Friction modification of synthetic gear oils.

Gear oils and gear oil additive packages that exhibit improved frictional properties for use in transmissions equipped with synchronizers are described. The lubricant compositions have a kinematic viscosity at 100°C in the range of 4 to 32 mm².s⁻¹ (cSt), and comprise: a) a base oil having at least 25%, preferably at least 50%, more preferably at least 75%, and most preferably 100% by weight of (i) hydrogenated poly-alpha-olefin oligomer oil or (ii) synthetic ester oil, or (iii) a combination of (i) and (ii); b) an amount of a gear oil additive package such that the gear oil lubricant satisfies or exceeds the specifications for API-GL4 service; and c) an amount in the range of 0.01 to 2 wt % based on the total weight of the lubricant of at least one alkali or alkaline earth metal salt of an oil-soluble sulfonic acid, the amount of said metal salt used being sufficient to improve the friction properties of the lubricant for use in manual transmissions, particularly those of the synchronizer type; said lubricant containing at most 100 ppm of metal as one or more additive components other than said metal salt, and having on a weight basis a boron content, if any, of not more than 1,000 ppm.
This invention relates to improving the frictional characteristics of gear oils in which the base oil is, or contains a significant quantity of, a synthetic oil such as a polyalpha-olefin oil (PAO) or a synthetic ester oil.

Modern commercial large vehicles equipped with manual transmissions of the synchronizer type are typically operated with conventional mineral oil-based transmission lubricants. Such lubricants contain additives for wear protection, corrosion protection, and other beneficial property improvements. The level and type of additive used depends on the performance requirements of the oil, including low temperature properties, or wear protection. Performance designations which are used include API-GL4 and API-GL5. More recently PG1, PG2 and API-GL7 are being defined. Additionally a degree of demulsification may be preferred. API-GL4 and lower performance specifications may be met using conventional crankcase mineral oil lubricants containing conventional levels of zinc dialkyldithiophosphates, sulfonates, or ashless dispersants. Mineral oil lubricants to meet all the above levels are based on P/S essentially ashless formulations, although up to at least API-GL5 has been met by P/S formulations containing significant levels of alkali metal borates and metal sulfonates (e.g., OLOA 9750 additive). As those skilled in the art are aware, "P/S" refers to gear oil additive packages in which a phosphorus and sulfur-containing antiwear and/or extreme pressure additive system is employed.

However, at the more extreme temperatures and other extreme conditions which many modern vehicles meet, great advantage may be obtained by utilizing fluids other than the more traditional mineral oils to formulate the transmission fluids. These synthetic fluids, as they are often termed, may be used with mineral oil or on their own. The synthetic oils/fluids of principal interest in this context comprise poly-α-olefin oils (PAO) and synthetic ester oils because of their thermal stability and desirable viscometric properties.

Unfortunately, unlike the traditional mineral oil-based transmission fluids, many of the synthetic fluids, which are based on the P/S essentially ashless additive systems, afford unsuitably low frictional properties in the synchronizer-based transmissions and thus cause poor synchronization of the gear changes. This negative aspect of such synthetic based gear oils may be conveniently observed as low friction and noisy gear change in the Zahnradfabrik Friedrichshafen A.G. synchronizer test (described and referred to hereinafter as the "ZF Synchronizer test"). To rectify this problem it is usually necessary to cause an appropriate increase in the frictional properties of the finished synthetic oil-based lubricant. But in doing so, it is important not to materially interfere with the other performance qualities of the finished gear oil.

It has now been found possible to beneficially increase the friction exhibited by finished gear lubricants based on synthetic oils such as PAO and synthetic ester oil and blends thereof of means of small amounts of an additive which will not materially affect the other performance capabilities of the finished lubricant. For example, as little as 0.1 wt % of a preferred additive in the oil, has enabled the finished lubricant to pass the ZF Synchronizer test conducted in the manner described hereinafter.

The additives used pursuant to this invention are alkali or alkaline earth metal salts of oil-soluble sulfonic acids, such as petroleum sulfonic acids, preferably alkyaryl sulfonic acids and, more preferably, alkylbenzene sulfonic acids. The metals of such salts preferably are those which have low toxicity and which present little or no concern from the environmental standpoint, namely, lithium, sodium, potassium, magnesium, and calcium. However, barium and strontium sulfonates can be used, if desired.

So far as is known, there have been only two types of API-GL5 gear oil compositions used in actual practice that apparently contain a metal sulfonate component. One is SPIRAX MB 90 (trademark of the Shell Oil Companies), a conventional mineral oil-based gear oil, which in Germany contained small amounts of barium, believed to be in the form of a barium sulfonate corrosion inhibitor.

The other type is based on use of gear oil additive packages containing high levels of potassium borate dispersion serving as an antiwear/extreme pressure agent. These packages are believed to contain low levels of calcium, presumably in the form of a sulfonate. These packages are apparently used primarily (if not exclusively) in conventional mineral oil stocks in forming finished gear oils. And in any event, the levels of the potassium borate used in the finished oils (e.g., 1-2 wt %) are sufficiently high as to seriously impair the results obtainable by the practice of this invention and thus are outside of the permissible concentrations of this invention.


Thus in accordance with any embodiment of this invention, there is provided a gear oil lubricant having a kinematic viscosity at 100°C in the range of 4 to 32 mm².s⁻¹ (cSt), and preferably in the range of 8 to 20 mm².s⁻¹ (cSt), and comprising:

a) a base oil having at least 25%, preferably at least 50%, more preferably at least 75%, and most preferably 100% by weight of (i) hydrogenated poly-alpha-olefin oligomer oil or (ii) synthetic ester oil, or (iii) a com-
b) an amount of a gear oil additive package such that the gear oil lubricant satisfies or exceeds the specifications for GL4 service; and

c) an amount in the range of 0.01 to 2 wt % based on the total weight of the lubricant of at least one alkali or alkaline earth metal salt of an oil-soluble sulfonic acid, the amount of said metal salt used being sufficient to improve the friction properties of the lubricant for use in manual transmissions, particularly those of the synchronizer type; said lubricant being essentially free of any metal additive component (i.e., the lubricant contains at most 100 ppm and preferably no more than 50 ppm of metal as one or more additive components other than said metal salt), and having on a weight basis a boron content, if any, of not more than 1,000 ppm, preferably not more than 300 ppm, and most preferably not more than 25 ppm.

