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(54) **USE OF NANOMATERIALS AS EFFECTIVE VISCOSITY MODIFIERS IN LUBRICATING FLUIDS**

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(57) **ABSTRACT**

Nanomaterials have been used as a supplement or replacement of traditional polymer-based viscosity modifiers for lubricants and other related fluids. Compared with traditional polymer-based viscosity modifiers, nanomaterials possess better viscosity-index modification functions, i.e., more even viscosity increase across the whole temperature range. Meanwhile, a cost-effective way of making nanomaterials have been developed based on commercially available graphite materials, and the resulting nanoparticles of graphite are nanodisks (nanoplates). Furthermore, it provides a viscosity modifier which exhibits temporary shear loss, which can contribute to fuel economy, but no permanent shear loss.

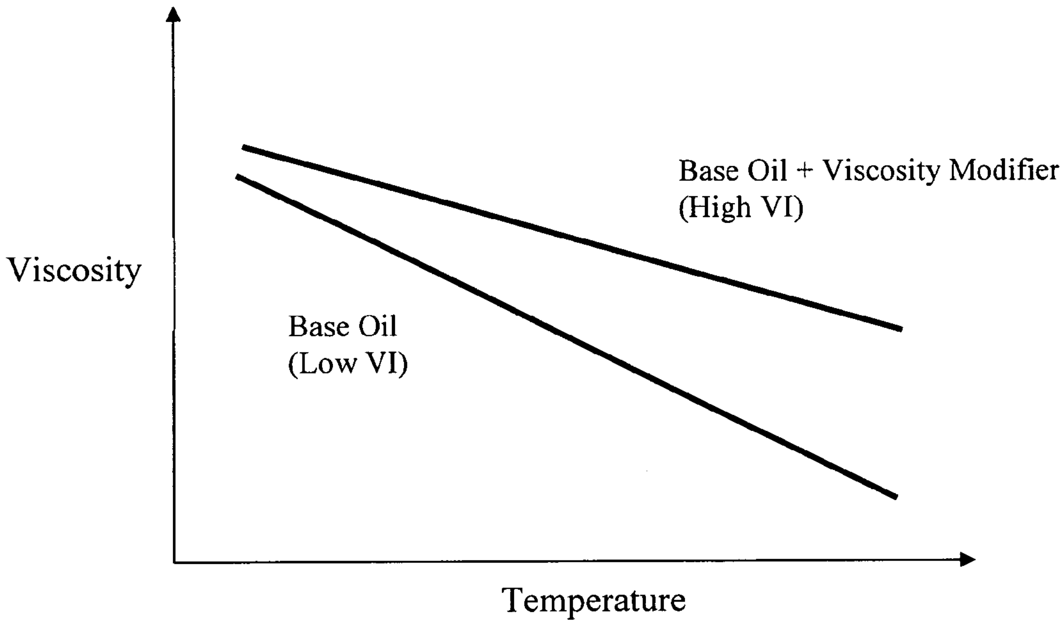
Base Oil + Viscosity Modifier
(High VI)
Viscosity
Base Oil
(Low VI)
Temperature

FIGURE 1

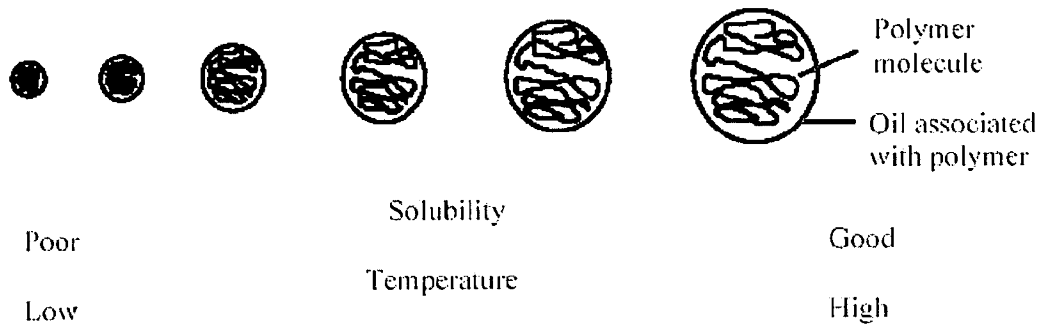
Polymer molecule
Oil associated with polymer
Solubility
Poor
Good
Temperature
Low
High

