(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) **World Intellectual Property Organization**
International Bureau

(43) **International Publication Date**
10 May 2013 (10.05.2013)

WIPO | PCT

(10) **International Publication Number**
WO 2013/066915 A1

(51) International Patent Classification:
C10M 169/04 (2006.01) *C10N 40/25* (2006.01)
C10N 30/02 (2006.01) *C10N 20/02* (2006.01)
C10N 30/08 (2006.01)

(21) International Application Number:
PCT/US2012/062654

(22) International Filing Date:
31 October 2012 (31.10.2012)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/554,140 1 November 2011 (01.11.2011) US

(71) Applicant: **EXXONMOBIL RESEARCH AND ENGINEERING COMPANY** [US/US]; 1545 Route 22 East, P.O. Box 900, Annandale, NJ 08801-0900 (US).

(72) Inventors: **BAILLARGEON, David, J.**; 112 Morningside Drive, Cherry Hill, NJ 08003 (US). **JETTER, Steven, M.**; 245 Hickory Corner Road, Hightstown, NJ 08520 (US). **SHOUGH, Anne, M.**; 414 Charles Arbors Lane, New Castle, DE 19720 (US). **DECKMAN, Douglas, Edward**; 5 Peachtree Lane, Mullica Hill, NJ 08062 (US). **KELLY, Kevin, John**; 507 Mandarin Court, Mullica Hill, NJ 08062 (US). **LYON, Kristen, A.**; 610 Myrtle Avenue, West Deptford, NJ 08086 (US). **MATTRAN, Donald, J.**; 3216 Labranch Street, Houston, TX 77004 (US). **PRINCE, Jessica, Lee**; 106 Sansom Lane, Depford, NJ 08096 (US).

(74) Agents: **MIGLIORINI, Robert, A.** et al.; EXXONMOBIL RESEARCH AND ENGINEERING COMPANY, 1545 Route 22 East, P.o. Box 900, Annandale, NJ 08801-0900 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

(54) Title: LUBRICANTS WITH IMPROVED LOW-TEMPERATURE FUEL ECONOMY

(57) Abstract: Lubricating oil compositions, formulated to a preselected viscosity grade that demonstrate stay-in-grade capability in a diesel injector shear stability test, are provided. The compositions comprise a major amount of a base oil of lubricating viscosity and a minor amount of (i) a viscosity modifier (VM) or mixtures thereof having a low shear stability index (SSI) and (ii) a VM or mixtures thereof having an SSI greater than that of the VM from (i).

WO 2013/066915 A1

LUBRICANTS WITH IMPROVED LOW-TEMPERATURE FUEL ECONOMY

FIELD

[0001] The present disclosure is directed to lubricating oil compositions for use in crankcase engine oils. More specifically, the disclosure is directed to crankcase engine oils that are effective in achieving improved low temperature fuel economy (FE) while simultaneously having high temperature, high shear viscosity (HTHS).

BACKGROUND

[0002] Lubricating oil compositions for use as crankcase engine oils comprise a major amount of a base oil and minor amounts of additives selected to enhance the performance characteristics of the base oil. For example, an important property of a lubricating oil is its ability to maintain a lubricating film between moving mechanical parts over a range of temperatures. This ability is a function of the viscometric properties of the lubricating oil. Typically, oil soluble, high molecular weight polymers are used to improve the viscometric performance of engine oil compositions. These materials commonly are referred to as viscosity modifiers (VM), and they function to reduce a decrease in the lubricating composition's viscosity upon an increase in temperature and the converse upon a decrease in temperature. Indeed, VMs are used to formulate lubricating compositions that meet the multigrade viscosity classification system of the Society of Automotive Engineers (SAE J300 specification) and are numerically numbered such as SAE 0W-20, 0W-30, 5W-30, 10W-30, 10W-40 and the like. In this system, the first number is related to a low temperature viscosity characteristic, and the second number, to high temperature viscosity characteristics.

[0003] It is well known that engine oils having low viscosities at low temperatures have desirable low temperature fuel economy (FE) performance. Unfortunately, lowering an engine oil viscosity can detrimentally affect high temperature performance. For example, a lower oil viscosity can result in lower film thickness as measured by high temperature, high shear (HTHS) viscosity, which is undesirable. Also, the use of VMs to improve the high temperature viscosity of the lubricating composition generally has an adverse affect on the low temperature properties.

[0004] One object of the present disclosure is to provide lubricating oil compositions that have improved low temperature FE performance.

