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(54) Title: MICROENCAPSULATION OF LUBRICANT ADDITIVES

(57) Abstract: Provided is a lubricating oil including a nonpolar lubricating oil base stock as a major component and microcapsules as a minor component. The microcapsules includes (i) a core containing a polar solvent and one or more polar lubricating oil additives having solubility in the polar solvent, and (ii) optionally a shell or membrane enclosing the core. The solubility of the polar lubricating oil additives in the nonpolar lubricating oil base stock is improved as compared to solubility achieved using a lubricating oil containing polar lubricating oil additives in a nonpolar lubricating oil base stock and not containing the microcapsules. A method of improving solubility of polar lubricating oil additives in a nonpolar lubricating oil base stock is also provided. The lubricating engine oils of this disclosure can be useful in automotive, marine, aviation, and industrial engine and machine components.

MICROENCAPSULATION OF LUBRICANT ADDITIVES

FIELD

[0001] This disclosure relates to lubricating engines using formulated lubricating oils to reduce wear and improve engine fuel efficiency. The formulated lubricating oils contain a major amount of a nonpolar lubricating oil base stock and a minor amount of microcapsules. The microcapsules comprise (i) a core containing a polar solvent and one or more polar lubricating oil additives having solubility in the polar solvent, and (ii) optionally a shell or membrane enclosing said core. The microcapsules are dispersed in the lubricating oil such that the lubricating oil exhibits improved anti-wear performance and improved engine fuel efficiency. The improved efficiency is enabled by the reduction of friction and improved elastohydrodynamic lubrication (EHL) film formation while using lower viscosity base stocks.

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] A major trend for passenger car engine oils (PCEOs) is an overall improvement in quality as higher quality base stocks become more readily available. Typically the highest quality PCEO products are formulated with highly saturated base stocks such as PAOs or GTL stocks. These highly saturated stocks require the use of Group V base stocks such as ester to improve additive and deposit solubility.

[0004] Another major trend is the gradual reduction in the maximum allowable phosphorus contained in an engine oil to improve operational life. As the phosphorus

content of engine oils is reduced, polar base stocks such as esters can accelerate wear and compromise vehicle durability.

[0005] Another major trend is the shift toward lower viscosity base stocks for improved fuel economy. This trend requires the use of use of high molecular weight polymers to provide protective films within lubricated contacts at high temperature. This approach has limitations in that these molecules increase the viscosity of the oil which has a negative impact on fuel economy and efficiency. These high molecular weight molecules are also sensitive to the harsh environment in the engine and typically degrade by oxidative chain scission and shear.

[0006] The current art is also limited in that conventional formulations tend to form acids which limit the life of the lubricant.

[0007] Therefore, there is a need for lubricating oils that provide appropriate solubility of lubricating oil additives and which also provide excellent surface performance, e.g., anti-wear and anti-corrosion performance. There is also a need to provide strong EHL films at contacts while using lower viscosity base stocks for improved fuel economy and efficiency.

SUMMARY

[0008] This disclosure relates to a lubricating oil comprising a nonpolar lubricating oil base stock as a major component and microcapsules as a minor component. The microcapsules are dispersed in the nonpolar lubricating oil base stock. The microcapsules comprise (i) a core containing a polar solvent and one or more polar lubricating oil additives having solubility in the polar solvent, and (ii) optionally a shell or membrane enclosing the core. The solubility of the polar lubricating oil additives in the nonpolar lubricating oil base stock is improved as compared to solubility achieved using a lubricating oil containing polar lubricating oil additives in a nonpolar lubricating oil base stock and not containing the microcapsules.

[0009] This disclosure also relates in part to a method of improving solubility of polar lubricating oil additives in a nonpolar lubricating oil base stock. The method comprises providing a lubricating oil comprising a nonpolar lubricating oil base stock as a major component and microcapsules as a minor component. The microcapsules are dispersed in the lubricating oil base stock. The microcapsules comprise (i) a core containing a polar solvent and one or more polar lubricating oil additives having solubility in the polar solvent, and (ii) optionally a shell or membrane enclosing the core. The solubility of the polar lubricating oil additives in the nonpolar lubricating oil base stock is improved as compared to solubility achieved using a lubricating oil containing polar lubricating oil additives in a nonpolar lubricating oil base stock and not containing the microcapsules.

[0010] This disclosure further relates in part to a lubricating oil comprising a nonpolar lubricating oil base stock as a major component and microcapsules as a minor component. The microcapsules are dispersed in the nonpolar lubricating oil base stock. The microcapsules comprise (i) a core containing a polar solvent and one or more polar lubricating oil additives having solubility in the polar solvent, and (ii) optionally a shell or membrane enclosing the core. The surface performance (e.g., anti-wear and anti-corrosion performance) in an engine is improved as compared to surface performance in an engine using a lubricating oil containing polar lubricating oil additives in a nonpolar lubricating oil base stock and not containing the microcapsules.

[0011] This disclosure yet further relates in part to a method of improving surface performance (e.g., anti-wear and anti-corrosion performance) of a lubricating oil in an engine lubricated with the lubricating oil. The method comprises using as the lubricating oil a formulated oil comprising a nonpolar lubricating oil base stock as a major component and microcapsules as a minor component. The microcapsules are dispersed in the lubricating oil base stock. The microcapsules comprise (i) a core containing a polar solvent and one or more polar lubricating oil additives having solubility in the polar solvent, and (ii) optionally a shell or membrane enclosing the core. The surface performance in the engine is improved as compared to surface performance in an engine achieved using a lubricating oil containing polar lubricating oil additives in a nonpolar lubricating oil base stock and not containing the microcapsules.

[0012] This disclosure also relates in part to a lubricating oil comprising a nonpolar lubricating oil base stock as a major component and microcapsules as a minor component. The microcapsules are dispersed in thed nonpolar lubricating oil base stock. The microcapsules comprise (i) a core containing a polar solvent and one or more polar lubricating oil additives having solubility in the polar solvent, and (ii) optionally a shell or membrane enclosing the core. The elastohydrodynamic lubrication (EHL) film formation at lubricating oil contacts in an engine is improved as compared to EHL film formation at lubricating oil contacts in an engine using a lubricating oil containing polar lubricating oil additives in a nonpolar lubricating oil base stock and not containing the microcapsules.

[0013] This disclosure further relates in part to a method of improving elastohydrodynamic lubrication (EHL) film formation at lubricating oil contacts in an engine lubricated with a lubricating oil. The method comprises using as the lubricating oil a formulated oil comprising a nonpolar lubricating oil base stock as a major component and microcapsules as a minor component. The microcapsules are dispersed in the lubricating oil base stock. The microcapsules comprise (i) a core containing a polar solvent and one or more polar lubricating oil additives having solubility in the polar solvent, and (ii) optionally a shell or membrane enclosing the core. The elastohydrodynamic lubrication (EHL) film formation at lubricating oil contacts in an engine is improved as compared to EHL film formation at lubricating oil contacts in an engine using a lubricating oil containing polar lubricating oil additives in a nonpolar lubricating oil base stock and not containing the microcapsules.

[0014] The advantages afforded by this disclosure include, for example, improved additive solubility beyond normal hydrocarbon base oil solubility limits, clarity and homogeneous finished lubricant phase, and enhanced surface performance through proper delivery of the performance additives. Enhanced performance is also achieved through improved EHL film formation.

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

BRIEF DESCRIPTION OF THE DRAWINGS

[0016] Fig. 1 graphically depicts the elastohydrodynamic lubrication (EHL) measurement of film thickness at 40°C of the NB:25417-145-3 encapsulated system, Spectrasyn®-4, and Mobil-1, 0W-20, as set forth in Example 1.

[0017] Fig. 2 graphically depicts the elastohydrodynamic lubrication (EHL) measurement of film thickness at 60°C of the NB:25417-145-3 encapsulated system, Spectrasyn®-4, and Mobil-1, 0W-20, as set forth in Example 1.

[0018] Fig. 3 graphically depicts the elastohydrodynamic lubrication (EHL) measurement of film thickness at 80°C of the NB:25417-145-3 encapsulated system, Spectrasyn®-4, and Mobil-1, 0W-20, as set forth in Example 1.

[0019] Fig. 4 graphically depicts the elastohydrodynamic lubrication (EHL) measurement of film thickness at 100°C of the NB:25417-145-3 encapsulated system, Spectrasyn®-4, and Mobil-1, 0W-20, as set forth in Example 1.

[0020] Fig. 5 graphically depicts friction versus temperature comparisons for encapsulated and unencapsulated ammonium tetrathiomolybdate including base stock control, dispersant control and tetraethylene glycol control.

[0021] Fig. 6 depicts an encapsulation system showing a polar solvent core with dissolved additive encapsulated within a lubricant.

[0022] Fig. 7 graphically depicts the measurement of capsule size using a Horiba laser light scattering particle size analyzer.

[0023] Fig. 8 is a 100x objective photograph of a macrocapsule (without polymer film) of polystyrene sulfonic acid (sodium salt) dissolved in tetraethylene glycol that is dispersed in oil without a dispersant.

[0024] Fig. 9 is a 100x objective photograph of a macrocapsule (with polymer film) of polystyrene sulfonic acid (sodium salt) dissolved in tetraethylene glycol that is dispersed in oil with a dispersant (i.e., PIBSA-PAM).

DETAILED DESCRIPTION

[0025] 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.

[0026] This disclosure is a special encapsulation technology for lubricants, which provides for the incorporation of sub-micron spheres of an insoluble polar solvent into a nonpolar basestock. This disclosure also provides a method of stabilizing the interface of the sphere with surfactants and an encapsulating polymer film. The invisible dispersed spheres provide the advantage of forming thick lubricating films while the surrounding basestock provides a relatively low overall viscosity to the oil. The encapsulated polar solvent can also be used to dissolve polar additives which are not soluble in the basestock and/or incorporate higher concentrations of additives which have low solubility in the basestock.

[0027] This encapsulation system can be used to efficiently transport polar molecules with a higher viscosity than the basestock to the contacts requiring elastohydrodynamic lubrication such as journal bearings. This system can be further used to solubilize and carry in the base-stock surface active ingredients such as friction modifiers, anti-wear additives and antioxidants critical to all lubricated contacts. The surfactant and polymer protective coating of the dispersed capsules also efficiently provides a sequestration and time-release mechanism which delivers the active ingredients at the high shear contacts where the capsules are ruptured.

[0028] In accordance with this disclosure, there is provided a means of incorporating hydrocarbon insoluble compounds into lubricant formulations. It also provides a protective system of nano-size capsules to carry additives and efficiently deliver them by

capsule rupture in the high shear environment of the lubricated contact. These encapsulated additives can be designed to impart better friction, anti-wear and antioxidant properties to the lubricant.

[0029] An additional benefit of this disclosure is the polar hydrocarbon carrier in which the additive is dissolved. The viscosity of this carrier can be maximized to provide a shear triggered protective film at the lubricated contact. The encapsulation of the high viscosity carrier provides the benefit of high film thickness within a relatively low viscosity lubricant. Furthermore, the polar hydrocarbon core can provide other benefits such as trapping and neutralizing acids formed during the oils use and providing a means to increase the thermal conductivity of the oil.

[0030] The lubricating engine oils of this disclosure can also be useful for applications irrespective of viscosity grade and/or base stock type. For example, the lubricating engine oils of this disclosure can be useful in automotive, marine, aviation, and industrial engine and machine components. The microencapsulation system of this disclosure can be used for a variety of applications, for example, isolating reactive additives, trapping water in lubricants, and the like. The lubricating oils of this disclosure can also be useful for lubricating machine components such as industrial paper machines, metal working tools, compressors, bearing greases, wind turbines, and the like.

[0031] In particular, this disclosure relates to microcapsules including a core containing one or more polar solvents and one or more lubricating oil additives in which the microcapsules are dispersed in one or more lubricating base oils of mineral, synthetic or natural origin, and optionally a polymer shell. This disclosure also relates to lubricating oils including the microcapsules. This disclosure further relates to the use of microcapsules as anti-wear, antioxidant and/or friction modifier additives for lubricant compositions.