It is to be noted that in the ZF. Synchronizer test the beneficial increase in friction exhibited by finished gear lubricants of this invention manifests itself in a substantial increase in the number of cycles during which the test can be performed without poor synchronization of the gear changes. For example, a finished synthetic oil-based gear oil devoid of a metal sulfonate additive may encounter substantial failure within 10,000 or 15,000 cycles. On the other hand, finished synthetic oil-based lubricants of this invention which contain a metal sulfonate component can achieve at least 50,000 and usually at least 100,000 cycles of trouble free operation in this test procedure.

It will be appreciated that in satisfying or exceeding the specifications for API-GL4 service, the gear oil additive package used as component b) may in fact satisfy the requirements for other performance specifications such as API-GL5, and including specifications not yet in being (or even envisioned) such as PG1, PG2 and API-GL7 or specifications of other countries such as comparable JIS gear oil standards, or the like. In short, the specifications of API-GL4 are to be considered minimum performance levels for the package. For example, if the requirements of the API-GL7 specification are more stringent for the most part than, say, API-GL4, the fact that an additive package satisfies the API-GL7 requirements inherently satisfies the minimum performance requirements for use in the practice of this invention, whether or not the package has actually been subjected to the API-GL4 performance tests.

Pursuant to another embodiment of this invention, there is provided a gear oil additive package which comprises (1) an oil-soluble phosphorus and sulfur-containing antiwear and/or extreme pressure additive component and (2) at least one alkali or alkaline earth metal salt of an oil-soluble sulfonic acid; said gear oil additive package being further characterized in that when blended with a base oil having a kinematic viscosity in the range of 4 to 32 cSt at 100°C and composed of at least 25% by volume of (i) hydrogenated poly-alpha-olefin oligomer oil or (ii) synthetic ester oil, or (iii) a combination of (i) and (ii) to form a lubricant containing from 0.01 to 2 wt % of said metal salt, said gear oil additive package provides a lubricant composition that:

A) satisfies or exceeds the specifications for API-GL4 service;

B) contains, if any, at most 100 ppm and preferably no more than 50 ppm of metal apart from the metal of said metal salt; and

C) has a boron content, if any, of not more than 1,000 ppm, preferably no more than 300 ppm, and most preferably not more than 25 ppm.

Still another aspect of this invention is the method of beneficially modifying the frictional characteristics of a low-friction synthetic lubricant composition containing a gear oil additive package such that the lubricant composition satisfies or exceeds the specifications for API-GL4 service, but does not exhibit satisfactory friction properties for use in manual transmissions, particularly those of the synchronizer type. The method comprises including in such lubricant composition an amount in the range of 0.01 to 2 wt % based on the total weight of the lubricant of at least one metal salt of an oil-soluble sulfonic acid such that the friction properties of said lubricant are improved for use in manual transmissions, particularly those of the synchronizer type.

In each of the above embodiments the metal of the sulfonate salt preferably is lithium, sodium, potassium, magnesium, or calcium, or a combination of two or more such metals. However, barium and/or strontium sulfonates can be used if desired.

In each of the embodiments of this invention, the metal sulfonate can be employed as a separate component (e.g., as a "top-treat" to the base oil with which the additive package has been or will be blended) or as a component of the additive package itself. Similarly, while use of additive packages is preferred, it is possible to blend the metal sulfonate and the respective components of the additive package into the base oil individually or in various compatible sub-combinations.

As noted above, the base oils are composed partially or entirely of a low-friction fluid such as PAO base oil and/or a synthetic ester lubricating oil. The PAO fluids are usually formed by oligomerization or co-oligomerization of 1-alkene hydrocarbon having 6 to 20 and preferably 8 to 16 carbon atoms in the molecule and hydrogenation of the resultant oligomer. Hydrogenated oligomers formed from 1-decene are particularly preferred. Methods for the production of such liquid oligomeric 1-alkene hydrocarbons are known and reported as described in patent EP 0 578 435 A1.
The specifications for API-GL4 and API-GL5 service are published in ASTM Publication STP-512A entitled "Laboratory Performance Tests for Automotive Gear Lubricants" (March 1987).

A number of gear oil additive packages (concentrates) that provide API-GL4 or API-GL5 performance are available in the marketplace. They generally contain at least a sulfur-phosphorus antiwear or extreme pressure additive.
additive system, one or more antioxidants, one or more corrosion inhibitors, and an antifoam additive, and may, and preferably do, contain a dispersant additive.

Pursuant to another embodiment of this invention, there is provided a gear oil additive package (concentrate) which comprises:

- a) at least one oil-soluble ashless dispersant, preferably a succinimide ashless dispersant and/or a succinic ester-amine ashless dispersant, and more preferably a Mannich base ashless dispersant;
- b) at least one oil-soluble metal-free sulphur-containing antiwear and/or extreme pressure agent;
- c) at least one oil-soluble metal-free phosphorus-containing antiwear and/or extreme pressure agent; and
- d) at least one alkali or alkaline metal salt of an oil-soluble sulfonic acid in an amount such that a lubricant composition formed by blending the additive package in a base oil having a kinematic viscosity in the range of 4 to 32 cSt at 100°C and composed of at least 25% by weight, preferably at least 50% by weight, and most preferably at least 75% by weight of (i) hydrogenated polyalpha-olefin oligomer oil or (ii) synthetic ester oil, or (iii) a combination of (i) and (ii) to form a lubricant containing from 0.01 to 2 wt % of said metal salt:
  A) satisfies or exceeds the specifications for API-GL4 service;
  B) contains, if any, no more than at most 100 ppm and preferably no more than 50 ppm of metal apart from the metal of said metal salt; and
  C) has a boron content, if any, of not more than 1,000 ppm, preferably not more than 300 ppm, and most preferably not more than 25 ppm.

Preferably, the metal of such salt is lithium, sodium, potassium, magnesium, or calcium, or a combination of two or more such metals.

