl aromatics and synthetic esters, i.e. Group IV and Group V oils are also well known base stock oils. The Group III base stock is highly paraffinic with saturates level higher than 90%, preferably 95%, a viscosity index greater than 125, preferably greater than 135, or more preferably greater than 140, very low aromatics of 3%, preferably less than 1%, and aniline point of 118 or higher.

**[0023]** Synthetic oils include hydrocarbon oil such as polymerized and interpolymers of olefins (polybutylenes, polypropylenes, propylene isobutylene copolymers, ethylene-olefin copolymers, and ethylene-alphaolefin copolymers, for example). Polyalphaolefin (PAO) oil base stocks, the Group IV API base

stocks, are a commonly used synthetic hydrocarbon oil. By way of example, PAOs derived from C<sub>6</sub>, C<sub>8</sub>, C<sub>10</sub>, C<sub>12</sub>, C<sub>14</sub>, C<sub>16</sub> olefins or mixtures thereof may be utilized. See U.S. Patent Nos. 4,956,122; 4,827,064; and 4,827,073, which are incorporated herein by reference in their entirety. Group IV oils, that is, the PAO base stocks have viscosity indices preferably greater than 130, more preferably greater than 135, still more preferably greater than 140.

**[0024]** PAOs are a class of hydrocarbons that can be manufactured by the catalytic oligomerization (polymerization to low-molecular-weight products) of linear  $\alpha$ -olefin (LAO) monomers. These typically range from 1-octene to 1-dodecene, or 1-octene to 1-tetradecene, with 1-decene being a preferred material, although oligomeric copolymers of lower olefins such as ethylene and propylene may also be used, including copolymers of ethylene with higher olefins as described in U.S. Patent No. 4,956,122 and the patents referred to therein, all of which are incorporated by reference in their entirety. PAO products have achieved importance in the lubricating oil market. Typically there are two classes of synthetic hydrocarbon fluids (SHF) produced from linear  $\alpha$ -olefins, the two classes of SHF being denoted as PAO and HVI-PAO (high viscosity index PAO's). PAO's of different viscosity grades are typically produced using promoted BF<sub>3</sub> or AlCl<sub>3</sub> catalysts.

**[0025]** Specifically, PAOs may be produced by the polymerization of olefin feed in the presence of a catalyst, such as AlCl<sub>3</sub>, BF<sub>3</sub>, or promoted AlCl<sub>3</sub> or BF<sub>3</sub>. Processes for the production of PAOs are disclosed, for example, in the following patents: U.S. Patent Nos. 3,149,178; 3,382,291; 3,742,082; 3,769,363; 3,780,128; 4,172,855 and 4,956,122, which are fully incorporated herein by reference. PAOs are also discussed in the following: Will, J. G. Lubrication Fundamentals, Marcel Dekker: New York, 1980. Subsequent to polymerization, the PAO lubricant range products are typically hydrogenated in order to reduce the residual unsaturation, generally to a level of greater than 90% of

hydrogenation. High viscosity PAO's may be conveniently made by the polymerization of an alpha-olefin in the presence of a polymerization catalyst such as Friedel-Crafts catalysts. These include, for example, boron trifluoride, aluminum trichloride, or boron trifluoride, promoted with water, with alcohols such as ethanol, propanol, or butanol, with carboxylic acids, or with esters such as ethyl acetate or ethyl propionate or ether such as diethyl ether, and diisopropyl ether. (See for example, the methods disclosed by U.S. Pat. Nos. 4,149,178 and. 3,382,291.) Other descriptions of PAO synthesis are found in the following: U.S. Patent No. 3,742,082; U.S. Patent No. 3,769,363; U.S. Patent No. 3,876,720; U.S. Patent No. 4,239,930; U.S. Patent No. 4,367,352; U.S. Patent No. 4,413,156; U.S. Patent No. 4,434,408; U.S. Patent No. 4,910,355; U.S. Patent No. 4,956,122; and U.S. Patent No. 5,068,487, all of which are incorporated in their entirety herein by reference.

**[0026]** Another class of HVI-PAOs may be prepared by the action of a supported, reduced chromium catalyst with an alpha-olefin monomer. Such PAOs are described in U.S. Patent No. 4,827,073; U.S. Patent No. 4,827,064; U.S. Patent No. 4,967,032; U.S. Patent No. 4,926,004; and U.S. Patent No. 4,914,254. Commercially available PAOs include SpectraSyn™ 2, 4, 5, 6, 8, 10, 40, 100 and SpectraSyn Ultra™ 150, SpectraSyn Ultra™ 300, SpectraSyn Ultra™ 1000, etc. (ExxonMobil Chemical Company, Houston, Tex.). Also included are PAOs prepared the presence of a metallocene catalyst with a non-coordinating anion activator and hydrogen as discussed in U.S. Published Patent Application No. 2008/0177121.

**[0027]** Esters in a minor amount may be useful in the lubricating oils of this disclosure. Additive solvency and seal compatibility characteristics may be secured by the use of esters such as the esters of dibasic acids with monoalkanols and the polyol esters of monocarboxylic acids. Esters of the former type include, for example, the esters of dicarboxylic acids such as phthalic acid,

succinic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkyl malonic acid, alkenyl malonic acid, etc., with a variety of alcohols such as butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, etc. Specific examples of these types of esters include dibutyl adipate, di(2-ethylhexyl) sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, etc.

**[0028]** Particularly useful synthetic esters are those which are obtained by reacting one or more polyhydric alcohols, preferably the hindered polyols such as the neopentyl polyols; e.g., neopentyl glycol, trimethylol ethane, 2-methyl-2-propyl-1,3-propanediol, trimethylol propane, pentaerythritol and dipentaerythritol with alkanoic acids containing at least 4 carbon atoms, preferably C<sub>5</sub> to C<sub>30</sub> acids such as saturated straight chain fatty acids including caprylic acid, capric acids, lauric acid, myristic acid, palmitic acid, stearic acid, arachic acid, and behenic acid, or the corresponding branched chain fatty acids or unsaturated fatty acids such as oleic acid, or mixtures of any of these materials.

**[0029]** Esters should be used in a amount such that the improved wear and corrosion resistance provided by the lubricating oils of this disclosure are not adversely affected. The esters preferably have a D5293 viscosity of less than 10,000 cP at -35°C.

**[0030]** Non-conventional or unconventional base stocks and/or base oils include one or a mixture of base stock(s) and/or base oil(s) derived from: (1) one or more Gas-to-Liquids (GTL) materials, as well as (2) hydrodewaxed, or hydroisomerized/cat (and/or solvent) dewaxed base stock(s) and/or base oils derived from synthetic wax, natural wax or waxy feeds, mineral and/or non-mineral oil waxy feed stocks such as gas oils, slack waxes (derived from the

solvent dewaxing of natural oils, mineral oils or synthetic oils; e.g., Fischer-Tropsch feed stocks), natural waxes, and waxy stocks such as gas oils, waxy fuels hydrocracker bottoms, waxy raffinate, hydrocrackate, thermal crackates, foots oil or other mineral, mineral oil, or even non-petroleum oil derived waxy materials such as waxy materials recovered from coal liquefaction or shale oil, linear or branched hydrocarbyl compounds with carbon number of 20 or greater, preferably 30 or greater and mixtures of such base stocks and/or base oils.

**[0031]** GTL materials are materials that are derived via one or more synthesis, combination, transformation, rearrangement, and/or degradation/deconstructive processes from gaseous carbon-containing compounds, hydrogen-containing compounds and/or elements as feed stocks such as hydrogen, carbon dioxide, carbon monoxide, water, methane, ethane, ethylene, acetylene, propane, propylene, propyne, butane, butylenes, and butynes. GTL base stocks and/or base oils are GTL materials of lubricating viscosity that are generally derived from hydrocarbons; for example, waxy synthesized hydrocarbons, that are themselves derived from simpler gaseous carbon-containing compounds, hydrogen-containing compounds and/or elements as feed stocks. GTL base stock(s) and/or base oil(s) include oils boiling in the lube oil boiling range (1) separated/fractionated from synthesized GTL materials such as, for example, by distillation and subsequently subjected to a final wax processing step which involves either or both of a catalytic dewaxing process, or a solvent dewaxing process, to produce lube oils of reduced/low pour point; (2) synthesized wax isomerates, comprising, for example, hydrodewaxed or hydroisomerized cat and/or solvent dewaxed synthesized wax or waxy hydrocarbons; (3) hydrodewaxed or hydroisomerized cat and/or solvent dewaxed Fischer-Tropsch (F-T) material (i.e., hydrocarbons, waxy hydrocarbons, waxes and possible analogous oxygenates); preferably hydrodewaxed or hydroisomerized/followed by cat and/or solvent dewaxing dewaxed F-T waxy

hydrocarbons, or hydrodewaxed or hydroisomerized/ followed by cat (or solvent) dewaxing dewaxed, F-T waxes, or mixtures thereof.

**[0032]** GTL base stock(s) and/or base oil(s) derived from GTL materials, especially, hydrodewaxed or hydroisomerized/ followed by cat and/or solvent dewaxed wax or waxy feed, preferably F-T material derived base stock(s) and/or base oil(s), are characterized typically as having kinematic viscosities at 100°C of from 2 mm<sup>2</sup>/s to 50 mm<sup>2</sup>/s (ASTM D445). They are further characterized typically as having pour points of -5°C to -40°C or lower (ASTM D97). They are also characterized typically as having viscosity indices of 80 to 140 or greater (ASTM D2270).

**[0033]** In addition, the GTL base stock(s) and/or base oil(s) are typically highly paraffinic (>90% saturates), and may contain mixtures of monocycloparaffins and multicycloparaffins in combination with non-cyclic isoparaffins. The ratio of the naphthenic (i.e., cycloparaffin) content in such combinations varies with the catalyst and temperature used. Further, GTL base stock(s) and/or base oil(s) typically have very low sulfur and nitrogen content, generally containing less than 10 ppm, and more typically less than 5 ppm of each of these elements. The sulfur and nitrogen content of GTL base stock(s) and/or base oil(s) obtained from F-T material, especially F-T wax, is essentially nil. In addition, the absence of phosphorous and aromatics make this materially especially suitable for the formulation of low SAP products.

**[0034]** The term GTL base stock and/or base oil and/or wax isomerase base stock and/or base oil is to be understood as embracing individual fractions of such materials of wide viscosity range as recovered in the production process, mixtures of two or more of such fractions, as well as mixtures of one or two or more low viscosity fractions with one, two or more higher viscosity fractions to produce a blend wherein the blend exhibits a target kinematic viscosity.

**[0035]** The GTL material, from which the GTL base stock(s) and/or base oil(s) is/are derived is preferably an F-T material (i.e., hydrocarbons, waxy hydrocarbons, wax).

**[0036]** Base oils for use in the formulated lubricating oils useful in the present disclosure are any of the variety of oils corresponding to API Group I, Group II, Group III, Group IV and Group V oils and mixtures thereof, preferably API Group II, Group III, Group IV and Group V oils and mixtures thereof, more preferably the Group III to Group V base oils due to their exceptional volatility, stability, viscometric and cleanliness features. Minor quantities of Group I stock, such as the amount used to dilute additives for blending into formulated lube oil products, can be tolerated but should be kept to a minimum, i.e. amounts only associated with their use as diluent/carrier oil for additives used on an “as-received” basis. Even in regard to the Group II stocks, it is preferred that the Group II stock be in the higher quality range associated with that stock, i.e. a Group II stock having a viscosity index in the range  $100 < VI < 120$ .