FIGURE 2


FIGURE 3

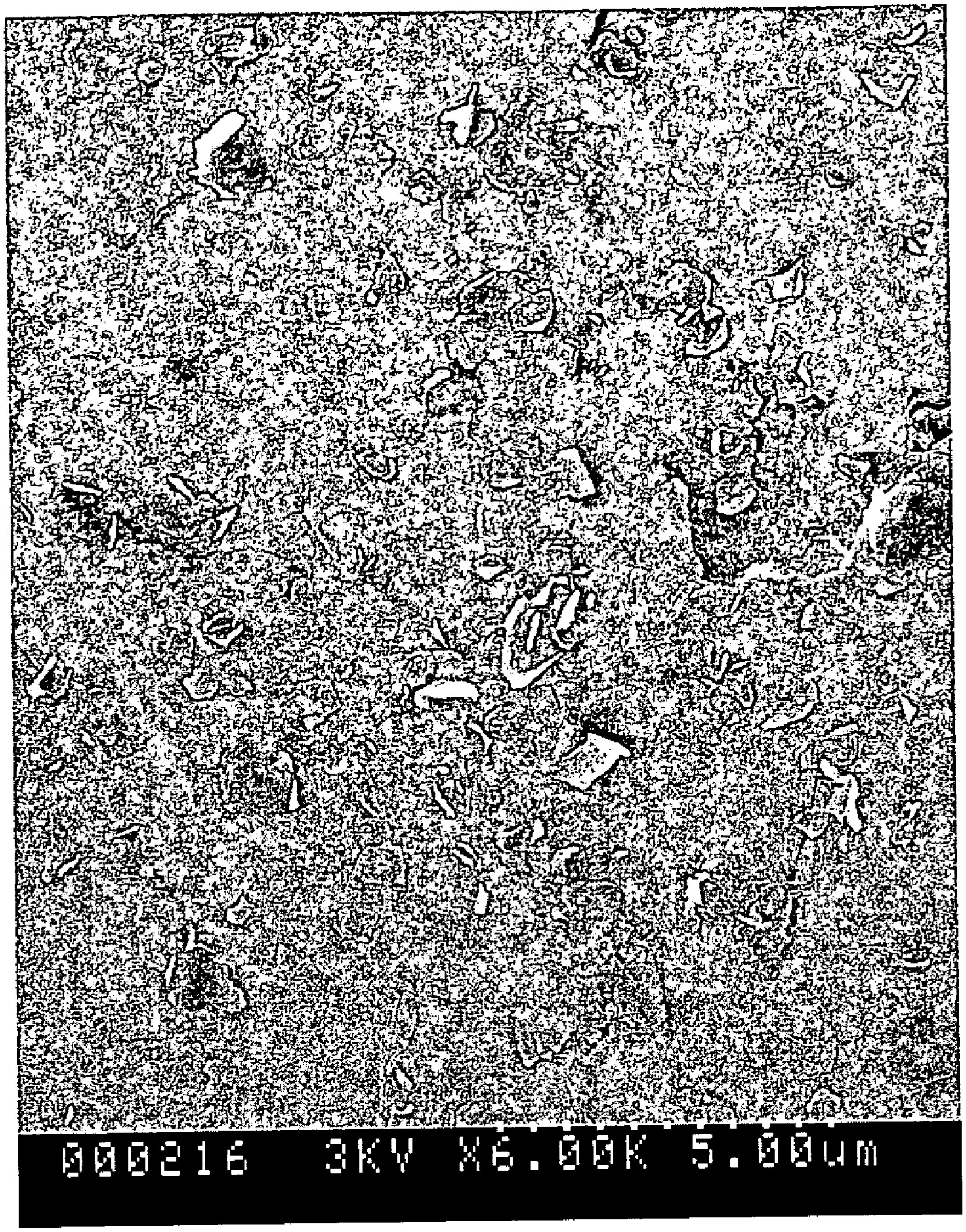


FIGURE 4

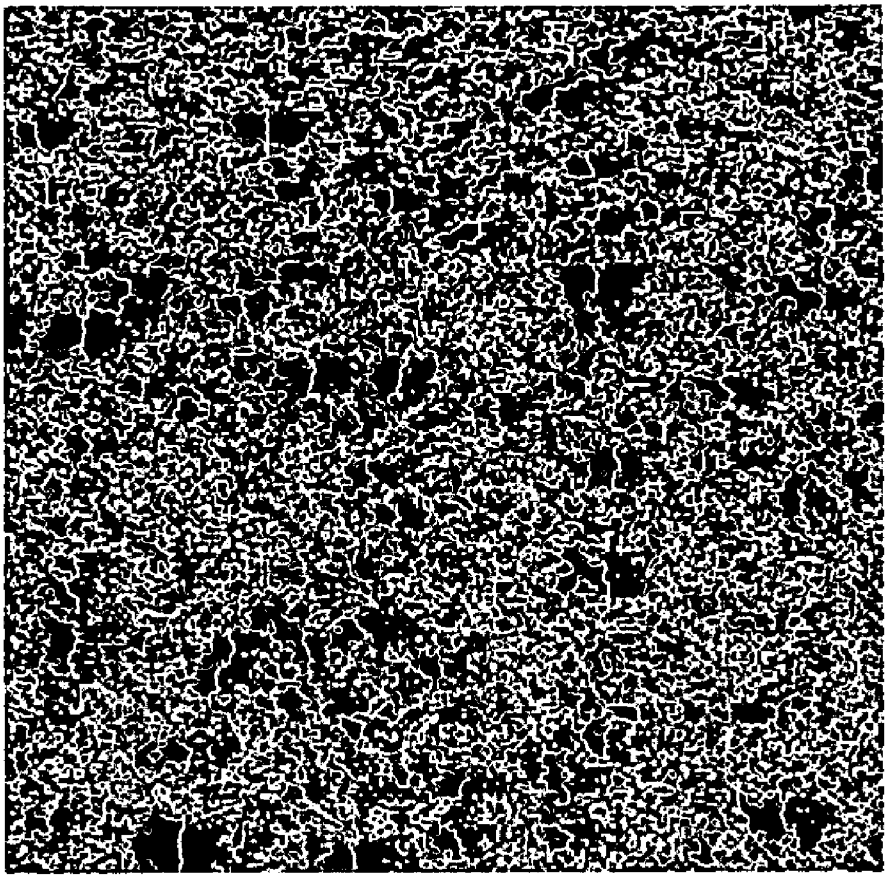

FIGURE 5

# USE OF NANOMATERIALS AS EFFECTIVE VISCOSITY MODIFIERS IN LUBRICATING FLUIDS

[0001] This application claims priority from U.S. Provisional Application Ser. No. 60/592,570 filed on Jul. 31, 2004 and Provisional Application Ser. No. 60/254,959 filed on Dec. 12, 2000 and U.S. Pat. No. 6,783,746 which issued on Aug. 31, 2004 from application Ser. No. 10/021,767 filed on Dec. 12, 2001 and application Ser. No. 10/929,636 filed on Aug. 30, 2004 and application Ser. No. 10/730,762 filed on Dec. 8, 2003 which claims priority from PCT/US02/16888 filed on May 30, 2002 and application Ser. No. 10/737,731 filed on Dec. 16, 2003 all of which are incorporated herein in their entirety.

## TECHNICAL FIELD

[0002] The present invention relates to a novel use of nanomaterial as a viscosity modifier for a lubricating oil and a lubricating oil composition. More particularly, the invention relates to a novel viscosity modifier for a lubricating oil capable of producing a lubricating oil composition having excellent viscosity index and lubricating oil compositions containing such a viscosity modifier.

## BACKGROUND OF THE INVENTION

[0003] The viscosity of petroleum products generally varies greatly with temperature, and for lubricating oils for automobiles, the temperature dependence of the viscosity is desired to be small. Therefore, a polymer has been widely used as a viscosity modifier having an effect of improving viscosity index for the purpose of decreasing the temperature dependence of the lubricating oils.

[0004] Viscosity index of a fluid is defined as the relationship of viscosity of that fluid to the temperature. It is determined by measuring the kinematic viscosities of the oil at 40 and 100° C. and then calculated by using the tables or formulas included in ASTM D 2270. High viscosity index fluids (e.g., a base oil with the addition of a viscosity modifier) tend to display less change in viscosity with temperature than low viscosity index fluids (e.g., that base oil), and the effect is illustrated in FIG. **1**.