[0005] Another object of the disclosure is to provide lubricating compositions for both gasoline and diesel engines that are effective over a broad range of lubricant viscosity and that they stay in grade as demonstrated by a diesel injector shear stability test.

[0006] Other objectives will become apparent from the detailed description that follows.

SUMMARY

[0007] One embodiment of the disclosure provides a lubricating oil composition formulated to a preselected SAE engine oil viscosity grade, said composition comprising:

(a) a major amount of a base oil of lubricating viscosity; and

(b) a minor amount of

(i) a viscosity modifier (VM) or mixtures thereof having a low shear stability index (SSI) , and

(ii) a VM or mixtures thereof having an SSI greater than the VM from (i);

(c) wherein the sheared kinematic viscosity at 100°C of the composition after 90 cycles in the diesel injector shear stability test (ASTM D7109) is equal to or greater than the minimum viscosity for the preselected grade before shearing; and

(d) wherein the sheared viscosity (c) is less than 20% lower relative to the unsheared composition viscosity.

[0008] In a preferred embodiment of the disclosure, the weight ratios of VM (ii) to VM (i) above, VM(ii)/VM(i), is in the range of from 0.01 to 1.5.

[0009] Another embodiment of the disclosure provides a method for lubricating an internal combustion engine comprising supplying the engine crankcase with the above lubricant composition whereby the composition is applied to the engine during operating conditions.

[0010] Other embodiments will become apparent from the detailed description and examples which follow.

DETAILED DESCRIPTION

[0011] 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.

[0012] It has now been found that an engine oil lubricant composition comprising a major amount of base oil and an effective amount of a mixture of high-SSI and low-SSI polymeric viscosity modifiers provides improved fuel efficiency while providing stay-in-grade viscosity retention for stable engine performance.

[0013] 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.

[0014] 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) 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/or 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 stocks generally 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 &/or	> 0.03% &	≥ 80 & < 120
Group II	≥ 90 &	≤ 0.03% &	≥ 80 & < 120
Group III	≥ 90 &	≤ 0.03% &	≥ 120
Group IV	Includes polyalphaolefins (PAO)		
Group V	All other base oil stocks not included in Groups I, II, III, or IV		

[0015] 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.

[0016] 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.

[0017] 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. Patents 4,956,122; 4,827,064; and 4,827,073.

[0018] 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.

[0019] 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 USP 4,149,178 or USP 3,382,291 may be conveniently used herein. Other descriptions of PAO synthesis are found in the following U.S. Patents 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 USP 4,218,330.

[0020] 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.

[0021] 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.

[0022] 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 dipenta-erythritol) 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.

[0023] Suitable synthetic ester components include the esters of trimethylol propane, trimethylol butane, trimethylol ethane, pentaerythritol and/or dipenta-erythritol 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).

[0024] 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.

[0025] 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 or Fischer-Tropsch processes, and mixtures of such base stocks.

[0026] The lubricating oil compositions of the disclosure comprise a major amount of a base oil of lubricating viscosity. In general, the base oil will comprise greater than 50 wt% based on the total weight of the composition, and typically, from 50 wt% to 99 wt%, and preferably, from 70 wt% to 95 wt%. 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. For example, suitable base oils may comprise one or more base stocks selected from Group III, Group IV and mixtures of Group III and Group IV base stocks. These base stock groups are defined in the American Petroleum Institute Publication "Engine Oil Licensing and Certification System", Fourteenth Edition, December 1966, Addendum I, December 1998. The base stock typically will have a kinematic viscosity (KV) at 100ºC, as determined by ASTM D445, of 1 cSt to 12 cSt (or mm^2/s) and preferably 1.5 cSt to 9 cSt (or mm^2/s). Mixtures of synthetic and natural base oils may be used if desired.

[0027] The compositions of the disclosure include a minor, but effective, amount of a mixture of VMs comprising (i) a VM or mixture of VMs, each having an SSI of 12 or less and (ii) a VM or mixture of VMs, each having an SSI greater than the VM of (i). In general, the VMs of (i) above will have SSIs in the range of 4 to 12, and preferably from 4 to 10, while the VMs of (ii) above will have SSIs in the range of 8 or higher, preferably from 12 to 65, and may include embodiments of VMs with SSIs of 24 or higher, 35 or higher, 45 or higher, and 50 or higher, for example.

[0028] The amount of the mixture of VMs (i) and (ii) in the composition may range from 0.01 wt% to 4 wt%, preferably from 0.01 wt% to 2 wt%, and more preferably from 0.1 wt% to 2 wt% on a solid polymer basis, based on the total weight of the composition.