[0032] As indicated above, the current art in formulating lubricants is limited by the oils solubility. It is an objective of this disclosure to solve this problem through the microencapsulation of polar solvents and polar lubricating oil additives in microparticles

optionally comprising a protective shell. Microencapsulation is a process via which a product is enclosed in hollow microparticles optionally comprising a shell or membrane (typically polymeric) enclosing a solid or liquid core containing the product. These microparticles, whose diameter is typically between 0.01 and 1000 μm, are designated under the term of microcapsules. Depending on the encapsulated molecules, applications are found in the areas of agriculture (fertilizers, pesticides), health (medications), cosmetics, textiles, and the like.

Lubricating Oil Base Stocks

[0033] A wide range of lubricating base oils is known in the art. Lubricating base oils that are useful in the present disclosure are both natural oils, and synthetic oils, and unconventional oils (or mixtures thereof) can be used unrefined, refined, or rerefined (the latter is also known as reclaimed or reprocessed oil). Unrefined oils are those obtained directly from a natural or synthetic source and used without added purification. These include shale oil obtained directly from retorting operations, petroleum oil obtained directly from primary distillation, and ester oil obtained directly from an esterification process. Refined oils are similar to the oils discussed for unrefined oils except refined oils are subjected to one or more purification steps to improve at least one lubricating oil property. One skilled in the art is familiar with many purification processes. These processes include solvent extraction, secondary distillation, acid extraction, base extraction, filtration, and percolation. Rerefined oils are obtained by processes analogous to refined oils but using an oil that has been previously used as a feed stock.

[0034] Groups I, II, III, IV and V are broad base oil stock categories developed and defined by the American Petroleum Institute (API Publication 1509; www.API.org) to create guidelines for lubricant base oils. Group I base stocks have a viscosity index of between 80 to 120 and contain greater than 0.03% sulfur and/or less than 90% saturates. Group II base stocks 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 stocks have a viscosity index greater than 120 and contain less than or equal to 0.03 % sulfur and greater than 90% saturates. Group IV includes polyalphaolefins (PAO). Group V

base stock includes base stocks not included in Groups I-IV. The table below summarizes properties of each of these five groups.

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

[0035] Natural oils include animal oils, vegetable oils (castor oil and lard oil, for example), and mineral oils. Animal and vegetable oils possessing favorable thermal oxidative stability can be used. Of the natural oils, mineral oils are preferred. Mineral oils vary widely as to their crude source, for example, as to whether they are paraffinic, naphthenic, or mixed paraffinic-naphthenic. Oils derived from coal or shale are also useful. Natural oils vary also as to the method used for their production and purification, for example, their distillation range and whether they are straight run or cracked, hydrorefined, or solvent extracted.

[0036] Group II and/or Group III hydroprocessed or hydrocracked basestocks, including synthetic oils such as polyalphaolefins, alkyl aromatics and synthetic esters are also well known basestock oils.

[0037] Synthetic oils include hydrocarbon oil. Hydrocarbon oils include oils such as polymerized and interpolymerized olefins (polybutylenes, polypropylenes, propylene isobutylene copolymers, ethylene-olefin copolymers, and ethylene-alphaolefin copolymers, for example). Polyalphaolefin (PAO) oil base stocks are commonly used synthetic hydrocarbon oil. By way of example, PAOs derived from C_8, C_{10}, C_{12}, C_{14} olefins or mixtures thereof may be utilized. See U.S. Patent Nos. 4,956,122; 4,827,064; and 4,827,073.

[0038] The number average molecular weights of the PAOs, which are known materials and generally available on a major commercial scale from suppliers such as ExxonMobil Chemical Company, Chevron Phillips Chemical Company, BP, and others, typically vary from 250 to 3,000, although PAO's may be made in viscosities up to 100 cSt (100°C). The PAOs are typically comprised of relatively low molecular weight hydrogenated polymers or oligomers of alphaolefins which include, but are not limited to, C_2 to C_{32} alphaolefins with the C_8 to C_{16} alphaolefins, such as 1-octene, 1-decene, 1-dodecene and the like, being preferred. The preferred polyalphaolefins are poly-1-octene, poly-1-decene and poly-1-dodecene and mixtures thereof and mixed olefin-derived polyolefins. However, the dimers of higher olefins in the range of C_{14} to C_{18} may be used to provide low viscosity basestocks of acceptably low volatility. Depending on the viscosity grade and the starting oligomer, the PAOs may be predominantly trimers and tetramers of the starting olefins, with minor amounts of the higher oligomers, having a viscosity range of 1.5 to 12 cSt.

[0039] The PAO fluids may be conveniently made by the polymerization of an alphaolefin in the presence of a polymerization catalyst such as the Friedel-Crafts catalysts including, for example, aluminum trichloride, boron trifluoride or complexes of boron trifluoride with water, alcohols such as ethanol, propanol or butanol, carboxylic acids or esters such as ethyl acetate or ethyl propionate. For example, the methods disclosed by U.S. Patent Nos. 4,149,178 or 3,382,291 may be conveniently used herein. Other descriptions of PAO synthesis are found in the following U.S. Patent Nos. 3,742,082; 3,769,363; 3,876,720; 4,239,930; 4,367,352; 4,413,156; 4,434,408; 4,910,355; 4,956,122; and 5,068,487. The dimers of the C_{14} to C_{18} olefins are described in U.S. Patent No. 4,218,330.

[0040] The hydrocarbyl aromatics can be used as base oil or base oil component and can be any hydrocarbyl molecule that contains at least 5% of its weight derived from an aromatic moiety such as a benzenoid moiety or naphthenoid moiety, or their derivatives. These hydrocarbyl aromatics include alkyl benzenes, alkyl naphthalenes, alkyl diphenyl oxides, alkyl naphthols, alkyl diphenyl sulfides, alkylated bis-phenol A, alkylated thiodiphenol, and the like. The aromatic can be mono-alkylated, dialkylated, polyalkylated, and the like. The aromatic can be mono- or poly-functionalized. The

hydrocarbyl groups can also be comprised of mixtures of alkyl groups, alkenyl groups, alkynyl, cycloalkyl groups, cycloalkenyl groups and other related hydrocarbyl groups. The hydrocarbyl groups can range from C_6 up to C_{60} with a range of C_8 to C_{20} often being preferred. A mixture of hydrocarbyl groups is often preferred, and up to three such substituents may be present. The hydrocarbyl group can optionally contain sulfur, oxygen, and/or nitrogen containing substituents. The aromatic group can also be derived from natural (petroleum) sources, provided at least 5% of the molecule is comprised of an above-type aromatic moiety. Viscosities at 100°C of approximately 3 cSt to 50 cSt are preferred, with viscosities of approximately 3.4 cSt to 20 cSt often being more preferred for the hydrocarbyl aromatic component. In one embodiment, an alkyl naphthalene where the alkyl group is primarily comprised of 1-hexadecene is used. Other alkylates of aromatics can be advantageously used. Naphthalene or methyl naphthalene, for example, can be alkylated with olefins such as octene, decene, dodecene, tetradecene or higher, mixtures of similar olefins, and the like. Useful concentrations of hydrocarbyl aromatic in a lubricant oil composition can be 2% to 25%, preferably 4% to 20%, and more preferably 4% to 15%, depending on the application.

[0041] Esters comprise a useful base stock. 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, alkyl succinic acid, alkenyl succinic acid, maleic acid, azelaic acid, suberic 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.

[0042] 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_5 to C_{30} acids such as saturated straight chain fatty acids including caprylic acid, capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, arachic acid, and behenic acid, or the corresponding branched chain fatty acids or unsaturated fatty acids such as oleic acid, or mixtures of any of these materials.

[0043] Suitable synthetic ester components include the esters of trimethylol propane, trimethylol butane, trimethylol ethane, pentaerythritol and/or dipentaerythritol with one or more monocarboxylic acids containing from 5 to 10 carbon atoms. These esters are widely available commercially, for example, the Mobil P-41 and P-51 esters of ExxonMobil Chemical Company).

[0044] Other useful fluids of lubricating viscosity include non-conventional or unconventional base stocks that have been processed, preferably catalytically, or synthesized to provide high performance lubrication characteristics.

[0045] Non-conventional or unconventional base stocks/base oils include one or more of a mixture of base stock(s) derived from one or more Gas-to-Liquids (GTL) materials, as well as isomerate/isodewaxate base stock(s) derived from natural wax or waxy feeds, mineral and or non-mineral oil waxy feed stocks such as slack waxes, natural waxes, and waxy stocks such as gas oils, waxy fuels hydrocracker bottoms, waxy raffinate, hydrocrackate, thermal crackates, or other mineral, mineral oil, or even non-petroleum oil derived waxy materials such as waxy materials received from coal liquefaction or shale oil, and mixtures of such base stocks.

[0046] 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.

[0047] 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^2/s to 50 mm^2/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).

[0048] 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.

[0049] The term GTL base stock and/or base oil and/or wax isomerate 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.

[0050] 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).

[0051] 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.

[0052] 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 diluents/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.

[0053] The base oil constitutes the major component of the engine oil lubricant composition of the present disclosure and typically is present in an amount ranging from 50 to 99 weight percent, preferably from 70 to 95 weight percent, and more preferably from 85 to 95 weight percent, based on the total weight of the composition. The base oil may be selected from any of the synthetic or natural oils typically used as crankcase lubricating oils for spark-ignited and compression-ignited engines. The base oil conveniently has a kinematic viscosity, according to ASTM standards, of 2.5 cSt to 12 cSt (or mm^2 /s) at 100°C and preferably of 2.5 cSt to 9 cSt (or mm^2/s) at 100°C. Mixtures of synthetic and natural base oils may be used if desired.

Microcapsules

[0054] The term "microcapsules" means hollow microcapsules comprising a solid or liquid core and optionally a shell or membrane (typically polymeric) enclosing the solid or liquid core. The microcapsules contain a polar solvent and one or more polar lubricating oil additives to be protected and to be released in controlled manner. These microparticles, having a diameter typically of less than 1000 μm, in particular of between 0.01 and 1000 μm, are designated under the term of microcapsules.

[0055] The microcapsules of this disclosure are approximately of spherical shape. When speaking in terms of diameter, or size of the microcapsules, reference is made to their largest dimension. The diameter of the microcapsules according to this disclosure is preferably between 0.01 and 50 μm, more preferably between 0.1 and 10 μm, or between 0.1 and 1.5 μm, or between 0.3 and 4 or between 0.4 and 3 or between 0.1 and 1 μm. It is desirable that the microcapsules should be of homogeneous size. It is also desirable that the preferably homogeneous size is of the order of a few hundred nanometers, typically less than 4 microns, for example less than 3 microns, in particular less than 1 or 2 microns, so as to facilitate the placing in suspension thereof in the lubricating oil in which they are to be incorporated as additives.

[0056] The core of the microparticles according to this disclosure comprises at least one polar solvent and at least one polar lubricating oil additive.

[0057] Illustrative polar solvents useful in the microparticles include, for example, glycols, alcohols, esters, ethers, carboxylic acids, amines, and other organic compounds containing one or more polar functional groups (e.g., phosphate, sulfonate, sulfate, silicone). In particular, useful polar solvents include monoethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, polyethylene glycol, triethylene glycol monomethyl ether, triethylene glocol dimethyl ether, tripropylene glycol, tripropylene glycol butyl ether (also known as Dowanol™ TPnB), tripropylene glycol methyl ether (also known as Dowanol™ TPM), diethylene glycol dimethyl ether (also known as diglyme), and the like.