**[0037]** In addition, the GTL base stock(s) and/or base oil(s) are typically highly paraffinic (>90% saturates), and may contain mixtures of monocycloparaffins and multicycloparaffins in combination with non-cyclic isoparaffins. The ratio of the naphthenic (i.e., cycloparaffin) content in such combinations varies with the catalyst and temperature used. Further, GTL base stock(s) and/or base oil(s) and hydrodewaxed, or hydroisomerized/cat (and/or solvent) dewaxed base stock(s) and/or base oil(s) typically have very low sulfur and nitrogen content, generally containing less than 10 ppm, and more typically less than 5 ppm of each of these elements. The sulfur and nitrogen content of GTL base stock(s) and/or base oil(s) obtained from F-T material, especially F-T wax, is essentially nil. In addition, the absence of phosphorous and aromatics make this material especially suitable for the formulation of low sulfur, sulfated ash, and phosphorus (low SAP) products.

**[0038]** The basestock component of the present lubricating oils will typically be from 50 to 90 weight percent of the total composition (all proportions and percentages set out in this specification are by weight unless the contrary is stated) and more usually in the range of 55 to 85 weight percent.

#### Coupled PAO-PAG Block Copolymer Components

**[0039]** The coupled PAO-PAG block copolymer components useful in this disclosure include those disclosed in U.S. Patent Application Publication No. 2012/0115763, the disclosure of which is incorporated herein by reference in its entirety.

**[0040]** The coupled PAO-PAG block copolymer components useful in this disclosure can be prepared by copolymerizing a functionalized hydrocarbon moiety and a functionalized polyether moiety, wherein the functionalized hydrocarbon moiety includes one or more functional end groups derived from: epoxides, amines, acids, acid chlorides, acid anhydrides, halogens, vinyl or vinylidene double bonds, aromatic rings or thiols, and wherein the functionalized polyether moiety includes one or more functional end groups derived from: epoxides, amines, acids, acid chlorides, acid anhydrides, halogens, vinyl or vinylidene double bonds, aromatic rings or thiols, wherein the end group of the polyether moiety is different than the end group of the hydrocarbon moiety, and wherein the hydrocarbon moiety and the polyether moiety are copolymerizable therewith.

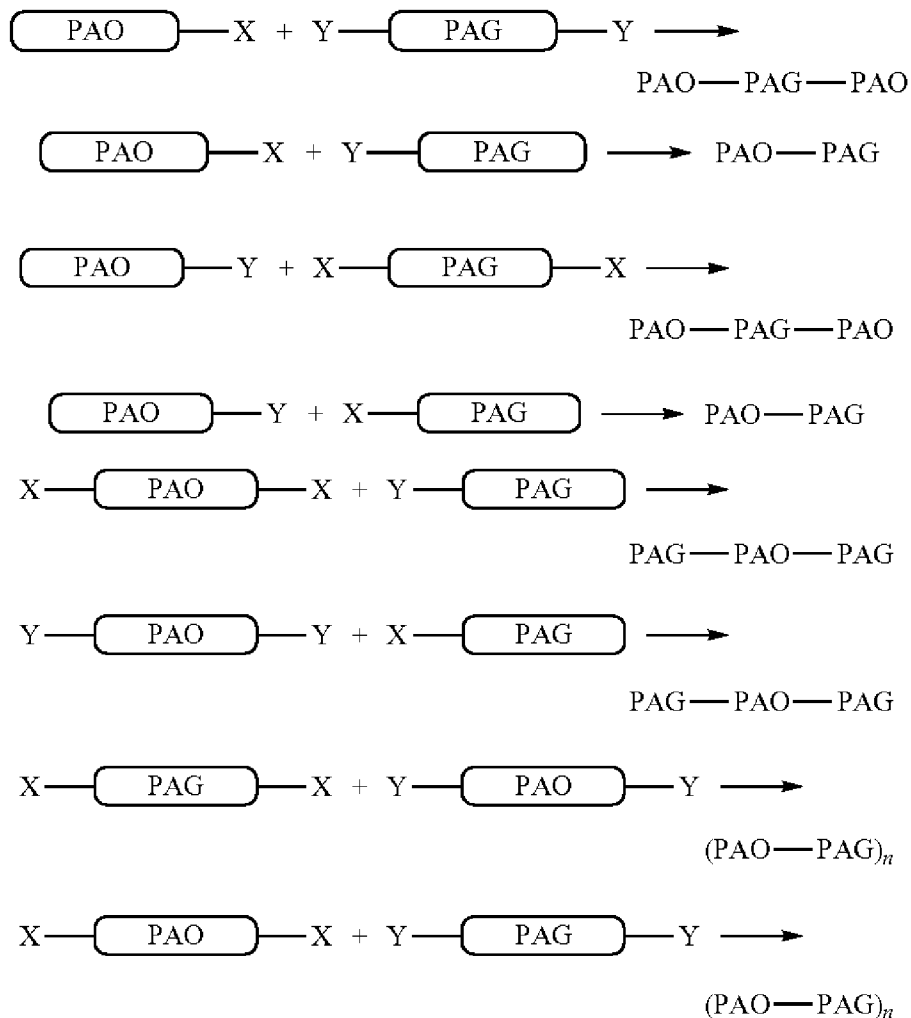
**[0041]** Preferably, the copolymerization takes place at a temperature of 0°C to 200°C, more preferably between 20°C to 120°C. The copolymerization takes place for a time of 0.5 hours to 36 hours, more preferably between 1 hour to 24 hours.

**[0042]** A lubricant base stock that exhibits desirable performance attributes due to the polymerization of a hydrocarbon moiety (e.g., poly- $\alpha$ -olefins (PAO)) having one or more functional end groups and a polyether moiety (e.g., polyalkylene glycols (PAG)) having one or more functional end groups. More particular, chemically coupled PAO-PAG block polymers of a hydrocarbon segment, such as those of poly- $\alpha$ -olefin (PAO), and a polyether segment, such as poly(alkylene glycol) (PAG), can be employed as low molecular weight synthetic lubricant base stocks.

**[0043]** The hydrocarbon segment can be a long chain alkane, a poly- $\alpha$ -olefin or a low molecular weight polyethylene, propylene, polybutene, polyisobutylene or ethylene- $\alpha$ -olefin macromer. The macromer is a unit having between 16 to 40 carbon atoms derived from ethylene, propylene or  $\alpha$ -olefins, and combinations of the foregoing. The olefin monomeric units are derived from one or more internal olefins. Alternatively, the olefin monomeric units are derived from one or more olefins including 1-hexene, 1-octene, 1-nonene, 1-decene, 1-undecene, 1-dodecene, 1-tetradecene, 1-hexadecene or 1-octadecene. Still further, the olefin monomeric unit is a low molecular weight oligomer prepared via a metallocene catalytic reaction. The low molecular weight oligomer is a dimer of 1-decene, 1-decene, 1-hexene, 1-tetradecene or mixtures thereof.

**[0044]** The polyether segment can be a polyalkylene glycol, such as ethylene glycol, propylene glycol, polybutylene glycol, or combinations thereof.

**[0045]** These segments are preferably coupled by chemical reaction of functional groups that can be attached to either the hydrocarbon segment and/or the polyether segment. Preferred schemes of coupling reactions are depicted below:

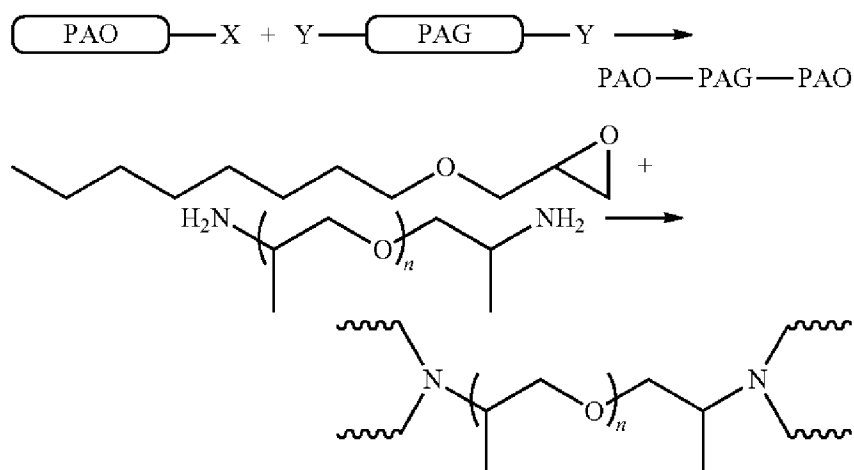


wherein X and Y are functional groups, such as amines, epoxides, acids, acid halides, halides, alcohols, esters, ketones, vinyl or vinylidene double bonds, substituted aromatic groups, phenols, and thiols.

**[0046]** As one example, the PAO/PAG block copolymers substantially maintain the respective benefits of both PAG and PAO fluids while unexpectedly eliminating or diminishing their respective disadvantages. Notably, the block copolymers provide surprisingly superior step-out fuel economy and energy efficiency when used in automotive engine lubricants and industrial and grease lubricants.

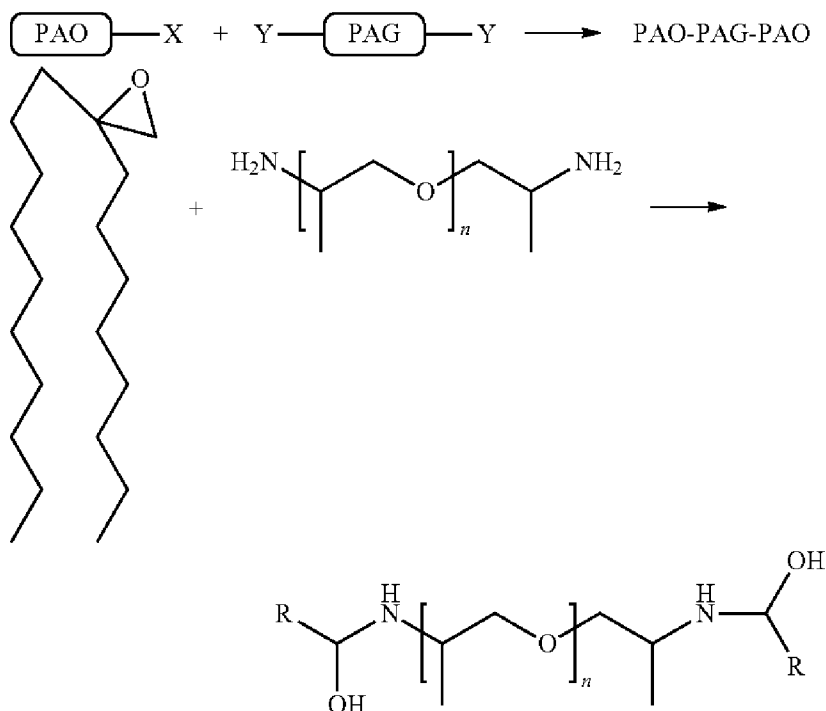
**[0047]** Three reaction sequences are particularly preferred in making the PAO-PAG block copolymers.

**[0048]** The first preferred sequence is the reaction of an alkyl glycidyl ether with a Jeffamine® polyetheramine to obtain a PAO-PAG block copolymer fluid.



