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(54) LUBRICANT AND ADDITIVE FORMULATION

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(57) **ABSTRACT**

A lubricant composition for use as a concentrate and motor oil having an enhanced thermal conductivity. One preferred composition contains a lubricant composition, nanomaterial, and a dispersing agent or surfactant for the purpose of stabilizing the nanomaterial. One preferred nanomaterial is a high thermal conductivity graphite, exceeding 80 W/m in thermal conductivity. Carbon nano material or nanostructures such as nanotubes, nanofibrils, and nanoparticles formed by grounding and/or milling graphite to obtain a mean particle size less than 500 nm in diameter, and preferably less than 100 nm, and most preferably less than 50 nm. Other high thermal conductivity carbon materials are also acceptable. To confer long-term stability, the use of one or more chemical dispersants or surfactants is useful. The graphite nanomaterials contribute to the overall fluid viscosity and providing a very high viscosity index. Particle size and dispersing chemistry is controlled to get the desired combination of viscosity and thermal conductivity increase from the lubricant. The resulting fluids have unique properties due to the high thermal conductivity and high viscosity index of the suspended particles, as well as their small size.

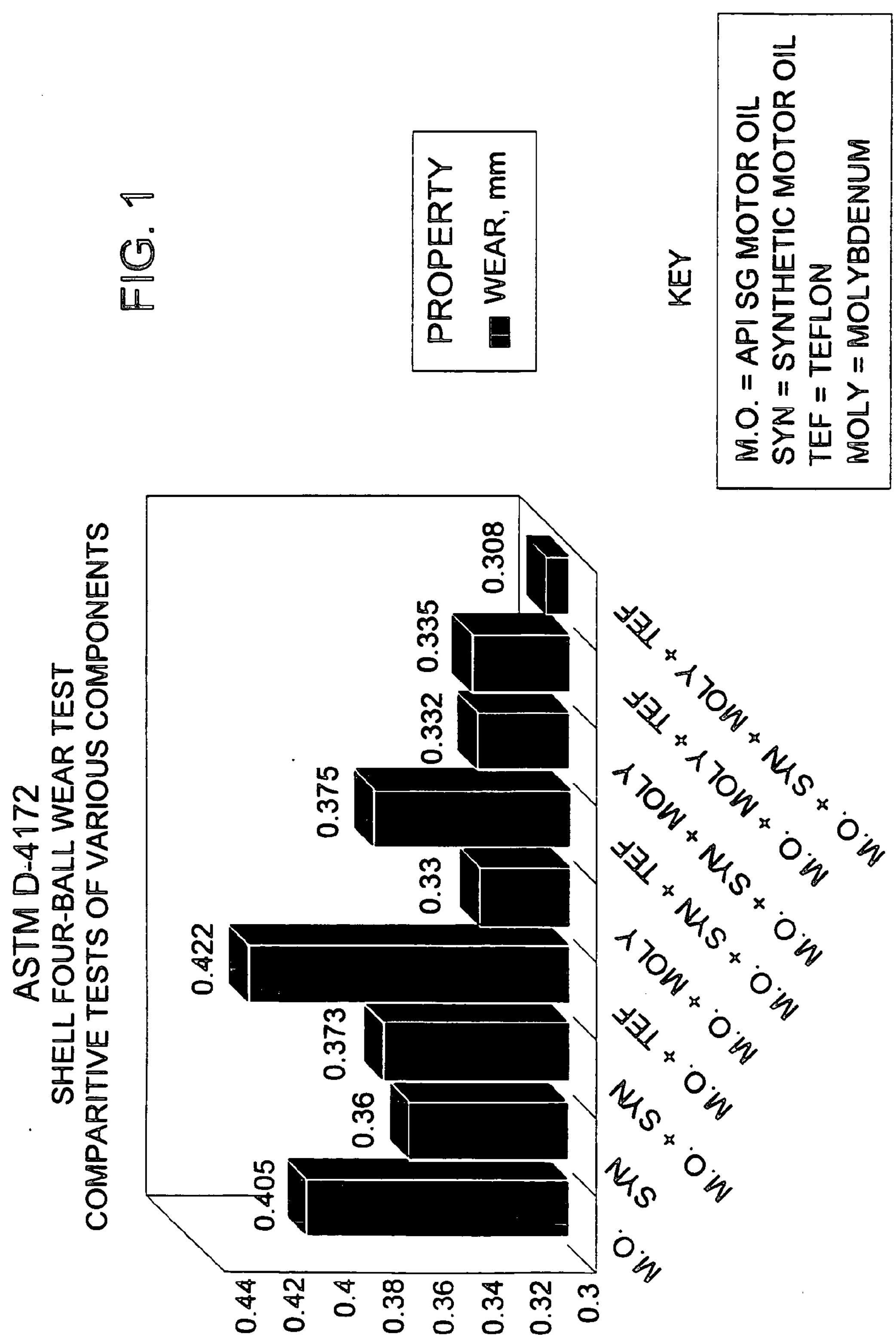
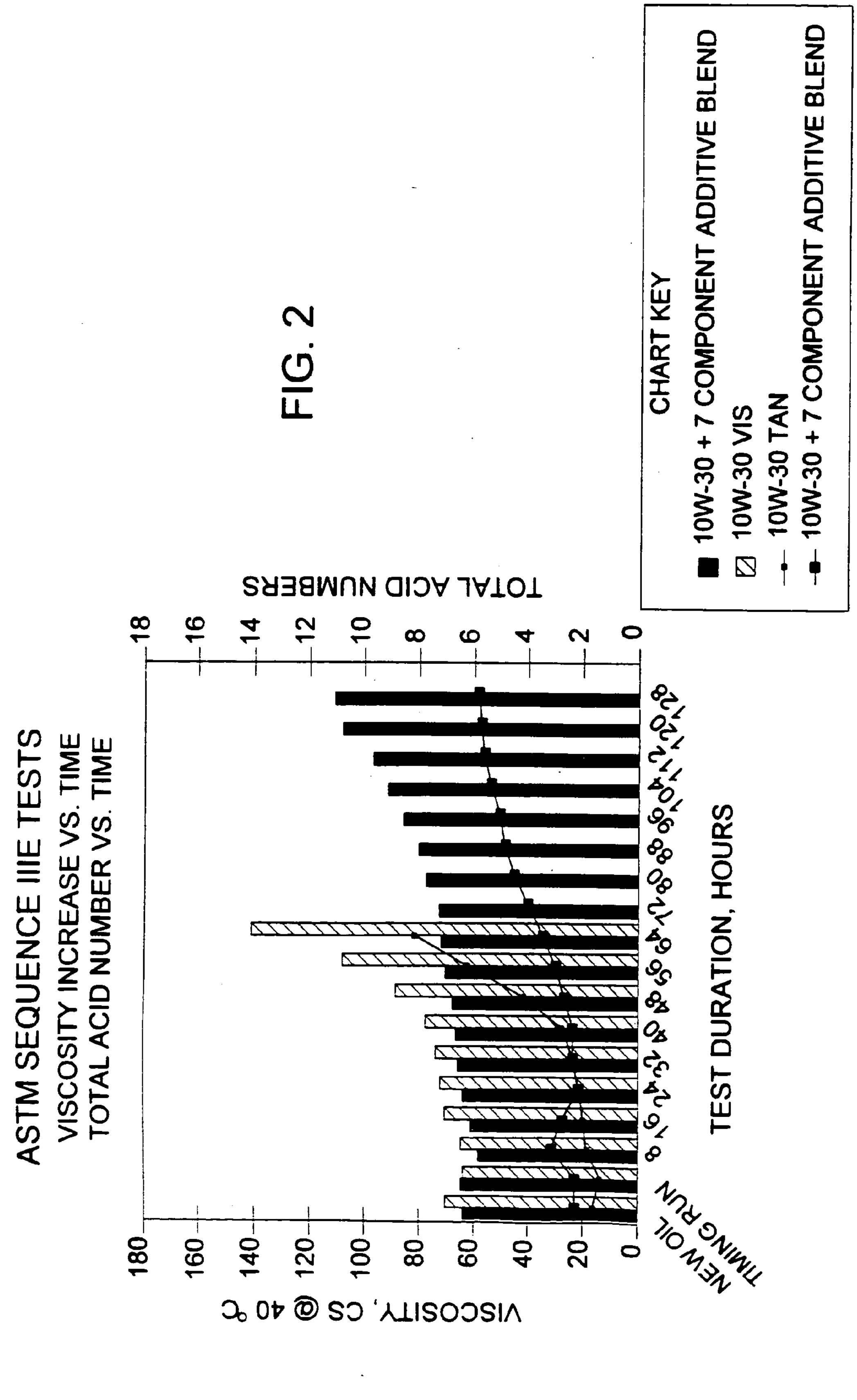

ASTM D-4172
SHELL FOUR-BALL WEAR TEST
COMPARITIVE TESTS OF VARIOUS COMPONENTS
0.44
0.42
0.4
0.38
0.36
0.34
0.32
0.3
0.405
0.36
0.373
0.422
0.33
0.375
0.332
0.335
0.308
M.O.
SYN
M.O. + SYN
M.O. + TEF
M.O. + MOLY
M.O. + SYN + TEF
M.O. + SYN + MOLY
M.O. + MOLY + TEF
M.O. + SYN + MOLY + TEF
PROPERTY
WEAR, mm
KEY
M.O. = API SG MOTOR OIL
SYN = SYNTHETIC MOTOR OIL
TEF = TEFLON
MOLY = MOLYBDENUM

FIG. 1

FIG. 2


ASTM SEQUENCE IIIE TESTS
VISCOSITY INCREASE VS. TIME
TOTAL ACID NUMBER VS. TIME
VISCOSITY, CS @ 40 °C
0 20 40 60 80 100 120 140 160 180
TOTAL ACID NUMBERS
0 2 4 6 8 10 12 14 16 18
NEW OIL
TIMING RUN
8 16 24 32 40 48 56 64 72 80 88 96 104 112 120 128
TEST DURATION, HOURS
CHART KEY
10W-30 + 7 COMPONENT ADDITIVE BLEND
10W-30 VIS
10W-30 TAN
10W-30 + 7 COMPONENT ADDITIVE BLEND

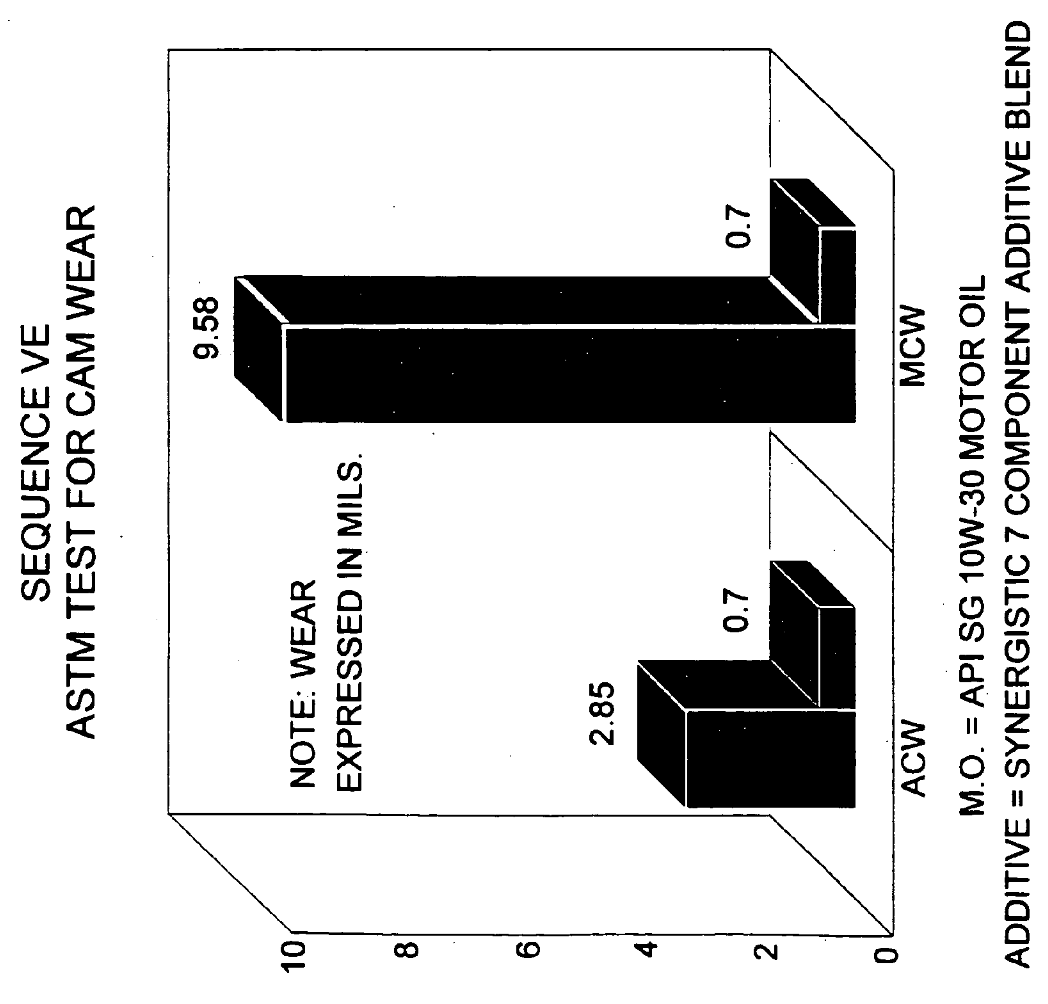
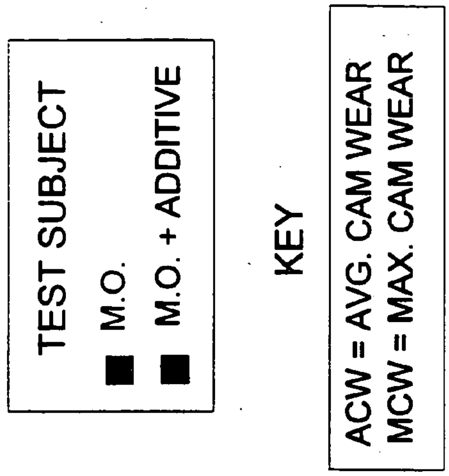