[0029] Importantly, the weight ratio of VM(ii)/VM(i) is from 0.01 to 1.5, preferably 0.05 to 1, and more preferably 0.05 to 0.8, and in further instances in the range of 0.1 to 0.8.

[0030] For the purposes of this disclosure, the VMs are selected from oil soluble or oil dispersible polymers typically used in crankcase lubricant compositions to improve the viscometric performance of the engine oil. Viscosity modifiers (VMs) are also known as VI improvers, viscosity index improvers, viscosity improvers, and thickeners.

[0031] 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 1,000,000, more typically 20,000 to 500,000, and even more typically between 50,000 and 200,000.

[0032] 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, copolymers of olefins and alpha-olefins, 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.

[0033] Olefin copolymers, are commercially available from Chevron Oronite Company LLC under the trade designation "PARATONE®" (such as "PARATONE® 8921", "PARATONE® 8941", "PARATONE® 8451", "PARATONE® 68530"); 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 "SV260". Other examples include "SV140", "SV150", "SV250", "SV270", and "SV300".

[0034] The compositions of the disclosure are formulated to meet any one of the SAE viscosity grades for engine oils such as xW-50, xW-40, xW-30, xW-20 and the like, where x = 15, 10, 5, or 0 and the like, and includes higher viscosity grades and lower viscosity grades, and includes grades not classifiable by SAE J300.

[0035] Compositions according to the disclosure are characterized by the fact that for any preselected viscosity grade, the sheared kinematic viscosity at 100^{o}C after 90 cycles in the diesel injector sheared stability test ASTM D 7109 is equal to or greater than the minimum viscosity (at 100^{o}C) for the preselected grade before shearing. Retention of kinematic viscosity at 100^{o}C within a single SAE viscosity grade classification by a fresh oil and its sheared version is evidence of an oil's stay-in-grade capability.

[0036] The compositions of the disclosure display stay-in-grade capability, and display a viscosity loss measured at 100ºC after 90 cycles in the diesel injector shear stability test of less than 25%, preferably less than 20%, more preferably less than 18%, and in some instances less than 14%.

[0037] The compositions of the present disclosure may also include other additives to improve or impart desired properties of the fully formulated compositions. These additives may be selected from conventional types of lubricant additives. Such additives include oxidation inhibitors, dispersants, detergents, corrosion inhibitors, metal deactivators, antiwear additives, extreme pressure additives, pour point depressants, seal compatibility agents, friction modifiers, defoamants and dyes. Each of these types of additives may be used in amounts commonly used in lubricant compositions.In general, on an active ingredient basis, the various lubricant additives will comprise from 0.5 wt% to 25 wt%, and preferably, from 2 wt% to 15 wt% based on the total weight of the composition.

[0038] While there are many different types of antiwear additives, for several decades the principal antiwear additive for internal combustion engine crankcase oils is a metal alkylthiophosphate and more particularly a metal dialkyldithiophosphate in which the metal constituent is zinc, or zinc dialkyldithiophosphate (ZDDP). 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. The ZDDP is typically used in amounts of from 0.4 to 1.4 wt% of the total lubricant oil composition, 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 lubricant composition.

[0039] 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".

[0040] Additional types of antiwear additives are effectively used in lubricant compositions and include, for example, metal-free, ashless, low-phosphorous, non-phosphorous, oligomeric, polymeric, zinc-containing, metal-containing (other than zinc), multi-functional chemical combinations of these, and other antiwear additives. All antiwear additives above, and the like, may be used individually and in combinations in lubricant compositions.

[0041] 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.

[0042] 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.

[0043] Chemically, many dispersants may be characterized as phenates, sulfonates, sulfurized phenates, salicylates, naphthenates, stearates, carbamates, thiocarbamates, phosphorous derivatives. 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 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. Patents 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.

[0044] 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.

[0045] Succinimides are formed by the condensation reaction between alkenyl succinic anhydrides and amines. Molar ratios can vary depending on the poly-amine. For example, the molar ratio of alkenyl succinic anhydride to TEPA can vary from 1:1 to 5:1. Representative examples are shown in U.S. Patents 3,087,936; 3,172,892; 3,219,666; 3,272,746; 3,322,670; and 3,652,616, 3,948,800; and Canada Pat. No. 1,094,044.

[0046] 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.

[0047] 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. Representative examples are shown in USP 4,426,305.

[0048] The molecular weight of the alkenyl 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, 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.