A finished lubricant composition containing at least the foregoing components a), b), c) and d) constitutes still another embodiment of this invention. Such finished lubricant satisfies or exceeds the specifications for API-GL4 service, and preferably satisfies or exceeds the specifications for API-GL5 service. Component a) of the foregoing additive package and finished lubricant composition most preferably is a Mannich base which includes or, alternatively, consists of boronated Mannich base ashless dispersant.

Yet another embodiment of this invention involves using as component a) a Mannich base dispersant and proportioning components a) and b) above in the additive package or in the finished lubricant composition such that the mass ratio (wt/wt) of nitrogen in the Mannich base dispersant to sulphur in the sulphur-containing antiwear and/or extreme pressure agent is in the range of 0.0005:1 to 0.5:1, and preferably in the range of 0.003:1 to 0.2:1.

In still further embodiments a Mannich base dispersant is employed as component a) and components a) and c) above are proportioned in the additive package or in the finished lubricant such that the mass ratio (wt/wt) of nitrogen in the Mannich base dispersant to phosphorus in the metal-free phosphorus-containing antiwear and/or extreme pressure agent is in the range of 0.005:1 to 5:1, and preferably in the range of 0.01:1 to 2:1.

In additional embodiments, any of the above additive concentrates and finished lubricant compositions further comprise at least one oil-soluble demulsifying agent.

In still other embodiments, any of the above additive concentrates and finished lubricant compositions further comprise at least one oil-soluble amine salt of a sulphur-free hydrocarbyl phosphoric acid.

Preferably the lubricant compositions of this invention have a halogen content, if any, of no more than 100 ppm, and more preferably no more than 30 ppm on a weight basis.

Other embodiments of this invention will appear hereinafter.

As is well known in the art, the ZF.Synchronizer test has been designed for the evaluation of oil performance in commercially available synchromesh units under endurance conditions with the bulk lubricant temperature controlled at a relatively high level. While it is important to simulate fairly closely the actual conditions met in service, the need to produce a test result in an acceptable period has to be taken into account. Briefly, two halves of a transmission synchromesh unit are repeatedly brought together under conditions of known force and speed differential until failure occurs. Failure may be defined in terms of synchromesh performance or overall wear. The test rig used in the procedure was designed with consideration of work done by Socin and Walters, SAE Paper Number 680008 entitled "Manual Transmission Synchronizers"; Fano, CEC TLPG4 Chairman's Final Report, 1985, entitled "Synchronmesh Test Method With Proposed Synchro Test Rig"; and Brugen, Thies and Naurian of Zahnradfabrik Friedrichshafen A.G. in a paper entitled "Einfluss Des Schmierstoffes auf die Schaltelemente Von Fahrzeuggetrieben". The two synchromesh units are assembled in a gear box which forms the oil reservoir and facilitates splash lubrication of components. Drive may be transmitted along the main shaft or via the layshaft gears to give an increased ratio. The input speed is kept constant by means of a DC drive control system and a large flywheel simulating vehicle inertia. On changing gear, the output shaft accelerates and decelerates the small flywheel which simulates clutch inertia. A pivot linkage connected to a
EXAMPLE A

To a reaction vessel are charged 38.0 parts of sulphurized isobutylene, 14.0 parts of a product formed by reaction of dicyclopentadiene with dithiophosphoric acid-0,0-dialkyl ester in which on a molar basis 40% of the alkyl groups are isopropyl, 40% are isobutyl and 20% are 2-ethylhexyl, 4.76 parts of dibutyl hydrogen phosphite, and 1.75 parts of 2-ethylhexyl acid phosphate. Throughout this addition, the components of the reaction vessel are agitation and maintained at 30°C for 10 minutes. To this mixture is added 6.0 parts of Primene® 81-R amine (a tert-alkyl primary amine mixture in the C12-C14 range; Rohm & Haas), and the mixture is stirred for 20 minutes without application of heat. Then another 4.9 parts of this tertiary alkyl monoamine product is added and the contents of the reaction vessel are maintained at 50°C for 1 hour with continuous stirring. While cooling the vessel contents to 40°C, 4.31 parts of oleic acid and 0.58 part of M530 defoamer (an antifoam concentrate of Monsanto Company) are added. Then, in a final stage and without application of heat, 1.8 parts of 2-tet-dodecyldithio-5-mercapto-1,3,4-thiadiazole, 12.3 parts of Amoco 9250 additive (a proprietary product of Amoco Corporation, which is believed to be a 48% oil concentrate of boronated Mannich base ashless dispersant and which contains about 1.1% nitrogen and about 0.2% boron), 0.77 parts of Pluronic L-121 demulsifier (an ethylene oxide-propylene oxide block copolymer of BASF Corporation) and 10.83 parts of process oil are added to the contents of the reaction vessel. The resulting additive concentrate is stirred for 60 minutes.

EXAMPLE B

To a reaction vessel are charged 38.3 parts of sulphurized isobutylene, 14.3 parts of di-tert-nonyl polysulfide, 5.7 parts of dibutyl hydrogen phosphite, 0.1 part of tolytriazole, and 2.9 parts of amyl acid phosphate. Throughout this addition, the components of the reaction vessel are agitation and maintained at 30°C for 10 minutes. To this mixture are added 3.7 parts of Primene 81-R amine, 3.7 parts of C16 and C18 primary amines, 1.0 part of octyl amine, and 3.2 parts of process oil, and the mixture is stirred for 20 minutes while maintaining the contents of the reaction vessel at 50°C for 1 hour with continuous stirring. Then, while cooling the contents to 40°C, 0.6 part of C95 dimer acid, 0.6 part of caprylic acid, 1.0 part of M530 defoamer, and 3.2 parts of process oil are added. Thereafter, without application of heat, 2.7 parts of 2-tet-dodecyldithio-5-mercapto-1,3,4-thiadiazole, 12.2 parts of Amoco 9250 additive, 0.5 part of Pluronic L-101 demulsifier (an ethylene oxide-propylene oxide block copolymer concentrate of BASF Corporation), 2.9 parts of phenolic antioxidant (ETHYL® antioxidant 733) and 3.4 parts of process oil are added to the contents of the reaction vessel. The resulting additive concentrate is stirred for 60 minutes.
EXAMPLE C