SEQUENCE VE
ASTM TEST FOR CAM WEAR
NOTE: WEAR
EXPRESSED IN MILS.
2.85
0.7
9.58
0.7
0
2
4
6
8
10
ACW
MCW
M.O. = API SG 10W-30 MOTOR OIL
ADDITIVE = SYNERGISTIC 7 COMPONENT ADDITIVE BLEND

FIG. 3


TEST SUBJECT
M.O.
M.O. + ADDITIVE
KEY
ACW = AVG. CAM WEAR
MCW = MAX. CAM WEAR

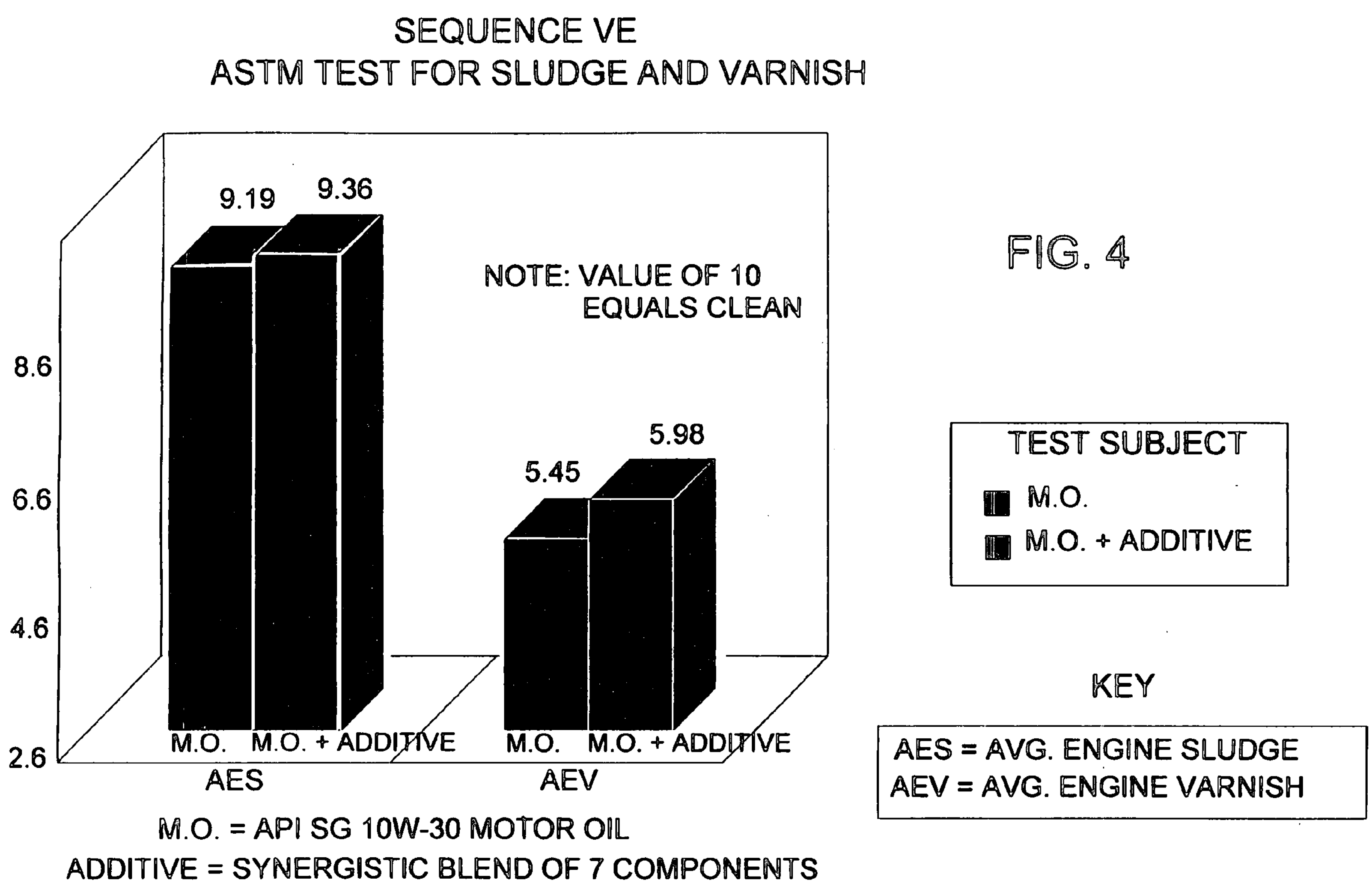

SEQUENCE VE
ASTM TEST FOR SLUDGE AND VARNISH
8.6
6.6
4.6
2.6
9.19
9.36
5.45
5.98
NOTE: VALUE OF 10 EQUALS CLEAN
M.O.
M.O. + ADDITIVE
M.O.
M.O. + ADDITIVE
AES
AEV
M.O. = API SG 10W-30 MOTOR OIL
ADDITIVE = SYNERGISTIC BLEND OF 7 COMPONENTS
TEST SUBJECT
M.O.
M.O. + ADDITIVE
KEY
AES = AVG. ENGINE SLUDGE
AEV = AVG. ENGINE VARNISH

FIG. 4

SEQUENCE VI
ASTM FUEL EFFICIENT ENGINE OIL DYNAMOMETER TEST

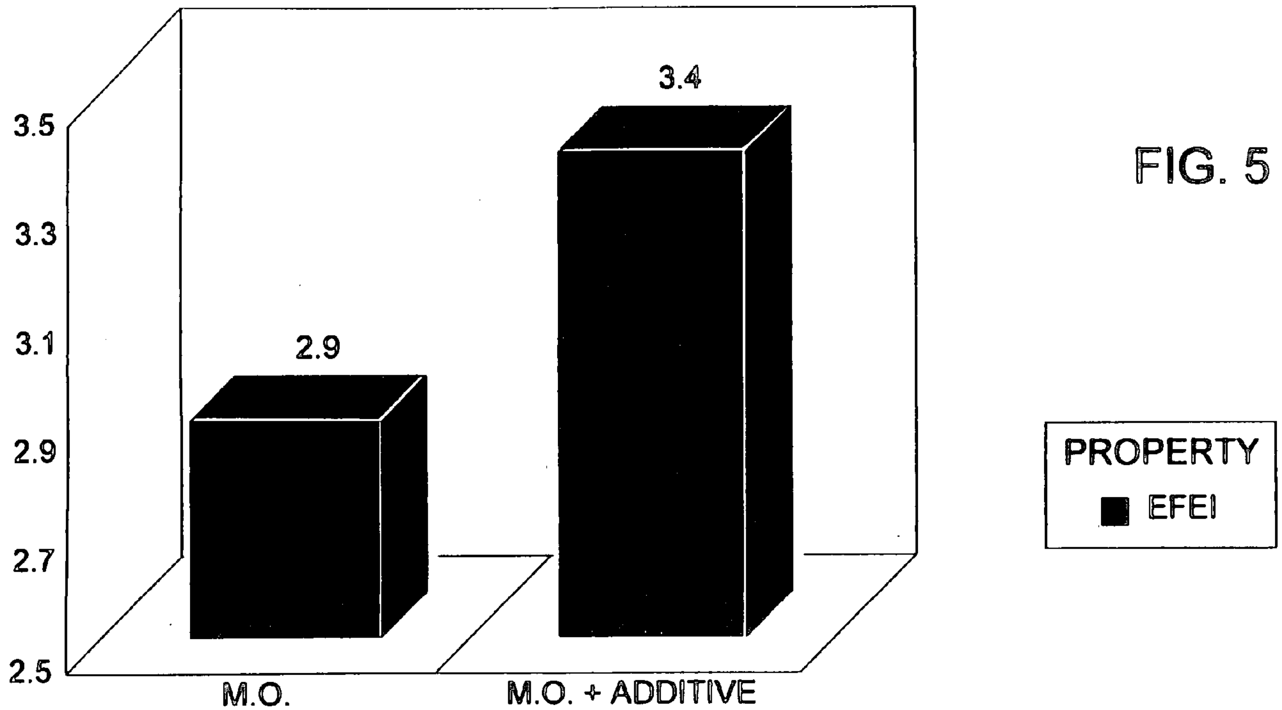
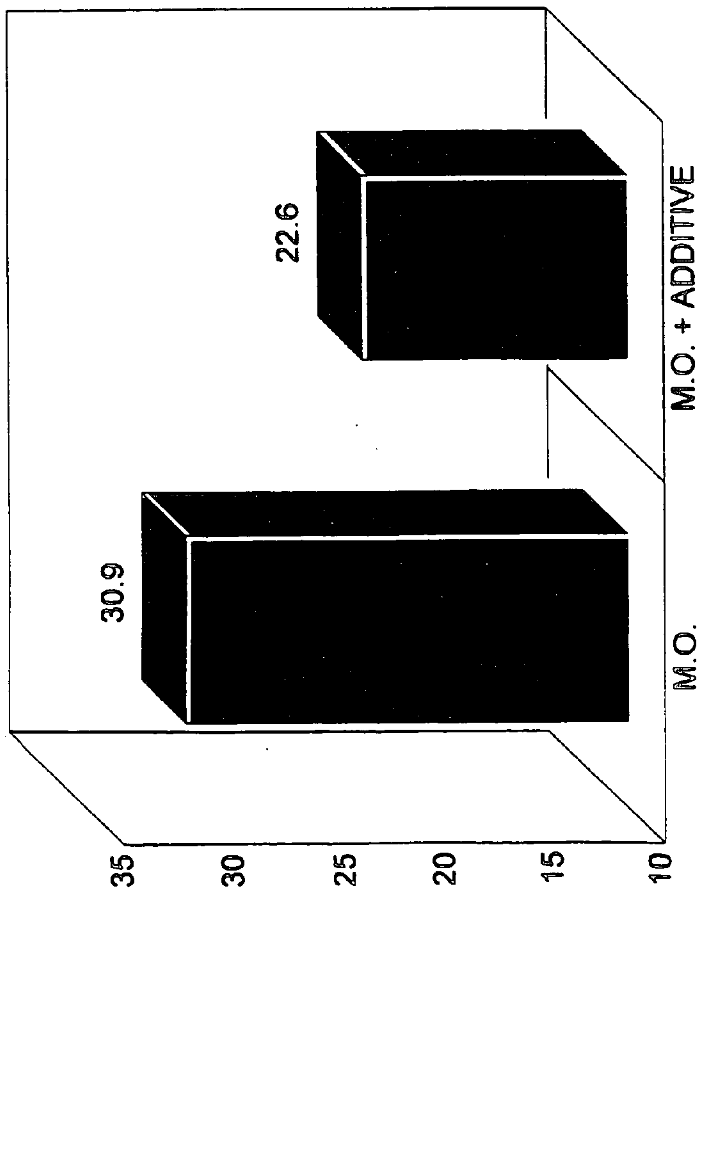


FIG. 5

EFEI = EQUIVALENT FUEL ECONOMY IMPROVEMENT
M.O. = API SG 10W-30 MOTOR OIL
ADDITIVE = SYNERGISTIC BLEND OF 7 COMPONENTS

FIG. 6

CRC L-38
CRANKCASE OXIDATION TEST



TOTAL ADJUSTED BEARING WEIGHT LOSS, mg
M.O. = API SG 5W-30 MOTOR OIL
ADDITIVE = SYNERGISTIC 7 COMPONENT ADDITIVE BLEND PLUS BORATE ESTER

LUBRICANT AND ADDITIVE FORMULATION

BACKGROUND OF THE INVENTION

[0001] This application is a Continuation-In-Part of copending U.S. application Ser. No. 10/206,852 filed on Jul. 26, 2002 which claims priority from Ser. No. 09/520,738 filed on Mar. 7, 2000; which claims priority from U.S. Pat. No. 6,034,038 which issued on Mar. 7, 2000; which claims priority from U.S. Pat. No. 5,962,377 issued on Oct. 5, 1999; which claims priority from U.S. Pat. No. 5,763,369 which issued on Jun. 9, 1998 and U.S. Pat. No. 5,641,731 which issued on Jun. 24, 1997; and U.S. application Ser. No. 10/737,731 filed on Dec. 16, 2003; Ser. No. 10/730,762 filed on Dec. 8, 2003 which claims priority from PCT/US02/16888 filed on May 30, 2002 and from 10/021,767 filed on Dec. 12, 2001 which claims priority from U.S. Provisional Application Ser. No. 60/254,959 filed on Dec. 12, 2000 all of which are incorporated by reference herein.