[0049] Mannich base dispersants are made from the reaction of alkylphenols, formaldehyde, and amines. See USP 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. Patents 3,697,574; 3,703,536; 3,704,308; 3,751,365; 3,756,953; 3,798,165; and 3,803,039.

[0050] 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 $HN(R)_2$ group-containing reactants.

[0051] Hydrocarbyl substituted amine ashless dispersant additives are well known to one skilled in the art; see, for example, U.S. Patents 3,275,554; 3,438,757; 3,565,804; 3,755,433, 3,822,209, and 5,084,197.

[0052] 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. Such additives may be used in an amount of 0.1 to 20 wt%, preferably 0.5 to 8 wt%.

[0053] Detergents are commonly used in lubricating compositions. 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.

[0054] 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.

[0055] 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.

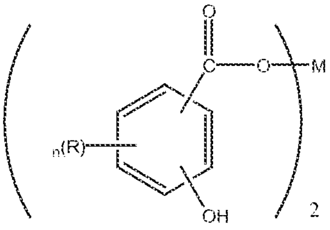
[0056] Preferred detergents include the alkali or alkaline earth metal salts of sulfonates, phenates, carboxylates, phosphates, and salicylates.

[0057] 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.

[0058] Klamann in “Lubricants and Related Products”, op cit discloses a number of overbased metal salts of various sulfonic acids which are useful as detergents and dispersants in lubricants. The book entitled “Lubricant Additives”, C. V. Smallheer and R. K. Smith, published by the Lezius-Hiles Co. of Cleveland, Ohio (1967), similarly discloses a number of overbased sulfonates that are useful as dispersants/detergents.

[0059] 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.

[0060] 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 a hydrogen atom or 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.

[0061] Hydrocarbyl-substituted salicylic acids may be prepared from phenols by the Kolbe reaction (see USP 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.

[0062] Alkaline earth metal phosphates are also used as detergents.

[0063] 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 USP 6,034,039 for example.

[0064] Preferred detergents include calcium phenates, calcium sulfonates, calcium salicylates, magnesium phenates, magnesium sulfonates, magnesium salicylates and other related components (including borated detergents). Typically, the total detergent concentration is 0.01 to 6.0 wt%, preferably, 0.1 to 3.5 wt%.

[0065] 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. Patents 4,798,684 and 5,084,197, for example.

[0066] 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).

[0067] 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.

[0068] 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-alphanaphthylamine; phenyl-alphanaphthylamine; and p-octylphenyl-alpha-naphthylamine.

[0069] Sulfurized alkyl phenols and alkali or alkaline earth metal salts thereof also are useful antioxidants.

[0070] 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 wt%, preferably 0.01 to 1.5 wt%, more preferably zero to less than 1.5 wt%, most preferably zero.

[0071] 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. USP 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 wt%, preferably 0.01 to 1.5 wt%.

[0072] 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 wt%, preferably 0.01 to 2 wt%.

[0073] 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 and often less than 0.1 percent.

[0074] 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 metal-ligand 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 USP 5,824,627; USP 6,232,276; USP 6,153,564; USP 6,143,701; USP 6,110,878; USP 5,837,657; USP 6,010,987; USP 5,906,968; USP 6,734,150; USP 6,730,638; USP 6,689,725; USP 6,569,820; WO 99/66013; WO 99/47629; WO 98/26030.

[0075] Ashless friction modifiers may have 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.

[0076] Useful concentrations of friction modifiers may range from 0.01 wt% to 10-15 wt% or more, often with a preferred range of 0.1 wt% to 5 wt%. 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.

[0077] 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 1, below.

[0078] Note that many of the additives are shipped from the manufacturer and used with a certain amount of base oil diluent in the formulation. 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 wt% indicated below are based on the total weight of the lubricating oil composition.

TABLE 1

Typical Amounts of Various Lubricant Oil Components

Compound	Approximate wt% (Useful)	Approximate wt% (Preferred)
Detergent	0.01-6	0.01-4
Dispersant	0.1-20	0.1-8
Friction Modifier	0.01-5	0.01-1.5
Viscosity Index Improver (solid polymer basis)	0.0-4	0.01-4, more preferably 0.01-1, most preferably
Antioxidant	0.1-5	0.1-1.5
Anti-wear Additive	0.01-6	0.01-4
Pour Point Depressant (PPD)	0.0-5	0.01-1.5
Anti-foam Agent	0.001-3	0.001-0.3
Base stock or base oil	Balance	Balance

[0079] 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.