[0005] Mineral oils, which are very effective lubricants at low temperatures, become less effective lubricants at high temperatures. At high temperatures, their film-forming ability (in the hydrodynamic lubrication regime) diminishes, because of a drop in viscosity. Prior to the use of viscosity modifiers and the introduction of multigrade oils, this problem was partly overcome through seasonal oil changes. The principal function of a viscosity modifier is to minimize viscosity variations with temperature. Viscosity modifiers are typically added to a low-viscosity oil to improve its high-temperature lubricating characteristics. These are organic polymers that minimize viscosity change with a change in temperature. This represents a practical means by which the operating range of mineral oils is extended to high temperature without adversely affecting their low-temperature fluidity. The mechanism is explained as follows.

[0006] At low temperature, the polymer molecules occupy a small volume (hydrodynamic volume) and therefore have a minimum association with the bulk oil. The effect should be little viscosity increase. The situation is reversed at high temperature because polymer chains extend or expand as a consequence of added thermal energy. This increases the association of the polymer with bulk oil because of an increase in surface area. The result is an effective increase in viscosity at this high temperature. FIG. **2** illustrates oil thickening by viscosity modifiers.

[0007] Olefin copolymers (OCP), polymethacrylates (PMA), hydrogenated styrene-diene (STD), and styrene-polyester (STPE) polymers are the most common types of viscosity modifiers used in modern lubricant formulations.

[0008] However, there is always some undesired viscosity increase at low temperature (under the operating temperature range) caused by these viscosity modifiers. That is, the viscosity index improvement by the polymers is limited. Moreover, these polymers contribute to a higher extreme-low-temperature viscosity and wax formulation.

[0009] When the surrounding temperature lowers, a wax component in a lubricating oil is crystallized and solidified to make the lubricating oil lose flowability, so a pour point depressant (PPD) is usually added into the lubricating oil to depress the solidification temperature. The pour point depressant functions to inhibit formation of a three-dimensional network attributed to crystallization of the wax component in the lubricating oil and to depress the pour point of the lubricating oil. Of the low-temperature properties of a lubricating oil containing a viscosity modifier, having an effect of improving viscosity index, and a pour point depressant, the viscosity at a high shear rate is determined by compatibility of a lubricating oil base with the viscosity modifier, but on the other hand, the viscosity at a low shear rate is greatly influenced by the pour point depressant. It is known that when an ethylene/α-olefin copolymer having specific composition is used as a viscosity modifier, the effect of the pour point depressant is markedly reduced because of an interaction between the copolymer and the pour point depressant (e.g., U.S. Pat. No. 3,697,429 and U.S. Pat. No. 3,551,336). Accordingly, the viscosity modifier to be blended with a lubricating oil which is required to have particularly excellent low-temperature properties is desired to exhibit an excellent effect of improving viscosity index and at the same time not to inhibit the function of the pour point depressant.

[0010] The thickening effect of particles to a fluid base is well known (P. C. Hiemenz and R. Rajagopalan, Principles of Colloid and Surface Chemistry, 3rd ed., Marcel Dekker, Inc., 1997, Chapter 4). The initial theory of explaining this was developed by Albert Einstein in 1906, and there have been various modifications and deviations in this theory, and the details of which are obviously out of the scope of the current invention. Nanoparticles have been added to a fluid for the purpose of increasing thermal conductivity (U.S. Pat. No. 6,221,275, U.S. Pat. No. 6,432,320, and U.S. Pat. No. 6,695,974). However, there has been little or no effort in addressing the issue of viscous thickening effect of these nanoparticles. In most of the cases this viscous thickening effect is undesirable, since the increased viscosity will results in more demand for pumping power, more energy loss due to internal fluid friction, and even malfunction or catastrophic failure of the machinery if the viscosity is way off the desired range.

[0011] However, in the current invention, with very careful formulation, the viscous thickening effect of the nanoparticles could be turned into an application as a revolutionary viscosity modifier. And because the nanoparticles are usually not polymer based, they are not going to cause compatibility issue with other polymeric additives/components in a lubricating fluid, and they are usually not contributing to wax formation by themselves.

[0012] It is common understanding in the lubricant industry that thinner fluid may provide better fuel economy if adequate film thickness is properly maintained. The reason is that the energy loss due to internal friction of fluid itself is less when the viscosity is lower. Therefore, if the viscosity modifier can be sheared down temporarily (but not permanently), fuel economy benefit could be observed. In the event of current invention, the nanodisks (or nanoplates) orient themselves in a laminar flow regime (Literature cited: Y. Yang, E. Grulke, Z. Zhang, G. Wu, Rheological Behavior of Carbon Nanotube and Graphite Dispersions, submitted to Langmuir), which indicates that temporary shear loss will be observed should the fluid be place in a shear field.

## SUMMARY OF THE INVENTION

[0013] In this invention, the use of nanoparticles as an effective viscosity modifier is illustrated. More specifically the use of carbon nanomaterial will be addressed. More specifically, cost-effective graphite materials and the process of making them into nanoparticles will be illustrated.

[0014] The use of nanoparticles in a fluid base is well know, as illustrated by the previous US Patents. The use of graphite in fluids such as lubricants is also 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 or larger, typically mean as 500-800 nm. The viscosity modification advantage of the graphite is not mentioned in the sales literature, nor is the product sold or promoted for its viscosity modification property.

[0015] 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 viscosity index of the fluid. 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 viscosity index. While graphite-containing automotive engine oil was once commercialized (Arco graphite), the potential to use graphite as a viscosity modifying material in this oil was not realized. The particle size of graphite used was larger (mean greater than one micron) than for the instnt invention as shown in FIG. **3**. 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.

[0016] 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.

[0017] Bulk graphite is available from POCO Graphite as a graphite foam, and is also available from the Carbide/Graphite Group, Inc. Graphite powders can be obtained from UCAR Carbon Company Inc., and from Cytec Carbon Fibers LLC. These bulk or powdery materials must be reduced to a nanometer-sized particles by various methods for use in the instant invention.

[0018] In this invention, fluids of enhanced viscosity index are prepared by dispersing nanometer-sized particles, especially carbon nanomaterials, 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.

[0019] The present invention provides at a minimum, a fluid of lubricant containing from 0.001% to 50% by weight nanoparticles, and preferably, from 0.01% to 25% by weight, and more preferably, from 0.1% to 20% by weight of nanoparticles. Preferably, however, a minimum of one or more chemical dispersing agents and/or surfactants are also added to achieve long-term stability. 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 "surfactanf" 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. The particle-containing fluid of the instant invention will have a viscosity index higher than the conventional fluid of the same type. The fluid can have any 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, or thermal property booster. 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.