TECHNICAL FIELD

[0002] The invention relates to the general field of additives to improve the performance of lubricating oils and function as an engine treatment oil additive and/or complete motor oil lubricants containing nanomaterial dispersed within engine oil, oil additive packages, and oil treatment concentrates which exhibit enhanced thermal conductivity as compared to conventional fluids without the nanomaterial dispersions.

DESCRIPTION OF THE PRIOR ART

[0003] Lubrication involves the process of friction reduction, accomplished by maintaining a film of a lubricant between surfaces which are moving with respect to each other. The lubricant prevents contact of the moving surfaces, thus greatly lowering the coefficient of friction. In addition to this function, the lubricant also can be called upon to perform heat removal, containment of contaminants, and other important functions. Additives have been developed to establish or enhance various properties of lubricants. Various additives which are used include viscosity improvers, detergents, dispersants, antioxidants, extreme pressure additives, and corrosion inhibitors.

[0004] Anti-wear agents, many of which function by a process of interactions with the surfaces, provide a chemical film which prevents metal-to-metal contact under high load conditions. Wear inhibitors which are useful under extremely high load conditions are frequently called "extreme pressure agents". Certain of these materials, however, must be used judiciously in certain applications due to their property of accelerating corrosion of metal parts, such as bearings. The instant invention utilizes the synergy between several chemical constituents to provide an additive formula which enhance the performance of conventional engine oil and inhibits the undesirable side effects which may be attributable to use of one of more of the chemical constituents when used at particular concentrations.

[0005] Several references teach the use of individual chemical components to enhance the performance of conventional engine oil. For instance, U.S. Pat. No. 4,879,045 by Eggerichs adds lithium soap to a synthetic base oil comprising diester oil and polyalphaolefins which can comprise an aliphatic diester of a carboxylic acid such as di-2-ethylhexylazelate, di-isodecyladipate, or ditridecyl-adipate, as set forth in the Encyclopedia of Chemical Technology, 34th addition, volume 14, pp 477-526, which describes lubricant additives including detergent-dispersant, viscosity index (VI) improvers, foam inhibitors, and the like.

[0006] The thermal conductivity of oils, e.g., mineral oil, polyalphaolefin, ester synthetic oil, ethylene oxide/propylene oxide synthetic oil, polyalkylene glycol synthetic oil, etc. is typically 0.12 to 0.16 W/m at room temperature, and thus they are inferior as heat transfer agents to water, since water has a much higher thermal conductivity, 0.61 W/m as set forth in Table 1. Usually these oils have many other important functions, and they are carefully formulated to perform to exacting specifications for example for friction and wear performance, low temperature performance, fuel efficiency performance etc. Often designers will desire a fluid with higher thermal conductivity than the conventional oil, but are restricted to oil due to the many other parameters the fluid must meet.

TABLE 1

Thermal conductivity of various materials (at room temperature)

Material	Thermal Conductivity (W/m)
Mineral oil	0.13
Typical fully-formulated engine oil	0.12–0.16
Ethylene glycol	0.253
Water	0.613
Commercial antifreeze	0.40
Graphite	80–700

[0007] The use of graphite in fluids such as lubricants is well known. The graphite is added as a friction reducing agent, which also carries some of the load imposed on the working fluid, and therefore helps to reduce surface damage to working parts. In order to be low friction, it is well known that the graphite layered structure must contain some water or other material to create the interlayer spacing and thereby lamellar structure. There are various commercially available graphite suspensions, e.g., from Acheson Colloid Co., which are specifically intended for use in lubricants. The size of the particles is varied for different dispersions, but the minimum average size for commercially available products is in the submicron range, typically mean as 500-800 nm (nanometers). The thermal advantage of the graphite is nor mentioned in the sales literature, nor is the product sold or promoted for its thermal conductivity property.

[0008] While there have been various patents filed on lubricants containing graphite, e.g. U.S. Pat. No. 6,169,059, there are none which specifically rely on graphite to improve the thermal conductivity of the fluid formulated for specific applications.

[0009] Furthermore, there are none which teach specifically the use of nanometer-sized graphite with mean particle size much significantly less than 1000 nm in order to increase thermal conductivity and that reducing particle size improves thermal conductivity. While graphite-containing automotive engine oil was once commercialized (Arco graphite), the potential to use graphite as a heat transfer improving material in this oil was not realized. The particle size of graphite used was larger (mean greater than one micron) than for the instant invention. As a result, the graphite had some settling tendency in the fluid. Graphite of this size also significantly affects the friction and wear properties of the fluid, and heretofore has been used to reduce friction and improve wear performance of the fluid, e.g. in metalworking fluids. On the other hand, the use of graphite in lubricants for recirculating systems was made unpopular, partly due to evidence that micron size graphite could "pile up" in restricted flow areas in concentrated contacts, thereby leading to lubricant starvation. No recognition of effect of graphite particle size on this phenomena was made.

[0010] Previously, naturally formed "nano-graphites" have not been available in the marketplace at all. Recently, Hyperion Catalysis International, Inc. commercialized carbon nanotubes or so-called carbon fibrils, which have a graphitic content, e.g., U.S. Pat. No. 5,165,909. Carbon nanotubes are typically hollow graphite-like tubules having a diameter of generally several to several tens nanometers. They exist in the form either as discrete fibers or aggregate particles of nanofibers. The thermal conductivity of the Hyperion Catalysis International, Inc. material is not stated in their product literature. However, the potential of carbon nanotubes to convey thermal conductivity in a material is mentioned in U.S. Pat. No. 5,165,909. Actual measurement of the thermal conductivity of the carbon fibrils they produced was not given in the patent, so the inference of thermal conductivity is general and somewhat speculative, based on graphitic structure.

[0011] Automotive engine oils have stringent requirements for viscosity, stability to oxidation, temperature and shear, low temperature fluidity, and static and dynamic coefficient of friction. Additionally, the heat transfer requirements are significant. It is generally necessary to use some form of cooling. Because of the relatively large particle size of conventional graphite dispersions, the use of graphite in these fluids is not known.

SUMMARY OF THE INVENTION

[0012] The present invention comprises various formulations of lubricant additive concentrates for addition to conventional engine oil or as motor oil lubricants incorporating said additives therein as complete formulas for improving the lubricating properties of the engine oil, enhance the performance of the engine, and reduce engine wear and possibly reduce the consumption of the oil.

[0013] One preferred embodiment of the engine treatment oil additive comprises a blend of chemical constituents including an oil soluble molybdenum additive, a dispersant inhibitor containing zinc dithiophosphate, and a viscosity index improvers in a synthetic base stock such as a polyalphaolefin. A selected synthetic constituent comprising a ester such as a diester, and/or a polyolester, provides optimal performance characteristics to the composition. The composition may include a mineral oil or a Group III hydrogenated oil as an additive to the base formula.

[0014] In this invention, fluids of enhanced thermal conductivity are prepared by dispersing nanometer-sized carbon nanomaterials of thermal conductivity higher than 80 W/m into the fluid. The term carbon nanomaterials used in this invention refers to graphite nanoparticles, carbon nanotubes or fibrils, and other nanoparticles of carbon with graphitic structure. Stable dispersion is achieved by physical and chemical treatments.

[0015] A metal containing a high pressure antiwear agent such as a borate compound and preferably a borate ester may be added optionally as a corrosion inhibitor for yellow metals.

[0016] A nonaqueous polytetrafluoroethylene compound may be added to further improve the lubricity of the composition.

[0017] The constituents may be combined to give particularly performance properties for formulating various embodiments of the lubricant additive concentrate for use with conventional crankcase engine oil or the formulation of a complete engine oil incorporating the additive concentrate package.

[0018] A preferred embodiment of the present invention comprises effective amounts of a combination of chemical constituents including an oil soluble molybdenum additive, base oil (synthetic, mineral, and/or Group III semi-synthetics), a dispersant inhibitor containing zinc dithiophosphate, and viscosity index improvers. Addition of selected synthetics such as polyalphaolefin and/or esters such as a diester or polyolester, and/or a nonaqueous polytetrafluoroethylene compound, and/or a antiwear/extreme pressure agent such as a metal containing borate compound such as a borate ester, may be used to formulate one or more embodiments of the additive in combination with a conventional crankcase lubricant containing mineral oil, synthetic oil, semi-synthetic, or combinations thereof up to 50 volume percent and more preferably from about 10 to 40 volume percent, more preferably from about 15 to 30 percent and most preferably from about 20 to about a 25% volume/percent after dilution with motor oil, wherein typically 1 quart is blended with 4 or 5 quarts of motor oil. The various constituents are preblended and/or sold as a complete motor oil formulation.

[0019] The additive is used in combination with a conventional crankcase lubricant containing mineral oil, synthetic oil or combinations thereof up to about 50 percent by volume, more preferably from about 10 to 40 percent by volume, more preferably from 15 to 30 percent by volume, and most preferably from about 20 to about a 25% volume/percent.

[0020] One preferred nanomaterial is a high thermal conductivity graphite, exceeding 80 W/m in thermal conductivity, and ground, milled, or naturally prepared with mean particle size less than 500 nm in diameter, and preferably less than 100 nm, and most preferably less than 50 nm. The graphite is dispersed in the fluid by one or more of various methods, including ultrasonication, milling, and chemical dispersion. It is contemplated that nanoparticles can be selected from any metal from the Group IV elements, such as carbon materials (carbon nanotubes, fullerenes, graphite, amorphous carbon, carbon particles, carbon fibrils and combinations thereof, etc.), silicone carbide, and clay materials, metal (including transition metals) particles (such as silver, copper, aluminum, etc.), metal oxides, alloy particles, and combinations thereof may be applicable to the instant invention.

[0021] Carbon nanotubes with a graphitic structure are another preferred type of nanomaterial or particles. Other high thermal conductivity carbon materials are also acceptable as long as they meet the thermal conductivity and size criteria set forth heretofore.

[0022] To confer long-term stability, an effective amount of one or more chemical dispersants or surfactants is preferred, although a special grinding procedure in base oil will also confer long term stability. The thermal conductivity enhancement, compared to the fluid without graphite, is proportional to the amount of nanomaterials added. The graphite nanoparticles or nanotubes contribute to the overall fluid viscosity, partly or completely eliminating the need for viscosity index improvers and providing a very high viscosity index. Particle size and dispersing chemistry is controlled to get the desired combination of viscosity and thermal conductivity increase from the base oil while controlling the amount of temporary viscosity loss in shear fields. The resulting fluids have unique properties due to the high thermal conductivity and high viscosity index of the suspended particles, as well as their small size.

[0023] The particle-containing fluid of the instant invention will have a thermal conductivity higher than the neat fluid, wherein the term 'neat' is defined as the fluid before the particles are added.

[0024] The fluid can have other chemical agents or other type particles added to it as well to impart other desired properties, e.g. friction reducing agents, antiwear or anticorrosion agents, detergents, antioxidants, dispersants to define a lubricant composition suitable for use in vehicle applications or the like. Furthermore, the term fluid in the instant invention is broadly defined to include pastes, gels, greases, and liquid crystalline phases in either organic or aqueous media, emulsions and microemulsions.

[0025] As set forth above, the preferred carbon nanomaterials are selected from graphitic carbon structures with bulk thermal conductivity exceeding 80 W/m. A preferred form of carbon nanomaterials is carbon nanotubes. Another preferred form of carbon nanomaterials is high thermal conductivity graphite. A preferred form of the high thermal conductivity graphite is Poco Foam from Poco Graphite. Another preferred form of high thermal conductivity graphite is graphite powders from UCAR Carbon Company Inc. Still another preferred form of high thermal conductivity graphite is graphite powders from Cytec Carbon Fibers LLC. Still another preferred form of graphite is bulk graphite from The Carbide/Graphite Group, Inc.

[0026] Of course, one of the major drawbacks concerning commercial use of the carbon nanotubes and other prepared carbon structures is the cost of preparation and availability of same for commercial applications. The instant invention has resulted in the development of a method of reducing very inexpensive graphite to a nanomaterial comprising particles, fabrils and flakes suitable for use and long term dispersion in lubricant compositions.

[0027] The carbon nanomaterial containing dispersion may also contain a large amount of one or more other chemical compounds, such as polymers, antiwear agents, friction reducing agents, anti-corrosion agents, detergents, metal passivating agents, antioxidants, antifoaming agents, corrosion inhibitors, pour point depressants, and viscosity index improvers that are not for the purpose of dispersing, but to achieve thickening or other desired fluid characteristics.

[0028] Another preferred embodiment of the engine treatment oil additive comprises a blend of chemical constituents including an oil soluble molybdenum additive, a synthetic, mineral, or Group III semi-synthetic base oil. Moreover, a dispersant inhibitor containing zinc dithiophosphate, polytetrafluoroethylene, and viscosity index improvers are blended together and added thereto. An extreme pressure antiwear agent such as a borate compound may also be utilized in the present composition.