[0080] As will be seen from the Examples herein, the compositions of the disclosure are sufficiently shear stable to provide stay-in-grade performance. Additionally, the compositions demonstrate surprising fuel economy performance in both diesel and gasoline engines. Thus, the compositions described herein are useful for lubricating diesel-powered and gasoline-powered, internal combustion engines such as those used for example in passenger vehicles, and in other classes of small engines such as used in lawn mowers and chain saws. They are also useful for lubricating diesel-powered engines such as those used in trucks, construction machinery and marine diesel engines.

[0081] Accordingly, an improved method for lubricating internal combustion engines is provided which comprises supplying to the engine, when operated, a lubricating composition of the present disclosure.

[0082] It should be understood that viscosities of the lubricant compositions, lubricating components, and basestocks are measured according to accepted procedures. Kinematic viscosity (KV) is measured using ASTM D445, D7279, and comparable methods. High temperature high shear viscosity (HTHS) is measured using ASTM D4683, CEC L-36, and comparable methods. Viscosity of such materials may also be usefully characterized as a function of temperature and shear rate, for example in the temperature range of 60°C to 160°C, and shear rate range of 10^3 sec^{-1} to 10^8 sec^{-1}.

EXAMPLES

[0083] The following examples further illustrate the present disclosure. These examples are presented by way of illustration and are not intended to limit the scope of the disclosure.

Example 1

[0084] A series of SAE 0W-30 diesel-type engine oils was formulated to substantially the same low HTHS viscosity, i.e. 3 to 3.1 mPa-s, and to substantially the same high HTHS viscosity, i.e. 3.4 to 3.6 mPa-s. The VM weight ratios ranged from 0.1 to 0.5. A major base oil in each instance is a Group III base oil, and each lubricant composition also contains Group IV and Group V base oils, and the same additives combination in substantially the same amounts. The example compositions along with a reference composition are shown in Table A.

Table A. Diesel Engine Oils, SAE 0W-30 – Compositions, Properties

			Lubricant Composition*				
Example	**VM Types (nominal SSI)**	**Active VM Wt Ratio High-SSI/Low-SSI**	**Active VMs (Wt%)**	**Base Stocks; GrpIII (Wt%)**	**Base Stocks; GrpIV (Wt%)**	**HTHS 10^6 sec^{-1}, 150°C (mPa-s)**	**KV100 mm^2/s**
A1	Paratone 8941 (50) SV200 (4)	0.15	1.1	75	6	3.56	12.2
A2	“	0.24	1.1	75	5	3.50	12.1
A3	“	0.40	1.0	75	4	3.47	12.0
B1	Paratone 8941 (50) SV200 (4)	0.15	0.8	74	4	3.11	10.0
B2	“	0.24	0.8	74	4	3.05	10.0
B3	“	0.41	0.7	74	3	3.13	10.1
Ref. 1	SV200 (4)	0.00	1.2	80	7	3.50	12.0

*Balance of lubricant compositions include additives, GrpV base stock.

Example 2

[0085] A series of SAE 0W-30 gasoline-type engine oils was formulated to the same low HTHS viscosity, i.e., 3 to 3.1 mPa-s, and to substantially the same high HTHS viscosity, i.e., 3.4 to 3.6 mPa-s. The VM weight ratios ranged from 0.1 to

0.5. The base oil in each instance is primarily a Group III base oil or a blend of Group III and Group IV base oils. Each lubricant composition also contains Group V base oil (alkyl aromatic and/or ester), and substantially the same additives combinations in substantially the same amounts. The example compositions along with reference compositions are shown in Table B.

Table B. Gasoline Engine Oils, SAE 0W-30 – Compositions, Properties

			Lubricant Composition*				
Example	**<u>VM Types</u> (nominal SSI)**	**Active VM Wt Ratio High-SSI/Low-SSI**	**Active VMs (Wt%)**	**Base Stocks; GrpIII (Wt%)**	**Base Stocks; GrpIV (Wt%)**	**HTHS 10^6 sec^{-1}, 150°C (mPa-s)**	**KV100 mm^2/s**
C1	Paratone 8941 (50) SV200 (4)	0.14	1.2	74	6	3.53	12.2
C2	“	0.24	1.1	74	5	3.56	12.3
C3	“	0.40	1.0	74	4	3.57	12.1
D1	SV300 (59) SV200 (5)	0.27	1.2	59	20	3.48	12.3
E1	SV140 (58) SV200 (4)	0.31	1.3	58	21	3.52	12.4
F1	Paratone 8941 (50) SV200 (4)	0.15	0.8	77	4	3.12	10.1
F2	“	0.24	0.8	76	4	3.14	10.1
F3	“	0.41	0.7	76	3	3.10	10.2
G1	SV261 (20) SV200 (4)	0.62	1.0	49	32	3.46	12.2
G2	SV151 (9) SV200 (4)	0.36	1.1	48	33	3.46	12.2
Ref. 2	SV200 (4)	0.00	1.2	80	7	3.50	12.0
Ref. 5	SV200 (4)	0.00	1.1	46	28	3.49	12.0

*Balance of lubricant compositions include additives, GrpV base stock.

