PERFORMANCE-ENHANCING ADDITIVES FOR LUBRICATING OILS

Inventors: David A. Dalman, Midland, MI (US);
Michael F. Rozniak, Saginaw, MI (US)

Correspondence Address:
PRICE HENEVELD COOPER DEWITT & LITTON, LLP
695 KENMOOR, S.E.
P O BOX 2567
GRAND RAPIDS, MI 49501 (US)

A lubricant exhibiting enhanced properties, including improved load-carrying capacity and wear reduction, includes synthetic and/or mineral oil as a major ingredient, and a performance-enhancing amount of vegetable oil. In addition to providing improved performance characteristics, the vegetable oil additive reduces the need for certain other additives, including pour point depressants and viscosity index improvers, thereby simultaneously lowering the overall cost of the lubricant.
Viscosity @ 100°C, Valvoline Syn Power 5W-30 Motor Oil

FIG. 1
FIG. 2
FIG. 3
FIG. 4
FIG. 5

Valvoline HPO SAE 30W Motor Oil

Coefficient of Friction

Load (lbs)
Valvoline HPO SAE 30W Motor Oil

- Pure Motor Oil
- Deodorized Corn Oil

FIG. 6
FIG. 7
Falex 4-Ball Test, Wear Scar Data, Blend with D. Corn Oil

Valvoline SynPower 5W-30 Motor Oil, @ 400 lbs load

FIG. 8
PERFORMANCE-ENHANCING ADDITIVES FOR LUBRICATING OILS

FIELD OF THE INVENTION

[0001] The invention relates to lubricant compositions containing vegetable oil, and more specifically, to such compositions that exhibit enhanced performance characteristics while achieving excellent high temperature oxidative stability.

BACKGROUND OF THE INVENTION

[0002] Vegetable oils, such as soybean oil, canola oil, sunflower oil, and coconut oil, have been proposed for use as automotive engine oil, 2-cycle engine oils, total loss lubricants (such as for logging machines, dust suppressants, railroad flange oils, chain saw bar/chain lubricants) and marine lubricants. Vegetable oils exhibit some performance benefits for these uses, but have been promoted primarily because of their better biodegradability and lower toxicity than the mineral oil-based products used today. A few commercial vegetable oil-based lubricants have found market application primarily in small engines. Canola/soybean oil-based products aimed at the automotive engine oil market have been in development for several years. In addition to issues of biodegradability and toxicity, this oil is said to provide lower oil consumption, lower wear, lower volatility, improved fuel economy, cleaner burning, and cause lower harmful exhaust emissions. The United Soybean Board and USDA have actively supported the development of this oil. Automobiles have been successfully operated using this oil, and more recently several significant fleet trials, including those of the USDA in Michigan, Michigan State University, The United States Postal Service, and many farmers of the Thumb Oilseed Producers Cooperative (TOPC) are in progress.

[0003] Vegetable oils are known to possess better inherent lubricity and higher viscosity index than mineral oils, and have been used alone as lubricants for applications were biodegradability is desired. However, vegetable oils are also known to have high pour point temperatures and poor thermal oxidative stability as compared with mineral oil-based lubricants.

[0004] Attempts to provide vegetable oils having improved thermal stability have focused on either increasing oleic acid content by hydrogenation and/or by genetically altering the vegetable crop, and/or by adding antioxidants. Typically, polyamine and hindered phenol antioxidants have been employed to overcome oxidation problems with vegetable oils.

[0005] Lubricating oils perform a number of functions. The primary function of a lubricant is to separate moving surfaces thus reducing abrasive wear. However, lubricants are typically expected to also protect surfaces from corrosion, absorb and transfer heat, and suspend and transfer particles and other contaminants. Designing a lubricant to perform all of these functions simultaneously is a complex task that requires careful selection and balancing of the properties of the base oil and the performance-enhancing additives.