[0029] One preferred composition contains an effective amount of at least one base oil such as mineral oil, hydrocracked mineral oil with high viscosity index, vegetable derived oils, polyalphaolefins, poly-internal-olefins, polyalkylglycols, polycyclopentadienes, propylene oxide or ethylene oxide based synthetics, silicone oils, phosphate esters or other synthetic esters, or any suitable base oil; an effective amount of at least one type of nanomaterial, preferably graphite nanoparticle or carbon nanotubes, and an effective amount of at least one dispersing agents or surfactants for the purpose of stabilizing the nanoparticles.

[0030] The improved performance of the engine additive in comparison with conventional crankcase lubricants is attributable to optimizing the design parameters for each of the individual chemical constituents and combining the chemical constituents to obtain surprisingly good results including improved: wear, oxidation resistance, viscosity stability, engine cleanliness, fuel economy, cold starting, reduced oil consumption, and inhibition of acid formation. The novel engine additive formulation comprises a combination of compounds, ingredients, or components, each of which alone is insufficient to give the desired properties, but when used in concert give outstanding lubricating properties. Additional components may be added to the engine additive formulation to enhance specific properties for special applications. Moreover, the formulation is compatible with engine warranty requirements, i.e., service classification API SH and SJ.

[0031] Moreover, viscosity index is defined as the relationship of viscosity to the temperature of a fluid. It is determined by measuring the kinematic viscosities of the oil at 40° C. and 100° C. and using the tables or formulas included in ASTM D2270. It is important to note that the smaller particles give the best thermal conductivity increase, and higher viscosity index of fluid, but also contribute to higher temporary viscosity loss in shear fields. A fluid made with heat transfer improvement of 20% at 100° C. may have an improvement of 60% or more when compared to a conventional fluid at 40° C. Therefore the heat transfer improvement due to the particles may be twofold, due to the higher thermal conductivity of the particles, and also due to the exceptional viscosity index of the particle-containing fluid.

[0032] The lubricating and oil-based functional fluid compositions of the present invention are based on natural and synthetic lubricating oils and mixtures thereof in combination with the additives.

[0033] The individual components can be separately blended into the base fluid or can be blended therein in various subcombinations. Moreover, the components can be blended in the form of separate solutions in a diluent. Blending the components used in the form of an oil additive concentrate simplifies the blending operations, reduces the likelihood of blending errors, and takes advantage of the compatibility and solubility characteristics afforded by the overall concentrate. Of course, the preblended complete motor oil is convenient to use and is often preferable for adding to an engine one quart or less at a time such as for routine maintenance of older cars having engine wear and requiring additional motor oil lubricant between oil changes. The complete motor oil does not require the consumer to determine the amount of additive required for optional performance when blending with a conventional motor oil in small quantifies between oil changes.

[0034] The combination of chemical constituents of the present invention are not disclosed by any known prior art references. The incorporation of molybdenum compounds, extreme antiwear compounds such as boric acid agents and/or a PFTE lubricant provide improved performance to motor oil and greases. Moreover, the incorporation of semi-synthetic oils defined by the American Petroleum Institute (API) as severely hydro cracked oils) provide an means to reduce the cost of lubricating oils while maintaining many of the desirable characteristics of synthetic oil.

[0035] These lubricating compositions are effective in a variety of applications including crankcase lubricating oils for spark-ignited and compression-ignited internal combustion engines, two-cycle engines, aviation piston engines, marine and low-load diesel engines, and the like. The invention will find use in a wide variety of lubricants, including motor oils, greases, sucker-rod lubricants, cutting fluids, and even spray-tube lubricants. The invention has the multiple advantages of saving energy, reducing engine or other hardware maintenance and wear, and therefore, provides an economical solution to many lubricating problems commonly encountered in industry or consumer markets. It is also contemplated that the formulation may be applicable to transaxle lubricants, gear lubricants, hydraulic fluids, and other lubricating oil compositions which can benefit from the incorporation of the compositions of the instant invention.

[0036] More particularly, one preferred concentrate for addition to conventional motor oil for improving the lubricating properties of the motor oil and enhancing the performance of the engine comprises the following chemical constituents: an oil soluble molybdenum additive, a ("synthetic base") such as polyalphaolefin (PAO), a synthetic polyolester, and/or a synthetic diester, a Dispersant Inhibitor (DI) package containing zinc dithiophosphate (ZDP) and which may also contain a detergent and/or corrosion inhibitor, such as CHEMALOY D-036; a Mineral Oil Base Stock; and a Viscosity Index Improver, such as for example, (SHELLVIS 90-SBR); and an extreme anti-wear agent (borate ester). The addition of a nonaqueous polytetrafluoroethylene, ("PTFE") provides additional protection and increased performance characteristics.

[0037] Bulk graphite with high thermal conductivity is available from Poco Graphite as a graphite foam, with thermal conductivity higher than 100 W/m, and is also available from the Carbide/Graphite Group, Inc. Graphite powders can be obtained from UCAR Carbon Company Inc., with thermal conductivity 10-500 W/m, and typically >80 W/m, and from Cytec Carbon Fibers LLC, with thermal conductivity 400-700 W/m. These bulk materials must be reduced to a nanometer-sized powder by various methods for use in the instant invention.

[0038] Utilization of these inexpensive sources of nanomaterials have not been released in lubrication formulations before and a point of novelty in the instant invention is the ability to reduce the graphite to produce an inexpensive nanomaterial having a particle size suitable for long term dispersion in lubricating compositions and the method of dispersing same.

[0039] As set forth above, the preferred carbon nanomaterials are selected from graphitic carbon structures with bulk thermal conductivity exceeding 80 W/m. A preferred form of carbon nanomaterials is carbon nanotubes. Another preferred form of carbon nanomaterials is high thermal conductivity graphite. A preferred form of the high thermal conductivity graphite is Poco Foam from Poco Graphite. Another preferred form of high thermal conductivity graphite is graphite powders from UCAR Carbon Company Inc. Still another preferred form of high thermal conductivity graphite is graphite powders from Cytec Carbon Fibers LLC. Still another preferred form of graphite is bulk graphite from The Carbide/Graphite Group, Inc.

[0040] Of course, one of the major drawbacks concerning commercial use of the carbon nanotubes and other prepared carbon structures is the cost of preparation and availability of same for commercial applications. The instant invention has resulted in the development of a method of reducing very inexpensive graphite to a nanomaterial comprising particles, fabrils and flakes suitable for use and long term dispersion in lubricant compositions.

[0041] Furthermore, the carbon nanomaterial dispersion can be pre-sheared, in a turbulent flow, such as a nozzle, or high pressure fuel injector, ultrasonic device, or mill in order to achieve a stable viscosity. This may be especially desirable in the case where carbon nanotubes with high aspect ratio are used as the graphite source, since they, even more than spherical particles, will thicken the fluid but loose viscosity when exposed in turbulent flows such as the flow regime in engines. Pre-shearing, e.g. by milling, sonicating, or passing through a small orifice, such as in a fuel injector, is a particularly effective way to disperse the particles and to bring them to a stable size so that their viscosity increasing effect will not change upon further use.

[0042] The milling process itself, or other pre-shearing process, can have a rather dramatic effect on the long term dispersion stability.

[0043] A novel method has been developed whereby graphite particles are milled to form a thick pasty liquid of particles with mean size less than 500 nanometers in diameter. The pasty liquid is then used as concentrate to prepare lubricants of various viscosity grades, and can be easily diluted to make a fluid with suitable viscosity for an engine oil. A very effective paste can be made by mixing particles in a viscous base fluid in a loading of 5% to 20' by weight and milling for a period of several hours. The base fluid preferably contains from 20% up to 100% of the dispersant/surfactant mixture with the remainder being natural, synthetic, or mineral base oil. Once the thermally conductive concentrate prepared by milling is diluted to liquid consistency with base oil and other fluid components, the entire fluid can (optionally) be passed through a small orifice to further increase the uniformity and decrease the size of dispersed particles.

[0044] The term dispersant in the instant invention refers to a surfactant added to a medium to promote uniform suspension of extremely fine solid particles, often of colloidal size. In the lubricant industry the term dispersant is generally accepted to describe the long chain oil soluble or dispersible compounds which function to disperse the "cold sludge" formed in engines. The term surfactant in the instant invention refers to any chemical compound that reduces surface tension of a liquid when dissolved into it, or reduces interfacial tension between two liquids or between a liquid and a solid. It is usually, but not exclusively, a long chain molecule comprised of two moieties; a hydrophilic moiety and a lipophilic moiety. The hydrophilic and lipophilic moieties refer to the segment in the molecule with affinity for water, and that with affinity for oil, respectively. These two terms, dispersant and surfactant, are mostly used interchangeably in the instant invention for often a surfactant has dispersing characteristics and many dispersants have the ability to reduce interfacial tensions.

[0045] Finally, a preferred composition of the instant invention provides improved lubricating properties and comprises a lubricant concentrate for dilution with conventional, synthetic blend, and/or fully synthetic motor oil. A lubricating composition comprising a major amount of an oil of lubricating viscosity and a minor amount of the concentrate aforementioned concentrate additive provides a complete motor oil with improved lubricating properties.

[0046] It is an object of the present invention to provide a method of preparing a lubricant as a stable dispersion of the carbon nanomaterials in a liquid medium with the combined use of dispersants/surfactants and physical agitation.

[0047] It is an object of the present invention to provide a in which the carbon nanomaterials are made from cost-effective high-thermal-conductivity graphite (with thermal conductivity higher than 80 W/m).

[0048] It is an object of the present invention to provide a method of developing a method of forming carbon nanomaterials from inexpensive bulk graphite.

[0049] It is an object of the present invention to provide a method of utilizing carbon nanotube, graphite flakes, carbon fibrils, carbon particles and combinations thereof.

[0050] It is an object of the present invention to provide a method of using carbon nanotubes which are either single-walled, or multi-walled, with typical aspect ratio of 500-5000.

[0051] It is an object of the present invention to provide a method wherein the said dispersants/surfactants are soluble or highly dispersible in the said liquid medium.

[0052] It is an object of the present invention to provide a process for preparing a lubricant composition containing nanomaterial by a) dissolving the said dispersants/surfactants or dispersant additive package into the base fluid; b) adding a high concentration (5-20% by weight) of the said carbon nanomaterials into the above mixture while being strongly agitated by high impact milling, and/or ultrasonication, to form a pasty liquid; and c) the pasty liquid obtained in b) is further diluted with base oil and additives as needed to make the final lubricant.

[0053] It is an object of the present invention to provide a method of using a liquid medium selected from a natural oil (vegetable or animal oil), or a synthetic oil, or a mineral oil or a combination thereof.

[0054] It is an object of the present invention to provide a method of defining an appropriate dispersants/surfactants for a liquid medium of the type used in the lubricant industry, whereby it is a surfactant or a mixture of surfactants with low HLB value (<8), preferably nonionic or mixture of nonionic and ionic surfactants.

[0055] It is an object of the present invention to provide that the dispersants can be the ashless polymeric dispersants used in the lubricant industry.

[0056] It is an object of the present invention to provide a uniform dispersion in the form of a gel or paste with designed viscosity of carbon nanomaterials in base oil medium.

[0057] It is an object of the present invention to provide a uniform dispersion in a form as a gel or paste of high thermal conductivity graphite nanoparticle in petroleum, natural, or synthetic liquid medium.

[0058] It is an object of the present invention to provide a uniform and stable dispersion in a form containing dissolved non-dispersing, other functional compounds in the liquid medium.

[0059] It is an object of the present invention to provide a uniform and stable dispersion in a form without polymeric viscosity index improvers, where all viscosity index improvement comes from the carbon nanomaterials.

[0060] It is an object of the present invention to provide a uniform and stable dispersion where due to the absence of polymeric materials the dispersion exhibits no permanent, only temporary loss in viscosity due to shear fields and turbulence.

[0061] Other objects, features, and advantages of the invention will be apparent with the following detailed description taken in conjunction with the accompanying drawings showing a preferred embodiment of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0062] A better understanding of the present invention will be had upon reference to the following description in conjunction with the accompanying drawings in which like numerals refer to like parts throughout the several views and wherein:

[0063] **FIG. 1** is a bar chart of ASTM D4172 four-ball wear results versus lube compositions;

[0064] **FIG. 2** is a multiple parameter graph of base oil compared to adiditized oil showing viscosity increase and acid number increase versus time in ASTM Sequence IIIE tests wherein the additive defined in Example 1 contains PTFE, but not a boron agent;

[0065] **FIG. 3** graphs ASTM Sequence VE test results of average (and maximum) cam wear for oil including the additive of the present invention defined in Example 1 containing PTFE, but not a boron agent, versus conventional motor oil;

[0066] **FIG. 4** graphs the substantial improvement in engine cleanliness in the Sequence VE test for the oil including the additive defined in Example 1 of the present invention containing PTFE, but not a borate agent, versus conventional motor oil;

[0067] **FIG. 5** graphs ASTM Sequence VI fuel economy and shows 17%1 improvement when using the additive defined by Example 1 of the present invention containing PTFE, but not a boron agent; and

[0068] **FIG. 6** graphs CRC L-38 Crankcase Oxidation Test and shows a 36.7% improvement from using the additive defined by Example 1 of the present invention including a boron agent.