<u>Example 3</u>

[0086] In this example, oil compositions A1, A2, A3 and B1 of Example 1 were tested in a passenger diesel vehicle with a start-of-test (SOT) temperature of 22°C, using the European NEDC fuel economy test protocol. The fuel economy improvement percent, %FEI, results are shown in Table C.

Table C. Diesel Vehicle Fuel Economy Improvement, %FEI
(Mercedes Benz C250 CDI; NEDC Procedure; SOT Temp = 22°C)

Example	**Active VM Wt Ratio High-SSI/Low-SSI**	**HTHS, 10^6 sec^{-1}, 150°C (mPa-s)**	**%FEI**
A1	0.15	3.56	0.59
A2	0.24	3.50	1.02
A3	0.40	3.47	1.33
B1	0.15	3.11	1.59
Reference 1 (Extrapolated from A1, A2, A3)	0	3.5	≤ 0.2
Reference 3 (Zero Reference MB 225.11)	0	3.5	0

[0087] As can be seen from oils A1 to A3, the %FEI increases with increasing VM wt ratios of high-SSI/low-SSI. In Reference 1, the VM wt ratio = 0, since only SV200 was used in that composition. Thus, oils A1 to A3, which each contain an effective amount of high-SSI VM, achieve significantly higher fuel efficiency, %FEI, than that of Reference 1 which contains zero high-SSI VM.

[0088] A comparison of oil B1 (HTHS viscosity of 3.11 mPa-s) with oil A1 (HTHS viscosity of 3.56 mPa-s) demonstrates that the same combination of high-SSI VM and low-SSI VM will provide positive %FEI for oils having different HTHS viscosities, both low and high viscosities, respectively.

Example 4

[0089] Gasoline-type engine oil compositions C1, C3, D1 and E1 of Example 2 were tested in a passenger gasoline vehicle with a start-of-test (SOT) temperature of 22°C, using the European NEDC fuel economy test protocol. The fuel economy improvement percent, %FEI, results are shown in Table D.

Table D. Gasoline Vehicle Fuel Economy Improvement, %FEI
(Mercedes Benz C200; NEDC Procedure; SOT Temp = 22°C)

Example	**Active VM Wt Ratio High-SSI/Low-SSI**	**HTHS, 10^6 sec^{-1}, 150°C (mPa-s)**	**%FEI**
C1	0.14	3.53	0.76
C3	0.40	3.57	1.36
D1	0.27	3.48	2.12
E1	0.31	3.52	1.00
Reference 2 (Extrapolated from C_1, C_3)	0	3.5	≤ 0.4
Reference 4 (Zero Reference MB 225.10)	0	3.5	0

[0090] The results for oils C1 and C3 demonstrate that %FEI increases with increasing VM wt ratio of high-SSI/low-SSI. The results for oils D1 and E1 demonstrate that different VM materials also can be used to achieve a positive %FEI result. The lubricant compositions of this Example, which each contain an effective amount of high-SSI VM, achieve significantly higher fuel efficiency, %FEI, than that of Reference 2 which contains zero high-SSI VM.

Example 5

[0091] Gasoline-type engine oil compositions G1 and G2 of Example 2 were tested in a Volkswagen gasoline engine with a start-of-test (SOT) temperature of -7°C, using the fuel economy test VW PV 1451. The fuel economy improvement percent, %FEI, results are shown in Table E.

Table E. Gasoline Vehicle Fuel Economy Improvement, %FEI (VW PV 1451)

Example	**Active VM Wt Ratio High-SSI/Low-SSI**	**HTHS, 10^6 sec^{-1}, 150°C (mPa-s)**	**%FEI**
G1	0.62	3.46	2.6
G2	0.36	3.46	2.6
Reference 5	0	3.49	2.2
Reference 6 (Zero Reference VW)	0	3.5	0

[0092] The results for oils G1 and G2 demonstrate that %FEI increases with increasing VM wt ratio of high-SSI/low-SSI. The lubricant compositions of this Example, which each contain an effective amount of high-SSI VM, achieve significantly higher fuel efficiency, %FEI, than that of Reference 5, which contains zero high-SSI VM, but which is otherwise essentially identical in composition.