[0006] Most lubricants are comprised primarily of mineral oil and/or synthetic oil, but typically contain numerous additives that improve the functionality and performance of the lubricant. Such additives are typically present in lubricants used for lubricating internal combustion engines in an amount from about 10% to about 30% of the formulated lubricant volume. Typical additives include antioxidants and/or oxidation inhibitors, dispersants, detergents, viscosity index improvers, corrosion inhibitors, anti-foam agents, pour point depressants, demulsifying agents, extreme pressure additives, and metal deactivators.

[0007] Antioxidants are added to prevent formation of acids, varnish, sludge, and viscosity increase, all of which would rapidly occur during operation of an internal combustion engine using a lubricant that does not include an effective antioxidant. Antioxidants and/or oxidation inhibitors decompose free radicals to hydro-peroxides before they cause oxidation. Conventional antioxidants include hindered amines, aromatic amines, hindered phenols, and dithiophosphate derivatives.

[0008] Dispersants are added to prevent agglomeration and settling of particulate matter. Detergents are employed to prevent deposits from accumulating on surfaces, such as ring grooves, and to neutralize harmful acids generated by combustion.

[0009] Viscosity index is a measure of the effect of temperature change on viscosity of the lubricant. In general, both mineral and synthetic oils tend to exhibit a very significant viscosity reduction with increasing temperature. Viscosity index improvers or viscosity modifiers are used to increase viscosity more at higher temperatures than at lower temperatures, thereby reducing the effect of temperature on viscosity. Viscosity modifiers are typically oil-soluble polymers (e.g., polymethacrylates, ethylene-propylene copolymers, etc.) having a molecular weight of from about 10,000 to about 1,000,000. Viscosity modifiers are relatively expensive and are typically mixed into oil base stock (mineral or synthetic) for engine lubricants at a relatively high concentration, such as up to about 10% by volume. As a result, viscosity modifiers have a major effect on the cost of engine lubricants. Pour point depressants are generally needed to lower the pour point of the lubricant to allow quicker flow and coating of engine components at lower temperatures. Pour point depressants are also typically relatively expensive polymer additives (e.g., polymethacrylates, vinyl acetate/fumaric acid ester copolymers, etc.).

[0010] It would be highly desirable to provide a lubricating oil that includes a relatively inexpensive performance-enhancing additive that does not adversely affect the important functional characteristics of the lubricating oil, and simultaneously reduces the need for expensive performance-enhancing additives, thereby providing enhanced performance characteristics at a reduced cost.

SUMMARY OF THE INVENTION

[0011] The invention provides lubricating oils utilizing vegetable oil as a performance-enhancing additive for mineral oil and/or synthetic oil-based lubricants.

[0012] In one aspect of the invention, it has been discovered that a mineral oil and/or synthetic oil-based lubricant exhibiting improved performance characteristics and exhibiting excellent high temperature oxidative stability can be prepared by adding a performance enhancing amount of a
vegetable oil having a low oleic content. This is contrary to the accepted practice of utilizing vegetable oils having a high oleic content in order to avoid problems with oxidative stability.

[0014] In accordance with another aspect of the invention, an improved lubricant containing a mineral and/or synthetic oil base is provided by including in the lubricant a performance-enhancing amount of a vegetable oil, and an alkylated diphenylamine, which imparts high-temperature oxidative stability to the lubricant.

[0015] In accordance with another aspect of the invention, an improved lubricant containing a mineral and/or synthetic oil base is provided by including in the lubricant a performance-enhancing amount of a vegetable oil, and an alkylated dihexylthiocarbonate salt, which imparts high-temperature oxidative stability to the lubricant.

[0016] These and other features, advantages and objects of the present invention will be further understood and appreciated by those skilled in the art by reference to the following specification, claims and appended drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017] FIG. 1 is a graph showing the effect of adding corn oil on the kinematic viscosity of a commercially available engine oil (Valvoline SynPower 5W-30).

[0018] FIG. 2 is a graph showing the temperature profile of a commercially available engine oil (Valvoline All Climate 5W-30) with the addition of corn oil.

[0019] FIG. 3 is a graph showing a typical 4-ball test result for determining coefficient of friction as a function of load.

[0020] FIG. 4 is a graph showing the typical bulk oil temperature profile as measured during a 4-ball test.