DESCRIPTION OF THE PREFERRED EMBODIMENT

[0069] Each of the preferred ingredients of the engine treatment oil additive formulation, whether mandatory or optional, is discussed below:

Oil Base Stocks

[0070] The complete motor oil formula and/or the concentrated additive contains preferably up to 95 percent by volume, more preferably from about 10 to about 95 percent by volume, more preferably from about 25 to about 90 percent by volume, more preferably from about 40 to about 85% by volume, and most preferably from about 55 to 75 percent by volume of a base stock composed of a mineral oil base stock, a severely hydrocracked oil base stock, and/or a synthetic base alone or blended together, and/or the following base stocks defined as Group I (solvent refined mineral oils), Group II (hydro cracked mineral oils), Group III (severely hydro cracked oil); Group IV (polyolefins), and Group V (esters, and napthenes). Typically the base oils from Groups III, IV and V together with additives are deemed synthetic oils. As used in the instant application, oils from Group III are deemed severly hydro cracked (semi-synthetic) base oils.

Synthetic Base Stock

[0071] Synthetic lubricating oils include hydrocarbon oils and halo-substituted hydrocarbon oils such as polymerized and interpolymerized olefins (e.g., polybutylenes, polypropylenes, propylene-isobutylene copolymers, chlorinated polybutylenes, poly(1-octenes), poly(1-decenes), etc., and mixtures thereof; alkylbenzenes (e.g., dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di-(2-ethylhexyl)benzenes, etc.); polyphenyls (e.g., biphenyls, terphenyls, alkylated polyphenyls, etc.), alkylated diphenyl, ethers and alkylated diphenyl sulfides and the derivatives, analogs and homologs thereof and the like.

[0072] Alkylene oxide polymers and interpolymers and derivatives thereof where the terminal hydroxyl groups have been modified by esterification, etherification, etc. constitute another class of known synthetic oils. These are exemplified by the oils prepared through polymerization of ethylene oxide or propylene oxide, the alkyl and aryl ethers of these polyoxyalkylene polymers (e.g., methylpolyisopropylene glycol either having an average molecular weight of 1000, diphenyl either of polyethylene glycol have a molecular weight of 500-1000, diethyl ether of polypropylene glycol having a molecular weight of 1000-1500, etc.) or mono- and polycarboxylic esters thereof, for example, the acetic acid esters, mixed C_3-C_{-8} fatty acid esters, esters, or the $C_{13}0\times0$ acid diester of tetraethylene glycol.

[0073] Another suitable class of synthetic oils comprises the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, alkyl succinic acids and alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, alkenyl malonic acids, etc.) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol diethylene glycol monoether, propylene glycol, etc.). Specific examples of these esters include dibutyl adipate, di(2-ethylhexyl) sebacate, di-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azealate, dioctyl phthalate, didecyl phthalate, dicicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid, and the like.

[0074] Esters useful as synthetic oils also include those made from C_5 to C_{12} monocarboxylic acids and polyols and polyol ethers such as neopentyl glycol, trimethylolpropane, pentaerythritol, dipentaerythritol, tripentaerythritol, etc. Other synthetic oils include liquid esters of phosphorus-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, diethyl ester of decylphosphonic acid, etc.), polymeric tetrahydrofurans and the like.

[0075] The concentrate additive and/or complete motor oil contains preferably up to 95 percent by volume, more preferably from about 10 to about 95 percent by volume, more preferably from about 25 to about 90 percent by volume, more preferably from about 40 to about 85% by volume, and most preferably from about 55 to 75 percent by volume of a synthetic, Group III severely hydro cracked (semi-synthetic), and/or mineral oil base stock used alone or blended together as a base stock.

[0076] One preferred synthetic base stock comprises at least a significant portion of a polyalphaolefin.

Polyalphaolefin (PAO)

[0077] Although not essential, the preferred synthetic base stock comprises at least a significant portion of a polyalphaolefin. Polyalphaolefin, ("PAO"), is a synthetic fluid effective at high temperatures, such as occurs during operation of internal combustion engines. It is also very effective at low temperatures. It is especially effective in the presence of diesters. Polyalphaolefin provides superior oxidation and hydrolytic stability and high film strength. Polyalphaolefin also has a high molecular weight, higher flash point, higher fire point, lower volatility, higher viscosity index, and lower pour point than mineral oil. U.S. Pat. No. 4,859,352 hereby incorporated by reference provides additional polyalphaolefin derivatives.

[0078] Preferred polyalphaolefins, ("PAO"), include those sold by EXXON-MOBIL USA as SHF fluids and those sold by Ethyl Corporation under the name ETHYLFLO, or ("ALBERMARLE"). PAO's include the ETHYL-FLOW series by Ethyl Corporation, "Albermarle Corporation", including ETHYL-FLOW 162, 164, 166, 168, and 174, having varying viscosities from about 2 to about 460 centistoke. Also useful are blends of about 56% of the 460 centistoke product and about 44% of the 45 centistoke product as set forth in U.S. Pat. No. 5,348,668 hereby incorporated by reference.

[0079] MOBIL SHF-42 from EXXON-MOBIL USA, EMERY 3004 and 3006, Equilon, and Quantum Chemical Company provide additional polyalphaolefins base stocks.

For instance, EMERY 3004 polyalphaolefin has a viscosity of 3.86 centistokes (cSt) at 212° F. (100 C.) and 16.75 cSt at +104 F. (40 C.). It has a viscosity index of 125 and a pour point of −98 F and it also has a flash point of +432 F. and a fire point of +478 F. Moreover, EMERY 3006 polyalphaolefin has a viscosity of 5.88 cSt at +212 F. and 31.22 cSt at +104 F. It has a viscosity index of 135 and a pour point of −87 F. It also has a flash point of +464 F. and a fire point of +514 F.

[0080] Additional satisfactory polyalphaolefins are those sold by Uniroyal Inc. under the brand SYNTON PAO-40, which is a 40 centistoke polyalphaolefin. Also useful are the ORONITE brand polyalphaolefins manufactured by CHEVRON-TEXACO Chemical Company.

[0081] It is contemplated that GULF SYNFLUID 4 cSt PAO, commercially available from Gulf Oil Chemicals Company, a subsidiary of CHEVRON-TEXACO Corporation, which is similar in many respects to EMERY 3004 may also be utilized herein. MOBIL SHF-41 PAO, commercially available from EXXON-MOBIL Chemical Corporation, is also similar in many respects to EMERY 3004.

[0082] Preferably the polyalphaolefins will have a viscosity of up to 100 centistoke and more typically in the range of about 2-10 centistoke at 100° C. with viscosities of 4 and 6 centistoke being particularly preferred.

[0083] Moreover, a preferred embodiment may incorporate up to 95 percent by volume, more preferably from 10 to 90 percent by volume, and more preferably from about 40 to 85 percent by volume of polyalphaolefins having a viscosity of about 4cSt at 100° C. such as is available from Ethyl Corporation under the trademark name of DURASYN 164.

[0084] A preferred concentrate embodiment may incorporate up to 85 percent by volume, more preferably from 5 to 85 percent by volume, more preferably from about 10 to 60 percent by volume, and most preferably from 10 to 30 percent by volume of polyalphaolefins having a viscosity of about 6cSt at 100° C. such as is available from Ethyl Corporation under the trademark name of DURASYN 166.

[0085] Moreover, an even more preferred embodiment of the present invention further providing even more enhanced performance characteristics utilizes synthetics which include a specific portion comprising esters, polyesters, or combinations thereof. One preferred embodiment utilizes polyolefins as the synthetic base stock together with at least a portion comprising esters and/or polyesters.

Esters

[0086] The most preferred synthetic based oil ester additives are polyolesters and diesters such as di-aliphatic diesters of alkyl carboxylic acids such as di-2-ethylhexylazelate, di-isodecyladipate, and di-tridecyladipate, commercially available under the brand name EMERY 2960 by Emery Chemicals, described in U.S. Pat. No. 4,859,352 to Waynick. Other suitable polyolesters are manufactured by EXXON-MOBIL Oil. Exxon-Mobil polyolester P-43, NP343 containing two alcohols, and Hatco Corp. 2939 are particularly preferred.

[0087] Diesters and other synthetic oils have been used as replacements of mineral oil in fluid lubricants. Diesters have outstanding extreme low temperature flow properties and good residence to oxidative breakdown.

[0088] The diester oil may include an aliphatic diester of a dicarboxylic acid, or the diester oil can comprise a dialkyl aliphatic diester of an alkyl dicarboxylic acid, such as di-2-ethyl hexyl azelate, di-isodecyl azelate, di-tridecyl azelate, di-isodecyl adipate, di-tridecyl adipate. For instance, Di-2-ethyl hexyl azelate is commercially available under the brand name of EMERY 2958 by Emery Chemicals.

[0089] Also useful are polyol esters such as EMERY 2935, 2936, and 2939 from Emery Group of Henkel Corporation and HATCO 2352, 2962, 2925, 2938, 2939, 2970, 3178, and 4322 polyol esters from Hatco Corporation, described in U.S. Pat. No. 5,344,579 to Ohtani et al. and MOBIL ester P 24 from EXXON-MOBIL USA. EXXON-MOBIL esters such as made by reacting dicarboxylic acids, glycols, and either monobasic acids or monohydric alcohols like EMERY 2936 synthetic-lubricant base stocks from Quantum Chemical Corporation and MOBIL P 24 from EXXON-MOBIL USA can be used. Polyol esters have good oxidation and hydrolytic stability. The polyol ester for use herein preferably has a pour point of about −100° C. or lower to −40° C. and a viscosity of about 2-460 centistoke at 100° C.

[0090] Although not essential, a preferred additive concentrate and/or motor oil comprises at least a portion of a ester. The concentrate additive and/or complete motor oil contains preferably up to 25 percent by volume, more preferably from about 5 to about 20 percent by volume, more preferably from about 5 to about 15 percent by volume, of a polyester or diester such as obtained from EMERY under the trademark 2960.

Severely Hydro Cracked Oils

[0091] A hydrogenated oil is a mineral oil subjected to hydrogenation or hydrocracking under special conditions to remove undesirable chemical compositions and impurities resulting in a base oil having synthetic oil components and properties. Typically the hydrogenated oil is defined by the American Petroleum Institute (API) as a Group III petroleum based stock with a sulfur level less than 0.03 with saturates greater than or equal to 90 and a viscosity index of greater than or equal to 120 may optionally be utilized in amounts up to 95 percent by volume, more preferably from 5.0 to 50 percent by volume and more preferably from 20 to 40 percent by volume when used alone or in combination with a synthetic or mineral oil.

[0092] The hydrogenated oil may be used as the sole base oil component of the instant invention providing superior performance to conventional motor oils with no other synthetic oil base or mineral oil base or used as a blend with mineral oil and/or synthetic oil. An example of such an oil is YUBASE-4. Other suppliers include CHEVRON-TEXACO Company. A complete motor oil or an additive concentrate embodiment may incorporate up to 95 percent by volume, more preferably from 5 to 85 percent by volume of the semi-synthetic as the oil base stock. When used in combination with another conventional synthetic oil such as those containing polyolefins or esters, or when used in combination with a mineral oil, the hydrogenated oil may be present in an amount of up to 95 percent by volume, more preferably from about 10 to 80 percent by volume, more preferably from 20 to 60 percent by volume and most preferably from 10 to 30 percent by volume of the base oil composition.

[0093] More particularly, the hydrogenated oil is a base oil for a lubricating oil consisting of a mineral oil and/or a synthetic oil, having a viscosity index of at least 120, and having a viscosity of from 2 to 3,000 CST at 100 degrees C. Hydrogenated oils can be obtained by subjecting raw materials for lubricating oils to hydrogenation treatment, using a hydrogenation catalyst such as cobalt or molybdenum with a silica-alumina carrier, and lubricating oil factions which can be obtained by the isomerization of waxes. The hydro cracked or wax-isomerized oils contain 90 percent by weight or greater of saturates and 300 ppm or less of sulfur.

Mineral Oil Base Stock

[0094] Although not essential, a mineral oil base stock may be incorporated in the present invention as a portion of the concentrate or a base stock to which the concentrate may be added to produce a motor oil. Particularly preferred as mineral oil base stocks are the ASHLAND 325 Neutral defined as a solvent refined neutral having a SABOLT UNIVERSAL of 325 SUS @ 100° F. and ASHLAND 100 Neutral defined as a solvent refined neutral having a SABOLT UNIVERSAL of 100 SUS @ 100° F., manufactured by MARATHON ASHLAND PETROLEUM and by others.