Example 6

[0093] The diesel-type oil compositions A1 to A3 and B1 to B3 of Example 1 were tested for shear stability using test method ASTM D7109. The KV at 100ºC after 90 cycles is shown in Table F.

Table F. Diesel Engine Oils, SAE 0W-30 – Shear Stability

			Diesel Injector Shear Stability-D7109			
Example	**Active VM Wt Ratio High-SSI/Low-SSI**	**HTHS 10^6 sec^{-1}, 150°C (mPa-s)**	**KV100 (fresh oil) mm^2/s**	**KV100 (90 cycles) mm^2/s**	**%Loss KV100 (90 cycles)**	**Stay-in-Grade (for SAE 0W-30, KV100 ≥ 9.3 mm^2/s**
A1	0.15	3.56	12.15	11.31	6.9	Yes
A2	0.24	3.50	12.10	10.96	9.4	Yes
A3	0.40	3.47	11.97	10.52	12.1	Yes
B1	0.15	3.11	9.96	9.52	4.4	Yes
B2	0.24	3.05	10.01	9.31	7.0	Yes
B3	0.41	3.13	10.05	9.13	9.2	No

[0094] Even though Example B3 contains a mixed high-SSI VM and low-SSI VM in the inventive range of VM weight ratio, it fails to meet the stay-in-grade shear stability requirement. This clearly demonstrates that viscosity retention and stay-in-grade shear stability represent a significant limitation to the use of mixed VM polymers in the instant disclosure. So stay-in-grade shear stability controls and limits the selection of VM weight ratio and VM concentrations to those compositions that are effective in providing improved fuel economy performance.

Example 7

[0095] Gasoline-type oil compositions C1 to C3, D1, E1 and F1 to F3 of Example 2 were tested for shear stability using test method ASTM D7109. The results are shown in Table G.

Table G. Gasoline Engine Oils, SAE 0W-30 – Shear Stability

			Diesel Injector Shear Stability – D7109			
Example	**Active VM Wt Ratio High-SSI/Low-SSI**	**HTHS 10^6 sec^{-1}, 150°C (mPa-s)**	**KV100 (fresh oil) mm^2/s**	**KV100 (90 cycles) mm^2/s**	**%Loss KV100 (90 cycles)**	**Stay-in-Grade (for SAE 0W-30, KV100 ≥ 9.3 mm^2/s**
C1	0.14	3.53	12.20	11.37	6.8	Yes
C2	0.24	3.56	12.27	11.14	9.2	Yes
C3	0.40	3.57	12.10	10.61	12.3	Yes
D1	0.27	3.48	12.27	10.2	<17	Yes
E1	0.31	3.52	12.35	10.1	<18	Yes
F1	0.15	3.12	10.11	9.59	5.1	Yes
F2	0.24	3.14	10.13	9.47	6.5	Yes
F3	0.41	3.10	10.19	9.26	9.1	No
G1	0.62	3.46	12.2	11.9	2.6	Yes
G2	0.36	3.46	12.2	12	2	Yes

[0096] Even though Example F3 contains a mixed high-SSI VM and low-SSI VM in the inventive range of VM weight ratio, it fails to meet the stay-in-grade shear stability requirement. This provides another illustration that viscosity retention and stay-in-grade shear stability represent a significant limitation to the use of mixed VM polymers in the instant disclosure.

[0097] 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.

[0098] 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.

[0099] 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 composition formulated to a preselected SAE engine oil viscosity, said composition comprising:

(a) a major amount of a base oil of lubricating viscosity; and

(b) a minor amount of

 (i) a viscosity modifier (VM) or mixtures thereof having a low shear stability index (SSI), and

 (ii) a VM or mixtures thereof having an SSI greater than the VM from (i);

(c) wherein the sheared kinematic viscosity at 100°C of the composition after 90 cycles in the diesel injector shear stability test (ASTM D7109) is equal to or greater than the minimum viscosity for the preselected grade before shearing; and

(d) wherein the sheared viscosity (c) is less than 25% lower relative to the unsheared composition viscosity.

2. The composition of claim 1 wherein the VM's of (i) therein have an SSI in the range of 4 to12.

3. The composition of claim 1 wherein the VMs of (ii) have an SSI in the range of 8 to 65 or higher.

4. The composition of claim 2 wherein the VM weight ratio of VM(ii) to VM(i) is in the range of 0.01 to 1.5.

5. The composition of claim 3 wherein the VM weight ratio of VM(ii) to VM(i) is in the range of 0.05 to 1.

6. The composition of claim 4 wherein the total amount of VM(i) and VM(ii) comprises from 0.1 wt% to 2.5 wt% of the total weight of the composition.