[0020] As set forth above, the nanomaterial could be of any commercially available nanoparticles, or any material which can be wet-milled into nanometer-sized particles using the process developed in this invention which will be explained in detail later. One of the preferable nanoparticles are carbon-based materials. A preferred form of carbon nanomaterials is carbon nanotubes. Another preferred form of carbon nanomaterials is graphite. A preferred form of graphite is POCO Foam from POCO Graphite. Another preferred form is graphite powders from UCAR Carbon Company Inc. Still another preferred form of graphite is graphite powders from Cytec Carbon Fibers LLC. Still another preferred form of graphite is bulk graphite from The Carbide/Graphite Group, Inc. Another preferable nanomaterial is aluminum oxide nanoparticles from Sasol.

[0021] The nanoparticle 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 additional conventional polymer-based viscosity improvers.

[0022] Furthermore, the nanomaterial dispersion can be pre-sheared, in a turbulent flow, such as a nozzle, or a high pressure fuel injector, a ultrasonic device, or a 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 modifying effect will not change upon further use in actual applications.

[0023] The milling process itself, or other pre-shearing process, can have a rather dramatic effect on the long term dispersion stability. It has been found that a preferred process is to mill the particles to 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 desired application as an automotive fluid, i.e., engine oil, automatic transmission fluid, gear oil, shock absorber oil, etc. 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 0% up to 100% of the dispersant/surfactant mixture with the remainder being natural, synthetic, or mineral base oil. Once the concentrate prepared by milling is diluted to liquid consistency with base oil and other lubricating fluid components, the entire fluid can (optionally) be passed through a small orifice device to further increase the uniformity and decrease the size of dispersed particles.

[0024] An important aspect of this invention is that the final lubricant should be prepared to give an acceptable lubricant film thickness at the maximum shear rate and temperature of use in the target application. The maximum concentration of particles in the final (diluted) lubricating fluid is limited by the relationship between viscosity increase of the fluid caused by the particles, and the temporary loss of viscosity (associated with the particles) at maximum temperature and shear rate of fluid use. In general, the viscosity of the lubricant of the instant invention will be matched with conventional fluid at high operating temperature, typically, 100° C., and the lower temperature viscosity of the lubricant of the instant invention will be lower than that of the conventional fluid. This means that the viscosity index of the particle-containing lubricant of the instant invention will be higher than that of the conventional fluid.

[0025] It is an object of the present invention to provide a viscosity modifier for a lubricating oil, which provides better viscosity index, and with no adverse effect to the low temperature properties of the fluid, than the currently used polymer-based viscosity modifiers.

[0026] It is an object of the present invention to provide a cost-effective material as a supplement or replacement for the conventional polymer-based viscosity modifiers.

[0027] It is an object of the present invention to development a cost-effective processing method for making the nanomaterial to be used as viscosity modifiers in lubricating oils.

[0028] It is an object of the present invention to use the cost-effective graphite as the source of the nanomaterials to be used as viscosity modifiers in lubricating oils.

[0029] It is an object of the present invention to provide a viscosity modifier which exhibits temporary shear loss, which will contribute to fuel economy upon use in a motor vehicle, but no permanent shear loss.

[0030] 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.

[0031] 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·K).

[0032] It is an object of the present invention to provide a method of developing a method of forming carbon nanomaterials from inexpensive bulk graphite.

[0033] 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.

[0034] It is an object of the present invention whereby the carbon nanomaterial can optionally be surface treated to be hydrophilic at surface for ease of dispersing into the aqueous medium.

[0035] 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.

[0036] 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.

[0037] 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.

[0038] 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 hydrophile-lipophile balance (HLB) value of 8 or less, preferably nonionic or mixture of nonionic and ionic surfactants.

[0039] It is an object of the present invention to dissolve a dispersant containing a surfactant a having a HLB of 8 or less in an amount of from 0.001 to 30.0 percent by weight of a lubricant liquid medium forming a dispersant liquid lubricant medium, adding nanomaterial having an aspect ratio of from 500 to 5,000 in an amount of from 0.001 to 10.0 percent by weight into the dispersant liquid lubricant medium with agitation, and forming a uniform suspension of colloidal size solid particles of nanomaterial having an enhanced thermal conductivity when compared to the same lubricant medium containing no nanomaterial.

[0040] It is an object of the present invention to dissolve a dispersant containing a surfactant a having a HLB of 8 or less in an amount of from 0.001 to 30.0 percent by weight of a lubricant liquid medium forming a dispersant liquid lubricant medium, adding carbon nanomaterial having an aspect ratio of from 500 to 5,000 in an amount of from 0.001 to 10.0 percent by weight into the dispersant liquid lubricant medium with agitation, and forming a uniform suspension of colloidal size solid particles of carbon nanomaterial having an enhanced thermal conductivity when compared to the same lubricant medium containing no carbon nanomaterial.

[0041] It is an object of the present invention to provide that the dispersants can be the ashless polymeric dispersants used in the lubricant industry.

[0042] 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.

[0043] 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.

[0044] It is an object of the present invention to provide a uniform dispersion in its final form as an automatic transmission fluid of relatively low viscosity (kinematic viscosity less than 10 centistokes at (100° C.).

[0045] 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.

[0046] 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.

[0047] 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.

[0048] It is an object of the present invention to provide a uniform and stable dispersion where the carbon nanomaterials are used to convey an extremely high viscosity index, >200, and even >300.

[0049] It is an object of the present invention to provide a uniform and stable dispersion where the thermal conductivity and heat transfer capability of the fluid is at least more than 20% improved compared to conventional mineral oil based automatic transmission fluids.

[0050] 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

[0051] 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:

[0052] FIG. **1** is a graph showing the effect of viscosity modifiers improving the viscosity index (VI) of a base oil;

[0053] FIG. **2** shows the working mechanism of a polymer-based viscosity modifier;

[0054] FIG. **3** shows a scanning electron microscope photomicrograph of a conventional graphite-containing oil;

[0055] FIG. **4** shows a scanning electron microscope photomicrograph of an automatic transmission fluid (ATF) oil sample containing the graphite nanodisks and platelets in a final automatic transmission fluid processed by the wet-milling method; and

[0056] FIG. **5** shows an atomic force microscope, (AFM) picture of the automatic transmission fluid of FIG. **4** wherein the grid size is 1×1 micron and the height is 5 nm showing the ATF oil sample containing the graphite nanodisks and platelets in a final automatic transmission fluid processed by the wet-milling method.

## DESCRIPTION OF THE PREFERRED EMBODIMENT

[0057] The present invention provides a nanomaterial-containing fluid medium that possesses higher viscosity index (smaller viscosity change tendency with temperature) compared to conventional fluids of the same medium. In the present invention the fluid medium is targeted in its lubrication, viscosity, friction, antioxidant and thermal management characteristics to perform in modern automotive machineries.