To a reaction vessel are charged 35.8 parts of sulphurized isobutylene, 3.6 parts of dibutyl hydrogen phosphite, 18.9 parts of a product formed by reaction of dicyclopentadiene with dithiophosphoric acid-0,0-dialkyl ester in which on a molar basis 40% of the alkyl groups are isopropyl, 40% are isobutyl and 20% are 2-ethylhexyl, and 1.7 parts of 2-ethylhexyl acid phosphate. Throughout this addition, the components of the reaction vessel are agitated and maintained at 30°C for 10 minutes. To this mixture are added 3.9 parts of C16 and C18 primary amines, 0.7 part of octyl amine, and 9.1 parts of process oil, and the mixture is stirred for 20 minutes while maintaining the contents of the reaction vessel at 50°C for 1 hour with continuous stirring. Then, while cooling the contents to 40°C, 0.7 part of caprylic acid, 0.7 part of M544 defoamer (an acrylate copolymer concentrate of Monsanto Company), and 5.8 parts of process oil are added. Thereafter, without application of heat, 12.0 parts of Amoco 9250 additive, 1.5 parts of 2-tert-dodecylthio-5-mercapto-1,3,4-thiadiazole, 0.8 part of Chemax HCO-5 (a hydrogenated castor oil ethoxylate concentrate of Chemax, Inc.), and 4.8 parts of process oil are added to the contents of the reaction vessel. The resulting additive concentrate is stirred for 60 minutes.

EXAMPLE D

To a reaction vessel are charged 35.1 parts of sulphurized isobutylene, 3.8 parts of dibutyl hydrogen phosphite, 16.6 parts of a product formed by reaction of dicyclopentadiene with dithiophosphoric acid-0,0-dialkyl ester in which on a molar basis 40% of the alkyl groups are isopropyl, 40% are isobutyl and 20% are 2-ethylhexyl, and 1.0 part of 2-ethylhexyl acid phosphate. Throughout this addition, the components of the reaction vessel are agitated and maintained at 30°C for 10 minutes. To this mixture are added 3.3 parts of C16 and C18 primary amines, and 8.3 parts of process oil, and the mixture is stirred for 20 minutes while maintaining the contents of the reaction vessel at 50°C for 1 hour with continuous stirring. Then, while cooling the contents to 40°C, 0.6 part of caprylic acid, 0.6 part of M544 defoamer, and 8.3 parts of process oil are added. Thereafter, without application of heat, 12.8 parts of Amoco 9250 additive, 1.3 parts of 2-tert-dodecylthio-5-mercapto-1,3,4-thiadiazole, and 8.3 parts of process oil are added to the contents of the reaction vessel. The resulting additive concentrate is stirred for 60 minutes.

EXAMPLES 1-4

A gear lubricant is formulated using respective Examples A-D above as follows:

<table>
<thead>
<tr>
<th>Additive package</th>
<th>6.5% wt</th>
</tr>
</thead>
<tbody>
<tr>
<td>AMOCO 421 Magnesium Sulfonate</td>
<td>0.35% wt</td>
</tr>
<tr>
<td>Diisodecyladipate</td>
<td>25% wt</td>
</tr>
<tr>
<td>ETHYLFLO 174 PAO</td>
<td>58.15% wt</td>
</tr>
<tr>
<td>ETHYLFLO 168 PAO</td>
<td>10.0% wt</td>
</tr>
</tbody>
</table>

EXAMPLES 5-8

Alternative lubricants of this invention are formulated using the respective additive packages of Examples A-D above as follows:

<table>
<thead>
<tr>
<th>Additive package</th>
<th>3.2% wt</th>
</tr>
</thead>
<tbody>
<tr>
<td>HITEC® 614 Calcium Sulfonate</td>
<td>0.1% wt</td>
</tr>
<tr>
<td>ETHYLFLO 170 PAO</td>
<td>80.7% wt</td>
</tr>
<tr>
<td>ETHYLFLO 174 PAO</td>
<td>6.0% wt</td>
</tr>
<tr>
<td>Diisodecyladipate</td>
<td>10.0% wt</td>
</tr>
</tbody>
</table>
EXAMPLE 9

A synthetic oil-based lubricating oil composition of this invention is formed by blending together the following components in the amounts specified:

- 6.5% of the additive package of Example A, B, C or D;
- 0.3% of HITEC® 611 Calcium Sulfonate;
- 39.9% of ETHYLFLO 168 poly-α-olefin oligomer oil (an 8 cSt base oil) (ETHYLFLO is a trademark of Ethyl Corporation);
- 43.3% of a low chlorine version of ETHYLFLO 174 poly-α-olefin oligomer oil (a 40 cSt base oil); and
- 10.0% of KETJENLUBE synthetic oil (KETJENLUBE is a trademark of Akzo Chemicals).

EXAMPLE 10

The ingredients listed below are pre-mixed in the relative proportions specified, heated to 60°C for 1.5 hours, and the resultant mixture is incorporated in an SAE 80W-90 synthetic fluid comprising 10.0% Ketjenlube 115 (Akzo Chemicals), 43.3% ETHYLFLO 174 PAO and 41.0% ETHYLFLO 168 PAO together with 0.2% w/w HITEC® 611 Calcium Sulfonate at a concentration of 5.5% w/w.

<table>
<thead>
<tr>
<th>Component</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfurized Isobutylene</td>
<td>3.9</td>
</tr>
<tr>
<td>Octyl Amine</td>
<td>0.6</td>
</tr>
<tr>
<td>Oleyl Amine</td>
<td>0.163</td>
</tr>
<tr>
<td>Octanoic Acid</td>
<td>0.5</td>
</tr>
<tr>
<td>2-Ethylhexyl-Acid Phosphate</td>
<td>0.196</td>
</tr>
<tr>
<td>Copper Deactivator</td>
<td>0.07</td>
</tr>
<tr>
<td>Antifoam</td>
<td>0.06</td>
</tr>
</tbody>
</table>

EXAMPLE 11

A gear oil additive concentrate of this invention is formed by heating at 50°C for one hour a mixture of sulfurized isobutylene, trihydrocarbyl ester of dithiophosphoric acid, octyl amine, bis-2-ethylhexylphosphate, oleylamine, alkyl acid phosphate, a friction modifier and a succinimide type dispersant. In the second stage of the procedure, oleic acid, antifoam agent, and process oil are added to the hot mixture produced in the first stage. The resultant concentrate is then allowed to cool to about 35°C, when metal deactivator and calcium sulfonate is added. The resultant concentrate contains (apart from amine tied up with phosphorus acids) approximately 21 mole % of sulphur per mole of amino nitrogen and approximately 0.56 chemical equivalent of weak acid (oleic acid) per equivalent of amino nitrogen. A gear oil is formed by blending this additive concentrate to a level of 6.5% w/w in an SAE 80W-90 synthetic fluid as in Example 10 above (equivalent to a concentration of 2.27 weight % of sulfurized isobutylene).