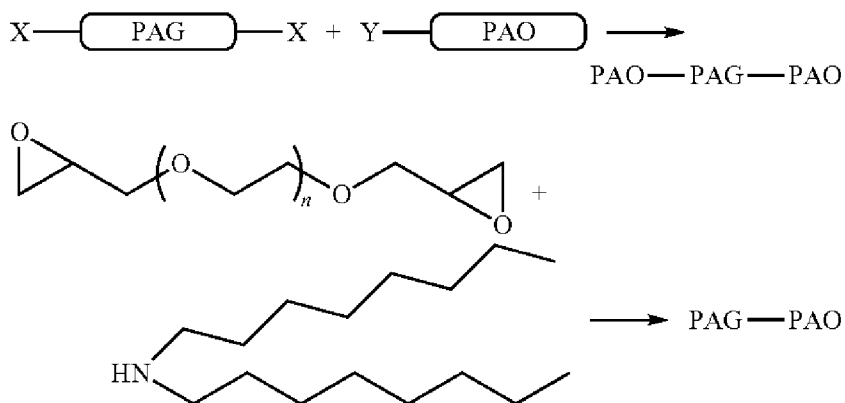
**[0049]** The PAO in above reaction is a C<sub>8</sub>/C<sub>10</sub> alkyl glycidyl ether wherein X is an epoxide and PAG is an polyether amine (Jeffamine®) wherein Y is an amine.

**[0050]** The second preferred sequence is the reaction of an alkyl epoxide (C<sub>20</sub>-epoxy) with a Jeffamine® polyetheramine to obtain a PAO-PAG block copolymer fluid.



**[0051]** The PAO-PAG shown above is similar to the structure depicted in the first sequence except the PAO is a long chain alkyl group (rather than a glycidyl ether) wherein X is an epoxide group and PAG is a polyether amine (Jeffamine®) wherein Y is an amine group.

**[0052]** The third preferred sequence is the reaction of a poly(alkylene glycol) diglycidyl ether with an alkylamine to obtain a PAO-PAG fluid.



**[0053]** The PAO/PAG block copolymer shown above has a diepoxide as a part of the polyether segment (PAG) and an amine as a part of hydrocarbon (PAO) segment, wherein X is an epoxide group and Y is an amine group.

**[0054]** Polyethylene glycol-containing diepoxides with dioctylamine can be reacted to obtain a low molecular weight synthetic fluid. For example, poly(ethyleneglycol) diglycidyl ether (MW of 526) and dioctylamine can be reacted to obtain a liquid product that has excellent lube properties like PAO. Besides poly(ethyleneglycol) diglycidyl ether, other diepoxides that contain polyether segments can be reacted with amines. Further, Armeen® amines other than dioctylamine can be reacted with epoxides.

**[0055]** Epoxides can be prepared by epoxidation of unhydrogenated PAO (PAO with terminal double bond) or of other hydrocarbon macromers, such as polyethylene (PE), polypropylene (PP), ethylene propylene (EP), ethylene butylene (EB), polyisobutylene (PIB), poly-n-butylene (PNB) macromers, or of alkyl glycidyl ethers.

**[0056]** The macromer is a having between 16 to 40 carbon atoms derived from ethylene, propylene, or  $\alpha$ -olefins, and combinations of the foregoing. The olefin monomeric units are derived from one or more internal olefins. Alternatively, the olefin monomeric units are derived from one or more olefins including 1-hexene, 1-octene, 1-nonene, 1-decene, 1-undecene, 1-dodecene, 1-tetradecene, or 1-octadecene. Still further, the olefin monomeric unit is a low molecular weight oligomer prepared via a metallocene catalytic reaction. The low molecular weight oligomer is a dimer of 1-decene, 1-decene, 1-hexene, 1-tetradecene or mixtures thereof.

**[0057]** Olefins are epoxidized using an epoxidation catalyst to produce a terminally epoxidized macromer. Epoxidation of the present olefin materials

can be affected using a peracid, such as performic acid, perbenzoic acid or m-chloroperbenzoic acid, as the oxidizing agent. The oxidation reaction can be performed using a preformed peracid to affect the epoxidation, or the peracid can be generated in-situ, for example by the addition of formic acid and hydrogen peroxide to produce performic acid. Formic acid can be added in a molar ratio to the olefin double bonds of from 10:1 to 30:1. Hydrogen peroxide can be added to the reaction mixture in a molar ratio to the olefin double bonds of from 1.01:1 to 5:1. Addition of both formic acid and H<sub>2</sub>O<sub>2</sub> to the reaction mixture results in the in situ formation of performic acid as an epoxidizing agent. Typically, the epoxidation is conducted at a temperature ranging from 25°C to 100°C, preferably from 30°C to 70°C. Suitable reaction times will generally range from 0.1 hour to 36 hours, such as from 1 hour to 24 hours. Epoxidation reactions can provide conversion from 50 to 100% of the double bonds into oxirane groups.

**[0058]** The epoxidation reaction is generally carried out in a liquid reaction medium. The reaction medium can comprise only the reactants essentially utilized in the process. More conventionally, however, the liquid reaction medium will comprise a suitable reaction solvent in which the reactants and catalyst materials can be dissolved, suspended or dispersed. Suitable reaction solvents include organic liquids which are inert in the reaction mixture. By “inert” is meant that the solvent does not deleteriously affect the oxidation reaction. Suitable inert organic solvents include aromatic hydrocarbons such as benzene, toluene, xylenes, benzonitrile, nitrobenzene, anisole, and phenyl nonane; saturated aliphatic hydrocarbons having from 5 to 20 carbons, such as pentane, hexane, and heptane; adiponitrile; halogenated hydrocarbons such as methylene chloride, 1,2-dichloroethane, chloroform, carbon tetrachloride and the like; non-fluorinated, substituted saturated aliphatic and/or aromatic hydrocarbons having from 1 to 20 carbons, including those selected from the group consisting of alcohols such as methanol, propanol, butanol, isopropanol,

and 2,4-di-*t*-butylphenol; ketones such as acetone; carboxylic acids such as propanoic acid and acetic acid; esters such as ethyl acetate, ethyl benzoate, dimethyl succinate, butyl acetate, tri-*n*-butyl phosphate, and dimethyl phthalate; ethers, such as tetraglyme; and mixtures thereof.

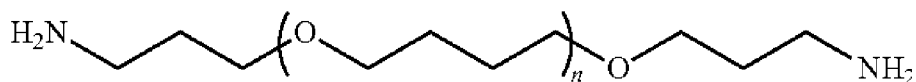
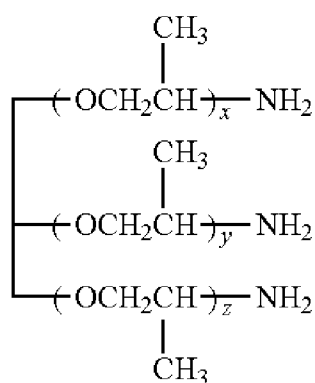
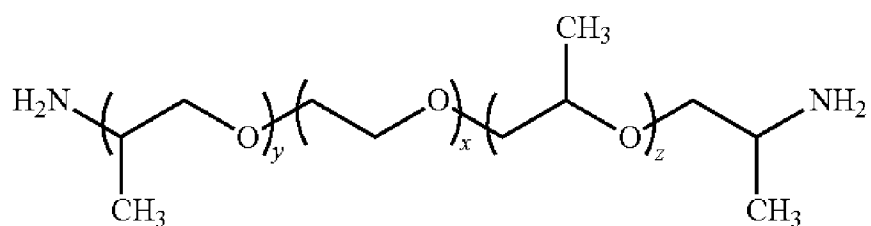
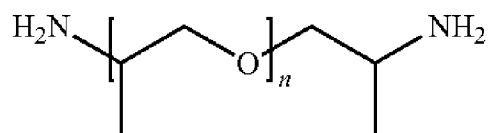
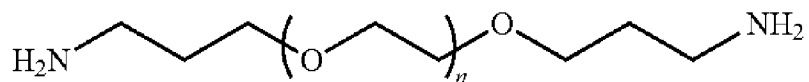
**[0059]** One type of epoxidation of olefins involves reaction of the material with a peracid, such as performic acid or *m*-chloroperbenzoic acid, to provide an epoxidized material having oxirane rings formed at the sites of the residual double bonds within the molecule. Catalytic epoxidation alternatives using hydrogen peroxide as an oxidizing agent instead of peracids can be used to epoxidize some unsaturated materials. Catalysts based on the use of high valent (d0), mostly Ti, V, Mo, W, and Re, metal complexes are known to promote alkene epoxidation with H<sub>2</sub>O<sub>2</sub>. Some notable effective epoxidation catalysts for use with hydrogen peroxide include titanium silicates, peroxophosphotungstates, manganese triazocyclononane, and methylrhenium trioxide.

**[0060]** A poly- $\alpha$ -olefin-polyalkyleneglycol (PAO-PAG) type fluid can be synthesized from a reaction of an alkyl epoxide (C<sub>20</sub>-epoxy) with a polyether amine. Polyether amines, such as the Jeffamine® polyetheramines, can be reacted with an epoxide terminated hydrocarbon molecule (PAO-epoxide or C<sub>20</sub>-epoxy) to obtain a low molecular weight synthetic fluid that can be used as synthetic base stock.

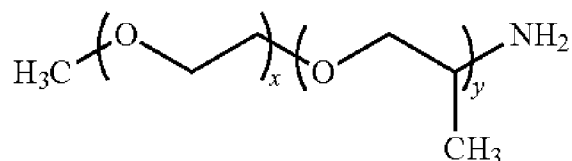
**[0061]** The Jeffamine® polyetheramines can be amine-terminated polyethers. The reaction of amine-terminated polyethers and epoxides can be carried out neat or in solvents like THF, MEK or ethanol. The temperature of the reaction can be 25°C to 60°C or higher. The reaction time can be a few hours to few days.

**[0062]** The Jeffamine® polyetheramines can be amine-terminated polyethers such as polyethylene oxide (PEO), polypropylene oxide (PPO) or combination of PEO/PPO copolymers. For example, some of the commercial polyethers include: poly(ethyleneglycol) bis(3-aminopropylether) (34901-14-9, mw 1500), poly(propyleneglycol) bis(2-aminopropylether) (mw 230), poly(propyleneglycol) bis(2-aminopropylether) (mw 400), poly(propyleneglycol) bis(2-aminopropylether) (9046-10-0, mw 2000), poly(propyleneglycol) bis(2-aminopropylether) (mw 4000), poly(propyleneglycol)-block-poly(ethyleneglycol)-block poly(propyleneglycol) bis(2-aminopropylether) (65605-36-9) (3.5:8.5) (PO:EO) (mw 600), poly(propyleneglycol)-block-poly(ethyleneglycol)-block poly(propyleneglycol) bis(2-aminopropylether) (3.5:15.5) (PO:EO) (mw 900), poly(propyleneglycol)-block-poly(ethyleneglycol)-block poly(propyleneglycol) bis(2-aminopropylether) (3.5:40.5) (PO:EO) (mw 2000), glycerol tris[poly(propylene glycol), amine terminated] ether (64852-22-8, mw 3000 or mw 440), poly(tetrahydrofuran), bis(3-aminopropyl) terminated (72088-96-1), and the like.