[0058] Illustrative polar lubricating oil additives useful in the microparticles include, for example, dispersants, detergents, corrosion inhibitors, rust inhibitors, metal deactivators, antioxidants, anti-wear agents and/or extreme pressure additives, anti-seizure agents, wax modifiers, viscosity index improvers, viscosity modifiers, fluid-loss additives, seal compatibility agents, friction modifiers, lubricity agents, anti-staining agents, chromophoric agents, defoamants, demulsifiers, emulsifiers, densifiers, wetting agents, gelling agents, tackiness agents, colorants, antifoam agents, and pour point depressants.

[0059] In particular, illustrative polar lubricating oil additives include friction modifiers such as ammonium tetrathiomolybdate, ammonium molybdate, sodium molybdate, sodium molybdenum dehydrate, molybdenum disulfide, molybdenum carbide, molybdenum (VI) oxide, molybdenum di-n-butyl dithiocarbamate, (propylcyclopentadienyl molybdenum tricarbonyl dimer, and the like; also organic and inorganic borated compounds and the like; antioxidants such as butylated hydroxytoluene (BHT), 2,6-di-tert-butyl phenol, 2,6-di-tert-butyl cresol, alkylated diphenylamines, and the like; and anti-wear agents such as zinc dialkyldithiophosphate (ZDDP), tricresyl phosphate, sulfurized olefins, elemental sulfur and compounds which produce sulfur in situ such as ammonium or sodium thiosulfate dissolved in the polar capsule core, and the like.

[0060] The microcapsules of this disclosure can optionally have a shell or membrane enclosing the core. The protective shell can insulate the polar solvent and polar lubricating oil additives from the outside environment, providing controlled release thereof in particular through rupture of the shell. In the microcapsules according to this disclosure, it may not be desired to obtain progressive diffusion of lubricating oil additives through the shell wall, but a release of lubricating oil additives at the metal-metal contact. It may not be desirable that the lubricating oil additives should be released other than by rupture of the microcapsules under strong pressure, of the order of GPa, existing at the contact.

[0061] The walls of the microcapsules can be slightly porous, formed of strongly cross-linked polymer. In an embodiment, for the production of the microcapsules according to this disclosure, di- or tri-functional monomers, i.e., monomers having several times the chemical function involved in the polymerization reaction, may be used.

[0062] The constituent polymers of the shell of the microcapsules according to this disclosure can have good heat resistance (i.e., do not degrade at extreme temperatures which may be encountered when in service, i.e., of the order of 150°C to 160°C), and good mechanical strength so that they can withstand the high shear levels encountered in engines. The shell of the microparticles according to this disclosure may be formed for example of polymers of polystyrene sulfonic acid (or salt), polyester, polyamide, polyurethane, polyurea type, or the copolymers thereof, optionally with other monomers, polyacrylonitriles, vinyl resins or aminoplast resins. Polyureas, known for their good properties, are particularly preferred. They also have good mechanical resistance and good heat resistance.

[0063] The microcapsules of this disclosure can be prepared by conventional methods known in the art. For example, a polar lubricating oil additive can be mixed with a polar solvent and the resulting product can be added to a lubricating oil base stock. The resulting product can be mixed under low and/or high shear conditions for a time (e.g., from 5 minutes to 2 hours) and at a temperature (e.g., from 15°C to 80°C) sufficient to form a homogeneous lubricant containing microcapsules.

[0064] The shell or membrane (typically polymeric) enclosing the solid or liquid core can be prepared by conventional methods known in the art. For example, an oil soluble cross-linking agent can be added to the oil continuous phase after the polar phase is dispersed. Alternatively, the functional groups on additive(s) in the oil continuous phase (such as the polyamine groups on typical dispersants) can be used to react with polymer(s) in the polar core and form a polymer film at the capsule interface.

[0065] The nonpolar lubricating oil base stock is present in an amount from 70 weight percent to 95 weight percent, preferably from 75 weight percent to 95 weight percent, and more preferably from 80 weight percent to 95 weight percent, based on the total weight of the lubricating oil. The microcapsules are present in the lubricating oil in an amount sufficient to impart to the lubricating oil improved anti-wear performance and improved engine fuel efficiency. In particular, the microcapsules can be present in an amount from 0.1 weight percent to 10 weight percent or greater, preferably from 0.25 weight percent to 9.5 weight percent, and more preferably from 0.5 weight percent to 9 weight percent, based on the total weight of the lubricating oil.

Other Additives

[0066] 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, 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, 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).

[0067] 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.

Dispersants

[0068] During engine operation, oil-insoluble oxidation byproducts are produced. Dispersants help keep these byproducts in solution, thus diminishing their deposition on metal surfaces. Dispersants used in the formulation of the lubricating oil may be ashless or ash-forming in nature. Preferably, the dispersant is ashless. So-called ashless dispersants are organic materials that form substantially no ash upon combustion. For example, non-metal-containing or borated metal-free dispersants are considered ashless. In contrast, metal-containing detergents discussed above form ash upon combustion.

[0069] 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.

[0070] Chemically, many dispersants may be characterized as phenates, sulfonates, sulfurized phenates, salicylates, naphthenates, stearates, carbamates, thiocarbamates, phosphorus derivatives. A particularly useful class of dispersants are the alkenylsuccinic derivatives, typically produced by the reaction of a long chain hydrocarbyl substituted succinic compound, usually a hydrocarbyl substituted succinic anhydride, with a polyhydroxy or polyamino compound. The long chain hydrocarbyl group constituting the oleophilic portion of the molecule which confers solubility in the oil, is normally a polyisobutylene group. Many examples of this type of dispersant are well known commercially and in the literature. Exemplary U.S. patents describing such dispersants are U.S. Patent Nos. 3,172,892; 3,215,707; 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.

[0071] Hydrocarbyl-substituted succinic acid and hydrocarbyl-substituted succinic anhydride derivatives are useful dispersants. In particular, succinimide, succinate esters, or succinate ester amides prepared by the reaction of a hydrocarbon-substituted succinic acid compound preferably having at least 50 carbon atoms in the hydrocarbon substituent, with at least one equivalent of an alkylene amine are particularly useful.

[0072] Succinimides are formed by the condensation reaction between hydrocarbyl substituted succinic anhydrides and amines. Molar ratios can vary depending on the polyamine. For example, the molar ratio of hydrocarbyl substituted succinic anhydride to TEPA can vary from 1:1 to 5:1. Representative examples are shown in U.S. Patent Nos. 3,087,936; 3,172,892; 3,219,666; 3,272,746; 3,322,670; and 3,652,616, 3,948,800; and Canada Patent No. 1,094,044.

[0073] Succinate esters are formed by the condensation reaction between hydrocarbyl substituted succinic anhydrides and alcohols or polyols. Molar ratios can vary depending on the alcohol or polyol used. For example, the condensation product of a hydrocarbyl substituted succinic anhydride and pentaerythritol is a useful dispersant.

[0074] Succinate ester amides are formed by condensation reaction between hydrocarbyl substituted succinic anhydrides and alkanol amines. For example, suitable alkanol amines include ethoxylated polyalkylpolyamines, propoxylated polyalkylpolyamines and polyalkenylpolyamines such as polyethylene polyamines. One example is propoxylated hexamethylenediamine. Representative examples are shown in U.S. Patent No. 4,426,305.

[0075] The molecular weight of the hydrocarbyl substituted succinic anhydrides used in the preceding paragraphs 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. The above products can also be post reacted with

boron compounds such as boric acid, borate esters or highly borated dispersants, to form borated dispersants generally having from 0.1 to 5 moles of boron per mole of dispersant reaction product.

[0076] Mannich base dispersants are made from the reaction of alkylphenols, formaldehyde, and amines. See U.S. Patent No. 4,767,551, which is incorporated herein by reference. Process aids and catalysts, such as oleic acid and sulfonic acids, can also be part of the reaction mixture. Molecular weights of the alkylphenols range from 800 to 2,500. Representative examples are shown in U.S. Patent Nos. 3,697,574; 3,703,536; 3,704,308; 3,751,365; 3,756,953; 3,798,165; and 3,803,039.

[0077] Typical high molecular weight aliphatic acid modified Mannich condensation products useful in this disclosure can be prepared from high molecular weight alkyl-substituted hydroxyaromatics or $HN®_2$ group-containing reactants.

[0078] Hydrocarbyl substituted amine ashless dispersant additives are well known to one skilled in the art; see, for example, U.S. Patent Nos. 3,275,554; 3,438,757; 3,565,804; 3,755,433, 3,822,209, and 5,084,197.

[0079] 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 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. A preferred dispersant is polyisobutylene succinimide polyamine (PIBSA-PAM). Such additives may be used in an amount of 0.1 to 20 weight percent, preferably 0.5 to 8 weight percent.

Detergents

[0080] A typical detergent is an anionic material that contains a long chain hydrophobic portion of the molecule and a smaller anionic or oleophobic hydrophilic

portion of the molecule. The anionic portion of the detergent is typically derived from an organic acid such as a sulfur acid, carboxylic acid, phosphorous acid, phenol, or mixtures thereof. The counterion is typically an alkaline earth or alkali metal.

[0081] Salts that contain a substantially stochiometric amount of the metal are described as neutral salts and have a total base number (TBN, as measured by ASTM D2896) of from 0 to 80. Many compositions are overbased, containing large amounts of a metal base that is achieved by reacting an excess of a metal compound (a metal hydroxide or oxide, for example) with an acidic gas (such as carbon dioxide). Useful detergents can be neutral, mildly overbased, or highly overbased.

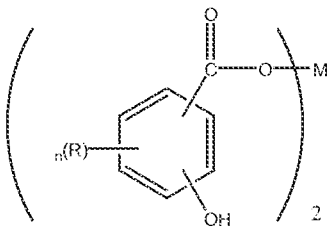
[0082] It is desirable for at least some detergent to be overbased. Overbased detergents help neutralize acidic impurities produced by the combustion process and become entrapped in the oil. Typically, the overbased material has a ratio of metallic ion to anionic portion of the detergent of 1.05:1 to 50:1 on an equivalent basis. More preferably, the ratio is from 4:1 to 25:1. The resulting detergent is an overbased detergent that will typically have a TBN of 150 or higher, often 250 to 450 or more. Preferably, the overbasing cation is sodium, calcium, or magnesium. A mixture of detergents of differing TBN can be used in the present disclosure.

[0083] Preferred detergents include the alkali or alkaline earth metal salts of sulfonates, phenates, carboxylates, phosphates, and salicylates, e.g., a mixture of magnesium sulfonate and calcium salicylate.

[0084] Sulfonates may be prepared from sulfonic acids that are typically obtained by sulfonation of alkyl substituted aromatic hydrocarbons. Hydrocarbon examples include those obtained by alkylating benzene, toluene, xylene, naphthalene, biphenyl and their halogenated derivatives (chlorobenzene, chlorotoluene, and chloronaphthalene, for example). The alkylating agents typically have 3 to 70 carbon atoms. The alkaryl sulfonates typically contain 9 to 80 carbon or more carbon atoms, more typically from 16 to 60 carbon atoms.

[0085] Alkaline earth phenates are another useful class of detergent. These detergents can be made by reacting alkaline earth metal hydroxide or oxide (CaO, $Ca(OH)_2$, BaO, $Ba(OH)_2$, MgO, $Mg(OH)_2$, for example) with an alkyl phenol or sulfurized alkylphenol. Useful alkyl groups include straight chain or branched C_1-C_{30} alkyl groups, preferably, C_4-C_{20}. Examples of suitable phenols include isobutylphenol, 2-ethylhexylphenol, nonylphenol, dodecyl phenol, and the like. It should be noted that starting alkylphenols may contain more than one alkyl substituent that are each independently straight chain or branched. When a non-sulfurized alkylphenol is used, the sulfurized product may be obtained by methods well known in the art. These methods include heating a mixture of alkylphenol and sulfurizing agent (including elemental sulfur, sulfur halides such as sulfur dichloride, and the like) and then reacting the sulfurized phenol with an alkaline earth metal base.