[0095] Other acceptable petroleum-base fluid compositions include white mineral, paraffinic and MVI naphthenic oils having the viscosity range of about 20-400 Centistoke. Preferred white mineral oils include those available from WITCO Corporation, ARCO BP Chemical Company, PSI and PENRECO. Preferred paraffinic oils include API Group I and Group II oils available from EXXON MOBIL USA, Group II oils available from MOTIVA ENTERPRISES, LLC., and Group II oils available from CHEVRON EXXON Corp. Preferred MVI naphthenic oils include solvent extracted oils available from EQUILON ENTERPRISES and SAN JOAQUIN REFINING, hydro treated oils available form EQUILON ENTERPRISES, and naphthenic oils sold under the names HYDROCAL and CALSOL by CALUMET, and naphthenic oils such as are described in U.S. Pat. No. 5,348,668 to Oldiges.

[0096] Mineral oil base stock can comprise the entire base oil typically up to 95% by volume, more preferably 5-85 percent by volume, more preferably 50-80 percent by volume and most preferably 70-80 percent by volume in the complete motor oil, but is not narrowly critical. More particularly, the mineral oil base stock can be used up to about 95 percent in the concentrate and up to 50 percent and preferably up to about 35 percent by volume of the motor engine oil upon dilution. Typically one unit of the concentrate is diluted with about 4 or 5 units of the motor oil which may be a fully synthetic, mineral oil, or blend.

[0097] Finally, vegetable oils may also be utilizes as the liquid medium in the instant invention. Soybean or rapeseed oil, particularly of the high oleic or mid oleic genetically engineered type, commercially available from Archer Daniels Midland Company, are good examples of these oils. Soybean oil is of interest because it has a high thermal conductivity itself.

Dispersants Used in Lubricant Industry

[0098] Dispersants used in the lubricant industry are typically used to disperse the "cold sludge" formed in gasoline and diesel engines, which can be either "ashless dispersants", or containing metal atoms. They can be used in the instant invention since they are found to be an excellent dispersing agent for nanoparticles with graphitic structure of this invention. They are also needed to disperse wear debris and products of lubricant degradation within the engine.

[0099] The ashless dispersants commonly used in the automotive industry contain an lipophilic hydrocarbon group and a polar functional hydrophilic group. The polar functional group can be of the class of carboxylate, ester, amine, amide, imine, imide, hydroxyl, ether, epoxide, phosphorus, ester carboxyl, anhydride, or nitrile. The lipophilic group can be oligomeric or polymeric in nature, usually from 70 to 200 carbon atoms to ensure oil solubility. Hydrocarbon polymers treated with various reagents to introduce polar functions include products prepared by treating polyolefins such as polyisobutene first with maleic anhydride, or phosphorus sulfide or chloride, or by thermal treatment, and then with reagents such as polyamine, amine, ethylene oxide, etc.

[0100] Of these ashless dispersants the ones typically used in the petroleum industry include N-substituted polyisobutenyl succinimides and succinates, alkyl methacrylate-vinyl pyrrolidinone copolymers, alkyl methacrylate-dialkylaminoethyl methacrylate copolymers, alkylmethacrylate-polyethylene glycol methacrylate copolymers, and polystearamides. Preferred oil-based dispersants that are most important in the instant application include dispersants from the chemical classes of alkylsuccinimide, succinate esters, high molecular weight amines, Mannich base and phosphoric acid derivatives. Some specific examples are polyisobutenyl succinimide-polyethylencpolyamine, polyisobutenyl succinic ester, polyisobutenyl hydroxybenzyl-polyethylcncpolyamine, bis-hydroxypropyl phosphorate. Commercial dispersants suitable for lubricating fluids are for example, Lubrizol 890 (an ashless PIB succinimide), Lubrizol 6420 (a high molecular weight PIB succinimide), ETHYL HITEC 646 (a non-boronated PIB succinimide). The dispersant may be combined with other additives used in the lubricant industry to form a ispersant-detergent (DI) additive package for lubricating fluids, e.g., LUBRIZOL 9677MX, and the whole DI package can be used as dispersing agent for the nanoparticle dispersions.

Other Types of Dispersants

[0101] Alternatively a surfactant or a mixture of surfactants with low HLB value (typically less than or equal to 8), preferably nonionic, or a mixture of nonionics and ionics, may be used in the instant invention.

[0102] The dispersants selected should be soluble or dispersible in the liquid medium. The dispersant can be in a range of up from 0.01 to 30 percent, more preferably in a range of from between 0.5 percent to 20 percent, more preferably in a range of from between 1 to 15 percent, and most preferably in a range of from between 2 to 13 percent. The carbon nanomaterials can be of any desired weight percentage in a range of from 0.001 up to 10 percent. For practical application it is usually in a range of from between 0.01 percent to 10 percent, and most preferably in a range of from between 0.1 percent to 5 percent. The remainder of the formula is the selected medium.

[0103] It is believed that in the instant invention the dispersant functions by adsorbing onto the surface of the carbon nanomaterials.

[0104] Though not narrowly critical, the Dispersant Inhibitor ("DI"), is exemplified by those which contain alkyl zinc dithiophosphates, succinimides, esters, or Mannich dispersant, calcium, magnesium, sodium sulfonates, phenates, phenylic and amine antioxidants, plus various friction modifiers such as sulfurized fatty acids. Dispersant inhibitors are readily available from Lubrizol, Ethyl, Oronite, a division of CHEVRON-TEXACO Chemical, and INFINEUM.

[0105] Generally acceptable are those commercial detergent inhibitor packages used in formulated engine oils meeting the API SH CD or higher performance specifications. Particularly preferred are dispersants such as LUBRIZOL 8955 having chemical and physical properties such as those described in U.S. Pat. No. 5,490,945 of the Lubrizol Corporation which is hereby incorporated by reference, ETHYL HITEC 1111 and 1131, and similar formulations available from INFINEUM, or Oronite, a division of CHEVRON-TEXACO Chemical.

[0106] An effective amount of an additive package which incorporates a dispersion inhibitor such as the one listed heretofore may also be utilized and include a conventional detergent and/or a corrosion inhibitor. Such an additive package may be utilized with or in substitution of a selected dispersion inhibitor or combinations thereof with each other and/or other dispersion inhibitors commercially available in an effective amount of up to 35 percent by volume, more preferably from about 0.5 to 25 percent by volume and more preferably from about 1 to 15 percent by volume of the complete motor oil formula and up to 6× that amount in the concentrate. The DI concentration is generally up to 15% by volume of the total formulation of the complete engine oil and more particularly from 5.0 to 15% by volume. Concentrations produced for dilution will generally be in these ranges.

[0107] Zinc dithiophosphate is a multi-function additive in that it functions as a corrosion inhibitor, antiwear agent, and antioxidants added to organic materials to retard oxidation.

[0108] Other metal dithiophosphates such as zinc isopropyl, methylamyl dithiophosphate, zinc isopropyl isooctyl dithiophosphate, barium di(nonyl) dithiophosphate, zinc di(cyclohexyl) dithiophosphate, copper di(isobutyl) dithiophosphate, calcium di(hexyl) dithiophosphate, zinc isobutyl isoamyl dithiophosphate, and zinc isopropyl secondary-butyl dithiophosphate may be applicable. These metal salts of phosphorus acid esters are typically prepared by reacting the metal base with the phosphorus acid ester such as set forth in U.S. Pat. No. 5,354,485 hereby incorporated by reference. Moreover, a preferred dispersion inhibitor is described in U.S. Pat. No. 5,490,945 hereby incorporated by reference which describes a compound containing at least one carboxylic derivative composition produced by reacting at least one substituted succinic acylating agent containing at least about 50 carbon atoms in the substituent with at least one amine compound containing at least one HN<group.

Pour Point Depressant

[0109] A pour point depressant in an effective amount of up to 10.0 volume percent of the complete engine oil formula and more preferably about 0.01 to 5.0 percent by weight and most preferably from about 0.1 to 1.0 percent by weight is not essential but can be utilized an embodiment of the formulation. Of course, a sufficient amount of the viscosity improver may also be incorporated in the base oils or motor oil to be treated. Also the pour point depressant is typically not concentrated 4× or 5× in the additive package. An example of a suitable pour point depressant is polymethacyrlate, alkylated bicyclic aromatics, styrene esters, polyfumerates, oligomerized alky phenyls, dialkyl esters of phthalate acid, ethylene vinyl acetate copolymers, and other mixed hydrocarbon polymers from LUBRIZOL, the ETHYL Corporation, or ROHMAX, a Division of Degussa. A commercially available pour point depressant is sold under the brand name of ACRYLOID 3008 which is a polymethyrlate formula.

Additive Packages

[0110] Additive packages which incorporate a dispersion inhibitor with a conventional detergent and/or a corrosion inhibitor may also be utilized with or in substitution of the dispersion inhibitor. For instance as set forth heretofore, such an additive package may comprise Lubrizol's LZ8955 and/or LZ9802 or combinations thereof with each other and/or other dispersion inhibitors in an effective amount of up to 35 percent by volume, more preferably from about 0.5 to 25 percent by volume and more preferably from about 1 to 10 percent by volume of the concentrate.

[0111] Because the base oils typically contain an effective amount of a pour point depressant and/or the motor oil to which the additive is added typically contain an effective amount of a pour point depressant, it would not typically be concentrated 4× or 5× in the additive package.

Viscosity Index Imrover (VI)

[0112] Viscosity improvers, ("VI"), include, but are not limited to, polyisobutenes, polymethacrylate acid esters, polyacrylate acid esters, diene polymers, polyalkyl styrenes, alkenyl aryl conjugated diene copolymers, polyolefins and multifunctional viscosity improvers and SHELLVIS 90, a linear styrene isoprene rubber in mineral oil base or SHELLVIS 260 a cyclic styrene isoprene compound.

[0113] The lubricant additive contain up to 15 percent by volume of a viscosity improver, more preferably from about 0.005-10 percent by volume, more preferably 0.05 to 8 and more preferably from 0.1 to 1.0 percent by volume. Of course, a sufficient amount of the viscosity improver may also be incorporated in the base oils or motor oil to be treated.

Molybdenum Additive

[0114] The most preferred molybdenum additive is an oil-soluble decomposable organo molybdenum compound, such as MOLYVAN 855 which is an oil soluble secondary diarylamine defined as substantially free of active phosphorus and active sulfur. The MOLYVAN 855 is described in Vanderbilt's Material Data and Safety Sheet as a organomolybdenum compound having a density of 1.04 and viscosity at 100 EC of 47.12 cSt. In general, the organo molybdenum compounds are preferred because of their superior solubility and effectiveness.

[0115] A less effective alternative molybdenum additive is MOLYVAN L is sulfonated oxymolybdenum dialkyldithiophosphate described in U.S. Pat. No. 5,055,174 by Howell hereby incorporated by reference.

[0116] MOLYVAN A made by R.T. Vanderbilt company, Inc., New York, N.Y., USA, is also an alternative additive which contains about 28.8 wt. % Mo, 31.6 wt. % C, 5.4 wt. % H., and 25.9 wt. % S. Also useful are MOLYVAN 855, 822, 856, and 807 in decreasing order of preference.

[0117] Also useful is SAKURA LUBE-500, which is more soluble Mo dithiocarbamate containing lubricant additive obtained from Asahi Denki Corporation and comprised of about 20.2 wt. % MO, 43.8 wt. % C, 7.4 wt. % H, and 22.4 wt. % S.

[0118] Also useful is MOLYVAN 807, a mixture of about 50 wt. % molybdenum ditridecyldithyocarbonate, and about 50 wt. % of an aromatic oil having a specific gravity of about 38.4 SUS and containing about 4.6 wt. molybdenum, also manufactured by R.T. Vanderbilt and marketed as an antioxidant and antiwear additive.

[0119] Other sources are molybdenum $Mo(Co)_6$, and Molybdenum octoate, $Mo(C_7H_{15}CO_2)_2$ containing about 8 wt-% Mo marketed by Aldrich Chemical Company, Milwaukee, Wis. and molybdenum naphthenethioctoate marketed by Shephard Chemical Company, Cincinnati, Ohio.

[0120] Inorganic molybdenum compounds such as molybdenum sulfide and molybdenum oxide are substantially less preferred than the organic compounds as described in 855, 822, 856, and 807.

[0121] Whereas 1% is equal to 10,000 parts per million (ppm), the preferred dosage in the molybdenum additive is up to 5.0 percent by mass. More preferably the preferred dosage is up to 3,000 ppm by mass, more preferably from about 100 ppm to about 2,000 ppm by mass, more preferably from about 300 to about 1,500 ppm by mass, more preferably from 300 to about 1000 ppm by mass of molybdenum.

Nanomaterials

[0122] One preferred type of graphitic particles are carbon nanotubes, the nanotubes can be either single-walled, or multi-walled, having a typical nanoscale diameter of 1-200 nanometers. More typically the diameter is around 10-30 nanometers. The length of the tube can be in submicron and micron scale, usually from 500 nanometers to 500 microns. More typical length is 1 micron to 100 microns. The aspect ratio of the tube can be from hundreds to thousands, more typical 500 to 5000. The surface of the nanotube can be treated chemically to achieve certain level of hydrophilicity, or left as is from the production. Unfortunately, the commercial availability of the prepared nanotubes is limited making them too expensive for incorporation into commodity type lubricants at this time.