**[0063]** The chemical structures of examples of amine-terminated polyethers are shown below:

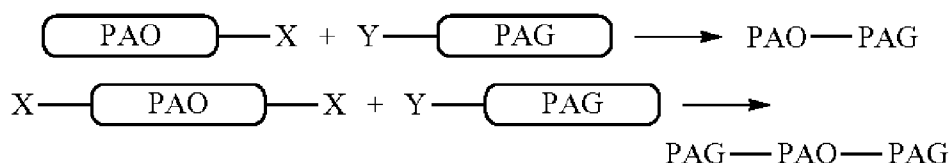


**[0064]** Jeffamine® polyetheramines can be monoamines that are prepared by reaction of a monohydric alcohol initiator with ethylene and/or propylene oxide, followed by conversion of the resulting terminal hydroxyl group to an amine. These products are produced by Huntsman as Jeffamine® monoamines (M series).



**[0065]** The molecular weights of the product can be 600, 1000, etc.

**[0066]** In this case, the sequence is the reaction of an alkyl epoxide or alkyl diepoxide with monoamine polyether to obtain a PAO-PAG fluid.



**[0067]** The reaction of amine-terminated polyethers and epoxides can be carried out neat or in solvents like THF, MEK or ethanol. The temperature of the reaction can be 25°C to 60°C or higher. The reaction time can be a few hours to few days.

**[0068]** The chemically coupled macromolecules of the present disclosure is useful as a lubricant base stock or a functional fluid and preferably has a 100°C kinematic viscosity of 1.5 cSt to 3000 cSt according to the ASTM D445 method. The copolymer has a 40°C kinematic viscosity of 3 to 15000 cSt. Preferred polymers exhibit a high viscosity index (VI). The VI typically ranges from 70 to 300 depending on viscosity, amount of hydrocarbon segment units, amount of alkylene oxide units, type of hydrocarbon segment or alkylene oxide units, method of synthesis, chemical compositions, and the like. Pour points are generally below -5°C even in the case of the higher molecular weight oligomers with viscosities (100°C) of 20 cSt or higher. Pour points (ASTM D97 or equivalent) generally range between -20 and -55°C and usually below -25°C.

Product viscosity may vary in view of factors such as polymerization conditions reaction temperature and reaction time. The lubricant fraction of the product will typically be a material having a viscosity between 4 cSt to 3000 cSt (at 100°C), but lower viscosity products between 1.5 cSt to 40 cSt (at 100°C) may also be obtained for use in lubricants in which a low viscosity base stock is desired.

**[0069]** The molecular weight of the polymer typically ranges from 200 to 20,000, typically from 300 to 10,000, and most typically from 350 to 7,500. Higher molecular weights and corresponding viscosities may be achieved by suitable choice of starting hydrocarbon segment, polyether segment and number of functional groups and reaction conditions. Values of the polydispersity index (PDI) are typically from 1.5 to 3.0, but can range from 1.01 to 6.

**[0070]** The polymer can take the form of a block copolymer or multi-blocks or dendritic or star type or combination of those. The polymer optionally may contain minor amounts of unreacted hydrocarbon segment or polyether segment as long as a homogeneous mixture can be obtained.

**[0071]** For automotive engine lubricant formulations, it is generally preferred to have lower viscosity fluids, e.g., below 10 cSt at 100°C. Lower viscosity is known to impart lower viscous drag thus offering better energy efficiency or fuel economy. Both low viscosity and high viscosity fluids are useful in industrial lubricant formulations to yield different ISO vis grad lubricants. For industrial lubricant formulations, it is generally important to use fluids of high VI and high hydrolytic stability.

**[0072]** For both engine and industrial lubricant application, it is important to have a lubricant formulation with a low friction coefficient. Generally fluids with low friction coefficients exhibit low frictional loss during lubrication and

fluids with high friction coefficients exhibit high frictional loss during lubrication. Low frictional loss is critical for improved energy or fuel efficiency of formulated lubricants.

**[0073]** Friction coefficients can be measured by a High Frequency Reciprocating Rig (HFRR) test. The test equipment and procedure are similar to the ASTM D6079 method except the test oil temperature is raised from 32°C to 195°C at 2°C/minute, 400 g load, 60 Hz frequency. The test can measure average friction coefficient and wear volume.

**[0074]** The PAO-PAG copolymers may take any form of block copolymer, such as diblock, repeating block, and the like.

**[0075]** Other teachings to useful PAO and PAG fluids and processes for making are disclosed in Synthetics, Mineral Oils, and Bio-Based Lubricants, Chemistry and Technology, by L. R. Rudnick, CRC Press, ©2006.

**[0076]** PAO-PAG fluids formed by combining a PAO type structure with a PAG structure maintain the benefits of both PAO (good VI, PP, and miscibility) and PAG (low friction coefficient) fluids. The fluids are very good lubricant base stocks. The fluids are soluble in hydrocarbon fluids. Thus, these fluids can be used along with other base stocks, such as poly- $\alpha$ -olefins, Group III+ type fluids (Visom, GTL, etc) and Group I-III base stocks.

#### Lubricant Compositions

**[0077]** The PAO-PAG block copolymer component useful in this disclosure may be included in an engine oil formulation to yield improved oxidative stability, wear resistance properties and frictional properties. In one form of the present disclosure, a lubricant composition for use in engine oil applications includes: i) a first base stock selected from a Group I base stock, a Group II base

stock and a combination thereof at 50 to 80 wt % of the lubricant composition, and ii) a block copolymer at 1 to 10 wt % of the lubricant composition, including: an “A” block of a functionalized hydrocarbon moiety including one or more functional end groups derived from: epoxides, amines, acids, acid chlorides, acid anhydrides, halogens, vinyl or vinylidene double bonds, aromatic rings or thiols; and a “B” block of a functionalized polyether moiety including one or more functional end groups derived from: epoxides, amines, acids, acid chlorides, acid anhydrides, halogens, vinyl or vinylidene double bonds, aromatic rings or thiols, wherein the end group of the polyether moiety is different than the end group of the hydrocarbon moiety, wherein the hydrocarbon moiety and the polyether moiety are copolymerizable therewith. Alternatively, the first base stock may be included at 55 to 75 wt %, or GO to 70 wt % of the lubricant formulation. In one advantageous form, the first base stock is included at 73 wt % of the lubricant composition and comprises 53 wt % of a Group I oil and 20 wt % of a Group II oil.

**[0078]** Alternatively, the block copolymer fluid may be included at 1 to 8 wt %, or 3 to 6 wt % of the lubricant composition. In one particularly advantageous form, the block copolymer fluid has a hydrocarbon moiety of a poly- $\alpha$ -olefin and a polyether moiety of a polyalkylene glycol and is included in the lubricant composition at 3 wt %.

#### Other Additives

**[0079]** The formulated lubricating oil useful in the present disclosure may additionally contain one or more of the other commonly used lubricating oil performance additives including but not limited to dispersants, other detergents, corrosion inhibitors, rust inhibitors, metal deactivators, other anti-wear agents and/or extreme pressure additives, anti-seizure agents, wax modifiers, viscosity index improvers, viscosity modifiers, fluid-loss additives, seal compatibility

agents, other friction modifiers, lubricity agents, anti-staining agents, chromophoric agents, defoamants, demulsifiers, emulsifiers, densifiers, wetting agents, gelling agents, tackiness agents, colorants, and others. For a review of many commonly used additives, see Klamann in *Lubricants and Related Products*, Verlag Chemie, Deerfield Beach, FL; ISBN 0-89573-177-0. Reference is also made to "Lubricant Additives" by M. W. Ranney, published by Noyes Data Corporation of Parkridge, NJ (1973).

**[0080]** The types and quantities of performance additives used in combination with the instant disclosure in lubricant compositions are not limited by the examples shown herein as illustrations.

#### Viscosity Modifiers/Improvers

**[0081]** The lubricant compositions disclosed herein may also include one or more viscosity modifiers/viscosity improvers as part of the lubricant composition. Viscosity modifiers (also known as Viscosity Index modifiers, VI modifiers, Viscosity index improvers, and VI improvers) increase the viscosity of the oil composition at elevated temperatures which increases film thickness, while having limited effect on viscosity at low temperatures.

**[0082]** Suitable viscosity improvers include high molecular weight hydrocarbons, polyesters and viscosity index improver dispersants that function as both a viscosity index improver and a dispersant. Typical molecular weights of these polymers are between 10,000 to 1,000,000, more typically 20,000 to 500,000, and even more typically between 50,000 and 200,000.

**[0083]** Examples of suitable viscosity improvers are polymers and copolymers of methacrylate, butadiene, olefins, or alkylated styrenes. Polyisobutylene is a commonly used viscosity index improver. Another suitable viscosity index improver is polymethacrylate (copolymers of various chain

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

**[0084]** The amount of viscosity modifier may range from zero to 25 wt %, or 0.2 to 20 wt %, or advantageously 3 to 15 wt %, or more advantageously 5 to 13 wt %, or still more advantageously 6 to 10 wt %, based on active ingredient and depending on the specific viscosity modifier used. In one particularly advantageous form, the viscosity modifier is an olefin copolymer viscosity modifier at 3 to 15 wt %, or 5 to 13 wt %, or 6 to 10 wt % of the lubricant composition. In one particularly advantageous form, the lubricant compositions disclosed herein include 6 to 7 wt % of an olefin copolymer viscosity modifier.

#### Additive Package

**[0085]** The lubricant compositions disclosed herein may also include an additive package including a combination of antioxidants, dispersants, detergents and antiwear agents. Further details on these additives are included below. The additive package may be included in the lubricant compositions at from 2 to 30 wt. %, 10 to 25 wt %, or 13 to 23 wt %, or 15 to 20 wt % of the lubricant composition. In one particularly advantageous form, the additive package is included at 17 wt% of the lubricant composition. One non-limiting exemplary additive package that includes the above combination of additives is supplied by Infineum and is designated Infineum D3426.

### Second Base Stock

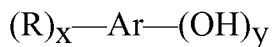
**[0086]** In addition to the first base stock and the PAO-PAG block copolymer component, the lubricant compositions disclosed herein may include a second base stock selected from a metallocene poly- $\alpha$ -olefin, a poly- $\alpha$ -olefin, a GTL base stock, and a Group III base stock. The second base stock may be included in the lubricant composition at from 5 to 45 wt %, or 10 to 40 wt %, or 15 to 35 wt %, or 20 to 30 wt %.