7. The composition of claim 5 wherein the total amount of VM(i) and VM(ii) comprises from 0.1 wt% to 2.5 wt% of the total weight of the composition.

8. The composition of claim 1 wherein the VMs are selected from vinylaromatic-diolefin copolymers.

9. The composition of claim 1 wherein the VMs are selected from olefin copolymers and vinylaromatic-diolefin copolymers.

10. The composition of claim 1 wherein the base oil comprises one or more base oils selected from Group III and Group IV oils and mixtures thereof.

11. The composition of claim 1 comprising one or more lubricant additives, selected from oxidation inhibitors, dispersants, detergents, corrosion inhibitors, metal deactivators, antiwear additives, extreme pressure additives, pour point depressants, seal compatibility agents, friction modifiers, defoamants and dyes.

12. In the method of lubricating an internal combustion engine by supplying a lubricating oil composition to the engine, the improvement comprising supplying an SAE multigraded lubricating oil composition to the engine, said oil composition comprising any of the compositions of claims 1 to 11, thereby enhancing the fuel efficiency of the engine while providing stay-in-grade viscosity retention for stable engine performance.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2012/062654

A. CLASSIFICATION OF SUBJECT MATTER
INV. C10M169/04
ADD. C10N30/02 C10N30/08 C10N40/25 C10N20/02

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)
C10M

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 02/10276 A2 (LUBRIZOL CORP [US]; HUANG CHOR [US]) 7 February 2002 (2002-02-07)	1-7,9-11
Y	page 1, lines 1-11; page 4, line 28 - page 5, line 3; page 6, lines 5-12; page 13, line 20 - page 14, line 18; page 24, lines 9-16; page 25, line 1; page 27, lines 7-14; claims 16,21; examples 1,2; tables 1-7 -----	1-12
X	US 5 888 946 A (ZAKARIAN JOHN A [US] ET AL) 30 March 1999 (1999-03-30)	1,4-7, 10,11
Y	column 2, lin 50 - column 3, line 35; column 5, lines 21-59; claims 1,3,4,8,9; examples 1-4,A,B ----- -/--	1-12

☒ Further documents are listed in the continuation of Box C.

☒ 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 28 January 2013	Date of mailing of the international search report 05/02/2013
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Renoth, Heinz

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2012/062654

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	US 5 520 832 A (ALEXANDER ALBERT G [CA]) 28 May 1996 (1996-05-28) column 2, lines 30-39; column 5, lines 27-33; claim 1; examples 1-15 -----	1-5,11 1-12
Y	WO 2006/068866 A1 (LUBRIZOL CORP [US]; BREON LEWIS D [US]; PATEL JAYRAM D [US]; SAMBUCHIN) 29 June 2006 (2006-06-29) paragraphs [0005], [0006], [0020], [0025] - [0055]; claims 8,11-14 -----	1-12
Y	EP 2 112 217 A1 (NIPPON OIL CORP [JP]) 28 October 2009 (2009-10-28) sentences 1,5,8,32,38; claims 1-3,6,7; examples -----	1-12

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2012/062654

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 0210276 A2	07-02-2002	AU 8087901 A	13-02-2002
		AU 2001280879 B2	05-10-2006
		CA 2416798 A1	07-02-2002
		EP 1309656 A2	14-05-2003
		JP 2004505152 A	19-02-2004
		US 2004038850 A1	26-02-2004
		WO 0210276 A2	07-02-2002
US 5888946 A	30-03-1999	CA 2257011 A1	30-06-1999
		US 5888946 A	30-03-1999
US 5520832 A	28-05-1996	CA 2161026 A1	29-04-1996
		US 5520832 A	28-05-1996
WO 2006068866 A1	29-06-2006	CN 101120077 A	06-02-2008
		EP 1844128 A1	17-10-2007
		JP 5004237 B2	22-08-2012
		JP 2008525583 A	17-07-2008
		US 2008096778 A1	24-04-2008
		US 2010212624 A1	26-08-2010
		WO 2006068866 A1	29-06-2006
EP 2112217 A1	28-10-2009	EP 2112217 A1	28-10-2009
		JP 2008184569 A	14-08-2008
		US 2010093578 A1	15-04-2010
		WO 2008093446 A1	07-08-2008