[0021] FIG. 5 is a 4-ball plot of the coefficient of friction versus load to incipient seizure point for a commercially available engine oil (Valvoline HPO SAE 30).

[0022] FIG. 6 is a comparison of the 4-ball test result for a commercially available engine oil (Valvoline HPO SAE 30) versus deodorized corn oil.

[0023] FIG. 7 is a coefficient of friction versus load plot for blends of both 10% and 20% deodorized corn oil added to commercially available engine oil.

[0024] FIG. 8 is a graph showing the area of scar induced on the balls during a 4-ball test as a function of the amount of corn oil in various blends of corn oil with commercially available engine oil.

DETAILED DESCRIPTION OF EMBODIMENTS

[0025] The lubricants, in accordance with the various aspects of this invention, contain a mineral and/or synthetic oil as a major component. Typically, the lubricants of this invention contain from about 50% to about 95% mineral oil and/or synthetic oil.

[0026] Synthetic lubricating oils include hydrocarbon oils and halo-substituted hydrocarbon oils such as polymerized and interpolymerized olefins (e.g., polybutylenes, polypropylene, propylene-isobutylene copolymers, chlorinated polybutylenes, poly(1-olefines), poly(1-decenes), etc., and mixtures thereof; alkylbenzenes (e.g., dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di-(2-ethylhexyl)benzenes, etc.); polychlorobenzenes (e.g., biphenyls, terphenyls, alkylated polychlorobenzenes, etc.); alkylated diphenyl ethers and alkylated diphenyl sulfides and derivatives and homologues thereof. Other suitable synthetic lubricating oils include alkylene oxide polymers and interpolymers and derivatives thereof where the terminal hydroxyl groups have been modified by esterification, etherification, etc. These are exemplified by oils prepared through polymerization of ethylene oxide or propylene oxide, the alkyl and aryl ethers of these polyoxyalkylene polymers (e.g., methylpolyisopropylene glycol ether, diphenyl ether of polyethylene glycol, diethyl ether of polypropylene glycol, etc.) or mono- and polycarboxylic esters thereof, such as acetic acid esters, mixed fatty acid esters, or acid diesters of tetrahydroxy glycol. Other suitable synthetic lubricating oils include esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, alkyl succinic acids, and alkyl sebacic 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-ethyl hexyl alcohol, ethylene glycol diethyleneglycol monoether, propylene glycol, etc.). Esters useful as synthetic oils also include those made from 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., tricyclophosphate, triethylphosphate, diethyl ether of decylyphosphonic acid, etc.), polymeric tetrahydrofurans, etc. One preferred synthetic lubricating oil comprises at least a significant portion of a polyalphaolefin. Polyalphaolefin oils provide superior oxidation, hydrolytic stability, and high film strength. Polyalphaolefin oils also have a high molecular weight, high flash point, high fire point, lower volatility, higher viscosity index, and lower pour point than mineral oil. Suitable polyalphaolefin oils are disclosed in U.S. Pat. No. 4,859,352, hereby incorporated by reference.

[0027] Suitable mineral oil lubricants or basestocks include white mineral, paraffinic and naphthenic oils having a viscosity of from about 20-400 centistokes.

[0028] The improved lubricating oils of this invention may be prepared by combining synthetic oil and/or mineral oil basestock, a performance-enhancing amount of vegetable oil, and other performance-enhancing additives. Alternatively, fully formulated lubricating oils comprising synthetic oil and/or mineral oil already in combination with conventional performance-enhancing additives may be combined with a performance enhancing amount of a vegetable oil. In the latter case, commercially available fully formulated lubricating oils may be combined with a performance-enhancing amount of vegetable oil. It has been found that such combinations provide improved characteristics such as higher load-carrying capacity and wear reduction. Further, it
has been discovered that by addition of an appropriate performance-enhancing amount of vegetable oil to a mineral oil and/or synthetic oil-based lubricant, the pour point temperature can be lowered, and the viscosity index can be improved, while thermal stability and oxidative stability can be maintained at an acceptable level. As a result, it is possible to reduce the amount of performance-enhancing additives needed, typically by about 5 to about 35%. In particular, on account of the improved viscosity index achieved by addition of a performance-enhancing amount of vegetable oil, it is possible to eliminate viscosity improver additives. Because of the enhanced anti-wear properties achieved by addition of a performance-enhancing amount of vegetable oil, the need for phosphorus anti-wear additives can be very substantially reduced. In addition to lowering the cost of the lubricant by requiring less phosphorus-containing anti-wear additives, a reduction in the amount of phosphorus-containing additives also extends the life of the catalytic converter and reduces air pollution. Specifically, it has been found that lubricants containing a performance-enhancing amount of vegetable oil in accordance with this invention can achieve excellent anti-wear properties while maintaining the total phosphorus content at less than 0.08%.