### Antioxidants

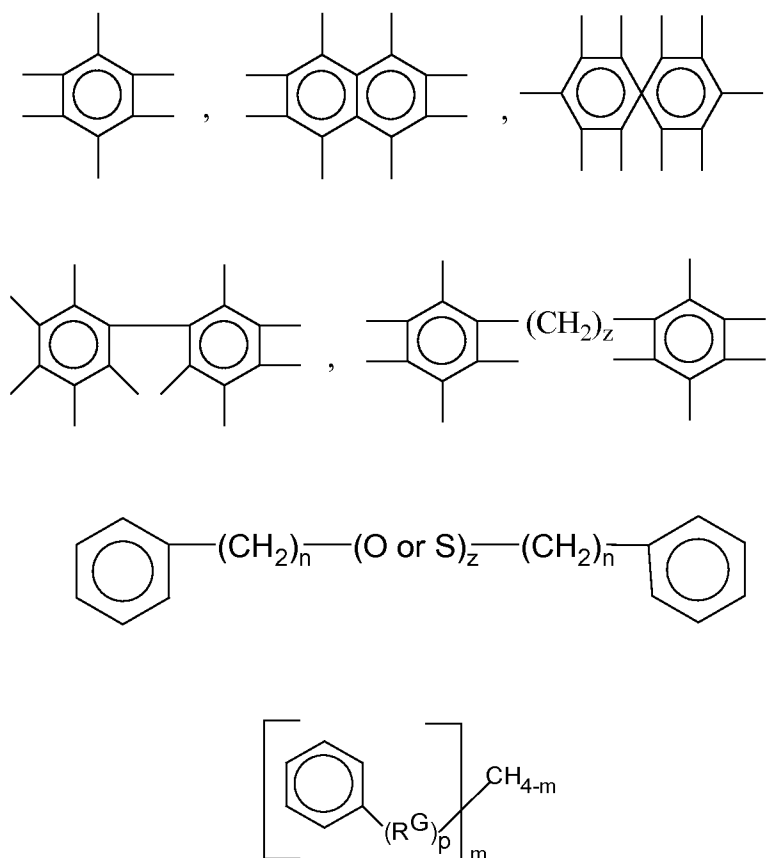
**[0087]** Typical antioxidant include phenolic antioxidants, aminic antioxidants and oil-soluble copper complexes.

**[0088]** The phenolic antioxidants include sulfurized and non-sulfurized phenolic antioxidants. The terms “phenolic type” or “phenolic antioxidant” used herein includes compounds having one or more than one hydroxyl group bound to an aromatic ring which may itself be mononuclear, e.g., benzyl, or polynuclear, e.g., naphthyl and spiro aromatic compounds. Thus “phenol type” includes phenol per se, catechol, resorcinol, hydroquinone, naphthol, etc., as well as alkyl or alkenyl and sulfurized alkyl or alkenyl derivatives thereof, and bisphenol type compounds including such bi-phenol compounds linked by alkylene bridges sulfuric bridges or oxygen bridges. Alkyl phenols include mono- and poly-alkyl or alkenyl phenols, the alkyl or alkenyl group containing from 3-100 carbons, preferably 4 to 50 carbons and sulfurized derivatives thereof, the number of alkyl or alkenyl groups present in the aromatic ring ranging from 1 to up to the available unsatisfied valences of the aromatic ring remaining after counting the number of hydroxyl groups bound to the aromatic ring.

**[0089]** Generally, therefore, the phenolic anti-oxidant may be represented by the general formula:



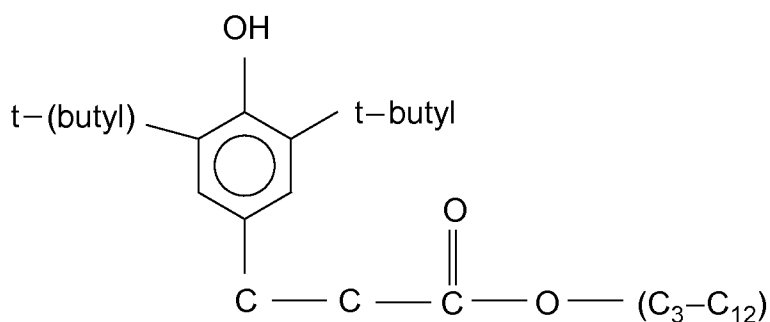
where Ar is selected from the group consisting of:



wherein R is a  $C_3$ - $C_{100}$  alkyl or alkenyl group, a sulfur substituted alkyl or alkenyl group, preferably a  $C_4$ - $C_{50}$  alkyl or alkenyl group or sulfur substituted alkyl or alkenyl group, more preferably  $C_3$ - $C_{100}$  alkyl or sulfur substituted alkyl group, most preferably a  $C_4$ - $C_{50}$  alkyl group,  $R^g$  is a  $C_1$ - $C_{100}$  alkylene or sulfur substituted alkylene group, preferably a  $C_2$ - $C_{50}$  alkylene or sulfur substituted alkylene group, more preferably a  $C_2$ - $C_2$  alkylene or sulfur substituted alkylene group, y is at least 1 to up to the available valences of Ar, x ranges from 0 to up

to the available valences of Ar-y, z ranges from 1 to 10, n ranges from 0 to 20, and m is 0 to 4 and p is 0 or 1, preferably y ranges from 1 to 3, x ranges from 0 to 3, z ranges from 1 to 4 and n ranges from 0 to 5, and p is 0.

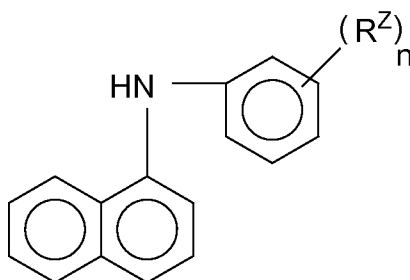
**[0090]** Preferred phenolic anti-oxidant compounds are the hindered phenolics and phenolic esters which contain a sterically hindered hydroxyl group, and these include those derivatives of dihydroxy aryl compounds in which the hydroxyl groups are in the o- or p-position to each other. Typical phenolic anti-oxidants include the hindered phenols substituted with C<sub>1</sub>+ alkyl groups and the alkylene coupled derivatives of these hindered phenols. Examples of phenolic materials of this type 2-t-butyl-4-heptyl phenol; 2-t-butyl-4-octyl phenol; 2-t-butyl-4-dodecyl phenol; 2,6-di-t-butyl-4-heptyl phenol; 2,6-di-t-butyl-4-dodecyl phenol; 2-methyl-6-t-butyl-4-heptyl phenol; 2-methyl-6-t-butyl-4-dodecyl phenol; 2,6-di-t-butyl-4 methyl phenol; 2,6-di-t-butyl-4-ethyl phenol; and 2,6-di-t-butyl 4 alkoxy phenol; and



**[0091]** Phenolic type antioxidants are well known in the lubricating industry and commercial examples such as Ethanox® 4710, Irganox® 1076, Irganox® L1035, Irganox® 1010, Irganox® L109, Irganox® L118, Irganox® L135 and the like are familiar to those skilled in the art. The above is presented only by way of exemplification, not limitation on the type of phenolic antioxidants which can be used.

**[0092]** The phenolic antioxidant can be employed in an amount in the range of 0.1 to 3 wt%, preferably 0.25 to 2.5 wt%, more preferably 0.5 to 2 wt% on an active ingredient basis.

**[0093]** Aromatic amine anti-oxidants include phenyl- $\alpha$ -naphthyl amine which is described by the following molecular structure:



wherein  $R^Z$  is hydrogen or a  $C_1$  to  $C_{14}$  linear or  $C_3$  to  $C_{14}$  branched alkyl group, preferably  $C_1$  to  $C_{10}$  linear or  $C_3$  to  $C_{10}$  branched alkyl group, more preferably linear or branched  $C_6$  to  $C_8$  and  $n$  is an integer ranging from 1 to 5 preferably 1. A particular example is Irganox L06.

**[0094]** Other aromatic amine anti-oxidants include other alkylated and non-alkylated aromatic amines such as aromatic monoamines of the formula  $R^8R^9R^{10}N$  where  $R^8$  is an aliphatic, aromatic or substituted aromatic group,  $R^9$  is an aromatic or a substituted aromatic group, and  $R^{10}$  is H, alkyl, aryl or  $R^{11}S(O)_xR^{12}$  where  $R^{11}$  is an alkylene, alkenylene, or aralkylene group,  $R^{12}$  is a higher alkyl group, or an alkenyl, aryl, or alkaryl group, and  $x$  is 0, 1 or 2. The aliphatic group  $R^8$  may contain from 1 to 20 carbon atoms, and preferably contains from 6 to 12 carbon atoms. The aliphatic group is a saturated aliphatic group. Preferably, both  $R^8$  and  $R^9$  are aromatic or substituted aromatic groups, and the aromatic group may be a fused ring aromatic group such as naphthyl. Aromatic groups  $R^8$  and  $R^9$  may be joined together with other groups such as S.

**[0095]** Typical aromatic amines antioxidants have alkyl substituent groups of at least 6 carbon atoms. Examples of aliphatic groups include hexyl, heptyl, octyl, nonyl, and decyl. Generally, the aliphatic groups will not contain more than 14 carbon atoms. The general types of such other additional amine anti-oxidants which may be present include diphenylamines, phenothiazines, imidodibenzyls and diphenyl phenylene diamines. Mixtures of two or more of such other additional aromatic amines may also be present. Polymeric amine antioxidants can also be used.

**[0096]** Another class of antioxidant used in lubricating oil compositions and which may also be present are oil-soluble copper compounds. Any oil-soluble suitable copper compound may be blended into the lubricating oil. Examples of suitable copper antioxidants include copper dihydrocarbyl thio- or dithio-phosphates and copper salts of carboxylic acid (naturally occurring or synthetic). Other suitable copper salts include copper dithiacarbamates, sulphonates, phenates, and acetylacetonates. Basic, neutral, or acidic copper Cu(I) and or Cu(II) salts derived from alkenyl succinic acids or anhydrides are known to be particularly useful.

**[0097]** Such antioxidants may be used individually or as mixtures of one or more types of antioxidants, the total amount employed being an amount of 0.20 to 6 wt %, or 0.50 to 5 wt %, or 0.75 to 3 wt % (on an as-received basis). Mixed ashless antioxidants are often preferred, including those chosen from aminic antioxidants and hindered phenolic antioxidants.

#### Detergents

**[0098]** In addition to the alkali or alkaline earth metal salicylate detergent which is an optional component in the present disclosure, other detergents may also be present. While such other detergents can be present, it is preferred that

the amount employed be such as to not interfere with the synergistic effect attributable to the presence of the salicylate. Therefore, most preferably such other detergents are not employed.

**[0099]** If such additional detergents are present, they can include alkali and alkaline earth metal phenates, sulfonates, carboxylates, phosphonates and mixtures thereof. These supplemental detergents can have total base number (TBN) ranging from neutral to highly overbased, i.e. TBN of 0 to over 500, preferably 2 to 400, more preferably 5 to 300, and they can be present either individually or in combination with each other in an amount in the range of from 0 to 10 wt%, preferably 0.5 to 5 wt% (active ingredient) based on the total weight of the formulated lubricating oil. Furthermore, mixtures of neutral detergents and overbased detergents may be useful.

**[00100]** Such additional other detergents include by way of example and not limitation calcium phenates, calcium sulfonates, magnesium phenates, magnesium sulfonates and other related components (including borated detergents).

**[00101]** Another optional component of the present lubricant compositions is one or more neutral/low TBN or mixture of neutral/low TBN and overbased/high TBN alkali or alkaline earth metal alkylsalicylate, sulfonate and/or phenate detergent preferably neutral/low TBN alkali or alkaline earth metal salicylate and at least one overbased/high TBN alkali or alkalene earth metal salicylate or phenate, and optionally one or more additional neutral and/or overbased alkali or alkaline earth metal alkyl sulfonate, alkyl phenolate or alkylsalicylate detergent, the detergent or detergent mixture being employed in the lubricant composition in an amount sufficient to achieve a sulfated ash content for the finished lubricant of 0.1 mass % to 2.0 mass %, preferably 0.1 to

1.5 mass %, more preferably 0.1 to 1.0 mass %, most preferably 0.1 to 0.7 mass %.