[0123] Therefor, a novel method has been developed to form nanomaterials suitable for use with commodity type lubricants at a low cost and capable of being produced in a large quantity using readily available equipment. Other acceptable form of graphite is a high-thermal-conductivity graphite commercially available, e.g. POCO FOAM, available from Poco Graphite, Inc., and graphite powders available from UCAR Carbon Company Inc. POCO FOAM is a high thermal conductivity foamed graphite, thermal conductivity typically in the range 100 to 150 W/m. A readily commercially available graphite is graphite powders from UCAR Carbon Company Inc., thermal conductivity of 10 to 500 W/m, and typically >80 W/m. Still another acceptable form of graphite is the high-thermal-conductivity graphite, Part#875G, from The Carbide/Graphite Group, Inc.

[0124] These graphite are prepared for the instant invention by pulverizing to a fine powder, dispersing chemically and physically in a fluid of choice, and then ball milled or otherwise size reduced until particle, flake, fibril or combinations thereof produce nanomaterial of a size of less than 500 nm mean size is attained. The preferred method is to disperse the graphite by ball milling in a viscous fluid of most additives (detergents, dispersants, etc.) and then diluting the obtained concentrate with base oil and other additives as needed to attain the final viscosity and performance characteristics. The finer the particle size attained upon milling, the better the thermal conductivity increase but also the more viscosity thickening effect of the pasty concentrate on the final blend. These effects must be balanced to attain a suitable lubricating film thickness at the maximum shear rate and temperature of fluid use. In general, any high thermal conductivity graphite can be used, provided that pulverization, milling and other described chemical and physical methods can be used to reduce the size of the final graphite dispersion to below a mean particle size of 500 nm or less.

[0125] In the process of making lubricating fluid such as the engine oil or engine treatment concentrate additive with the nanomaterial, the mechanical process and sequence of adding the components are important in order to fully take advantage of the high viscosity index of the nanoparticles and to make the final fluid product with exceptionally high viscosity index. High impact mixing is necessary to achieve a homogeneous dispersion. Ball mill is one of the examples of a high impact mixer. In the instant invention, an Eiger Mini Mill (Model: M250-VSE-EXP) is used as the high impact ball mill. It utilizes high wear resistant zirconia beads as the grinding media and circulates the dispersion constantly during milling.

[0126] To achieve the best milling effect and therefore the best viscosity index improvement, the proper milling procedure has been developed. Firstly a 5% to 20% by weight of graphite powders, and more preferably 10% by weight of graphite powders, in base oil dispersion is milled into a paste state. Usually this step takes about 3 to 4 hours. Then add the appropriate effective amount of at least one dispersing agent(s), usually 1 to 2 times of the weight of graphite, into the mill. With the addition of dispersing agent(s) the paste changes from paste into liquid almost instantly, and extended milling becomes possible. For most cases the extended milling period is 4 hours. It should be pointed out that if the mixture in the mill turns into a paste, the recirculation of it becomes very difficult and thus a poor milling is resulted. It is also found that if the dispersing agent(s) is(are) added into the mill at the very beginning, the viscosity index of the final nanofluids made from the milling process is not as high.

[0127] Graphite nanomaterials are obtained by pulverizing big graphite chunks weight several pounds or kilograms obtained from The Carbide/Graphite Group. The resulting pulverized material is size-selected through a mesh filter to be less than 75 μm. Thirty (30) grams of the above pulverized graphite particles and 270 grams of a base oil, DURASYN 162 (a commercial 2 centistokes polyalphaolefin) were added into the Eiger Mini Mill (Model: M250-VSE-EXP). The milling speed was gradually increased to 4000 rpm. In about 4 hours the above mixture turned into thick paste. About 60 grams of this paste was discharged and labeled Paste 'A'. Forty-eight (48) grams of a dispersant package from Lubrizol, LUBRIZOL 9677MX, was added to the rest of the mixture in the mill. The paste became very thin, and successful recirculation was restored. Stopped the mill after another 4 hours of milling and labeled the discharged paste as Paste "B" Paste "C" was obtained by milling a mixture of 30 grams of graphite with diameter less than 75 μm, 60 grams of LUBRIZOL 9677MX, and 270 grams of DURASYN 162 at 4000 rpm for 8 hours. Note here the dispersing agent LUBRIZOL 9677MX was added into the mill at the very beginning. Then engine oil concentrates can be formulated using the above three pastes as concentrates respectively. The final compositions were exactly the same by weight and ingredients except for the graphite material: 2% graphite, 4% LUBRIZOL 9677 MX, 18% DURASYN 162, 76% DURASYN 166 (a commercial 6 centistokes polyalphaolefin base oil) (all percentage by weight). Example 1 illustrates the 100° C. viscosity and viscosity index (VI) of the fluids. It was also found that the graphite particle size before milling was an important variable to control the viscosity modification effect as well. For example, starting with graphite smaller than 10 (obtained as graphite powder from UCAR Carbon Company Inc.) and following the same procedure as Paste B, a thin Paste D was obtained. The particle size is measured by atomic force microscopy (AFM), and the graphite nanoparticles appear to be flakes or a plate-like structure, with average diameter of around 50 nm and thickness around 5 nm.

[0128] The present invention provides at a minimum, a fluid of lubricant containing less than 10% by weight graphite nanoparticles. Preferably, however, a minimum of one or more chemical dispersing agents and/or surfactants is also added to achieve long term stability.

Polytetrafluoroethylene Additive

[0129] Polytetrafluoroethylene sold commercially under the trademark of TEFLON by the DUPONT Corporation. It is a solid lubricant which can be defined as an oil soluble functional additive. The term "oil soluble" water-insoluble functional additive refers to a functional additive which is not soluble in water above a level of about 1 gram per 100 ml of water at 25 EC., but is soluble in mineral oil to the extent of at least 1 gram per liter at 25 EC.

[0130] These functional additives can also include frictional polymer formers, which are polymer forming materials which are dispersed in a liquid carrier at low concentration and which polymerize at rubbing or contacting surfaces to form protective polymeric films on the surfaces. The polymerization are believed to result from the heat generated by the friction and, possibly, from catalytic and/or chemical action of the freshly exposed surface.

[0131] It is theorized that polytetrafluoroethylene, ("PTFE"), containing lubricants provide enhanced lubrication by virtue of the fact that the PTFE particles somehow become attached to the surfaces of the engine thus lubricated, thereby creating a renewable coating of PTFE. The composition may contain a mixture of a carrier lubricant medium, such as mineral oil, a quantity of fluoropolymer particles, such as ground and sintered particles of polytetrafluoroethylene which are well dispersed in the carrier lubricant. It is important that these particles are well dispersed in the carrier lubricant in order to prevent coagulation, agglomeration, and/or settling.

[0132] The size of the PTFE particles is selected based on the consideration that the PTFE particles may actually become attached within the pores of the surface thus coated. The frictional forces applied by the moving parts of the engine wipe after the composition is applied to it removing excess lubricant and working the lubricant into the surface by the exertion of heat and pressure to the surface to enhance penetration of the lubricant into the surface. Thus, it is thought that the PTFE may become attached to the surface, and particularly within the pores of the surface.

[0133] It is thought that the other additives in the additive package aid in bonding of the PTFE particles to the surface lowering the coefficient of friction of the surface and reducing fluid drag on the surface.

[0134] The PTFE for use with selected embodiments of the present invention are preferably a nonaqueous dispersion of fine particles in colloidal form. A preferred average particle size would be in the range of from about 0.05-3.0 micrometers (microns) and can be in any convenient nonaqueous media; e.g., synthetic or mineral base oil, compatible with the remainder of the formulation. Commercial PTFE dispersions which are suitable for the invention include ACHINSON SLA 1612 manufactured by Acheson Colloids Company, Michigan.

[0135] The preferred dosage of PTFE in the selected concentrate additive is up to 10.0 percent by weight, preferably from about 0.01 to about 10 weight percent, more preferably from about 0.05 to about 5 weight percent, and most preferably from about 0.01-3 weight percent PTFE.

Anti-Wear Extreme Pressure Agents

[0136] The preferred anti-wear extreme pressure agent is a boron antiwear/extreme pressure agent, preferably a borate ester, a boric acid, other boron compounds such as a boron oxide. The boron compound is hydrolytically stable and is utilized for improved antiwear, antiweld, extreme pressure and/or friction properties, and perform as a rust and corrosion inhibitor for copper bearings and other metal engine components. The borated ester compound acts as an inhibitor for corrosion of metal to prevent corrosion of either ferrous or non-ferrous metals (e.g. copper, bronze, brass, titanium, aluminum and the like) or both, present in concentrations in which they are effective in inhibiting corrosion.

[0137] Patents describing techniques for making basic salts of sulfonic, carboxylic acids and mixtures thereof include U.S. Pat. Nos. 5,354,485; 2,501,731; 2,616,911; 2,777,874; 3,384,585; 3,320,162; 3,488,284; and 3,629,109. The disclosure of these patents are hereby incorporated by reference. Methods of preparing borated overbased compositions are found in U.S. Pat. Nos. 4,744,920; 4,792,410; and

PCT publication WO 88/03144. The disclosure of these references are hereby incorporated by reference. The oil-soluble neutral or basic salts of alkali or alkaline earth metals salts may also be reacted with a boron compound.

[0138] The borate ester utilized in the preferred embodiment is manufactured by EXXON-MOBIL USA under the product designation of ("MCP 1286") and MOBIL ADC700. Test data show the viscosity at 100° C. using the D-445 method is 2.9 cSt; the viscosity at 40° C. using the D-445 method is 11.9; the flash point using the D-93 method is 146; the pour point using the D-97 method is −69; and the percent boron as determined by the ICP method is 5.3%.

[0139] The preferred dosage of boron compound in the total crankcase lubricant is up to 10.0 volume percent, more preferably from about 0.01 to about 10.0 volume %, more preferably from about 0.01 to about 5 volume %, and most preferably from about 0.1-3.0 volume %. An effective elemental boron range of up to 1000 ppm or less than 1% elemental boron. Thus, a preferred concentration of elemental boron is from 100 to 1000 ppm and more preferably from 100 to 300 ppm and most preferably in one preferred embodiment as set forth in Table 3 about 166 ppm.

[0140] As demonstrated in **FIG. 6**, the engine treatment oil additive formulation was found to comply with all requirements of engine additives specification CRC L-38 for a Crankcase Oxidation Test showing the Total Adjusted Bearing Weight Loss comparing the blend of Components comprising the engine treatment oil additive with an API SG 5w-30 Motor Oil. The surprisingly good results show the total adjusted bearing weight loss was reduced from 30.9 mg for the Motor Oil without the engine treatment oil additive to 22.6 mg. for the motor oil used in combination with the engine treatment oil additive.

[0141] Other corrosion resisting compounds which may be used together with boron or independently may be selected from the group comprising dimercapto, thiediapoles, and benzotriazoles, benzotriazole derivatives, benzothiazole, benzothiazole derivatives, triazole, triazole derivatives, benzoimidazole, and benzoiidazole derivitives in levels of to 1% by weight.

Other Additives

[0142] The invention also contemplates the use of an effective amount of other additives in the lubricating and functional fluid compositions of this invention. Such additives include, for example, detergents and dispersants of the ash-producing or ashless type, corrosion and oxidation-inhibiting agents, pour point depressing agents, auxiliary extreme pressure and/or antiwear agents, color stabilizers and anti-foam agents.

Physical Agitation

[0143] The physical mixing includes high shear mixing, such as with a high speed mixer, homogenizers, microfluidizers, a Kady mill, a colloid mill, etc., high impact mixing, such as attritor, ball and pebble mill, etc., and ultrasonication methods or passing through a small orifice such as a fuel injector. Turbulent flows of any type will assist mixing.

[0144] Ball milling is the most preferred physical method in the instant invention since it is effective at rapidly reducing the graphite particles to very small size while simultaneously dispersing them into a concentrated paste as previously described. The concentrate can then be diluted with base oil and other additives to hit a final target viscosity, depending on the maximum temperature and shear conditions anticipated in the lubricant application. For further size reduction and reducing particle maximum size the diluted oil can be passed through a small orifice such as a fuel injector. The raw material mixture may be pulverized by any suitable known dry or wet grinding method. One grinding method includes pulverizing the raw material mixture in the fluid mixture of the instant invention to obtain the concentrate, and the pulverized product may then be dispersed further in a liquid medium with the aid of the dispersants described above. However, pulverization or milling reduces the carbon nanotube average aspect ratio. A detailed description has been given in an earlier section of the instant invention.

[0145] Ultrasonication is another physical method in the instant invention since it is less destructive to the carbon nanomaterial structure than the other methods described. Ultrasonication can be done either in the bath-type ultrasonicator, or by the horn-type ultrasonicator. More typically, horn-type ultrasonication is applied for higher energy output. Sonication at the medium-high instrumental intensity for up to 30 minutes, and usually in a range of from 10 to 20 minutes is desired to achieve better homogeneity.