Vegetable oils are extracted from the seeds, fruit, or nuts of plants, and are generally considered to be a mixture of mixed glycerides, primarily triglycerides of long chain carboxylic acids. Natural vegetable oils also contain free fatty acids, typically in relatively low amounts. The triglycerides are typically comprised of three fatty acids of varying lengths and configurations covalently bonded to a glycerol backbone. The fatty acid components (both free and bound) include polyunsaturated fatty acids (those having two or more carbon-carbon double bonds), monounsaturated fatty acids (having a single carbon-carbon double bond) and saturated fatty acids (not having any carbon-carbon double bonds). In general, it has been believed that vegetable oils suitable for use as lubricants must contain relatively high levels of monounsaturated fatty acid components (i.e., have a high oleic content). The term “oleic content” refers to the percentage of free and bound fatty acids that are monounsaturated. Typically, it has been recommended that vegetable oils used for lubricants, such as for internal combustion engines and the like, should have an oleic content that is at least 60% in order to prevent problems associated with thermal oxidative decomposition. However, it has been discovered that vegetable oils having a relatively low oleic content can be utilized as an effective performance-enhancing additive in a lubricating composition that exhibits excellent thermal oxidative resistance when the low oleic content vegetable oil is utilized in an appropriate amount and/or is utilized in combination with specific types of antioxidants. In particular, it has been found that vegetable oils having an oleic content of less than 60% may be utilized as a performance-enhancing additive for a lubricant when used in an amount of from about 5% to about 25%, and more typically and/or preferably from about 20% to about 25% by volume of the lubricant. In fact, it has been discovered that vegetable oils having an oleic content less than 50%, and even less than 20% provide performance-enhancing characteristics without imparting unacceptable thermal oxidative resistance. Examples of low oleic vegetable oils that can be utilized in their natural form (i.e., without requiring hydrogenation processing) include canola oil, soybean oil, and corn oil, with corn oil being preferred. Deodorized vegetable oils are preferred. Especially preferred is deodorized corn oil, which provides improved load-carrying capacity. Deodorization of vegetable oils is well known in the art and refers to distillation processes (typically steam stripping processes) that are utilized for removing volatile components from the non-volatile triglyceride oil.

In order to further enhance thermal oxidative resistance, it is generally desirable to add an antioxidant to the lubricant. In accordance with an aspect of this invention, it has been discovered that while most conventional antioxidants are not particularly effective at improving the oxidative stability of highly unsaturated vegetable oils, alkylated diphenylamines and dialkylidithiocarbamates are very effective at imparting excellent thermal oxidative stability to lubricants containing a performance-enhancing amount of vegetable oil (including low oleic content vegetable oils). Suitable commercially available products that may be used for imparting enhanced thermal oxidative stability include Vanlube® AZ additive, which comprises zinc diarylthiocarbamate; Molyvan® 822 additive, which comprises molybdenum dialkylidithiocarbamate; Vanlube® SL additive, which comprises a mixture of alkylated diphenylamines; Vanlube® 818-D which is a mixture of about 95% methylene bis (N,N-dibutylidithiocarbamate) and about 5% of a dodecenylnonadecyl acid adduct added as a rust inhibitor; and Vanlube® 7723 which is comprised entirely or almost entirely of methylene bis (N,N-dibutylidithiocarbamate).