**[00102]** The TBN of the neutral/low TBN alkali or alkaline earth metal alkyl salicylate, alkyl phenate or alkyl sulfonate is 150 or less mg KOH/g of detergent, preferably 120 or less mg KOH/g, most preferably 100 or less mg KOH/g while the TBN of the overbased/high TBN alkali or alkaline earth metal alkyl salicylate, alkyl phenate or alkyl sultanate is 160 or more mg KOH/g, preferably 190 or more mg KOH/g, most preferably 250 or more mg KOH/g, TBN being measured by ASTM D-2896.

**[00103]** The mixture of detergents may be added to the lubricant composition in an amount up to 10 vol % based on active ingredient in the detergent mixture, preferably in an amount up to 8 vol % based on active ingredient, more preferably up to 6 vol % based on active ingredient in the detergent mixture, most preferably between 1.5 to 5.0 vol %, based on active ingredient in the detergent mixture.

**[00104]** By active ingredient is meant the amount of additive actually constituting the name detergent or detergent mixture chemicals in the formulation as received from the additive supplier, less any diluent oil included in the material. Additives are typically supplied by the manufacturer dissolved, suspended in or mixed with diluent oil, usually a light oil, in order to provide the additive in the more convenient liquid form. The active ingredient in the mixture is the amount of actual desired chemical in the material less the diluent oil.

#### Dispersants

**[00105]** During engine operation, oil-insoluble oxidation byproducts are produced. Dispersants help keep these byproducts in solution, thus diminishing

their deposition on metal surfaces. Dispersants may be ashless or ash-forming in nature. Preferably, the dispersant is ashless. So called ashless dispersants are organic materials that form substantially no ash upon combustion. For example, non-metal-containing or borated metal-free dispersants are considered ashless. In contrast, metal-containing detergents discussed above form ash upon combustion.

**[00106]** Suitable dispersants typically contain a polar group attached to a relatively high molecular weight hydrocarbon chain. The polar group typically contains at least one element of nitrogen, oxygen, or phosphorus. Typical hydrocarbon chains contain 50 to 400 carbon atoms.

**[00107]** A particularly useful class of dispersants are the alkenylsuccinic derivatives, typically produced by the reaction of a long chain substituted alkenyl succinic compound, usually a substituted succinic anhydride, with a polyhydroxy or polyamino compound. The long chain group constituting the oleophilic portion of the molecule which confers solubility in the oil, is normally a polyisobutylene group. Many examples of this type of dispersant are well known commercially and in the literature. Exemplary U.S. patents describing such dispersants are U.S. Patent Nos. 3,172,892; 3,215,707; 3,219,666; 3,316,177; 3,341,542; 3,444,170; 3,454,607; 3,541,012; 3,630,904; 3,632,511; 3,787,374 and 4,234,435. Other types of dispersant are described in U.S. Patent Nos. 3,036,003; 3,200,107; 3,254,025; 3,275,554; 3,438,757; 3,454,555; 3,565,804; 3,413,347; 3,697,574; 3,725,277; 3,725,480; 3,726,882; 4,454,059; 3,329,658; 3,449,250; 3,519,565; 3,666,730; 3,687,849; 3,702,300; 4,100,082; 5,705,458. A further description of dispersants may be found, for example, in European Patent Application No. 471 071, to which reference is made for this purpose.

**[00108]** Hydrocarbyl-substituted succinic acid compounds are popular dispersants. In particular, succinimide, succinate esters, or succinate ester amides prepared by the reaction of a hydrocarbon-substituted succinic acid compound preferably having at least 50 carbon atoms in the hydrocarbon substituent, with at least one equivalent of an alkylene amine are particularly useful.

**[00109]** Succinimides are formed by the condensation reaction between alkenyl succinic anhydrides and amines. Molar ratios can vary depending on the amine or polyamine. For example, the molar ratio of alkenyl succinic anhydride to TEPA can vary from 1:1 to 5:1.

**[00110]** Succinate esters are formed by the condensation reaction between alkenyl succinic anhydrides and alcohols or polyols. Molar ratios can vary depending on the alcohol or polyol used. For example, the condensation product of an alkenyl succinic anhydride and pentaerythritol is a useful dispersant.

**[00111]** Succinate ester amides are formed by condensation reaction between alkenyl succinic anhydrides and alkanol amines. For example, suitable alkanol amines include ethoxylated polyalkylpolyamines, propoxylated polyalkylpolyamines and polyalkenylpolyamines such as polyethylene polyamines. One example is propoxylated hexamethylenediamine.

**[00112]** The molecular weight of the alkenyl succinic anhydrides will typically range between 800 and 2,500. The above products can be post-reacted with various reagents such as sulfur, oxygen, formaldehyde, carboxylic acids such as oleic acid, and boron compounds such as borate esters or highly borated dispersants. The dispersants can be borated with from 0.1 to 5 moles of boron per mole of dispersant reaction product.

**[00113]** Mannich base dispersants are made from the reaction of alkylphenols, formaldehyde, and amines. Process aids and catalysts, such as oleic acid and sulfonic acids, can also be part of the reaction mixture. Molecular weights of the alkylphenols range from 800 to 2,500 or more.

**[00114]** Typical high molecular weight aliphatic acid modified Mannich condensation products can be prepared from high molecular weight alkyl-substituted hydroxyaromatics or  $\text{HN(R)}_2$  group-containing reactants.

**[00115]** Examples of high molecular weight alkyl-substituted hydroxyaromatic compounds are polypropylphenol, polybutylphenol, and other polyalkylphenols. These polyalkylphenols can be obtained by the alkylation, in the presence of an alkylating catalyst, such as  $\text{BF}_3$ , of phenol with high molecular weight polypropylene, polybutylene, and other polyalkylene compounds to give alkyl substituents on the benzene ring of phenol having an average 600-100,000 molecular weight.

**[00116]** Examples of  $\text{HN(R)}_2$  group-containing reactants are alkylene polyamines, principally polyethylene polyamines. Other representative organic compounds containing at least one  $\text{HN(R)}_2$  group suitable for use in the preparation of Mannich condensation products are well known and include the mono- and di-amino alkanes and their substituted analogs, e.g., ethylamine and diethanol amine; aromatic diamines, e.g., phenylene diamine, diamino naphthalenes; heterocyclic amines, e.g., morpholine, pyrrole, pyrrolidine, imidazole, imidazolidine, and piperidine; melamine and their substituted analogs.

**[00117]** Examples of alkylene polyamine reactants include ethylenediamine, diethylene triamine, triethylene tetraamine, tetraethylene pentaamine, pentaethylene hexamine, hexaethylene heptaamine, heptaethylene octaamine,

octaethylene nonaamine, nonaethylene decamine, and decaethylene undecamine and mixture of such amines having nitrogen contents corresponding to the alkylene polyamines, in the formula  $H_2N-(Z-NH-)_nH$ , mentioned before, Z is a divalent ethylene and n is 1 to 10 of the foregoing formula. Corresponding propylene polyamines such as propylene diamine and di-, tri-, tetra-, pentapropylene tri-, tetra-, penta- and hexaamines are also suitable reactants. The alkylene polyamines are usually obtained by the reaction of ammonia and dihalo alkanes, such as dichloro alkanes. Thus the alkylene polyamines obtained from the reaction of 2 to 11 moles of ammonia with 1 to 10 moles of dichloroalkanes having 2 to 6 carbon atoms and the chlorines on different carbons are suitable alkylene polyamine reactants.

**[00118]** Aldehyde reactants useful in the preparation of the high molecular products useful in this disclosure include the aliphatic aldehydes such as formaldehyde (also as paraformaldehyde and formalin), acetaldehyde and aldol (3-hydroxybutyraldehyde). Formaldehyde or a formaldehyde-yielding reactant is preferred.

**[00119]** Preferred dispersants include borated and non-borated succinimides, including those derivatives from mono-succinimides, bis-succinimides, and/or mixtures of mono- and bis-succinimides, wherein the hydrocarbyl succinimide is derived from a hydrocarbylene group such as polyisobutylene having a Mn of from 500 to 5000 or more or a mixture of such hydrocarbylene groups. Other preferred dispersants include succinic acid-esters and amides, alkylphenol-polyamine-coupled Mannich adducts, their capped derivatives, and other related components. Such additives may be used in an amount of 0.1 to 20 wt%, preferably 0.1 to 8 wt%, more preferably 1 to 6 wt% (on an as-received basis) based on the weight of the total lubricant.

### Pour Point Depressants

**[00120]** Conventional pour point depressants (also known as lube oil flow improvers) may also be present. Pour point depressant may be added to lower the minimum temperature at which the fluid will flow or can be poured. Examples of suitable pour point depressants include alkylated naphthalenes polymethacrylates, polyacrylates, polyarylamides, condensation products of haloparaffin waxes and aromatic compounds, vinyl carboxylate polymers, and terpolymers of dialkylfumarates, vinyl esters of fatty acids and allyl vinyl ethers. Such additives may be used in amount of 0.0 to 0.5 wt%, preferably 0 to 0.3 wt%, more preferably 0.001 to 0.1 wt% on an as-received basis.

### Corrosion Inhibitors/Metal Deactivators

**[00121]** Corrosion inhibitors are used to reduce the degradation of metallic parts that are in contact with the lubricating oil composition. Suitable corrosion inhibitors include aryl thiazines, alkyl substituted dimercapto thiodiazoles thiadiazoles and mixtures thereof. Such additives may be used in an amount of 0.01 to 5 wt%, preferably 0.01 to 1.5 wt%, more preferably 0.01 to 0.2 wt%, still more preferably 0.01 to 0.1 wt% (on an as-received basis) based on the total weight of the lubricating oil composition.

### Seal Compatibility Additives

**[00122]** Seal compatibility agents help to swell elastomeric seals by causing a chemical reaction in the fluid or physical change in the elastomer. Suitable seal compatibility agents for lubricating oils include organic phosphates, aromatic esters, aromatic hydrocarbons, esters (butylbenzyl phthalate, for example), and polybutenyl succinic anhydride and sulfolane-type seal swell agents such as Lubrizol 730-type seal swell additives. Such additives may be used in an amount of 0.01 to 3 wt%, preferably 0.01 to 2 wt% on an as-received basis.

### Anti-Foam Agents

**[00123]** Anti-foam agents may advantageously be added to lubricant compositions. These agents retard the formation of stable foams. Silicones and organic polymers are typical anti-foam agents. For example, polysiloxanes, such as silicon oil or polydimethyl siloxane, provide antifoam properties. Anti-foam agents are commercially available and may be used in conventional minor amounts along with other additives such as demulsifiers; usually the amount of these additives combined is less than 1 percent, preferably 0.001 to 0.5 wt%, more preferably 0.001 to 0.2 wt%, still more preferably 0.0001 to 0.15 wt% (on an as-received basis) based on the total weight of the lubricating oil composition.

### Inhibitors and Antirust Additives

**[00124]** Anti-rust additives (or corrosion inhibitors) are additives that protect lubricated metal surfaces against chemical attack by water or other contaminants. One type of anti-rust additive is a polar compound that wets the metal surface preferentially, protecting it with a film of oil. Another type of anti-rust additive absorbs water by incorporating it in a water-in-oil emulsion so that only the oil touches the surface. Yet another type of anti-rust additive chemically adheres to the metal to produce a non-reactive surface. Examples of suitable additives include zinc dithiophosphates, metal phenolates, basic metal sulfonates, fatty acids and amines. Such additives may be used in an amount of 0.01 to 5 wt%, preferably 0.01 to 1.5 wt% on an as-received basis.