EXAMPLE 12

A mixture is formed from sulphurized isobutylene, oleylamine, octanoic acid, trihydrocarbyl dithiophosphate, a succinimide dispersant and a friction modifier in weight proportions of approximately 11.7:2.8:0.7:5:5.1:1 respectively. This mixture is heated at 60°C for one hour. To this hot mixture in a second stage are added octylamine, bis-2-ethylhexyl phosphate, an amine salt of a dihydrocarbyl thiophosphate and antifoam agent in weight proportions of approximately 0.2:0.4:3:3:0.2, respectively. Thereafter a mineral oil and a metal deactivator are added so that the resultant concentrate contains approximately 35% of the initial sulfurized isobutylene and approximately 18.3% of the mineral oil diluent. Excluding amine that is tied up with phosphorus acids, the additive concentrate contains approximately 18 mole % of sulfur per mole of amino nitrogen and approximately 0.6 equivalent of weak acid per equivalent of amino nitrogen. 3.25% of this additive package together with 0.3% of HITEC® 611 calcium sulfonate is dissolved in a semi-synthetic fluid comprising 15% di(tridecyl)adipate, 25% ETHYLFLO 168 PAO, and 56.45% of mineral oil (Shell HVI 850b).
EXAMPLE 13

The procedure of Example 12 for producing the additive concentrate is repeated with the following modifications: the bis-2-ethylhexyl phosphate, the octylamine and the antifoam agent are included in the first stage, the oleyl amine, the dispersant and the friction modifier are introduced into the second stage reaction mixture, and the second stage reaction mixture is held at 50°C for 30 minutes. 6.5% of this additive package together with 0.5% of Amoco 421 magnesium sulfonate is dissolved in a fluid comprising a mixture of ETHYL-FLO 168 PAO and mineral oil (Shell HVI 650b) to give a gear lubricant of SAE 80W-90 viscosity grade.

EXAMPLE 14

The procedure of Example 13 is repeated except that the first stage reaction mixture is heated to 50°C for 20 minutes and the second stage reaction mixture is held at 50°C for one hour. 6.5% of this additive package together with 0.25% of HiTEC®631 barium sulfonate is dissolved in a mixture of di(tridecyl)adipate (30%) and 63.25% mineral oil to give an SAE 80W-90 semi-synthetic gear lubricant.

EXAMPLE 15

The procedure of Example 12 for producing the additive concentrate is repeated except that the octylamine is added in the first stage reaction, the octanoic acid is added in the second stage reaction mixture, the first stage reaction mixture is maintained at 50°C for one hour, and the amine salt of a dihydrocarbyl thiophosphate is added in a final stage along with the mineral oil and metal deactivator. 3.0% of HiTEC® 611 high base sulfonate is stirred into the additive package which is then used to formulate synthetic and semi-synthetic lubricants suitable for use in manual automotive transmissions where a synchronization system is utilized.

EXAMPLE 16

The procedure of Example 12 for producing the additive concentrate is repeated with the following modifications: the octylamine and the trihydrocarbyl dithiophosphate are introduced into the first stage reaction mixture, and the octanoic acid is introduced into the second stage reaction mixture. This additive package is dissolved at 5.0% together with 0.2% of Lubrizol 6477 high base sulfonate in a synthetic fluid comprising a mixture of 25% of a poly-a-olefin made from dodecene, 44.8% of a poly-α-olefin made from decene (ETHYL-FLO 168 PAO) and 25% of di(tridecyl)adipate.

EXAMPLE 17

A lubricating fluid of SAE 90 grade viscosity characteristics is blended with a commercially available additive package (HiTEC® 2375 additive: Ethyl Petroleum Additives, Ltd.; Ethyl Petroleum Additives, Inc.; Ethyl S.A.; Ethyl Canada Limited) in quantities such that the oil contains sulfurized isobutylene (2.27% w/w) and an alkylamine/alkylphosphate/alkylphosphite/alkylthiophosphate mixture (0.56%w/w). The oil also contains octanoic acid in a proportion such that there are approximately 136 moles of sulfur per mole of said acid. The sulfurized isobutylene itself is HiTEC® 309 additive. The alkylamine is entirely neutralized by the phosphorus acids present. 3.75% of this additive package is used in combination with 0.2% HiTEC® 631 barium sulfonate to formulate a semi-synthetic lubricant comprising 15% di(isodecyl)adipate, 30% ETHYLFLO 168 PAO and 56.05% Shell mineral oil (HVI 650b).

EXAMPLE 18

Stage 1. To a reaction vessel are charged 43.4 parts of sulfurized isobutylene, 4.44 parts of dibutyl hydrogen phosphite, 4.99 parts of C₁₂-C₁₄ tertiary alkyl primary amine (Primene 81R; Rohm & Haas Chemical Company), 1.16 parts of 2-ethylhexyl acid phosphate, and 2.56 parts of process oil. Throughout this addition, wherein the sulfurized isobutylene, phosphite and amines are added in the order named, the components of the reaction vessel are agitated. An exothermic reaction occurs on bringing the sulfurized isobutylene, phosphite and amines into contact with each other, and the rate of addition is controlled so that the temperature does not exceed 60°C. Concurrently a slight negative pressure is maintained on the reaction vessel in order to remove any volatiles produced during the exothermic reaction. The temperature of the reaction vessel is maintained at 55-60°C for 60 minutes while continuing the agitation. The mixture is then cooled to 40°C.