[0058] One of the preferred nanomaterials are carbon nanotubes. The nanotubes can be either single-walled, double-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 50 nanometers to 100 microns. More typical length is 500 nanometers to 50 microns. The aspect ratio of the tube (which is defined by the average length of the tubes divided by the average diameter) can be from hundreds to thousands, more typical 100 to 2000. The surface of the nanotube can be treated chemically to achieve certain level of hydrophilicity, or left as is from the production.

**[0059]** Another preferred form of nanomaterials are commercially available graphite, e.g. POCO Foam, available from POCO Graphite, Inc., and graphite powders available from UCAR Carbon Company Inc.

**[0060]** POCO Foam is a high thermal conductivity foamed graphite, thermal conductivity typically in the range 100 to 150 W/m·K. A readily commercially available graphite is graphite powders from UCAR Carbon Company Inc. Still another preferred nanomaterial is the high thermal conductivity bulk graphite, Part#875G, from The Carbide/Graphite Group, Inc. Either of these graphite is 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 a particle size of less than 500 nm diameter mean size is attained. Graphite nanoparticles this small usually exhibit the morphology as "nanodisk" or "nanoplate", i.e., disk-like or plate-like particles in the nanometer-size scale, with average diameter much larger than the average thickness of particles. The preferred method is to disperse the graphite by ball milling in a viscous fluid of certain 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 viscosity thickening effect of the pasty concentrate to the final blend. The viscous thickening effect must be carefully balanced to attain a suitable lubricating film thickness at the maximum shear rate and temperature of fluid use. In general, any commercially available graphite material 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 (in diameter). FIG. **4** and FIG. **5**, respectively, show a scanning electron microscopic picture and an atomic force microscopic picture of the graphite nanodisks/nanoplates in a final automatic transmission fluid processed by the wet-milling method.

**[0061]** Another preferred nanomaterial is aluminum oxide nanoparticles from Sasol North America. These are particles surface-treated to improve dispersability in fluid. Typical particle size is 25 nm.

**[0062]** In the process of making the lubricating fluid with the nanoparticles, the mechanical process and sequence of adding the components are crucial 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. To achieve the best milling effect and therefore the best viscosity index improvement, the proper milling procedure has been developed. Firstly if the material is in bulk state, it must first be size reduced into powders (with average size less than 100 microns). Then a 5% to 20% by weight of powder form of the material, and more preferably 10% by weight of the powders, in base oil dispersion is milled into a paste state. Usually this step takes about 3 to 4 hours. Then add appropriate amount of dispersing agent(s), usually 1 to 2 times of the weight of particle, 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 added into the mill at the very beginning, the viscosity index of the final nanofluids made from the milling process is not as high.

Example of Making the Fluids

**[0063]** Graphite particles are obtained by pulverizing big graphite chunks from The Carbide/Graphite Group, and size-selected through a mesh filter to be less than 75 μm. 30 grams of the above graphite particles and 270 grams of DURASYN 162 (a commercial 2 centistokes polyalphaolefin, abbreviated hereafter as 2 cSt PAO) 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. Discharged 60 grams of this paste and labeled it as Paste A. For the rest of the mixture in the mill, added 48 grams of a dispersant and inhibitor package (DI package) from Lubrizol, LUBRIZOL 9677MX, into the mill and the paste became very thin, and successful recirculation 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 we formulate three automatic transmission fluids A through C, using the above three pastes as concentrate, and their final composition is exactly the same: 2% graphite, 4% LUBRIZOL 9677 MX, 18% DuraSyn 162, 76% Durasyn 166 (a commercial 6 centistokes polyalphaolefin, abbreviated hereafter as 6 cSt PAO) (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 very critical on the viscosity modification effect as well. For example, starting with graphite smaller than 10 μm (obtained as graphite powder from UCAR Carbon Company Inc.) and following the same procedure as Paste B, a thin Paste D was obtained.

Oil Basestocks

**[0064]** The petroleum liquid medium can be any petroleum distillates or synthetic petroleum oils, greases, gels, or oil-soluble polymer composition. More typically, it is the mineral basestocks or synthetic basestocks used in the lube industry, e.g., Group I (solvent refined mineral oils). Group II (hydrocracked mineral oils), Group III (severely hydrocracked oils, sometimes described as synthetic or semi-synthetic oils), Group IV (PAOs), and Group V (esters, naphthenes, and others). One preferred group includes the polyalphaolefins, synthetic esters, and polyalkylglycols.

**[0065]** 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. 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.

**[0066]** Another suitable class of synthetic oils comprises the esters of dicarboxylic acids (e.g., phtalic 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.

**[0067]** 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.

**[0068]** Preferred polyalphaolefins (PAO), include those sold by Mobil Chemical Company 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 viscosity from about 2 to about 460 centistokes.

**[0069]** MOBIL SHF-42 from Mobil Chemical Company, EMERY 3004 and 3006, and Quantum Chemical Company provide additional polyalphaolefins basestocks. For instance, EMERY 3004 polyalphaolefin has a viscosity of 3.86 centistokes at 212° F. (100° C.) and 16.75 centistokes 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 centistokes at 212° F. and 31.22 centistokes 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.

**[0070]** Additional satisfactory polyalphaolefins are those sold by Uniroyal Inc. under the brand SYNTON PAO-40, which is a 40 centistokes polyalphaolefin. Also useful are the ORONITE brand polyalphaolefins manufactured by Chevron Chemical Company.

**[0071]** It is contemplated that Gulf SYNFLUID 4 centistokes PAO, commercially available from Gulf Oil Chemicals Company, a subsidiary of Chevron Corporation, which is similar in many respects to EMERY 3004 may also be utilized herein. MOBIL SHF-41 PAO, commercially available from Mobil Chemical Corporation, is also similar in many respects to EMERY 3004.

**[0072]** Preferably the polyalphaolefins will have a viscosity in the range of about 2-100 centistokes at 100° C., with viscosity of 4 and 10 centistokes being particularly preferred.

**[0073]** The most preferred synthetic base 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 Mobil Oil. MOBL polyolester P43, M-045 containing two alcohols, and Hatco Corp. 2939 are particularly preferred.

**[0074]** 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 resistance to oxidative breakdown.

**[0075]** 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-ethylhexyl azelate is commercially available under the brand name of EMERY 2958 by Emery Chemicals.

**[0076]** 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 Mobil Chemical Company. 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 Mobil Chemical Company 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 centistokes at 100° C.