### Antiwear Agents

**[00125]** Antiwear agents or additives may also be included in the present disclosure. Non-limiting exemplary antiwear agents include ZDDP, zinc dithiocarbamates, molybdenum dialkyldithiophosphates, molybdenum

dithiocarbamates, other organo molybdenum-nitrogen complexes, sulfurized olefins, etc.

**[00126]** A metal alkylthiophosphate and more particularly a metal dialkyl dithio phosphate in which the metal constituent is zinc, or zinc dialkyl dithio phosphate (ZDDP) may be present in the lubricating oils of the present disclosure. ZDDP can be primary, secondary or mixtures thereof. ZDDP compounds generally are of the formula  $\text{Zn}[\text{SP}(\text{S})(\text{OR}^1)(\text{OR}^1)(\text{OR}^2)]_2$  where  $\text{R}^1$  and  $\text{R}^2$  are  $\text{C}_1\text{-C}_{18}$  alkyl groups, preferably  $\text{C}_2\text{-C}_{12}$  alkyl groups. These alkyl groups may be straight chain or branched and can be derived from primary alcohols, secondary alcohols and mixtures thereof.

**[00127]** Preferable zinc dithiophosphates which are commercially available include secondary zinc dithiophosphates such as those available from for example, the Lubrizol Corporation under the trade designations “LZ 677A”, “LZ 1095” and “LZ 1371”, from for example Chevron Oronite under the trade designation “OLOA 262” and from, for example, Afton Chemical under the trade designation “HITEC 7169”.

**[00128]** The ZDDP is typically used in amounts of from 0.4 wt % to 1.2 wt %, preferably from 0.5 wt % to 1.0 wt %, and more preferably from 0.6 wt % to 0.8 wt %, based on the total weight of the lubricating oil, although more or less can often be used advantageously. Preferably, the ZDDP is a secondary ZDDP and present in an amount of from 0.6 to 1.0 wt % of the total weight of the lubricating oil.

**[00129]** The term “organo molybdenum-nitrogen complexes” embraces the organo molybdenum-nitrogen complexes described in U.S. Patent 4,889,647. The complexes are reaction products of a fatty oil, dithanolamine and a molybdenum source. Specific chemical structures have not been assigned to the

complexes. U.S. Patent 4,889,647 reports an infrared spectrum for a typical reaction product of that disclosure; the spectrum identifies an ester carbonyl band at  $1740\text{ cm}^{-1}$  and an amide carbonyl band at  $1620\text{ cm}^{-1}$ . The fatty oils are glyceryl esters of higher fatty acids containing at least 12 carbon atoms up to 22 carbon atoms or more. The molybdenum source is an oxygen-containing compound such as ammonium molybdates, molybdenum oxides and mixtures.

**[00130]** Other organo molybdenum complexes which can be used in the present disclosure are tri-nuclear molybdenum-sulfur compounds described in EP 1 040 115 and WO 99/31113 and the molybdenum complexes described in U.S. Patent No. 4,978,464.

#### Friction Modifiers

**[00131]** A friction modifier is any material or materials that can alter the coefficient of friction of a surface lubricated by any lubricant or fluid containing such material(s). Friction modifiers, also known as friction reducers, or lubricity agents or oiliness agents, and other such agents that change the ability of base oils, formulated lubricant compositions, or functional fluids, to modify the coefficient of friction of a lubricated surface may be effectively used in combination with the base oils or lubricant compositions of the present disclosure if desired. Friction modifiers that lower the coefficient of friction are particularly advantageous in combination with the base oils and lube compositions of this disclosure. Friction modifiers may include metal-containing compounds or materials as well as ashless compounds or materials, or mixtures thereof. Metal-containing friction modifiers may include metal salts or metalligand complexes where the metals may include alkali, alkaline earth, or transition group metals. Such metal-containing friction modifiers may also have low-ash characteristics. Transition metals may include Mo, Sb, Sn, Fe, Cu, Zn, and others. Ligands may include hydrocarbonyl derivative of alcohols, polyols,

glycerols, partial ester glycerols, thiols, carboxylates, carbamates, thiocarbamates, dithiocarbamates, phosphates, thiophosphates, dithiophosphates, amides, imides, amines, thiazoles, thiadiazoles, dithiazoles, diazoles, triazoles, and other polar molecular functional groups containing effective amounts of O, N, S, or P, individually or in combination. In particular, Mo-containing compounds can be particularly effective such as for example Mo-dithiocarbamates, Mo(DTC), Mo-dithiophosphates, Mo(DTP), Mo-amines, Mo (Am), Mo-alcoholates, Mo-alcohol-amides, etc. See U.S. Patent Nos. 5,824,627, 6,232,276, 6,153,564, 6,143,701, 6,110,878, 5,837,657, 6,010,987, 5,906,968, 6,734,150, 6,730,638, 6,689,725, 6,569,820; and also WO 99/66013; WO 99/47629; and WO 98/26030.

**[00132]** Ashless friction modifiers may also include lubricant materials that contain effective amounts of polar groups, for example, hydroxyl-containing hydrocarbyl base oils, glycerides, partial glycerides, glyceride derivatives, and the like. Polar groups in friction modifiers may include hydrocarbyl groups containing effective amounts of O, N, S, or P, individually or in combination. Other friction modifiers that may be particularly effective include, for example, salts (both ash-containing and ashless derivatives) of fatty acids, fatty alcohols, fatty amides, fatty esters, hydroxyl-containing carboxylates, and comparable synthetic long-chain hydrocarbyl acids, alcohols, amides, esters, hydroxy carboxylates, and the like. In some instances fatty organic acids, fatty amines, and sulfurized fatty acids may be used as suitable friction modifiers.

**[00133]** Useful concentrations of friction modifiers may range from 0.01 weight percent to 10-15 weight percent or more, often with a preferred range of 0.1 weight percent to 5 weight percent. Concentrations of molybdenum-containing materials are often described in terms of Mo metal concentration. Advantageous concentrations of Mo may range from 10 ppm to 3000 ppm or more, and often with a preferred range of 20-2000 ppm, and in some instances a

more preferred range of 30-1000 ppm. Friction modifiers of all types may be used alone or in mixtures with the materials of this disclosure. Often mixtures of two or more friction modifiers, or mixtures of friction modifier(s) with alternate surface active material(s), are also desirable.

Typical Amounts of Various Lubricant Oil Components

| Compound             | Approximate wt%<br>(useful) | Approximate wt%<br>(preferred) |
|----------------------|-----------------------------|--------------------------------|
| Friction Modifiers   | 0.01-15                     | 0.01-5                         |
| Antiwear Additives   | 0.01-6                      | 0.01-4                         |
| Detergents           | 0.01-8                      | 0.01-4                         |
| Dispersants          | 0.1-20                      | 0.1-8                          |
| Antioxidants         | 0.01-5                      | 0.01-1.5                       |
| Anti-foam Agents     | 0.001-1                     | 0.001-0.1                      |
| Corrosion Inhibitors | 0.01-5                      | 0.01-1.5                       |
| Co-basestocks        | 0-50                        | 0-40                           |
| Base Oils            | Balance                     | Balance                        |

Lubricant Composition Properties

**[00134]** The lubricant compositions including the PAO-PAG block copolymer fluid described above provide improved emulsion characteristics, and also improved oxidative stability (PDSC) and elastomer compatibility (ACEA) in engine oil lubrication applications. The use of these PAO-PAG block copolymers are desirable in engine oils in the presence of salicylate, sulfonate and phenate detergents, along with antioxidants and ashless antioxidants, along with succinimide based dispersants, along with zinc dialkyldithiophosphates, along with organic and metallic friction modifiers, along with corrosion inhibitors, along with defoamants and in the presence of Group I, Group II, Group III, Group IV and Group V base oils. The PAO-PAG block copolymer are useful in all engine oil applications, but are particularly useful in low

viscosity fluids with a kinematic viscosity at 100°C between 9 and 13 cSt, more preferred at a kinematic viscosity range at 100°C between 5 and 9, and even more preferential below 5 cSt at 100°C. Furthermore, the use of the PAO-PAG block copolymers are desirable in engine oils with low sulfated ash levels (measured by ASTM D874) of 1 wt% or less, more preferred at levels 0.8 wt% or less.

**[00135]** In terms of emulsion as measured by as measured by ASTM D7563, the ability of the engine lubricating oil of this disclosure contaminated with water and fuel to emulsify water contamination is improved as compared to the ability of an engine lubricating oil contaminated with water and fuel to emulsify water contamination using a lubricating oil containing a minor component other than the coupled block copolymer.

**[00136]** In terms of oxidative stability as measured by PDSC, thermo-oxidative stability is improved as compared to thermo-oxidative stability achieved using a lubricating oil containing a minor component other than the coupled block copolymer.

**[00137]** In terms of elastomer compatibility as measured by ACEA, elastomer compatibility is improved as compared elastomer compatibility achieved using a lubricating oil containing a minor component other than the coupled block copolymer.

**[00138]** In the above detailed description, the specific embodiments of this disclosure have been described in connection with its preferred embodiments. However, to the extent that the above description is specific to a particular embodiment or a particular use of this disclosure, this is intended to be illustrative only and merely provides a concise description of the exemplary embodiments. Accordingly, the disclosure is not limited to the specific

embodiments described above, but rather, the disclosure includes all alternatives, modifications, and equivalents falling within the true scope of the appended claims. Various modifications and variations of this disclosure will be obvious to a worker skilled in the art and it is to be understood that such modifications and variations are to be included within the purview of this application and the spirit and scope of the claims.

**[00139]** The following are examples of the present disclosure and are not to be construed as limiting.

### **EXAMPLES**

**[00140]** Lubricating oils were prepared for ASTM D7563 testing. Three baseline candidates using typical levels of engine oil additives were used and compared to samples top-treated (1-5 wt%) with commercial PAGs (“capped PAG”) and a synthesized derivative of PAG (“coupled PAG”). The samples are identified in the figures.

**[00141]** The samples were tested in accordance with ASTM D7563. ASTM D7563 measures the ability of an oil to emulsify water and E85 fuel. In the Examples, 10 vol% water and 10 vol% fuel were mixed into the lubricating oil sample and stored for 24 hours at 0°C at 25°C. Afterwards, the amount of oil, water, and emulsion was observed and reported. In ASTM D7563, an emulsion is desirable (i.e., no observable aqueous layer at the bottom of the container).

**[00142]** In Fig. 1, two graphs show results of the ASTM D7563 E85 emulsion testing. One test was conducted at 0°C and the other test conducted at 25°C. The presence of any amount of a water phase was a failing result. Comparative examples A, B and C all showed very poor failing results. The comparative example top treated with the coupled PAG, at 5 wt%, showed very good passing

emulsion properties, above the commercially available PAGs. The use of the coupled PAG, in typical engine oil, at 1-3 wt%, more preferably at 3-5 wt% can reduce the aqueous phase separation from 12-14 vol% to 0 vol%.