Stage 2. In a separate reactor, 0.69 part of M-544 defoamant (Monsanto Chemical Company), 0.73 part
of caprylic acid, 0.50 part of a mixture of C₁₂ and C₁₄ tert-alkyl primary monoamines (Primene 81R), and 2.87 parts of process oil are agitated together for 15 minutes. The solution so formed is added to the Stage 1 product. Concurrently, added is 19.63 parts of a product formed by reaction of dicyclopentadiene with dithiophosphoric acid-0,0-dialkyl ester in which on a molar basis 40% of the alkyl groups are isopropyl, 40% are isobutyl and 20% are 2-ethylhexyl. Agitation is continued for 15 minutes, and the temperature is kept at 30-40°C. The pH of the resultant solution is approximately 6.9.

Stage 3. To the agitated solution of Stage 2 are added 3.0 parts of 2-tert-dodecyldithio-1,3,4-thiadiazole and 16.03 parts of process oil. Agitation is continued for 15 minutes while keeping the temperature at 30-40°C. The finished product is a bright clear amber liquid typically having a sulfur content of about 23.7% (wt) and a phosphorus content of about 2.35% (wt).

EXEMPLARY 19

Stage 1. The procedure of Stage 1 of Example 18 is repeated using 34.97 parts of sulfurized isobutylene, 3.00 parts of dibutyl hydrogen phosphate, 5.60 parts of C₁₆₋₁₈ alkyl monoamine, 0.01 part of n-octyl amine, 0.98 part of 2-ethylhexyl ester phosphate, and 2.65 parts of process oil.

Stage 2. The product of Stage 1 is cooled to 40°C with continued agitation. Added to this product after the temperature reaches 40°C, is 16.61 parts of a product formed by reaction of dicyclopentadiene with dithiophosphoric acid-0,0-dialkyl ester in which on a molar basis 40% of the alkyl groups are isopropyl, 40% are isobutyl and 20% are 2-ethylhexyl.

Stage 3. In a separate reactor, 0.58 part of M-544 defoamant (Monsanto Chemical Company), 0.62 part of caprylic acid, 0.62 part of a C₉₆ dicarboxylic acid (formed by dimerization of oleic acid), and 2.65 parts of process oil are agitated together for 15 minutes. The resulting solution is added to the product from Stage 2. Agitation is continued for 15 minutes.

Stage 4. To the agitated mixture of Stage 3 are added 2.6 parts of 2-tert-dodecyldithio-1,3,4-thiadiazole and 2.65 parts of process oil. After these two components are added, 0.75 parts of dibutyl hydrogen phosphate is added to the mixture. Agitation is continued for 15 minutes.

Stage 5. To the agitated mixture of Stage 4 are added 23.07 parts of a mixture composed of 55% (wt) of a boronated succinimide (HiTEC® 648 additive; Ethyl Petroleum Additives, Inc.; Ethyl Petroleum Additives, Ltd.; Ethyl S.A.; Ethyl Canada Ltd.) and 45% (wt) of process oil, and 2.65 parts of additional process oil. Agitation is continued for 15 minutes to ensure complete blending of the components. The finished product is pumped through a filter. The product is a bright clear amber liquid typically containing, on a weight basis, about 19.3% sulfur, about 2.0% phosphorus, about 0.62% nitrogen, and about 0.16% boron. This concentrate is dissolved in a synthetic fluid at 3.5% together with 0.1% Amoco 421 magnesium sulfonate. In this case the synthetic fluid comprises 25% of a synthetic dibasic ester di(tridecyl)adipate and a 10 cSt (10 mm²·s⁻¹) poly-α-olefin, ETHYLFLO 170 PAO.

EXEMPLARY 20

Stage 1. The procedure of Stage 1 of Example 18 is repeated using 31.26 parts of sulfurized isobutylene, 2.44 parts of dibutyl hydrogen phosphate, 3.18 parts of C₁₆₋₁₈ alkyl monoamine, 0.63 part of n-octyl amine, 0.80 part of 2-ethylhexyl acid phosphate, and 5.19 parts of process oil. The pH of the resulting mixture is approximately 7.0.

Stage 2. In a separate reactor, 0.47 part of M-544 defoamant (Monsanto Chemical Company), 0.51 part of caprylic acid, 0.51 part of a C₉₆ dicarboxylic acid (formed by dimerization of oleic acid), and 5.19 parts of process oil are agitated together for 15 minutes. The solution so formed is added to the Stage 1 product. Concurrently, added is 10.66 parts of a product formed by reaction of dicyclopentadiene with dithiophosphoric acid-0,0-dialkyl ester in which on a molar basis 40% of the alkyl groups are isopropyl, 40% are isobutyl and 20% are 2-ethylhexyl. Agitation is continued for 60 minutes, and the temperature is kept at 40°C.

Stage 3. To the agitated solution of Stage 2 is added 2.14 parts of 2,5-dimethylthio-1,3,4-thiadiazole and 5.19 parts of process oil. Then 0.61 part of dibutyl hydrogen phosphate is added to the mixture. Agitation is continued for 15 minutes.

Stage 4. To the agitated solution from Stage 3 are added 10.32 parts of a mixture composed of 55% (wt) of a boronated succinimide (HiTEC® 648 additive; Ethyl Petroleum Additives, Inc.; Ethyl Petroleum Additives, Ltd.; Ethyl S.A.; Ethyl Canada Ltd.) and 45% (wt) of process oil, 6.24 parts of alkenylsuccinic anhydride produced from a mixture of olefins made by isomerizing a 1-olefin mixture containing 49% C₂₀, 42% C₂₂, and 8% C₂₄ 1-olefins, and 14.66 parts of additional process oil. Agitation
is continued for 15 minutes to ensure complete blending of the components. The finished product is pumped through a filter. The product is a bright clear amber liquid typically containing, on a weight basis, about 17.5% sulfur, and about 1.6% phosphorus. This product is dissolved in a fluid comprising 0.5% calcium sulfonate (HiTEC® 611 additive), 27% Lubrizol 3174 shear stable viscosity index improver, 40% of a synthetic ester di(iso-decyl)adipate and 32.5% of ETHYLFLO 168 PAO.