[0146] The instant method of forming a stable dispersion of carbon nanomaterials in a solution consist of three steps. First select the appropriate concentrate of dispersant or mixture of dispersing and other additives for the carbon nanomaterials, and the medium, and dissolve the dispersant into the liquid medium to form a concentrate solution (keeping in mind the final additive concentrations desired following dilution); secondly add a high concentration of the carbon nanomaterials into the dispersant-containing solution, initiate strongly agitating, ball milling, or ultrasonicating, or any combination of physical methods named; following an agitation time of several hours, the resulting paste will be extremely stable and easily dilutable into more base oil and additives to give the final desired concentrations of additives and the desired final viscosity.

EXPERIMENTAL RESULTS

[0147] The novel engine treatment oil additive comprises a combination of chemical constituents including an oil soluble molybdenum additive, polyalphaolefin, ester such as a polyolester or diester, dispersant inhibitor containing zinc dithiophosphate, and viscosity index improvers. A polytetrafluoroethylene compound increases the effect of the other chemical constituents considerably. A borate ester may also be incorporated in the blend with or without the polytetrafluoroethylene additive providing an even greater improvement in the oxidation inhibition capabilities thereof. The blend is typically used in combination with a conventional crankcase lubricant such as a mineral oil, synthetic, or mineral/oil synthetic blend at about a 20 to about a 25% volume/percent. The improved performance of the engine additive in comparison with conventional mineral oil crankcase lubricants is attributable to optimizing the design parameters for each of the individual chemical constituents and combining the chemical constituents according to the present invention to obtain surprisingly good results including improved: wear, oxidation resistance, viscosity stability, engine cleanliness, fuel economy, cold starting, and inhibition of acid formation. The novel engine additive formulation comprises a combination of compounds, ingredients, or components, each of which alone is insufficient to give the desired properties, but when used in concert give outstanding lubricating properties.

[0148] It is theorized that the combination of chemical constituents comprising the instant invention result in a reduction of friction between the moving parts of the engine so that in operation an extremely fine film of the chemical constituents is formed on the metal surfaces. At the high temperature and high pressure within the engine, the surface active ingredients react with the film continuously forming an extremely thin lubricating layer thereon having an extremely low coefficient of friction and wear even under extreme temperature and pressure providing superior lubrication during the start-up and running phase of the engine.

EXPERIMENTAL EVALUATION

[0149] The following Examples provide the results of tests performed comparing the combination of formula components of the present invention with conventional API SG motor oil. The Examples exemplify the technology previously described. The combination of the formula components in the Examples provide excellent performance at high temperatures while also maintaining excellent performance at moderately elevated temperatures and normal temperatures, as well as provide resistance to ferrous and copper corrosion, improved wear, oxidation resistance, viscosity stability, engine cleanliness, fuel economy, cold starting, inhibition of acid formation, and other desirable high performance properties greater than exhibited by the individual components.

Example 1

The Invention Using Mo. Synthetic, PTFE, DI and VI Additive

[0150] The additive package is designed for addition to conventional motor oil in the crankcase of an internal combustion engine is prepared in a 2000 gallon jacketed, stirred vessel heated to approximately 40 EC. First there is added 600 gallons of polyalphaolefins (PAO 4 cSt) obtained from Ethyl Corporation under the trademark DURASYN 164; 43 gallons of PAO 6 centistoke DURASYM 166 obtained from the same source and 93 gallons of diester obtained under the brand name EMERY 2960. Stirring continues during the addition of all the ingredients. The above mixture is termed "synthetic" and is a synthetic base stock. To the synthetic is added 123 gallons of dispersant inhibitor (DI) package obtained under the brand name LUBRIZOL 8955, Lubrizol Corporation; 5 gallons of an 8% concentrate of SHELL VIS 1990 viscosity index improver, 25 gallons of MOLYVAN 855 obtained from R. T. Vanderbilt and Company, and 52 gallons of SLA 1612 obtained from Acheson Colloids, a 20% concentration of colloidal DUPONT TEFLON® brand PTFE. The resulting mixture is stirred for an additional 30 minutes, sampled and tested for viscosity, metal concentration, and other quality control checks.

[0151] The resulting concentrate is bottled into one quart containers and a single container is added to the four quarts of conventional motor oil in a five quart crank case of an automobile.

[0152] The result is improved wear (**FIGS. 1 and 3**), oxidation resistance (**FIG. 2**), viscosity stability (**FIG. 2**), engine cleanliness (**FIG. 4**), fuel economy (**FIG. 5**), cold starting (Table 2, and inhibited acid formation (**FIG. 2**).

Example 2

The Invention of Example 1 Under Standard Tests

[0153] When one of the one quart formulations prepared in Example 1 is tested under conventional lubricant test procedures, results are as given in Tables 1 and 2, and **FIGS. 1-5**. Note that the Shell four-ball wear test ASTM D4172 of **FIG. 1** and Table 1 is a bench test indicative of wear performance of a lubricant.

[0154] When the same ingredients of Example 1 are formulated while omitting one or more of the ingredients, the comparative results are as shown in Table 1 and **FIG. 1**.

TABLE 1

	ASTM 4172 Shell Four Ball								
TEST	AC	SYN	AC + SYN	AC + TEF	AC + MOLY	AC + SYN + TEF	AC + SYN + MOLY	AC + MOLY + TEF	AC + SYN + MOLY + VI + DI*
Shell Four-Ball Wear, mm	0.405	0.360	0.373	0.422	0.330	0.375	0.332	0.335	0.308

MO Motor Oils, VALVOLINE 10W30 All-Climate
SYN VALVOLINE 5W30 Synthetic, includes DI and VI
AC + SYN 10W30 AC + (20%) 5W30 Synthetic
MOLY Molybdenum
TEF TEFLON ®
ADDITIVE Invention of Example 1

[0155]

TABLE 2

	ASTM 4742 - 88 Oxidation				
Sample	RFOUT (min)**	TFOUT (min)*	Ruler***	CCS@20NC cP	TP1@20NF cP
A	180	138	211	3,030	12,540
C	370	279	322	2,160	9,360

Note:
A 10W30 All Climate (Motor Oil Control)
*C 80% Control plus 20% Additive
**Thin Film Oxygen Uptake
***Modified test of ASTM 4742
Remaining useful Life Evaluation Routine

[0156] As can be seen from Tables 1 and 2, and **FIGS. 1 through 5**, the results using this additive show a remarkable improvement when compared to a conventional motor oil tested without the additive of the invention.

Example 3

[0157] A grease composition according to the invention of Example 1 can be conventionally mixed with a lithium soap of a fatty acid to thicken the composition and to result in an improved grease.

Example 4

[0158] A boron containing compound, more particularly a borate ester was added to the additive produced in Example 1. As demonstrated in **FIG. 6**, the engine treatment oil additive formulation was found to comply with all requirements of engine additives specification CRC L-38 for a Crankcase Oxidation Test showing the Total Adjusted Bearing weight Loss comparing the blend of Components comprising the engine treatment oil additive with an API SG 5w-30 Motor Oil. The surprisingly good results show the total adjusted bearing weight loss was reduced from 30.9 mg for the Motor Oil without the engine treatment oil additive to 22.6 mg. for the motor oil used in combination with the engine treatment oil additive.

[0159] As set forth herebelow, Table 3 shows various additive combinations and the preferred formulas by weight and/or volume percent.

TABLE 3

ADDITIVE COMPOSITIONS

Parameter	Units	Preferred	More Preferred	Most Preferred	Target Formulation Vol. %
Base Stock	Vol. %	Up to 95	25–90	60–85	74
Polyolefins	Vol. %	15–85	25–80	50–75	65
Diesters	Vol %	1–25	3–20	5–15	9.5
Viscosity Improver 100%	Wt. %	0.05–5	0.07–3	0.1–2	6.5
Molybdenum (Mo)	Wt. %	0.05–5	0.07–3	0.1–2	2.5
PTFE	Wt. %	0.01–10	0.0005–5	0.1–3	20
Dispersant (12.3% vol.)	Vol. %	0 . . . 5–35	1–25	5–20	12.3
Dilution Before Use:	Vol. Lubr. Vol. Addit	0.25	0.5–15	1–10	4–5
Borate Esters	Vol. %	0.01–1.0 10–1000 ppm	0.05–.7 50–700 ppm	0.1–.5 10–500 ppm	1 1000 ppm

Modifications

[0160] Specific compositions, methods, or embodiments discussed are intended to be only illustrative of the invention disclosed by this specification. Variation on these compositions, methods, or embodiments are readily apparent to a person of skill in the art based upon the teachings of this specification and are therefore intended to be included as part of the inventions disclosed herein.

[0161] Reference to documents made in the specification is intended to result in such patents or literature cited are expressly incorporated herein by reference, including any patents or other literature references cited within such documents as if fully set forth in this specification.

[0162] The foregoing detailed description is given primarily for clearness of understanding and no unnecessary limitations are to be understood therefrom, for modification will become obvious to those skilled in the art upon reading this disclosure and may be made upon departing from the spirit of the invention and scope of the appended claims. Accordingly, this invention is not intended to be limited by the specific exemplifications presented hereinabove. Rather, what is intended to be covered is within the spirit and scope of the appended claims.

1. An engine oil lubricant concentrate used in combination with a crankcase lubricant for dilution with a mineral oil, a synthetic oil, a semi-synthetic severely hydro cracked oil, and combinations thereof, said lubricant concentrate comprising:

from 0.05 weight percent to 5.0 weight percent of an oil soluble molybdenum additive;

from 10.0 volume percent to 95 volume percent of a base oil comprising selected from the group consisting of a synthetic base oil, a mineral oil, a severely hydro cracked oil, alone and in combination one with another;

from 0.5 volume percent to 35.0 volume percent of a dispersant inhibitor containing zinc dithiophosphate;

from 0.5 weight percent to 25.0 weight percent of a viscosity index improver;

an effective amount of nano structures; and

an effective amount of a boron compound containing an effective amount of less than 1000 ppm of an elemental boron.

2. An engine oil lubricant concentrate used in combination with a conventional crankcase lubricant comprising a mineral oil, a synthetic oil, a semi-synthetic severely hydro cracked oil, and combinations thereof, said lubricant concentrate comprising:

from 0.05 weight percent to 5.0 weight percent of an oil soluble molybdenum additive;

from 10.0 volume percent to 95 volume percent of a synthetic base oil, a mineral oil, a severely hydro cracked oil, and combinations thereof;

from 0.5 volume percent to 35.0 volume percent of a dispersant inhibitor;

from 0.5 weight percent to 25.0 weight percent of a viscosity index improver; and

an effective amount of a nanostructure.

3. The lubricant concentrate according to claim 2, wherein said synthetic base oil comprises from 10.0 volume percent to 95 volume percent of an ester.

4. The lubricant concentrate according to claim 2, wherein said synthetic base comprises from 10.0 volume percent to 95 volume percent of a diester.

5. The lubricant concentrate according to claim 2, wherein said synthetic base stock comprises from 10.0 volume percent to 95 volume percent of a polyalphaolefin.

6. The lubricant concentrate according to claim 2, wherein said synthetic oil comprises from 10.0 volume percent to 95 volume percent of a polyalphaolefin in combination with an ester.

7. The lubricant concentrate according to claim 2, comprising from 1.0 to 3.0 weight percent of said oil soluble molybdenum additive.

8. The lubricant concentrate according to claim 2 wherein said synthetic base stock comprises at least 10% polyalphaolefins.

9. The lubricant concentrate according to claim 2, said dispersant inhibitor containing zinc dithiophosphate.

10. The lubricant concentrate according to claim 2, wherein said viscosity index improver is selected from the group consisting of polyisobutenes, polymethacrylate acid esters, polyacrylate acid esters, diene polymers, polyalkyl styrenes, alkenyl aryl conjugated diene copolymers, polyolefins, and combinations thereof.

11. The lubricant concentrate of claim 2, wherein said diester is a di-aliphatic diesters of alkyl carboxylic acid.

12. The lubricant concentrate of claim 11, wherein said di-aliphatic diesters of alkyl carboxylic acid is selected from the group consisting of di-2-ethylhexylazelate, di-isodecyladipate, and di-tridecyladipate.

13. The lubricant concentrate of claim 3, wherein said ester has a pour point of less than −100° C. and a viscosity of from 2 to 460 centistoke at 100° C.

14. The lubricant of concentrate of claim 2, wherein said base oil is a combination of a mineral oil and a severely hydro cracked oil.

15. The lubricant concentrate of claim 2, wherein said base oil is a synthetic oil.

16. The lubricant concentrate of claim 5, wherein said polyalphaolefin is has a viscosity of from 2 to 460 centistoke.

17. The lubricant concentrate of claim 5, wherein said polyalphaolefin has a viscosity of from 2 to 10 centistoke at 200° C.

18. The lubricant concentrate of claim 5, wherein said polyalphaolefin has a viscosity of from 4 to 6 centistoke at 200° C.

19. The lubricant concentrate of claim 2, wherein said synthetic base stock comprises from 25 to 90 percent by volume.

20. The lubricant concentrate of claim 2, wherein said synthetic base stock comprises from 60 to 85 percent by volume.

21. (canceled)

22. (canceled)

23. (canceled)

24. (canceled)

25. (canceled)

26. (canceled)

27. (canceled)

28. (canceled)

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30. (canceled)

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38. (canceled)

39. (canceled)

40. (canceled)

41. (canceled)

42. (canceled)

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