The use of vegetable oil as a performance-enhancing additive in accordance with the invention has several advantages, including: (a) reducing or eliminating the need for viscosity index improver additives, thus resulting in better retention of viscosity when the oil is exposed to high temperature and high rates of shear; (b) reducing or eliminating the need for phosphorus-containing compounds such as anti-wear additives, thus extending the active life of automobile catalytic converters; (c) lowering wear of engine components under high-load operation, even while also lowering the level of extreme pressure and anti-wear additives; (d) achieving high fuel economy due to lower formulation coefficient of friction during standard operating conditions in hydrodynamic lubrication; (e) lowering the cost for synthetic engine oils based on polyalphaolefin and/or ester-based stocks; and (f) lowering the pour point temperature for mineral oil-based engine oils.

Table I presents results of thin film oxygen uptake tests (TFOUT). The tests utilized a rotating pressure vessel in a hot oil bath. The vessel was charged with oxygen gas to 90 psig and run until the oxygen pressure decreased, which was an indication that antioxidants in the additive package had been exhausted. The longer the test runs (in minutes), the better the oxidative resistance of the formulation. Sample A is an unmodified commercially available Valvoline HPO SAE 30 motor oil. Sample B is a blend comprising 80% of the commercially available motor oil and 20% (by volume) of corn oil. Sample C is a blend comprising 98.4% (by weight) of Sample B and 1.6% (by weight) of Vanlube® 818D additive. Sample D is a blend comprising 98.4% (by weight) of Sample B and 1.6% (by weight) of Vanlube® SL additive. Sample E is a blend comprising 98.4% (by weight) of Sample B and 1.6% (by weight) of Vanlube® AZ.
Likewise, the Thermo-Oxidation Engine Oil Simulation Test (TEOST) was run on the same formulations as described in Table I. TEOST is one of the ILSAC GF-3 bench tests required before running the American Petroleum Institute (API) engine oil deposit test (Sequence IIII). In this procedure, the test oil was preloaded with an oxidation catalyst and circulated over a hot (285° C.) metal finger for 24 hours. During that time, deposits were formed on the finger as a result of oxidation breakdown of the oil. This is a very severe test and gives a good indication of the ability of an oil formulation to pass the IIII engine test. The results in Table II show that, with the addition of 20% corn oil to the SAE 30 engine oil, the level of deposit formation is increased. However, with the addition of supplemental antioxidant compounds the deposit formation is reduced from between 19% and 74%.

Viscosity is an important property of engine oils. The change in viscosity over a range in temperature is another important measure of engine oil performance. It is desirable to have a low enough viscosity for an engine to start easily at low temperatures yet maintain a high enough viscosity to prevent excessive wear at high temperatures. Vegetable oils have lower kinematic viscosities than do most formulated engine oils. Thus, by adding vegetable oils to engine oils, a linear decrease in viscosity is observed. Some examples of the viscosity change due to blending vegetable oils with commercial engine oils are shown in Table III.

**FIG. 1** shows the near-linear effect of adding vegetable oils to engine oils on the kinematic viscosity at 100° C. There is a very substantial viscosity decrease with increasing temperature for mineral oils. To level out the viscosity versus temperature property of mineral oil-based engine oils, one of several synthetic polymers, called viscosity index improvers (VI), are added. Although viscosity index improvers are effective under certain conditions, they are subject to temporary loss of effectiveness at high shear rates, such as are routinely encountered in an engine. It is desirable to minimize or eliminate these additives. Vegetable oils have a naturally higher viscosity index (over 200) than mineral oils. The addition of vegetable oils to a variety of engine oils linearly increases the viscosity index of the blended oil. The last column of Table III shows the viscosity index for several blended oils. The bottom of the Table shows the viscosity index of several pure vegetable oils. A mineral oil generally has a viscosity index of about 100. Vegetable oils typically have a viscosity index of from about 215 to about 230. Addition of vegetable oil(s) to commercial engine oils increases the viscosity index of the blend in a linear fashion.