**[0077]** Group III oils are often referred to as hydrogenated oil to be used as one of the preferred base oil components of the instant invention providing superior performance to conventional lubricating oils with no other synthetic oil base or mineral oil base.

**[0078]** 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 mineral oil based oil having synthetic oil components and properties. Typically the hydrogenated oil is defined as a Group III petroleum based stock with a sulfur level less than 0.03, severely hydrotreatd and isodewaxed with saturates greater than or equal to 90 and a viscosity index of greater than or equal to 120, and may optionally be utilized in amounts up to 90 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 in combination with a synthetic or mineral oil.

[0079] The hydrogenated oil my be used as the preferred base oil component of the instant invention providing superior performance to conventional motor oils with no other synthetic oil base or mineral oil base. When used in combination with another conventional synthetic oil such as those containing polyalphaolefins 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.

[0080] A Group I or II mineral oil basestock may be incorporated in the present invention as a portion of the concentrate or a basestock to which the concentrate may be added. Preferred as mineral oil basestocks are the Marathon Ashland Petroleum (MAP) 325 Neutral defined as a solvent refined neutral having a Sabolt Universal viscosity of 325 SUS at 100° F. and MAP 100 Neutral defined as a solvent refined neutral having a S abolt Universal viscosity of 100 SUS at 100° F., both manufactured by the Marathon Ashland Petroleum.

[0081] Other acceptable petroleum-base fluid compositions include white mineral, paraffinic and MVI naphthenic oils having the viscosity range of about 20-400 centistokes. Preferred white mineral oils include those available from Witco Corporation, Arco Chemical Company, PSI and Penreco. Preferred paraffinic oils include solvent neutral oils available from Exxon Chemical Company, HVI neutral oils available from Shell Chemical Company, and solvent treated neutral oils available from Arco Chemical Company. Preferred MVI naphthenic oils include solvent extracted coastal pale oils available from Exxon Chemical Company, MVI extracted/acid treated oils available from Shell Chemical Company, and naphthenic oils sold under the names HYDROCAL and CALSOL by Calumet, and described in U.S. Pat. No. 5,348,668 to Oldiges.

[0082] 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

### Dispersants used in Lubricant Industry

[0083] 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 moving parts housing of an automobile.

[0084] 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.

[0085] Of these ashless dispersants the ones typically used in the petroleum industry include N-substitued 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 transmission fluid 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 "dispersant-detergent (DI)" additive package for a lubricant, e.g., LUBRIZOL™ 9677MX (used in transmission fluids), and the whole DI package can be used as dispersing agent for the nanoparticle dispersions.

[0086] 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 have been found to be an excellent dispersing agent for soot, an amorphous form of carbon particles generated in the engine crankcase and incorporated with dirt and grease.

[0087] 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.

[0088] Of these ashless dispersants the ones typically used in the petroleum industry include N-substituted polyisobutenyl succinimides and succinates, allyl 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-polyethylenepolyamine, polyisobutenyl succinic ester, polyisobutenyl hydroxybenzyl-polyethylenepolyamine, bis-hydroxypropyl phosphorate. The dispersant may be combined with other additives used in the lubricant industry to form a "dispersant-detergent (DI)" additive package, e.g., LUBRIZOL™ 9802A, and the whole DI package can be used as dispersing agent for the nanostructure suspension.

[0089] For instance, LUBRIZOL 9802A is described in the technical brochure (MATERIAL SAFETY DATA SHEET No. 1922959-1232446-3384064) by The Lubrizol Corporation in Wickliffe, Ohio and is hereby incorporated by reference. LUBRIZOL 9802A is described as a motor oil additive is believed to contain as an active ingredient a zinc dithiophosphate and/or zinc alkyldithiophosphate.

[0090] LUBRIZOL 4999 is described in its Technical Brochure (MATERIAL SAFETY DATA SHEET No. 1272553-1192556-3310026) by the Lubrizol Corporation in Wickliffe, Ohio and is hereby incorporated by reference. LUBRIZOL 9802A is described as a engine oil additive and contains as an active ingredient from 5 to 9.9 percent of a zinc alkyldithiophosphate.

[0091] LUBRIZOL 7720C in amounts of about 40% and LUBRIZOL 5186B in amounts of up to about 1% are especially useful for shock absorber nanofluids containing nanostructures.

[0092] OLOA 9061 is described in Technical Brochure "MATERIAL SAFETY DATA SHEET No. 006703" by Chevron Chemical Company LLC and is hereby incorporated by reference. OLOA 9061 is described as zinc alkyl dithiophosphate compound.

[0093] IGEPAL CO-630 is described in Technical Brochure "MATERIAL SAFETY DATA SHEET" from Rhodia Inc. and is hereby incorporated by reference. IGEPAL CO-630 is described as a nonylphenoxy poly(ethyleneoxy) ethanol, branched compound.

## Other Types of Dispersants

[0094] 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.

[0095] The dispersant for the oily liquid medium is a surfactant with low hydrophile-lipophile balance (HLB) value (HLB <8) or a polymeric dispersant of the type used in the lubricant industry. It is preferably nonionic, or a mixture of nonionics and ionics. A preferred dispersant for the aqueous liquid medium is of high HLB value (HLB >10), preferably a nonylphenoxypoly(ethyleneoxy)ethanol-type surfactant. Of course, other alcohol based glycols having a high HLB value can be used as well. The uniform dispersion of nanotubes is obtained with a designed viscosity in the liquid medium. The dispersion of nanotubes may be obtained in the form of a paste, gel or grease, in either a petroleum liquid medium or an aqueous medium.

[0096] 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 25 percent, more preferably in a range of from between 1 to 20 percent, and most preferably in a range of from between 2 to 15 percent. The nanoparticle material can be of any desired weight percentage in a range of from 0.001 up to 50 percent. For practical application it is usually in a range of from between 0.01 percent to 25 percent, and most preferably in a range of from between 0.1 percent to 20 percent. The remainder of the formula is the selected medium and other desired additives.

[0097] It is believed that in the instant invention the dispersant functions by adsorbing onto the surface of the nanoparticle material.

## Other Chemical Compounds

[0098] This dispersion may also contain a large amount of one or more other chemical compounds, preferably polymers, not for the purpose of dispersing, but to achieve additional thickening or other desired fluid characteristics. These can be added but reduce the amount of particulate that can be used without excessive thickening.