**[00143]** Samples were also tested using Pressure Differential Scanning Calorimetry (PDSC) at 210°C and 100 psi air. This test measures enthalpy change over time. The point at which a significant exotherm occurs is considered the induction time. A greater resistance to oxidation induction is desirable. A baseline candidate was compared to samples top-treated (3-5 wt%) with commercial PAGs, a coupled PAG and a polyetheramine precursor to the synthesized PAG. The results are set forth in Fig. 2. The coupled PAG was the only component top-treat that improved the oxidation induction time of Comparative Example D.

**[00144]** Elastomer compatability performance was evaluated for four Association des Constructeurs Europeens D'Automobiles (ACEA) elastomers: Viton, Acrylate, Silicone, and Nitrile. A baseline candidate (Comparative Example D) was compared to samples top-treated (1-5 wt%) with commercial PAGs coupled PAGs and a polyetheramine. The results are shown in Fig. 3. Three component top-treated samples showed no-harm in ACEA elastomer compatibility testing. The coupled PAG (Comparative Example D + 3 wt% coupled PAG) provided benefits for Nitrile and Polyacrylate compatibility and exhibited no harm for Viton and Silicone compatibility.

**[00145]** All patents and patent applications, test procedures (such as ASTM methods, UL methods, and the like), and other documents cited herein are fully incorporated by reference to the extent such disclosure is not inconsistent with this disclosure and for all jurisdictions in which such incorporation is permitted.

**[00146]** When numerical lower limits and numerical upper limits are listed herein, ranges from any lower limit to any upper limit are contemplated. While the illustrative embodiments of the disclosure have been described with particularity, it will be understood that various other modifications will be apparent to and can be readily made by those skilled in the art without departing from the spirit and scope of the disclosure. Accordingly, it is not intended that the scope of the claims appended hereto be limited to the examples and descriptions set forth herein but rather that the claims be construed as encompassing all the features of patentable novelty which reside in the present disclosure, including all features which would be treated as equivalents thereof by those skilled in the art to which the disclosure pertains.

**[00147]** The present disclosure has been described above with reference to numerous embodiments and specific examples. Many variations will suggest themselves to those skilled in this art in light of the above detailed description. All such obvious variations are within the full intended scope of the appended claims.

**CLAIMS:**

1. A method selected from:

(a) a method for improving the ability of an engine lubricating oil contaminated with water and fuel to emulsify water contamination by using as the engine lubricating oil a formulated oil comprising a lubricating oil base stock as a major component and a coupled block copolymer as a minor component; wherein the coupled block copolymer comprises:

an “A” block of a functionalized hydrocarbon moiety including one or more functional end groups derived from: epoxides, amines, acids, acid chlorides, acid anhydrides, halogens, vinyl or vinylidene double bonds, aromatic rings or thiols; and

a “B” block of a functionalized polyether moiety including one or more functional end groups derived from: epoxides, amines, acids, acid chlorides, acid anhydrides, halogens, vinyl or vinylidene double bonds, aromatic rings or thiols;

wherein the end group of the polyether moiety is different than the end group of the hydrocarbon moiety, and the hydrocarbon moiety and the polyether moiety are copolymerizable therewith; and

wherein, in an engine lubricated with said lubricating oil, the ability of the engine lubricating oil contaminated with water and fuel to emulsify water contamination is improved as compared to the ability of an engine lubricating oil contaminated with water and fuel to emulsify water contamination using a lubricating oil containing a minor component other than the coupled block copolymer; and

(b) a method for improving thermo-oxidative stability and elastomer compatibility in an engine lubricated with a lubricating oil by using as the lubricating oil a formulated oil comprising a lubricating oil base stock as a major component and a coupled block copolymer as a minor component; wherein the coupled block copolymer comprises:

an “A” block of a functionalized hydrocarbon moiety including one or more functional end groups derived from: epoxides, amines, acids, acid chlorides, acid anhydrides, halogens, vinyl or vinylidene double bonds, aromatic rings or thiols; and

a “B” block of a functionalized polyether moiety including one or more functional end groups derived from: epoxides, amines, acids, acid chlorides, acid anhydrides, halogens, vinyl or vinylidene double bonds, aromatic rings or thiols;

wherein the end group of the polyether moiety is different than the end group of the hydrocarbon moiety, and the hydrocarbon moiety and the polyether moiety are copolymerizable therewith; and

wherein, in an engine lubricated with said lubricating oil, thermo-oxidative stability and elastomer compatibility are improved as compared to thermo-oxidative stability and elastomer compatibility achieved using a lubricating oil containing a minor component other than the coupled block copolymer.

2. The method of claim 1 wherein the lubricating oil base stock comprises a Group I, II, III, IV or V base oil stock.

3. The method of claim 1 wherein the lubricating oil base stock comprises a poly alpha olefin (PAO) base stock.

4. The method of claim 1 wherein the hydrocarbon moiety is a poly- $\alpha$ -olefin and the polyether moiety is a polyalkylene glycol, and wherein the poly- $\alpha$ -olefin is difunctional and the polyalkylene glycol is difunctional.
5. The method of claim 4 wherein the polyalkylene glycol is a Jeffamine® polyetheramine, and wherein the the Jeffamine® polyetheramine is at least one amine selected from the group consisting of: poly(propyleneglycol) bis(2-aminopropylether), and poly(propyleneglycol)-block-poly(ethyleneglycol)-block poly(propyleneglycol) bis(2-aminopropylether).
6. The method of claim 1 wherein the hydrocarbon moiety is an alkyl glycidyl ether, Armeen® amine or dioctylamine.
7. The method of claim 1 wherein the block copolymer comprises a diblock copolymer or a repeating diblock copolymer, and wherein the the block copolymer has an average molecular weight of 200 to 20000.
8. The method of claim 1 wherein the coupled block copolymer is present in an amount sufficient for the lubricating oil to pass ILSAC GF-5 specification and/or ASTM D7563, or wherein the ability of the engine lubricating oil to emulsify water and fuel as measured by ASTM D7563 shows no observable aqueous layer.
9. The method of claim 1 wherein the the lubricating oil base stock is present in an amount of 50 to 90 wt % of the lubricant composition, and the coupled block copolymer is present in an amount of 1 to 10 wt % of the lubricant composition.

10. The method of claim 1 wherein the lubricating oil further comprises one or more of a viscosity improver, antioxidant, ashless antioxidant, antiwear, detergent, dispersant, pour point depressant, corrosion inhibitor, metal deactivator, seal compatibility additive, anti-foam agent, inhibitor, and anti-rust additive.

11. A lubricating engine oil selected from:

(a) a lubricating engine oil comprising a lubricating oil base stock as a major component and a coupled block copolymer as a minor component; wherein the coupled block copolymer comprises:

an "A" block of a functionalized hydrocarbon moiety including one or more functional end groups derived from: epoxides, amines, acids, acid chlorides, acid anhydrides, halogens, vinyl or vinylidene double bonds, aromatic rings or thiols; and

a "B" block of a functionalized polyether moiety including one or more functional end groups derived from: epoxides, amines, acids, acid chlorides, acid anhydrides, halogens, vinyl or vinylidene double bonds, aromatic rings or thiols;

wherein the end group of the polyether moiety is different than the end group of the hydrocarbon moiety, and wherein the hydrocarbon moiety and the polyether moiety are copolymerizable therewith; and

wherein, in an engine lubricated with said lubricating oil, the ability of the engine lubricating oil contaminated with water and fuel to emulsify water contamination is improved as compared to the ability of an engine lubricating oil contaminated with water and fuel to emulsify water contamination using a lubricating oil containing a minor component other than the coupled block copolymer; and

(b) a lubricating engine oil comprising a lubricating oil base stock as a major component and a coupled block copolymer as a minor component; wherein the coupled block copolymer comprises:

an “A” block of a functionalized hydrocarbon moiety including one or more functional end groups derived from: epoxides, amines, acids, acid chlorides, acid anhydrides, halogens, vinyl or vinylidene double bonds, aromatic rings or thiols; and

a “B” block of a functionalized polyether moiety including one or more functional end groups derived from: epoxides, amines, acids, acid chlorides, acid anhydrides, halogens, vinyl or vinylidene double bonds, aromatic rings or thiols;

wherein the end group of the polyether moiety is different than the end group of the hydrocarbon moiety, and wherein the hydrocarbon moiety and the polyether moiety are copolymerizable therewith; and

wherein, in an engine lubricated with said lubricating oil, thermo-oxidative stability and elastomer compatibility are improved as compared to thermo-oxidative stability and elastomer compatibility achieved using a lubricating oil containing a minor component other than the coupled block copolymer.

12. The lubricating engine oil of claim 11 wherein the lubricating oil base stock comprises a Group I, II, III, IV or V base oil stock.

13. The lubricating engine oil of claim 11 wherein the lubricating oil base stock comprises a poly alpha olefin (PAO) base stock.

14. The lubricating engine oil of claim 11 wherein the hydrocarbon moiety is a poly- $\alpha$ -olefin and the polyether moiety is a polyalkylene glycol, and wherein the polyalkylene glycol is difunctional and the poly- $\alpha$ -olefin is difunctional.

15. The lubricating engine oil of claim 14 wherein the polyalkylene glycol is a Jeffamine® polyetheramine, and wherein the the Jeffamine® polyetheramine is at least one amine selected from the group consisting of:

poly(propyleneglycol) bis(2-aminopropylether), and poly(propyleneglycol)-block-poly(ethyleneglycol)-block poly(propyleneglycol) bis(2-aminopropylether).

16. The lubricating engine oil of claim 11 wherein the hydrocarbon moiety is an alkyl glycidyl ether, Armeen® amine or dioctylamine.

17. The lubricating engine oil of claim 11 wherein the block copolymer comprises a diblock copolymer or a repeating diblock copolymer, and wherein the the block copolymer has an average molecular weight of 200 to 20000.

18. The lubricating engine oil of claim 11 wherein the coupled block copolymer is present in an amount sufficient for the lubricating oil to pass ILSAC GF-5 specification and/or ASTM D7563, or wherein the ability of the engine lubricating oil to emulsify water and fuel as measured by ASTM D7563 shows no observable aqueous layer.

19. The lubricating engine oil of claim 11 wherein the the lubricating oil base stock is present in an amount of 50 to 80 wt % of the lubricant composition, and the coupled block copolymer is present in an amount of 1 to 10 wt % of the lubricant composition.

20. The lubricating engine oil of claim 11 wherein the lubricating oil further comprises one or more of a viscosity improver, antioxidant, ashless antioxidant, antiwear, detergent, dispersant, pour point depressant, corrosion inhibitor, metal deactivator, seal compatibility additive, anti-foam agent, inhibitor, and anti-rust additive.

21. The method of claim 10 wherein the lubricating oil comprises a lubricating oil base stock selected from a Group I, II, III, IV or V base oil stock, a poly- $\alpha$ -olefin (PAO)- polyalkylene glycol (PAG) coupled block copolymer, a salicylate, sulfonate or phenate based detergent, an ashless antioxidant, a succinimide based dispersant, a zinc dialkyldithiophosphate (ZDDP), a friction modifier, a corrosion inhibitor, and a defoamant.

22. The lubricating engine oil of claim 20 which comprises a lubricating oil base stock selected from a Group I, II, III, IV or V base oil stock, a poly- $\alpha$ -olefin (PAO)- polyalkylene glycol (PAG) coupled block copolymer, a salicylate, sulfonate or phenate based detergent, an ashless antioxidant, a succinimide based dispersant, a zinc dialkyldithiophosphate (ZDDP), a friction modifier, a corrosion inhibitor, and a defoamant.