[0086] Metal salts of carboxylic acids are also useful as detergents. These carboxylic acid detergents may be prepared by reacting a basic metal compound with at least one carboxylic acid and removing free water from the reaction product. These compounds may be overbased to produce the desired TBN level. Detergents made from salicylic acid are one preferred class of detergents derived from carboxylic acids. Useful salicylates include long chain alkyl salicylates. One useful family of compositions is of the formula



where R is an alkyl group having 1 to 30 carbon atoms, n is an integer from 1 to 4, and M is an alkaline earth metal. Preferred R groups are alkyl chains of at least C_{11}, preferably C_{13} or greater. R may be optionally substituted with substituents that do not interfere with the detergent's function. M is preferably, calcium, magnesium, or barium. More preferably, M is calcium.

[0087] Hydrocarbyl-substituted salicylic acids may be prepared from phenols by the Kolbe reaction (see U.S. Patent No. 3,595,791). The metal salts of the hydrocarbyl-substituted salicylic acids may be prepared by double decomposition of a metal salt in a polar solvent such as water or alcohol.

[0088] Alkaline earth metal phosphates are also used as detergents and are known in the art.

[0089] Detergents may be simple detergents or what is known as hybrid or complex detergents. The latter detergents can provide the properties of two detergents without the need to blend separate materials. See U.S. Patent No. 6,034,039.

[0090] Preferred detergents include calcium phenates, calcium sulfonates, calcium salicylates, magnesium phenates, magnesium sulfonates, magnesium salicylates and other related components (including borated detergents) in any combination. A preferred detergent includes magnesium sulfonate and calcium salicylate.

[0091] The detergent concentration in the lubricating oils of this disclosure can range from 1.0 to 6.0 weight percent, preferably 2.0 to 5.0 weight percent, and more preferably from 2.0 weight percent to 4.0 weight percent, based on the total weight of the lubricating oil.

Antioxidants

[0092] Antioxidants retard the oxidative degradation of base oils during service. Such degradation may result in deposits on metal surfaces, the presence of sludge, or a viscosity increase in the lubricant. One skilled in the art knows a wide variety of oxidation inhibitors that are useful in lubricating oil compositions. See, Klamann in Lubricants and Related Products, op cite, and U.S. Patent Nos. 4,798,684 and 5,084,197, for example.

[0093] Useful antioxidants include hindered phenols. These phenolic antioxidants may be ashless (metal-free) phenolic compounds or neutral or basic metal salts of certain

phenolic compounds. Typical phenolic antioxidant compounds are the hindered phenolics which are the ones 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 antioxidants include the hindered phenols substituted with C_6+ 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; and 2-methyl-6-t-butyl-4-dodecyl phenol. Other useful hindered mono-phenolic antioxidants may include for example hindered 2,6-di-alkyl-phenolic proprionic ester derivatives. Bis-phenolic antioxidants may also be advantageously used in combination with the instant disclosure. Examples of ortho-coupled phenols include: 2,2′-bis(4-heptyl-6-T-butyl-phenol); 2,2′-bis(4-octyl-6-t-butyl-phenol); and 2,2′-bis(4-dodecyl-6-t-butyl-phenol). Para-coupled bisphenols include for example 4,4′-bis(2,6-di-t-butyl phenol) and 4,4′-methylene-bis(2,6-di-t-butyl phenol).

[0094] Non-phenolic oxidation inhibitors which may be used include aromatic amine antioxidants and these may be used either as such or in combination with phenolics. Typical examples of non-phenolic antioxidants include: alkylated and non-alkylated aromatic amines such as aromatic monoamines of the formula $R^8R^9R^{10}N$ where R^8 is an aliphatic, aromatic or substituted aromatic group, R^9 is an aromatic or a substituted aromatic group, and R^{10} is H, alkyl, aryl or $R^{11}S(O)_XR^{12}$ where R^{11} is an alkylene, alkenylene, or aralkylene group, R^{12} is a higher alkyl group, or an alkenyl, aryl, or alkaryl group, and x is 0, 1 or 2. The aliphatic group R^8 may contain from 1 to 20 carbon atoms, and preferably contains from 6 to 12 carbon atoms. The aliphatic group is 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 amine antioxidants useful in the present compositions include diphenylamines, phenyl naphthylamines, phenothiazines, imidodibenzyls and diphenyl phenylene diamines. Mixtures of two or more aromatic amines are also useful. Polymeric amine antioxidants can also be used. Particular examples of aromatic amine antioxidants useful in the present disclosure include: p,p′-dioctyldiphenylamine; t-octylphenyl-alpha-naphthylamine; phenyl-alphanaphthylamine; and p-octylphenyl-alpha-naphthylamine.

[0096] Sulfurized alkyl phenols and alkali or alkaline earth metal salts thereof also are useful antioxidants.

[0097] Preferred antioxidants include hindered phenols, arylamines. These antioxidants may be used individually by type or in combination with one another. Such additives may be used in an amount of 0.01 to 5 weight percent, preferably 0.01 to 1.5 weight percent, more preferably zero to less than 1.5 weight percent, most preferably zero.

Anti-Wear Additives

[0098] A metal alkylthiophosphate and more particularly a metal dialkyl dithio phosphate in which the metal constituent is zinc, or zinc dialkyl dithio phosphate (ZDDP) is a component of the lubricating oils of this disclosure. ZDDP can be primary, secondary or mixtures thereof. ZDDP compounds generally are of the formula $Zn[SP(S)(OR^1)(OR^2)]_2$ where R^1 and R^2 are C_1-C_{18} alkyl groups, preferably C_2-C_{12} alkyl groups. These alkyl groups may be straight chain or branched.

[0099] 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".

[00100] The ZDDP is typically used in amounts of from 0.4 weight percent to 1.2 weight percent, preferably from 0.5 weight percent to 1.0 weight percent, and more preferably from 0.6 weight percent to 0.8 weight percent, based on the total weight of the lubricating oil, although more or less can often be used advantageously. Preferably, the ZDDP is a secondary ZDDP and present in an amount of from 0.6 to 1.0 weight percent of the total weight of the lubricating oil.

[00101] ZDDP is one of the most successful anti-wear additives ever used in lubricants. This additive is fairly cost effective and provides exceptionally durable anti-wear tribofilms on ferrous surfaces under extreme lubrication conditions. ZDDP forms protective films on ferrous surfaces within a very short period of time. This additive forms pad-like polymeric tribofilms at the rubbing contact and thus prevents wear. It is believed that ZDDP undergoes thermal decomposition at the tribological contact followed by the reactions with reactive iron surfaces or iron oxides that forms glassy phosphate films. These films contain minimal iron meaning that the formation of tribofilm requires minimal loss of iron from the rubbed surfaces. The chain lengths of the phosphate decreases with the depth of the tribofilm and the layers near the surface were mostly dominated by iron sulphides and iron oxides.

[00102] Using an optical interferometry technique, it has been demonstrated that the formation of ZDDP tribofilm takes several tens of minutes. The friction coefficients during the film formation period initially increases and then gradually decreases and finally reaches to steady sate. The increase of friction is a result of initial wear (adhesive/abrasive wear) that generates enough nascent iron to react with the thermally decomposed ZDDP. As soon as the ZDDP tribofilm starts to dominate the contact between two interacting surfaces, friction starts to decrease. Since the film formation of ZDDP is primarily influenced by the initial wear, the nature of wear influences the uniformity as well as growth rate of ZDDP tribofilm to a great extent.

[00103] Uniform anti-wear tribofilms are desirable over the non-uniform patchy tribofilms. This is because the uniform tribofilm can resist the applied load more uniformly and thereby generates distributed stresses within the tribofilm. In contrast, in the case of non-uniform tribofilms, the applied load is mainly taken by the high spots

resulting in more concentrated stresses and thereby causing more failure of tribofilms. This disclosure reveals that NGP materials enable the formation of uniform ZDDP tribofilms by controlling the initial wear process.

Pour Point Depressants (PPDs)

[00104] Conventional pour point depressants (also known as lube oil flow improvers) may be added to the compositions of the present disclosure if desired. These pour point depressant may be added to lubricating compositions of the present disclosure to lower the minimum temperature at which the fluid will flow or can be poured. Examples of suitable pour point depressants include polymethacrylates, polyacrylates, polyarylamides, condensation products of haloparaffin waxes and aromatic compounds, vinyl carboxylate polymers, and terpolymers of dialkylfumarates, vinyl esters of fatty acids and allyl vinyl ethers. U.S. Patent Nos. 1,815,022; 2,015,748; 2,191,498; 2,387,501; 2,655, 479; 2,666,746; 2,721,877; 2,721,878; and 3,250,715 describe useful pour point depressants and/or the preparation thereof. Such additives may be used in an amount of 0.01 to 5 weight percent, preferably 0.01 to 1.5 weight percent.

Seal Compatibility Agents

[00105] Seal compatibility agents help to swell elastomeric seals by causing a chemical reaction in the fluid or physical change in the elastomer. Suitable seal compatibility agents for lubricating oils include organic phosphates, aromatic esters, aromatic hydrocarbons, esters (butylbenzyl phthalate, for example), and polybutenyl succinic anhydride. Such additives may be used in an amount of 0.01 to 3 weight percent, preferably 0.01 to 2 weight percent.

Antifoam Agents

[00106] Anti-foam agents may advantageously be added to lubricant compositions. These agents retard the formation of stable foams. Silicones and organic polymers are typical anti-foam agents. For example, polysiloxanes, such as silicon oil or polydimethyl siloxane, provide antifoam properties. Anti-foam agents are commercially available and

may be used in conventional minor amounts along with other additives such as demulsifiers; usually the amount of these additives combined is less than 1 weight percent and often less than 0.1 weight percent.

Friction Modifiers

[00107] 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 hydrocarbyl 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; WO 99/66013; WO 99/47629; and WO 98/26030.

[00108] 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.

[00109] 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.

Viscosity Index Improvers

[00110] Viscosity index improvers (also known as VI improvers, viscosity modifiers, and viscosity improvers) can be included in the lubricant compositions of this disclosure. Preferably, the method of this disclosure obtains improvements in fuel economy without sacrificing durability by a reduction of high-temperature high-shear (HTHS) viscosity to a level lower than 2.6 cP through reduction or removal of viscosity index improvers or modifiers.

[00111] Viscosity index improvers provide lubricants with high and low temperature operability. These additives impart shear stability at elevated temperatures and acceptable viscosity at low temperatures.

[00112] Suitable viscosity index 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 1,500,000, more typically 20,000 to 1,200,000, and even more typically between 50,000 and 1,000,000.

[00113] Examples of suitable viscosity index improvers are linear or star-shaped 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.

[00114] Olefin copolymers, are commercially available from Chevron Oronite Company LLC under the trade designation "PARATONE®" (such as "PARATONE® 8921" and "PARATONE® 8941"); from Afton Chemical Corporation under the trade designation "HiTEC®" (such as "HiTEC® 5850B"; and from The Lubrizol Corporation under the trade designation "Lubrizol® 7067C". Polyisoprene polymers are commercially available from Infineum International Limited, e.g. under the trade designation "SV200"; diene-styrene copolymers are commercially available from Infineum International Limited, e.g. under the trade designation "SV 260".

[00115] In an embodiment of this disclosure, the viscosity index improvers may be used in an amount of less than 2.0 weight percent, preferably less than 1.0 weight percent, and more preferably less than 0.5 weight percent, based on the total weight of the formulated oil or lubricating engine oil.

[00116] In another embodiment of this disclosure, the viscosity index improvers may be used in an amount of from 0.0 to 2.0 weight percent, preferably 0.0 to 1.0 weight

percent, and more preferably 0.0 to 0.5 weight percent, based on the total weight of the formulated oil or lubricating engine oil.

[00117] When lubricating oil compositions contain one or more of the additives discussed above, the additive(s) are blended into the composition in an amount sufficient for it to perform its intended function. Typical amounts of such additives useful in the present disclosure are shown in Table A below.