Another important property of lubricating oils is the pour point temperature. There is concern about sufficient pumpability, cold cranking, and the formation of gels upon slow cooling. If the specified criteria are not met, the results of engine wear can be catastrophic. Blending 20% by volume of deodorized corn oil with Valvoline HPO SAE 30 engine oil provides a Newtonian oil containing no viscosity index improver additive. A comparison of certain low temperature properties of a 20% corn oil/80% commercial mineral oil-based lubricant blend with SAE requirements for a 10W-30 oil is presented in Table IV. The blend of SAE 30 oil with corn oil (20%) meets all of the requirements for an SAE 10W-30 engine oil except the low-temperature cranking at -25° C. However, the viscosity in this temperature range falls so rapidly with temperature that the SAE requirements can be met by increasing the amount of corn oil to
about 21-22%. Because there are no viscosity index improver additives in the formulation, the high shear viscosity requirement is easily met. The significance of this formulation is the possibility of providing a fully formulated multi-grade engine oil that does not contain any viscosity index improver additives that could degrade under high shear conditions.

### TABLE IV

<table>
<thead>
<tr>
<th>Test</th>
<th>Low Temp. Cranking, Max. cP</th>
<th>Low Temp. Pumping, Max. cP</th>
<th>100°C Viscosity, cP</th>
<th>150°C High Shear, Min. cP</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAE Req. 7000</td>
<td>60,000</td>
<td>9.3-12.5</td>
<td>2.9</td>
<td></td>
</tr>
<tr>
<td>SAE 30 with 8,864</td>
<td>32,800</td>
<td>9.50</td>
<td>3.2</td>
<td></td>
</tr>
<tr>
<td>Corn oil</td>
<td>No yield stress</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

[0037] The pour point temperature of a lubricant is the temperature at which the oil ceases to flow. If the ambient temperature is lower than the pour point temperature, oil cannot flow to lubricate critical engine parts. The pour point of a mineral oil is usually a function of the formation of waxy crystal structures upon slow cooling of the oil. Pour point depressants are a normal part of an engine oil additive package and are designed to prevent the formation of these waxy crystalline structures. It is desirable in an engine oil to have a pour point below -35°C and preferably as low as -40°C. One of the often-cited deficiencies against using vegetable oils as engine lubricants is that vegetable oils have a relatively high pour point temperature. As seen in Table V, the vegetable oils have typical pour point temperatures in the range of -11°C to -20°C. However, blending vegetable oils into commercial engine oils actually lowers the pour point temperature of the blends. This is a synergistic behavior. The major effect is with mineral oil-based lubricants, which are more prone to form waxy crystals, rather than synthetic (e.g., polyalphaolefin-based) lubricants. The effect of vegetable oil addition to a commercially available engine oil (Valvoline All Climate 5W-30) is illustrated in FIG. 2.

[0038] A Falex Thrust Washer Machine in the 4-ball test configuration was used for evaluating friction and wear. These tests were run by rotating one steel ball against three stationary balls while adding load (weights) in increments. This step-loading sequence (described in ASTM D-4172) determines the coefficient of friction (COF) versus load to the point of failure or "incipient seizure." FIG. 3 shows a typical friction plot for a 4-ball test and illustrates the typical effect of load on coefficient of friction. Each of the plots shown in FIGS. 3-7 can be divided into four regions. In the first (hydrodynamic) region, there is not any contact between the steel surfaces. The only resistance to sliding is due to the lubricant viscosity, and thus, the COF is very low (less than 0.05). The viscosity of the lubricant in this region is high enough to separate the metal surfaces. In the second region (the lubrication or boundary regime) the metal surfaces are in slight contact and the lubricant is only partially able to support the higher imposed load. At this point, there is a small wear scar forming on the steel balls. The viscosity of the lubricant is barely able to support the much higher load. Not only is the load very high but also the frictional heating has reduced the oil viscosity significantly. In the third region, the anti-wear additives in the formulation take over the task of preventing catastrophic wear by forming alloys with steel that allow the steel to continue sliding with relatively low friction. As the anti-wear additives are used up or decompose at higher temperatures, the steel reaches close to its melting point and would weld together except that the test is stopped before this occurs.