**EXAMPLE E**

An additive concentrate is prepared as follows:

14 parts by weight of trihydrocarbyl dithiophosphate [where two of the substituents are a mixture of isopropyl, n-butyl and 2-ethylhexyl (in a 40:40:20 ratio) and the third substituent is derived from dicyclopentadiene] is stirred at approximately 30°C with 38 parts of sulfurized isobutylene, 1.75 parts 2-ethylhexyl acid phosphate, and 4.76 parts of dibutyl hydrogen phosphate.

6 parts of a tertiary alkyl primary amine (PRIMENE 81R) is added and allowed to react. After approximately 30 minutes a polyisobutylene substituted succinimide dispersant at 2.42 parts by weight and a further 4.9 parts of PRIMENE 81R is added and the resultant mixture stirred at about 55°C for one hour.

0.57 parts of polyalkylacrylate antifoamant, 4.31 parts of oleic acid and 5.63 parts of mineral oil are stirred into the mixture which is subsequently allowed to cool to below 40°C.

1.8 parts of a thiadiazole (HiTEC® 314 additive) is then added to the mixture which is allowed to cool to room temperature.

**EXAMPLE 21**

Into the additive concentrate prepared as in Example E above are stirred 3.15 parts of HiTEC® 611 calcium sulfonate and 11.85 parts of mineral oil to give an additive package suitable for formulating gear oils.

**EXAMPLE 22**

Into the additive concentrate prepared as in Example E above is stirred 15 parts of HiTEC® 614 calcium sulfonate to give an additive concentrate.

**EXAMPLE 23**

Into the additive concentrate prepared as in Example E above are stirred 3.0 parts of Amoco 421 magnesium sulfonate and 12.0 parts of mineral oil.

**EXAMPLE 24**

Into the additive concentrate prepared as in Example E above are blended 1.0 part of sodium alkyl benzene sulfonate, 2.0 parts of HiTEC® 611 calcium sulfonate and 12.0 parts of mineral oil.

**EXAMPLE 25**

The following Table gives examples of gear oil formulations containing the respective additive packages described in Examples 21-24 above.
EXAMPLE F

A chemical composition is prepared as follows:

6.26 parts of a trihydrocarbyl dithiophosphate [where two of the substituents are a mixture of isopropyl, n-butyl and 2-ethylhexyl (in a 40:40:20 ratio) and the third substituent is derived from dicyclopentadiene] is stirred with 44 parts of sulfurized isobutylene, 5.33 parts dibutyl hydrogen phosphite and 1.94 parts of 2-ethylhexylacid phosphate for 10 minutes at about 30°C. To this mixture is added 0.6 parts of octylamine followed by a mixture of 6.0 parts PRIMENE 81R amine and 1.2 parts oleylamine. The resulting mixture is then heated to about 55°C for about 1 hour after which time heating is terminated and the following acidic mixture is added:

**ACIDIC MIXTURE**

- 5 parts mineral oil
- 2.2 parts oleic acid
- 0.5 part polyalkylacrylate antifoamant
- 0.3 part caprylic acid
- 0.116 part TOLAD 9308 (Petrolite)
- 0.106 part polyethylene/propylene block copolymer
- 0.777 part TOLAD 370 (Petrolite)

After cooling and stirring to below 40°C, 9.33 parts of Amoco 9250, 1.2 parts of a thiadiazole (HiTEC 314 additive) and 15.781 parts mineral oil are added.

EXAMPLE 26

The composition formed as described in Example F above is mixed 50:50 by weight with calcium sulfonate (HiTEC 611 additive and used in formulating transmission oils as described in Example 27 below.
EXAMPLE 27

<table>
<thead>
<tr>
<th></th>
<th>(I)</th>
<th>(II)</th>
<th>(III)</th>
<th>(IV)</th>
<th>(V)</th>
<th>(VI)</th>
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<tbody>
<tr>
<td>Composition of Example 26</td>
<td>0.2</td>
<td>1.0</td>
<td>0.3</td>
<td>0.2</td>
<td>0.9</td>
<td>1.0</td>
</tr>
<tr>
<td>Composition of Example F</td>
<td>3.75</td>
<td>7.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anglamol 99 (Low Chlorine)</td>
<td>--</td>
<td>--</td>
<td>3.9</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Anglamol 9000</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>7.0</td>
<td>--</td>
</tr>
<tr>
<td>Mobilab G521T</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>5.0</td>
<td>--</td>
</tr>
<tr>
<td>Diisodecyl adipate</td>
<td>10.0</td>
<td>20.0</td>
<td>20.0</td>
<td>20.0</td>
<td>25.0</td>
<td>20.0</td>
</tr>
<tr>
<td>ETHYL FLO 168 PAO</td>
<td>--</td>
<td>11.5</td>
<td>--</td>
<td>10.0</td>
<td>17.1</td>
<td>--</td>
</tr>
<tr>
<td>ETHYL FLO 170 PAO</td>
<td>80.0</td>
<td>--</td>
<td>70.0</td>
<td>--</td>
<td>--</td>
<td>74.0</td>
</tr>
<tr>
<td>ETHYL FLO 174 PAO</td>
<td>6.05</td>
<td>--</td>
<td>5.8</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Mineral oil (Shell HV1650b)</td>
<td>--</td>
<td>60</td>
<td>--</td>
<td>64.8</td>
<td>50</td>
<td>--</td>
</tr>
</tbody>
</table>

EXAMPLE 28

A semi-synthetic gear fluid of this invention is formed from Anglamol 99 gear additive package at 3.9% and barium sulfonate (HiTEC 631 additive) at 0.2% in a mixture of 10% diisodecyl adipate, 25% hydrotreated mineral oil (Shell XHVI 5.2) and 60.9% mineral oil (Shell HVI 650b).

EXAMPLE 29

Blended together are Anglamol 6004A gear additive package at 6.5%, HiTEC 614® calcium sulfonate at 0.5%, diisodecyl adipate at 10%, ETHYL FLO 174 PAO at 6.0% and ETHYL FLO 170 PAO at 77% to give an SAE 80W fluid of this invention.

EXAMPLE 30

With a mixture of 33.2% of diisodecyl adipate and 60% of ETHYL FLO 174 PAO are blended 6.6% Mobilad G521T gear additive package and 0.2% Amoco 421 magnesium sulfonate to give a gear lubricant of the invention.