[00118] It is noted that many of the additives are shipped from the additive manufacturer as a concentrate, containing one or more additives together, with a certain amount of base oil diluents. Accordingly, the weight amounts in the table below, as well as other amounts mentioned in this specification, are directed to the amount of active ingredient (that is the non-diluent portion of the ingredient). The weight percent (wt%) indicated below is based on the total weight of the lubricating oil composition.

TABLE 1

Typical Amounts of Other Lubricating Oil Components

Compound	Approximate wt% (Useful)	Approximate wt% (Preferred)
Dispersant	0.1-20	0.1-8
Detergent	1.0-6.0	2.0-4.0
Friction Modifier	0.01-5	0.01-1.5
Antioxidant	0.1-5	0.1-1.5
Pour Point Depressant (PPD)	0.0-5	0.01-1.5
Anti-foam Agent	0.001-3	0.001-0.15
Viscosity Index Improver (solid polymer basis)	0.0-2	0.0-1

[00119] The foregoing additives are all commercially available materials. These additives may be added independently but are usually precombined in packages which can be obtained from suppliers of lubricant oil additives. Additive packages with a

variety of ingredients, proportions and characteristics are available and selection of the appropriate package will take the requisite use of the ultimate composition into account.

[00120] The following non-limiting examples are provided to illustrate the disclosure.

EXAMPLES

Example 1

[00121] Figs. 1-4 show the film forming properties of ammonium tetrathiomolybdate dissolved in tetraethylene glycol and encapsulated in Spectrasyn®-4 (referred to as NB:25417-145-3 in Figs. 1-4). The ammonium tetrathiomolybdate was first dissolved in tetraethylene glycol and the resulting product was added to Spectrasyn®-4 under low shear mixing followed by high shear mixing. Spectrasyn®-4 is a commercially available metallocene polyalphaolefin (mPAO). The data shown in Figs. 1-4 was taken using an elastohydrodynamic lubrication (EHL) instrument at 40°C, 60°C, 80°C and 100°C. The NB:25417-145-3 encapsulated system was compared to Spectrasyn®-4 alone as a control, and also commercially available Mobil-1, 0W-20, a fully formulated motor oil.

[00122] The composition of the encapsulated system NB:25417-145-3 was as follows:

2% Dispersed Phase – 5% ammonium tetrathiomolybdate dissolved in tetraethylene glycol

98% Continuous Phase – 9% Stock 5929 PIBSA-PAM (polyisobutylene succinimide polyamine) dispersant in PAO4

[00123] The encapsulated system NB:25417-145-3 shows superior retention of film thickness as a function of temperature compared to the unencapsulated control (i.e., Spectrasyn®-4) and fully formulated motor oil (i.e., Mobil-1, 0W-20).

Example 2

[00124] The above system NB:25417-145-3 was further stabilized by forming a polymer film at the interface of the two phases. This was achieved by dissolving in the polar dispersed phase a high molecular weight polymer (i.e., polystyrene sulfonic acid (or salt)) that reacted at the interface with the polyamine head of the dispersant (i.e., PIBSA-PAM (polyisobutylene succinimide polyamine)) molecule.

[00125] The composition of the encapsulated system NB:25417-145-3 was as follows:

2% Dispersed Phase – 1% polystyrene sulfonic acid (or salt) 5% ammonium tetrathiomolybdate dissolved in tetraethylene glycol

98% Continuous Phase – 9% Stock 5929 PIBSA-PAM (polyisobutylene succinimide polyamine) dispersant in PAO4

Example 3

[00126] Fig. 5 shows friction versus temperature comparisons for encapsulated and unencapsulated ammonium tetrathiomolybdate. The device used for the comparisons was a High Frequency Reciprocating Rig (HFRR). Friction data was collected while ramping temperature from 30°C to 200°C. In Fig. 5, the blue line is PAO4 basestock as a control. The green line is PAO4 basestock with polyisobutylene succinimide polyamine (PIBSA-PAM) dispersant. This is the external or continuous phase of the encapsulated system. The turquoise line is encapsulated ammonium tetrathiomolybdate $(NH_4)_2MoS_4$ of this disclosure. The purple line is tetraethylene glycol which is the polar core solvent. The pink line is unencapsulated ammonium tetrathiomolybdate dissolved in tetraethylene glycol (i.e., polar core with dissolved friction modifier). The yellow line is molybdenum disulfide (MoS_2 solid) dispersed in PAO4. Ammonium tetrathiomolybdate decomposes to molybdenum disulfide at high temperatures. The red line is another tetraethylene glycol control for the polar core. The turquoise line and pink line clearly show the benefit of the ammonium tetrathiomolybdate friction modifier unencapsulated in the polar core solvent and encapsulated in PAO4. The encapsulation system enables the additive to be dispersed in PAO4 in invisible submicron capsules.

The encapsulated version also showed the best friction reduction at the highest test temperature (200°C).

[00127] Fig. 6 shows a model encapsulation system of a polar core solvent, i.e., tetraethylene glycol, with a dissolved additive, i.e., ammonium tetrathiomolybdate, encapsulated within a lubricant, i.e., PAO4. The shell of the microparticles according to this disclosure can be formed of polymers of polystyrene sulfonic acid (or salt). PIBSA-PAM is a dispersant useful in this disclosure.

[00128] Fig. 7 shows the measurement of capsule size using a Horiba LA910 laser light scattering particle size analyzer. The device measured a mean particle size of 0.096 microns for the microencapsulation system. The encapsulation according to this disclosure is unique relative to typical emulsions in that the microcapsules can be infinitely diluted without coalescence. Particles of this size are not visible (completely clear), but are larger than a typical micro emulsion which is in the range of 5 to 200 nm.

[00129] Fig. 8 is a 100x objective photograph of a macrocapsule (without polymer film) of polystyrene sulfonic acid (sodium salt) dissolved in tetraethylene glycol that is dispersed in oil without a dispersant. Fig. 9 is a 100x objective photograph of a macrocapsule (with polymer film) of polystyrene sulfonic acid (sodium salt) dissolved in tetraethylene glycol that is dispersed in oil with a dispersant (i.e., PIBSA-PAM). The photographs are macrocapsules formed using very low shear to make them visible by optical microscopy. The friction and EHL data set forth herein was generated without a polymer film.

[00130] 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.

[00131] 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.

[00132] 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 lubricating oil comprising a nonpolar lubricating oil base stock as a major component and microcapsules as a minor component; wherein said microcapsules are dispersed in said nonpolar lubricating oil base stock; and wherein said microcapsules comprise (i) a core containing a polar solvent and one or more polar lubricating oil additives having solubility in said polar solvent, and (ii) optionally a shell or membrane enclosing said core; wherein the solubility of the polar lubricating oil additives in the nonpolar lubricating oil base stock is improved as compared to solubility achieved using a lubricating oil containing polar lubricating oil additives in a nonpolar lubricating oil base stock and not containing said microcapsules.

2. The lubricating oil of claims 1, 7 and 8 wherein the nonpolar lubricating oil base stock comprises a Group I, Group II, Group III, Group IV or Group V base oil.

3. The lubricating oil of claims 1, 2, 7 and 8 wherein the one or more polar solvents are selected from the group consisting of glycols, alcohols, esters, ethers, carboxylic acids, amines, and organic compounds containing one or more polar functional groups; and the one or more polar lubricating oil additives are selected from the group consisting of dispersants, detergents, corrosion inhibitors, rust inhibitors, metal deactivators, antioxidants, anti-wear agents and/or extreme pressure additives, anti-seizure agents, wax modifiers, viscosity index improvers, viscosity modifiers, fluid-loss additives, seal compatibility agents, friction modifiers, lubricity agents, anti-staining agents, chromophoric agents, defoamants, demulsifiers, emulsifiers, densifiers, wetting agents, gelling agents, tackiness agents, colorants, antifoam agents, and pour point depressants.

4. The lubricating oil of claims 1-3, 7 and 8 wherein the nonpolar lubricating oil base stock is present in an amount from 70 weight percent to 95 weight percent, and the microcapsules are present in an amount from 0.1 weight percent to 10 weight percent or greater, based on the total weight of the lubricating oil.

5. The lubricating oil of claims 1-4, 7 and 8 wherein the shell or membrane is polymeric, and the polymer is selected from polystyrenes, polyesters, polyurethanes,

polyamides, polyureas, or the copolymers thereof; polyacrylonitriles, vinyl resins or aminoplast resins.

6. The lubricating oil of claims 1-5, 7 and 8 wherein the microcapsules have a diameter of between 0.01 μm and 50 μm.

7. A lubricating oil comprising a nonpolar lubricating oil base stock as a major component and microcapsules as a minor component; wherein said microcapsules are dispersed in said nonpolar lubricating oil base stock; and wherein said microcapsules comprise (i) a core containing a polar solvent and one or more polar lubricating oil additives having solubility in said polar solvent, and (ii) optionally a shell or membrane enclosing said core; wherein surface performance in an engine is improved as compared to surface performance in an engine using a lubricating oil containing polar lubricating oil additives in a nonpolar lubricating oil base stock and not containing said microcapsules.

8. The lubricating oil of claim 7 wherein surface performance comprises increasing thickness of a lubricating film at contacts requiring elastohydrodynamic lubrication (EHL) in said engine.

9. A method of improving solubility of polar lubricating oil additives in a nonpolar lubricating oil base stock, said method comprising providing a lubricating oil comprising a nonpolar lubricating oil base stock as a major component and microcapsules as a minor component; wherein said microcapsules are dispersed in said lubricating oil base stock; wherein said microcapsules comprise (i) a core containing a polar solvent and one or more polar lubricating oil additives having solubility in said polar solvent, and (ii) optionally a shell or membrane enclosing said core; wherein the solubility of the polar lubricating oil additives in the nonpolar lubricating oil base stock is improved as compared to solubility achieved using a lubricating oil containing polar lubricating oil additives in a nonpolar lubricating oil base stock and not containing said microcapsules.

10. The method of claims 9 and 13-15 wherein the nonpolar lubricating oil base stock comprises a Group I, Group II, Group III, Group IV or Group V base oil; the one or more

polar solvents are selected from the group consisting of glycols, alcohols, esters, ethers, carboxylic acids, amines, and organic compounds containing one or more polar functional groups; and the one or more polar lubricating oil additives are selected from the group consisting of dispersants, detergents, corrosion inhibitors, rust inhibitors, metal deactivators, antioxidants, anti-wear agents and/or extreme pressure additives, anti-seizure agents, wax modifiers, viscosity index improvers, viscosity modifiers, fluid-loss additives, seal compatibility agents, friction modifiers, lubricity agents, anti-staining agents, chromophoric agents, defoamants, demulsifiers, emulsifiers, densifiers, wetting agents, gelling agents, tackiness agents, colorants, antifoam agents, and pour point depressants.

11. The method of claims 9, 10 and 13-15 wherein the nonpolar lubricating oil base stock is present in an amount from 70 weight percent to 95 weight percent, and the microcapsules are present in an amount from 0.1 weight percent to 10 weight percent or greater, based on the total weight of the lubricating oil.

12. The method of claims 9-11 and 13-15 wherein the shell or membrane is polymeric, and the polymer is selected from polystyrenes, polyesters, polyurethanes, polyamides, polyureas, or copolymers thereof; polyacrylonitriles, vinyl resins or aminoplast resins.

13. A method of improving surface performance of a lubricating oil in an engine lubricated with the lubricating oil, said method comprising using as the lubricating oil a formulated oil comprising a nonpolar lubricating oil base stock as a major component and microcapsules as a minor component; wherein said microcapsules are dispersed in said lubricating oil base stock; wherein said microcapsules comprise (i) a core containing a polar solvent and one or more polar lubricating oil additives having solubility in said polar solvent, and (ii) optionally a shell or membrane enclosing said core; wherein surface performance in the engine is improved as compared to surface performance in an engine achieved using a lubricating oil containing polar lubricating oil additives in a nonpolar lubricating oil base stock and not containing said microcapsules.