[0039] At the same time that torque (resistance to rotation) is recorded, the temperature of the oil is measured by means of a thermocouple placed between the stationary balls. The measurement of the oil temperature is important because frictional heating reduces the oil viscosity to the point that it can no longer help support load, and at the point of incipient seizure, is even itself decomposing. The temperature rise tracks very closely to the load-bearing determination followed by resistance to sliding (torque) versus applied load. A plot of the temperature rise versus applied load is shown in FIG. 4.

[0040] FIG. 5 shows the 4-ball plot of coefficient of friction versus load to the incipient seizure point for a commercially available mineral oil-based Newtonian oil that...
does not contain a viscosity index improver. The plot follows the pattern described for a typical engine oil shown in FIG. 3. Incipient seizure occurs at about 550 pounds of load. Amazingly, when the result for uninhibited deodorized corn oil is superimposed on the same plot (as shown in FIG. 6), it is revealed that corn oil has a higher load-carrying capacity than the fully formulated commercially available engine oil.

FIG. 7 shows the result from two additional 4-ball tests superimposed on the same plot. In this case, blends containing the same commercially available motor oil (Valvoline HPO SAE30) with 10% and 20% corn oil were tested under the same conditions. Surprisingly, even while diluting the total additive package in the formulated commercial motor oil, the 10% blend exceeded the load-carrying capability of either the commercially available oil or the corn oil. Further, the 20% blend was better than the 10% corn oil blend and exceeded the limits of the test. This is a surprising and remarkable synergistic behavior.

High wear (loss of material) is observed during cold starts for various automobile components, including camshafts, cam followers and main shaft journal bearings. High wear also occurs while running engines under high-load conditions. It is possible to follow the wear rate during the 4-ball test with a micrometer attached to the load arm and/or one can optically measure the diameter of the wear scar at the end of the test using a Nikon Profile Projector. We made two observations using these techniques. First, with mineral oil-based commercial engine oils, the balls after the test are usually black and smell like sulfur. This is most likely a residue of the interaction of steel at high temperature with zinc dialkyldithiophosphate (ZDDP) anti-wear additive to form iron sulfide (FeS). It is interesting that after the addition of corn oil to the engine oil at the 10% and 20% levels, the balls remained bright and shiny. Apparently, corn oil is very effective as a boundary lubricant that extends the load-carrying capability of the formulation without the formation of other surface slip agents.

Another effect of using corn oil as an additive for engine oils is a partial reduction of wear. By the time the point of incipient seizure is reached, the wear scar is typically a deep gouge in the lower steel balls. However, by stopping the test at an intermediate point where boundary lubrication is operative (e.g., 400 pounds load) the diameter of the scar can be measured by optical means. FIG. 8 shows the reduction in wear scar by the addition of 10% and 20% corn oil to a commercially available engine oil (Valvoline SynPower 5W-30).

Phosphorus derived from the most used anti-wear/antioxidant compound (zinc dialkyldithiophosphate, ZDDP) is known to carry over with blow-by exhaust gases from the engine into the catalytic converter, where it poisons the platinum catalyst. The United States Environmental Protection Agency is expected to require automakers to reduce the phosphorus level in engine oils from the current typical level of 0.1% to less than 0.08% to extend the life of the catalytic converter and reduce air pollution. One might assume that dilution of current engine oils with anything not containing phosphorus would accomplish this goal. In fact, analysis of our 20% blend with corn oil by Inductively Coupled Plasma showed phosphorus reduction from 0.096% to 0.075%, thus meeting the new EPA requirement. The reason that automakers do not simply reduce ZDDP levels is that they are concerned about the potential of greater engine wear. However, in the case of 20% corn oil formulations, wear is reduced and load-carrying capability is greater even at 20% lower ZDDP levels. The actual reduction of phosphorus levels in the engine oils is shown in Table VI.