[0099] The viscosity improvers used in the lubricant industry can be used in the instant invention for the oil medium for the purpose of achieving additional thickening, which include olefin copolymers (OCP), polymethacrylates (PMA), hydrogenated styrene-diene (STD), and styrene-polyester (STPE) polymers. Olefin copolymers are rubber-like materials prepared from ethylene and propylene mixtures through vanadium-based Ziegler-Natta catalysis. Styrene-diene polymers are produced by anionic polymerization of styrene and butadiene or isoprene. Polymethacrylates are produced by free radical polymerization of alkyl methacrylates. Styrene-polyester polymers are prepared by first co-polymerizing styrene and maleic anhydride and then esterifying the intermediate using a mixture of alcohols.

[0100] Other compounds which can be used in the instant invention in the oil medium include: acrylic polymers such as polyacrylic acid and sodium polyacrylate, high-molecular-weight polymers of ethylene oxide such as Polyox® WSR from Union Carbide, cellulose compounds such as carboxymethylcellulose, polyvinyl alcohol (PVA), polyvinyl pyrrolidone (PVP), xanthan gums and guar gums, polysaccharides, alkanolamides, amine salts of polyamide such as Disparlon AQ series from King Industries, hydrophobically modified ethylene oxide urethane (e.g., Acrysol series from Rohmax), silicates, and fillers such as mica, silicas, cellulose, wood flour, clays (including organoclays) and nanoclays, and resin polymers such as polyvinyl butyral resins, polyurethane resins, acrylic resins and epoxy resins.

[0101] Chemical compounds such as seal swell agents or plasticizers can also be used in the instant invention and may be selected from the group including phthalate, adipates, sebacate esters, and more particularly: glyceryl tri(acetoxystearate), epoxidized soybean oil, epoxidized linseed oil, N,n-butyl benzene sulfonamide, aliphatic polyurethane, epoxidized soy oil, polyester glutarate, polyester glutarate, triethylene glycol caprate/caprylate, long chain alkyl ether, dialkyl diester glutarate, monomeric, polymer, and epoxy plasticizers, polyester based on adipic acid, hydrogenated dimer acid, distilled dimer acid, polymerized fatty acid trimer, ethyl ester of hydrolyzed collagen, isostearic acid and sorbian oleate and cocoyl hydrolyzed keratin, PPG-12/PEG-65 lanolin oil, dialkyl adipate, alkylaryl phosphate, alkyl diaryl phosphate, modified triaryl phosphate, triaryl phosphate, butyl benzyl phthalate, octyl benzyl phthalate. alkyl benzyl phthalate, dibutoxy ethoxy ethyl adipate, 2-ethylhexyldiphenyl phosphate, dibutoxy ethoxy ethyl formyl, diisopropyl adipate, diisopropyl sebacate, isodecyl oleate, neopentyl glycol dicaprate, neopenty giycol diotanoate, isohexyl neopentanoate, ethoxylated lanolins, polyoxyethylene cholesterol, propoxylated (2 moles) lanolin alcohols, propoxylated lanoline alcohols, acetylated polyoxyethylene derivatives of lanoline, and dimethylpolysiloxane. Other plasticizers which may be substituted for and/or used with the above plasticizers including glycerine, polyethylene glycol, dibutyl phthalate, and 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate, and diisononyl phthalate all of which are soluble in a solvent carrier. Other seal swelling agents such as LUBRIZOL 730 can also be used.

**[0102]** Antioxidants are an important part of transmission fluids. General classes include zinc dialkyldithiophosphates, alkyl and aryl phenols, alkyl and aryl amines, and sulfuinzed olefins. Commercial examples are CIBA L57 (phenyl amine) and ETHYL HITEC 1656.

**[0103]** Pour point depressants, either of polymethyl methacrylate or ethylene propylene olefin co-polymer type are useful to decrease the low temperature Brookfield viscosity of the ATF. Examples include ROHMAX 3008, ROHMAX 1-333, LUBRIZOL 6662A.

**[0104]** Friction Modifiers are used to control friction and torque characteristics of the fluid. Commercial examples include LUBRIZOL 8650 and HITEC 3191.

## Physical Agitation

**[0105]** 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.

**[0106]** Ball milling is the most preferred physical method in the instant invention since it is effective at rapidly reducing 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 target vehicle 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 modifies the average aspect ratio of rod-like nanomaterials, e.g., carbon nanotubes. A detailed description has been given in an earlier section of the instant invention.

**[0107]** Ultrasonication is another physical method in the instant invention since it may be less destructive to the nanomaterial structure than the other methods described. Ultrasonication can be done either in the bath-type ultrasonicator, or by the horn-type ultrasonicator (or called the "wand"). 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.

**[0108]** The instant method of forming a stable dispersion of nanomaterials in a solution consist of three steps. First select the appropriate concentrate of dispersant or mixture of dispersing and other additives for the nanomaterial, and the oily 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 nanomaterials, e.g., graphite nanoparticles or carbon nanotubes, into the dispersant-containing solution, initiate strong agitation: 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 oils and additives to give the final desired concentrations of additives and the desired final viscosity.

## EXAMPLES

**[0109]** 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. 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.

**[0110]** An automatic transmission fluid D was formulation with the same composition as automatic transmission fluid (ATF) A and result is list in Example 1 as well. The particle size is measured by atomic force microscopy (AFM), and FIG. **5** illustrates an AFM picture of ATF B. The graphite nanoparticles are plate-like structure, with average diameter is around 50 nm and thickness around 5 nm (as we described earlier, nanodisk or nanoplate).

### Example 1

Automatic Transmission Fluids and Viscosity Data

**[0111]**

| | ATF | | | | |
|---|---|---|---|---|---|
| | A | B | C | D | E* |
| From Concentrate | Paste A | Paste B | Paste C | Paste D | N/A |
| Kinematic viscosity at 100° C., cSt | 7.55 | 19.68 | 10.83 | 7.48 | 7.15 |

-continued

| | ATF | | | | |
|---|---|---|---|---|---|
| | A | B | C | D | E* |
| Kinematic viscosity at 40° C., cSt | 28.44 | 29.32 | 28.77 | 27.85 | 33.67 |
| Viscosity Index | 254 | 634 | 395 | 257 | 183 |

*E is an off-the-shelf regular commercial ATF (MERCON V).