14. The method of claim 13 wherein improving surface performance comprises increasing thickness of a lubricating film at contacts requiring elastohydrodynamic lubrication (EHL) in said engine.

15. The method of claims 13 and 14 wherein the lubricating oil is used in automotive, marine, aviation, and industrial engine and machine component applications.

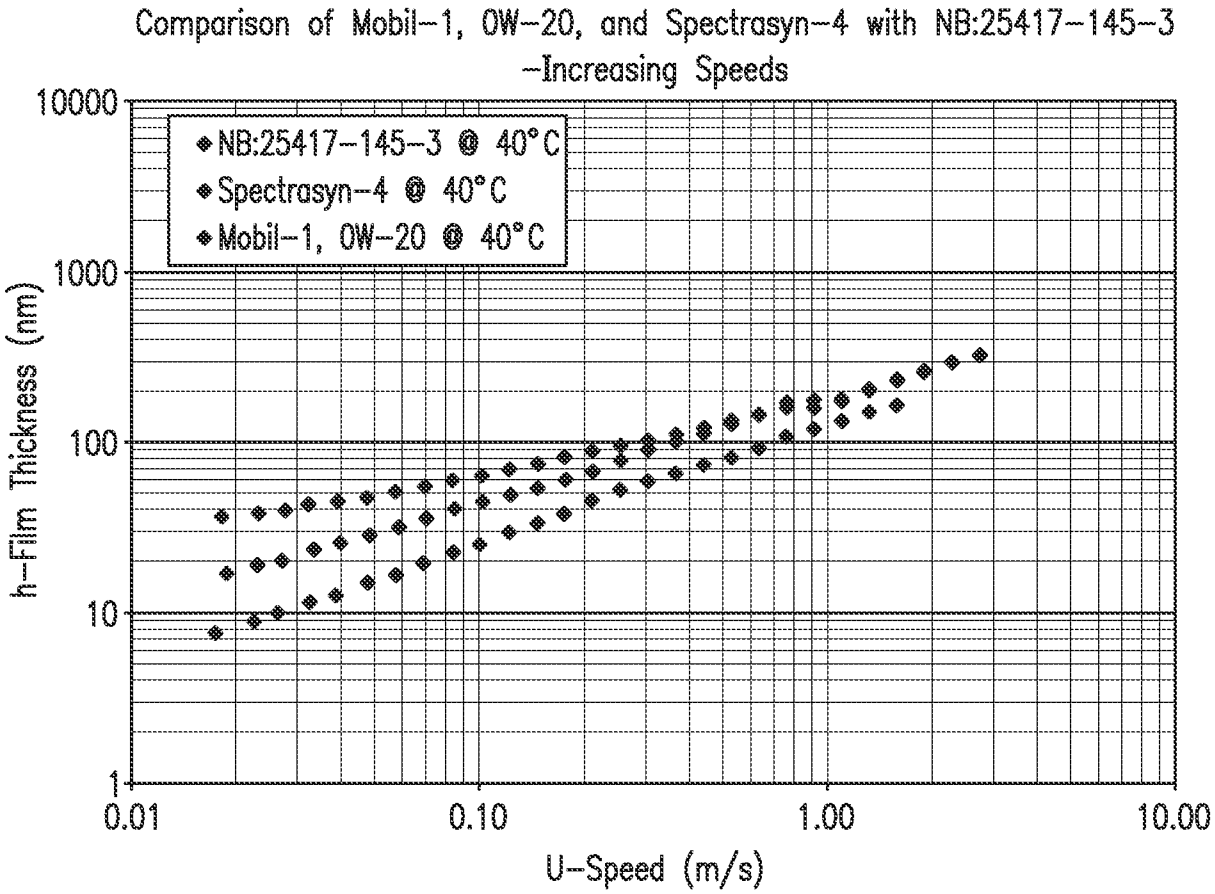

Comparison of Mobil-1, 0W-20, and Spectrasyn-4 with NB:25417-145-3
-Increasing Speeds
NB:25417-145-3 @ 40°C
Spectrasyn-4 @ 40°C
Mobil-1, 0W-20 @ 40°C
h-Film Thickness (nm)
10000
1000
100
10
1
0.01
0.10
1.00
10.00
U-Speed (m/s)

FIG. 1

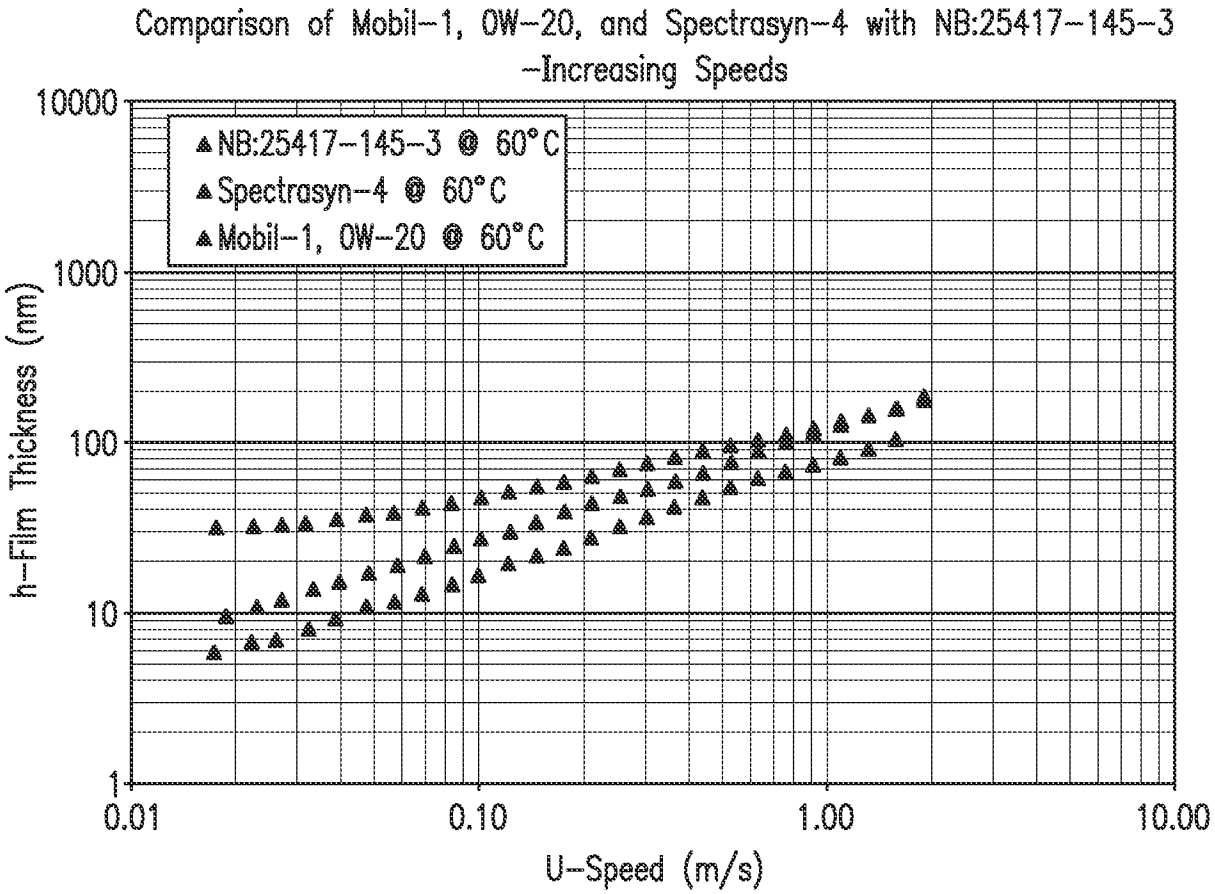
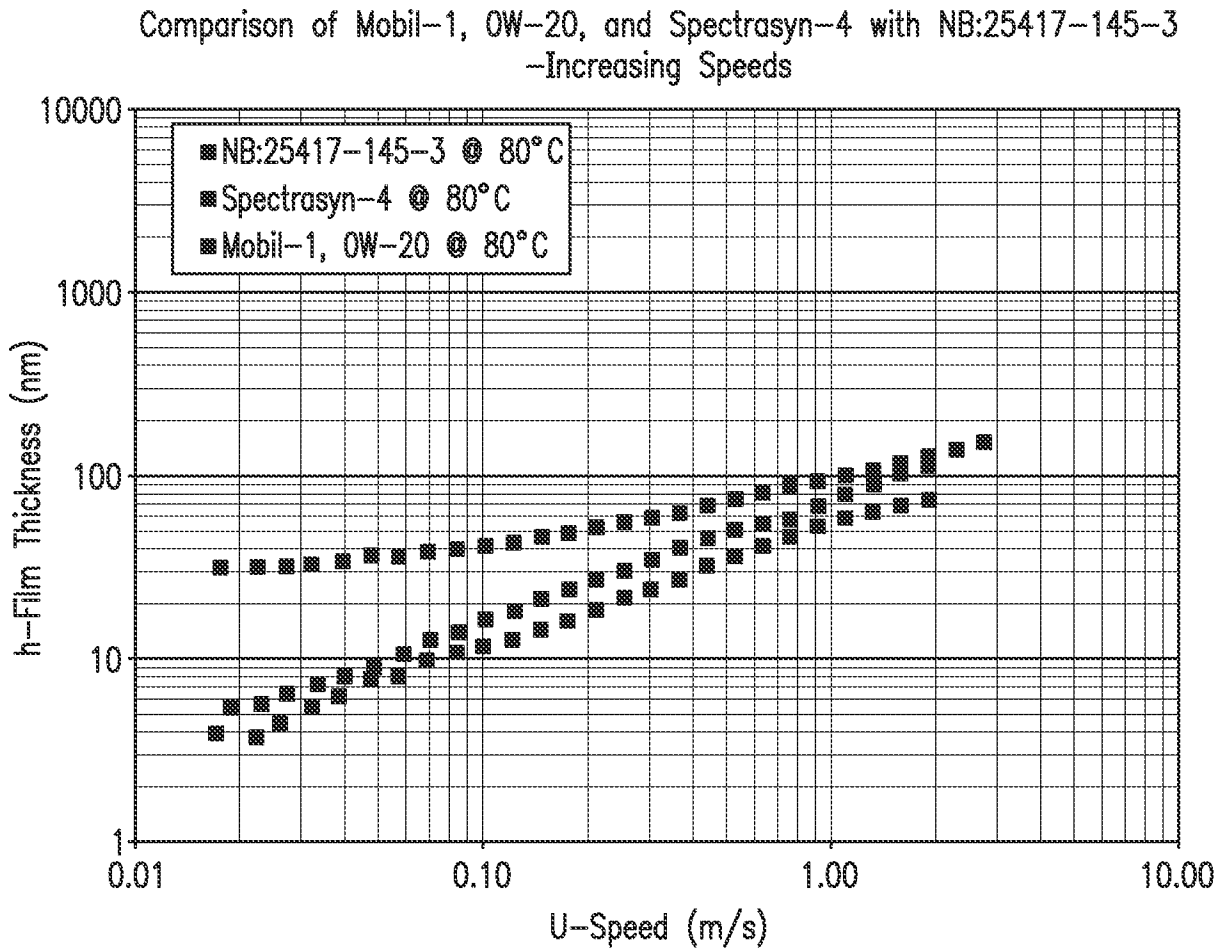

Comparison of Mobil-1, 0W-20, and Spectrasyn-4 with NB:25417-145-3
-Increasing Speeds
NB:25417-145-3 @ 60°C
Spectrasyn-4 @ 60°C
Mobil-1, 0W-20 @ 60°C
h-Film Thickness (nm)
10000
1000
100
10
1
0.01
0.10
1.00
10.00
U-Speed (m/s)

FIG. 2


Comparison of Mobil-1, 0W-20, and Spectrasyn-4 with NB:25417-145-3
-Increasing Speeds
NB:25417-145-3 @ 80°C
Spectrasyn-4 @ 80°C
Mobil-1, 0W-20 @ 80°C
h-Film Thickness (nm)
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1000
100
10
1
0.01
0.10
1.00
10.00
U-Speed (m/s)