### Table VI

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Valvoline SAE 30</th>
<th>SAE 30 + 20% Corn Oil</th>
<th>20% Corn oil + 1.5% Valvolute® 818D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphorus</td>
<td>0.0958%</td>
<td>0.0752%</td>
<td>0.0750%</td>
</tr>
<tr>
<td>Zinc</td>
<td>0.1064%</td>
<td>0.0860%</td>
<td>0.0876%</td>
</tr>
</tbody>
</table>

The above description is considered that of the preferred embodiments only. Modifications of the invention will occur to those skilled in the art and to those who make or use the invention. Therefore, it is understood that the embodiments shown in the drawings and described above are merely for illustrative purposes and not intended to limit the scope of the invention, which is defined by the following claims as interpreted according to the principles of patent law, including the doctrine of equivalents.

The invention claimed is:

1. A lubricant exhibiting excellent high temperature oxidative stability, comprising:
   from about 95% to about 75% (by volume) of a mineral and/or synthetic oil optionally containing performance-enhancing additives; and
   from about 5% to about 25% (by volume) of a vegetable oil having an oleic content of less than 50%.

2. The lubricant of claim 1, wherein the vegetable oil is corn oil.

3. The lubricant of claim 1, wherein the vegetable oil is deodorized corn oil.

4. The lubricant of claim 1, further comprising a dialkylthiophosphoramide salt.

5. The lubricant of claim 1, further comprising zinc dialkyldithiocarbamate in an amount effective to enhance oxidative stability.

6. The lubricant of claim 1, wherein pour point depressant additives are not present or are present in an amount less than 0.5%.

7. The lubricant of claim 1, wherein the vegetable oil comprises from about 20% to about 25% of the lubricant by volume.

8. The lubricant of claim 1, having a pour point temperature less than ~37°F.

9. The lubricant of claim 1, wherein the vegetable oil comprises greater than 20% of the lubricant by volume.

10. The lubricant of claim 1, wherein the vegetable oil comprises greater than 10% corn oil by volume, and further comprises an antioxidant.

11. The lubricant of claim 10, wherein the antioxidant is a dialkyldithiocarbamate salt.

12. The lubricant of claim 11, wherein the dialkyldithiocarbamate salt is zinc dialkyldithiocarbamate.

13. The lubricant of claim 11, wherein the dialkyldithiocarbamate salt is a molybdenum dialkyldithiocarbamate.
14. The lubricant of claim 10, wherein the antioxidant is an alkylated diphenylamine.
15. The lubricant of claim 10, wherein the antioxidant comprises methylene bis (N,N-dibutylthioclormate).
16. The lubricant of claim 1, wherein the vegetable oil is corn oil and comprises from 20% to 25% by weight of the lubricant, and wherein the viscosity index improver additives are not present.
17. The lubricant of claim 1, wherein phosphorus-containing additives are not present or wherein phosphorus-containing additive(s) are present in an amount less than 0.08% (by weight).
18. An internal combustion engine lubricated with the lubricant of claim 1.
19. An automotive transmission lubricated with the lubricant of claim 1.
20. A lubricant comprising:
   synthetic and/or mineral oil;
   a performance-enhancing amount of vegetable oil; and
   an antioxidant selected from dialkyldithiocarbamate salts, alkylated diphenylamines, and methylene bis (N,N-dibutylthioclormate).
21. The lubricant of claim 20, wherein the vegetable oil is corn oil.
22. The lubricant of claim 20, wherein the vegetable oil is deodorized corn oil.
23. The lubricant of claim 20, wherein the vegetable oil comprises from about 20% to about 25% of the lubricant by volume.
24. The lubricant of claim 20, wherein the dialkyldithiocarbamate salt is zinc diamyldithiocarbamate.
25. The lubricant of claim 20, wherein the dialkyldithiocarbamate salt is a molybdenum dialkyldithiocarbamate.
26. The lubricant of claim 20, wherein the antioxidant is an alkylated diphenylamine.
27. The lubricant of claim 20, wherein the vegetable oil is corn oil and comprises from 20% to 25% by weight of the lubricant, and wherein the viscosity index improver additives are not present.
28. The lubricant of claim 20, wherein phosphorus-containing additives are not present or wherein phosphorus-containing additive(s) are present in an amount less than 0.08% (by weight).

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