Example 2

Engine Oil

**[0112]**

| | Product | |
|---|---|---|
| | Conventional Engine Oil | Nanoparticle-containing Engine oil |
| Composition | Valvoline DURABLEND 5W-30 | 90% DURABLEND 5W-30<br>9% DURASYN 162<br>1% Graphite |
| Process | | Bulk graphite is pulverized, and milled in DURASYN 162 to obtain a paste. The paste is added to DURABLEND 5W-30 |
| Viscosity @ 100° C. | 10.66 | 10.90 |
| Viscosity @ 40° C. | 61.14 | 54.34 |
| Viscosity Index | 166 | 197 |

Example 3

Shock Absorber Oil

**[0113]**

| | Product | |
|---|---|---|
| | Conventional Shock Oil | Nanoparticle-containing Shock oil |
| | Composition | |
| VISTA LPA 210 | 62.40 | 77.70 |
| LUBRIZOL 7720C | 36.87 | 20.66 |
| LUBRIZOL 5186B | 0.30 | 0.30 |
| Tricresyl phosphate | 0.22 | 0.22 |
| F-655C defoamer | 0.20 | |
| Blue Dye | 0.01 | 0.01 |
| Graphite | | 1.11 |
| Process | | Graphite obtained as powders (UCAR), and milled in VISTA LPA 210/LZ 7720C to obtain a concentrate. Then the other ingredients are added to make the final formulation |

-continued

| | Product | |
|---|---|---|
| | Conventional Shock Oil | Nanoparticle-containing Shock oil |
| Viscosity @ 100° C. | 8.97 | 7.77 |
| Viscosity @ 40° C. | 29.75 | 12.45 |
| Viscosity Index | 307 | 732 |

Example 4

Automatic Transmission Fluid (ATF)

**[0114]**

| | Product | | |
|---|---|---|---|
| | Conventional Mercon V ATF | Nanoparticle-containing ATF #1 | Nanoparticle-containing ATF #2 |
| | Composition | | |
| 2 cSt PAO | | 36.00 | 34.00 |
| 4 cSt PAO | | 51.50 | 53.50 |
| LUBRIZOL | | 10.50 | 10.50 |
| | ATF DI Package | | |
| Graphite | | 2.00 | 2.00 |
| Process | | Graphite obtained as powders (UCAR), and milled in 2 cSt PAO/DI package to obtain a concentrate. Then other ingredients are added to make the final formulation | Graphite foam (POCO) was pulverized, and milled in 2 cSt PAO/DI package to obtain a concentrate. Then other ingredients are added to make the final formulation |
| Viscosity @ 100° C. | 7.70 | 7.57 | 7.37 |
| Viscosity @ 40° C. | 36.20 | 16.01 | 16.96 |
| Viscosity Index | 190 | 527 | 475 |

Example 5

Gear Lubricant

**[0115]**

| | Product | |
|---|---|---|
| | Conventional Gear Oil | Nanoparticle-containing Gear Oil |
| | Composition | |
| YUBASE 100N | 47.70 | |
| 4 cSt PAO | 15.00 | 9.00 |

-continued

| | Product | |
|---|---|---|
| | Conventional Gear Oil | Nanoparticle-containing Gear Oil |
| 6 cSt PAO | | 67.00 |
| LUBRIZOL Gear Oil DI Package | 10.00 | 10.00 |
| LUBRIZOL 3174 | 26.30 | 12.00 |
| VISCOPLEX 0-112 | 1.00 | 1.00 |
| Graphite | | 1.00 |
| Process | | Graphite obtained as powders (UCAR), and milled in 4 cSt PAO/DI package to obtain a concentrate. Then the other ingredients are added to make the final formulation |
| Viscosity @ 100° C. | 14.21 | 14.79 |
| Viscosity @ 40° C. | 98.63 | 65.06 |
| Viscosity Index | 148 | 240 |

**[0116]** To demonstrate the temporary shear loss effect, a regular DEXRON III ATF and a nanofluid ATF were tested for high-temperature-high-shear (HTHS) viscosity, ASTM D 4683. This technique measures the high-temperature (150° C.) high-shear-rate viscosity of motor oils; very high shear rates ($10^6$ $s^{-1}$) are obtained by using an extremely small gap between the rotor and stator wall. Low number means more temporary shear loss under the test conditions.

Example 6

HTHS Viscosity of a DEXRON III ATF and a Nanofluid ATF

**[0117]**

| | DEXRON III ATF | Nanofluid ATF |
|---|---|---|
| Graphite nanodisk | 0 | 2% |
| 100° C. Kinematic Viscosity | 7.2 cSt | 7.55 cSt |
| HTHS Viscosity (150° C., $10^6$ $s^{-1}$) | 2.06 cP | 1.74 cP |

**[0118]** To demonstrate that there is no permanent shear loss to these nanodisk-containing fluids, a standard European gear lubricant test, CEC L-45-T-93, was run on a SYNPOWER 75W-90 and on a nanofluid gear oil. This test is designed to permanently shear down the non-shear-stable polymers in the formulation through a special taper roller bearing rig.

Example 7

Permanent Shear Test Data on a SYNPOWER 75W-90 and a Nanofluid Gear Oil

**[0119]**

| | SYNPOWER 75W-90 | Nanofluid Gear Oil |
|---|---|---|
| Graphite nanodisk | 0 | 1% |
| 100° C. Kinematic Viscosity before shear | 14.90 cSt | 18.14 cSt |
| 100° C. Kinematic Viscosity after shear | 13.96 cSt | 17.47 cSt |
| Percent Viscosity Loss due to shear | 6.31 | 3.69 |

**[0120]** 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 exemplification presented herein above. Rather, what is intended to be covered is within the spirit and scope of the appended claims.

**1**. The method of using nanomaterials as an effective viscosity modifier for a lubricating oil, which provides better viscosity index, and with no adverse effect to the low temperature properties of the fluid, than the currently used polymer-based viscosity modifiers.

**2**. The method of claim 1 in which the nanomaterials are made from carbon.

**3**. The method of claim 1 in which the nanomaterials are carbon nanotubes.

**4**. The method of claim 1 in which the nanomaterials are graphite nanoparticles.

**5**. The method of claim 3 wherein said carbon nanotube is either single-walled, double-walled, or multi-walled, with typical aspect ratio of 100-2000.

**6**. The method of claim 4 wherein said graphite nanoparticles are made by ball milling commercially available bulk graphite or graphite powders or graphite foams into the desired particle size, preferably with average diameter less than 500 nanometers.

**7**. The method of claim 4 wherein said graphite nanoparticles are in the form of nanodisks (or nanoplates).

**8**. The method of claim 1 wherein said nanomaterials are used in the final lubricating formulation in the weight percentage of from 0.001% to 50%, or more preferably from 0.01% to 25%, or more preferably from 0.1% to 20%.

**9**. The method of claim 1 in which the said lubricating fluid can be engine oil for either gasoline or diesel engines, transmission fluid, gear oil, hydraulic fluid, shock absorber oil, or any other lubricating fluid used in a modern vehicle.

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