FIG. 3

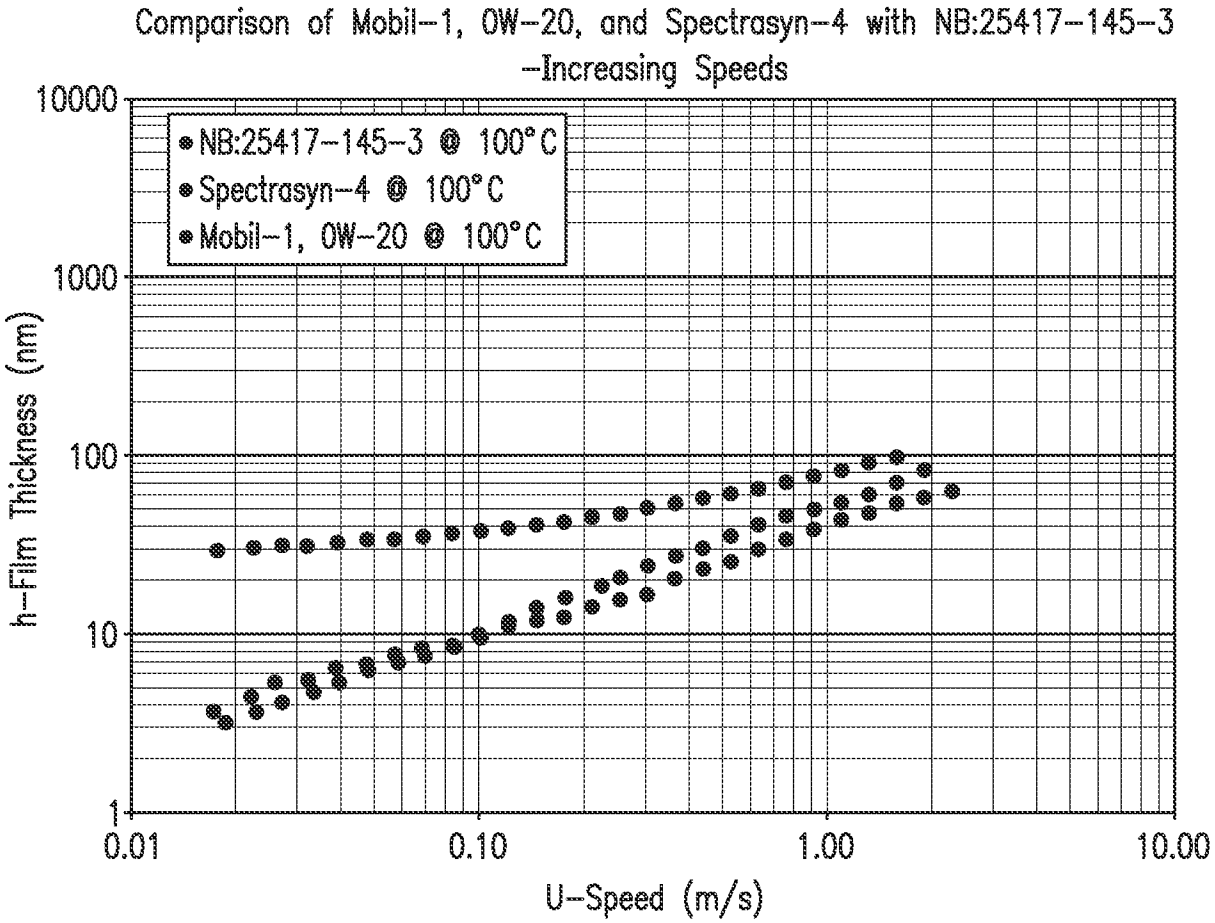

Comparison of Mobil-1, 0W-20, and Spectrasyn-4 with NB:25417-145-3
-Increasing Speeds
NB:25417-145-3 @ 100°C
Spectrasyn-4 @ 100°C
Mobil-1, 0W-20 @ 100°C
h-Film Thickness (nm)
10000
1000
100
10
1
0.01
0.10
1.00
10.00
U-Speed (m/s)

FIG. 4

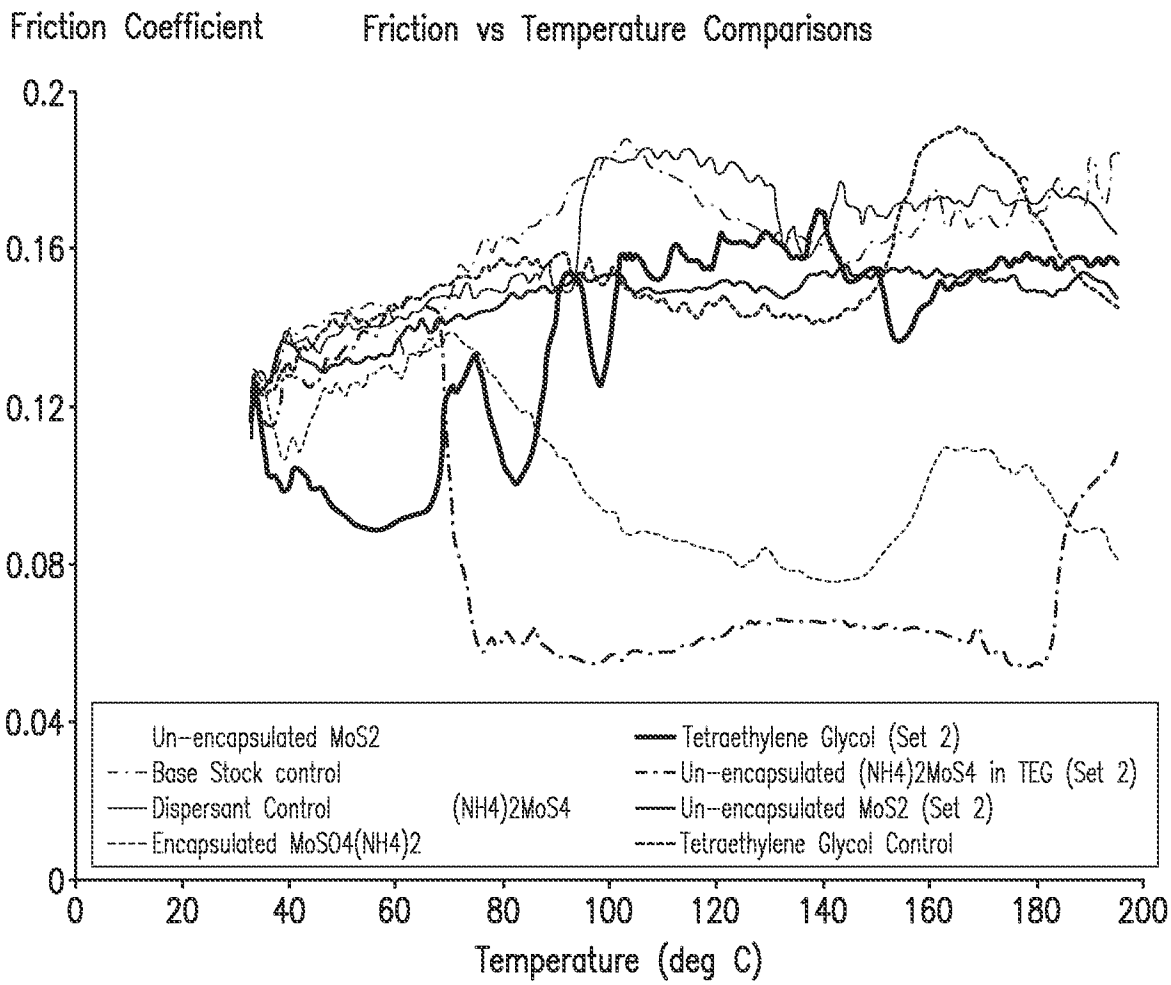

Friction Coefficient
Friction vs Temperature Comparisons
0.2
0.16
0.12
0.08
0.04
0
0
20
40
60
80
100
120
140
160
180
200
Temperature (deg C)
Un-encapsulated MoS2
Base Stock control
Dispersant Control
Encapsulated MoSO4(NH4)2
(NH4)2MoS4
Tetraethylene Glycol (Set 2)
Un-encapsulated (NH4)2MoS4 in TEG (Set 2)
Un-encapsulated MoS2 (Set 2)
Tetraethylene Glycol Control

FIG. 5

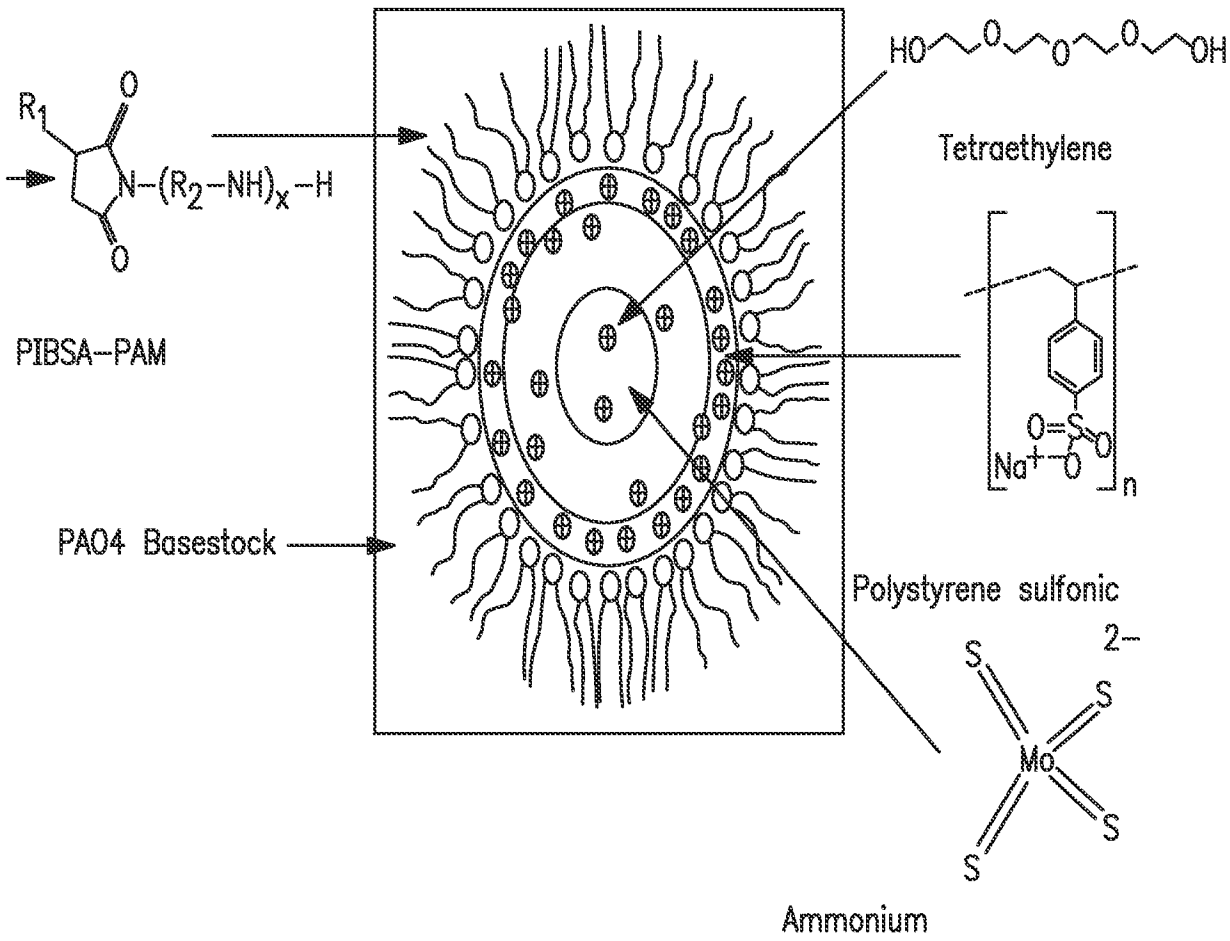
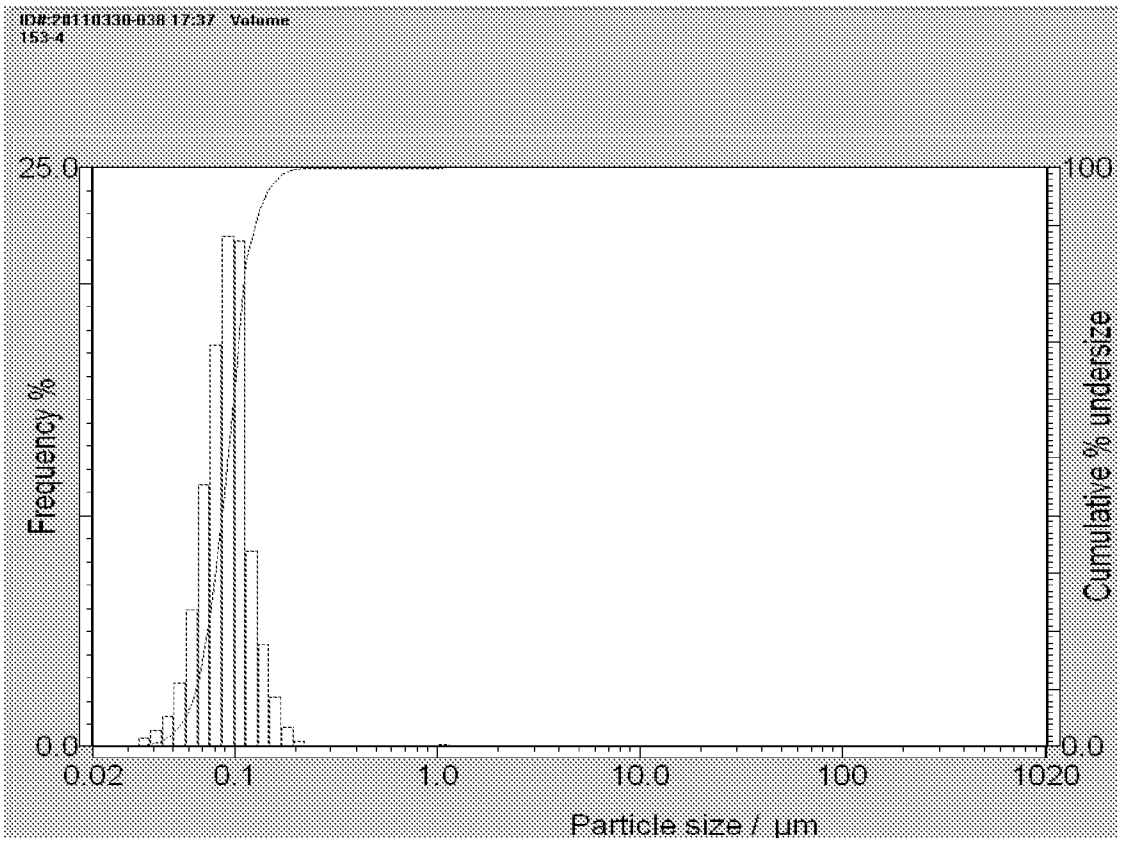

PIBSA–PAM
PAO4 Basestock
Tetraethylene
Polystyrene sulfonic
Ammonium

FIG. 6

Fig. 7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Cumulative % undersize
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1.0
10.0
100
1020
Particle size / µm

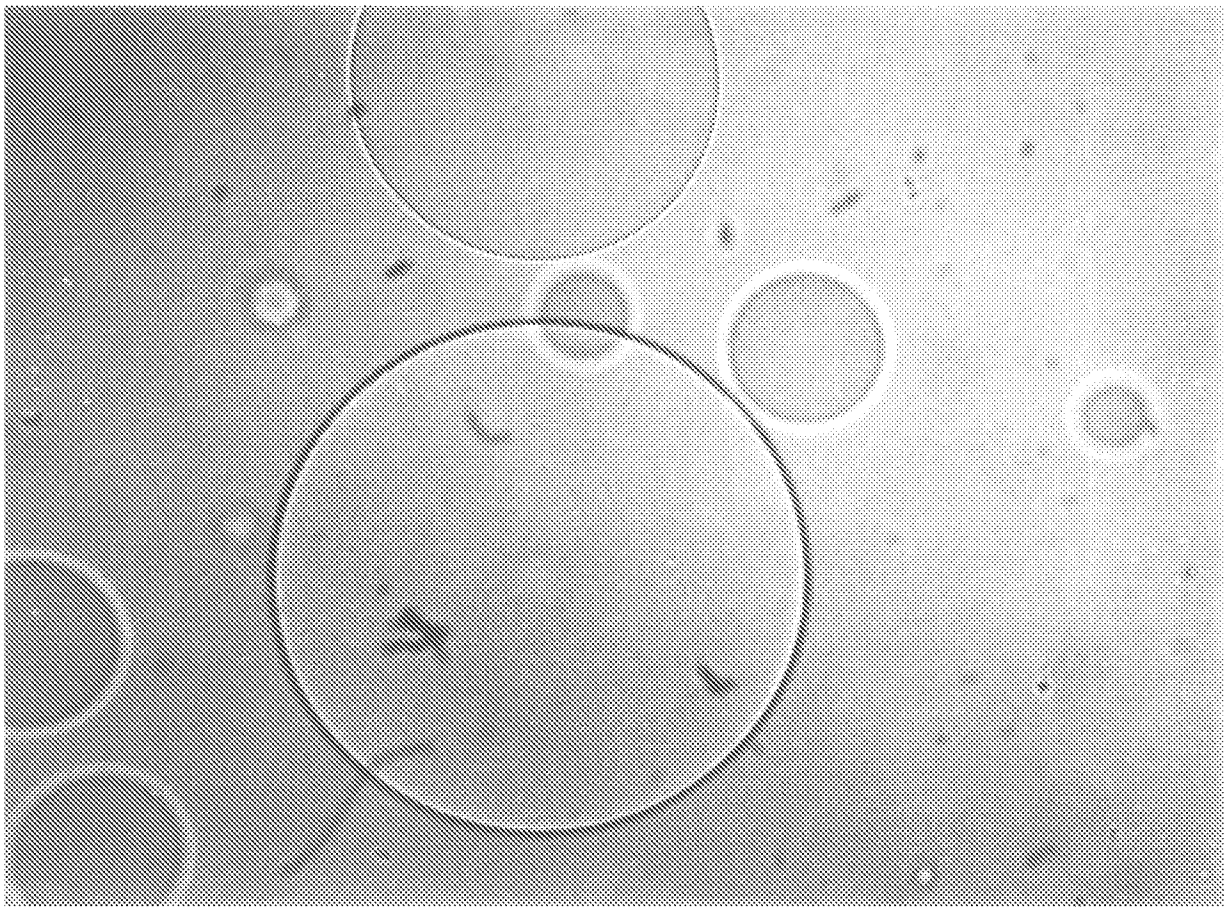

FIG. 8

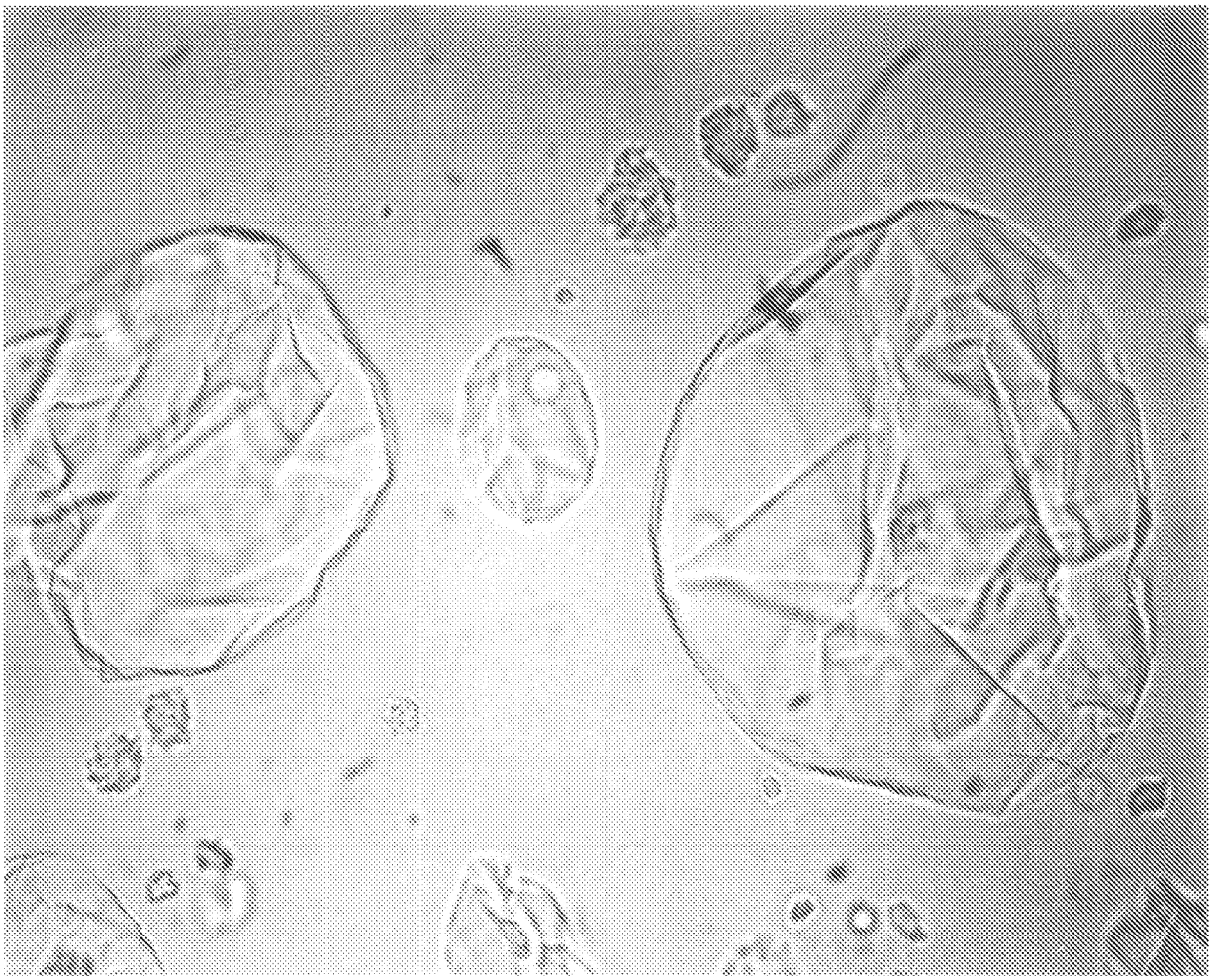

FIG. 9

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2013/058146

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01J13/02 C10M171/06
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01J C10M C10N

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2007 177165 A (NSK LTD) 12 July 2007 (2007-07-12) last sentence of [0021]; paragraphs [0014], [0019], [0024], [0029] paragraphs [0039] - [0043]; claims 1,2 abstract -----	1-12,15
Y	US 2004/002429 A1 (FORBUS THOMAS R [US] FORBUS JR THOMAS R [US]) 1 January 2004 (2004-01-01) paragraphs [0001], [0007] - [0010] paragraphs [0024], [0031], [0034]; claims 1,26,27,56 ----- -/--	1-15

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

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

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

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
28 November 2013	02/01/2014

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Bork, Ana-Maria

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	DE 10 2009 031342 A1 (DAIMLER AG [DE]) 5 January 2011 (2011-01-05) paragraphs [0001], [0005], [0006], [0009] paragraphs [0014], [0015], [0020], [0027]	1-15
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