EXAMPLE 31

A semi-synthetic gear lubricant of the invention is formed when 8.0% of Anglamol 6043U gear additive is blended with 0.2% HiTEC 631 barium sulfonate, 35% of di(tridecyl) adipate and 56.8% of mineral oil (Shell HVI 650b).

EXAMPLE 32

Blended together are 6.5% of a low chlorine version of Anglamol 99 gear additive, 0.5% HiTEC 631 barium sulfonate, 1.5% HiTEC 623 pour point depressant, 65% mineral oil (Shell HVI 650b) and 26.5% of ETHYL FLO 168 PAO to give a semisynthetic gear lubricant of the invention.

EXAMPLE 33

With a mixture of 7.0% Anglamol 9000 gear additive, 0.1% HiTEC 611 calcium sulfonate and 1.0% HiTEC 623 pour point depressant are blended 33% diisodecyl adipate and 58.9% Shell HVI 650b mineral oil to give a semi-synthetic gear fluid of the invention.
EXAMPLE 34

A semi-synthetic gear lubricant of the invention is formed when 8.0% of Anglamol 8043U gear additive is blended with 0.1% potassium alkylbenzene sulfonate, 0.1% HiTEC 611 calcium sulfonate, 35% di(tridecyl)adipate and 56.8% of mineral oil.

EXAMPLE 35

Blended together are 6.5% of a low chlorine version of Anglamol 99 gear additive, 0.2% sodium alkylbenzene sulfonate, 0.2% Amoco 421 magnesium sulfonate, 0.2% HiTEC 614 calcium sulfonate, 1.5% HiTEC 623 pour point depressant, 65% mineral oil (Shell HVI 650b) and 26.5% of diisodecyl adipate to give a lubricant of the invention suitable for use in manual transmissions and final drives of certain motor vehicles.

It will of course be appreciated by those skilled in the art that the various above three Anglamol products (The Lubrizol Corporation) and the above Mobilad product (Mobil Chemical Company) are all gear oil additive packages based on use of phosphorus- and sulfur-containing antiwear and/or extreme pressure additive componentry.

The performance improvements achievable by the practice of this invention are illustrated, but by no means limited, by the results of various ZF.Synchronizer tests conducted as described hereinabove. Table I summarizes the results of tests in which a gear additive package (HiTEC® 380 additive; Ethyl Petroleum Additives, Ltd., Bracknell, England) was blended into various base oils at API-GL4 dosage levels. In Table I all percentages are by weight, and:

<table>
<thead>
<tr>
<th>Run No.</th>
<th>% HITEC 380</th>
<th>% PAO (I)</th>
<th>% ESTER</th>
<th>% MIN. OIL</th>
<th>%PAO (II)</th>
<th>ZF RESULTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.2</td>
<td>--</td>
<td>--</td>
<td>96.8</td>
<td>--</td>
<td>PASS</td>
</tr>
<tr>
<td>2</td>
<td>3.2</td>
<td>96.8</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>FAIL</td>
</tr>
<tr>
<td>3</td>
<td>3.2</td>
<td>86.8</td>
<td>10</td>
<td>--</td>
<td>--</td>
<td>FAIL</td>
</tr>
<tr>
<td>4</td>
<td>6.5</td>
<td>86.8</td>
<td>10</td>
<td>--</td>
<td>--</td>
<td>FAIL</td>
</tr>
<tr>
<td>5</td>
<td>3.2</td>
<td>71.8</td>
<td>25</td>
<td>--</td>
<td>--</td>
<td>FAIL</td>
</tr>
<tr>
<td>6</td>
<td>3.2</td>
<td>71.8</td>
<td>25</td>
<td>--</td>
<td>--</td>
<td>FAIL</td>
</tr>
<tr>
<td>7</td>
<td>3.2</td>
<td>36.8</td>
<td>--</td>
<td>60</td>
<td>--</td>
<td>FAIL</td>
</tr>
<tr>
<td>8</td>
<td>6.5</td>
<td>32.2</td>
<td>10</td>
<td>--</td>
<td>50.8</td>
<td>PASS</td>
</tr>
</tbody>
</table>

It will be seen by comparing the results of Run Nos. 2-7 with Run No. 1 that the fluids containing the synthetic oils failed the tests whereas the mineral oil based fluid passed. Run No. 8 shows that inclusion in the synthetic oil based fluid of a small amount of a metal sulfonate pursuant to this invention improved the frictional properties of the blend to such an extent that it passed the test.
Table II summarizes the results of additional ZF-Synchronizer tests which demonstrate the practice and advantages of this invention.

Run Nos. 11-14 represent the practice of this invention as these gear oils contained, respectively, 2.0, 1.0, 0.2 and 0.1% of a metal sulfonate (HiTEC® 611 additive). In Run No. 15 the gear oil contained, for comparative purposes, 1.0% of an alkenyl succinimide friction modifier of the type described in EP 20,037. The oil of Run No. 16 contained 3.5% of a polyisobutenyl succinimide ashless dispersant (HiTEC® 646 additive; Ethyl Petroleum Additives, Inc.; Ethyl Petroleum Additives, Ltd. and their affiliated companies). The foregoing percentages are on an "as received basis" and thus include solvent oils. The succinimide friction modifier of Run No. 15 contained no diluent. As in the case of Table I, all percentages are by weight, also "PAO (I)", "PAO (II)", and "ESTER" have the same meanings as in Table I.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>% HITEC 380</th>
<th>% PAO (I)</th>
<th>% PAO (II)</th>
<th>% ESTER</th>
<th>ZF RESULT</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>3.2</td>
<td>46.8</td>
<td>25.0</td>
<td>25</td>
<td>FAIL</td>
</tr>
<tr>
<td>10</td>
<td>6.5</td>
<td>80.0</td>
<td>3.5</td>
<td>10</td>
<td>FAIL</td>
</tr>
<tr>
<td>11</td>
<td>3.2</td>
<td>78.8</td>
<td>6.0</td>
<td>10</td>
<td>PASS</td>
</tr>
<tr>
<td>12</td>
<td>3.2</td>
<td>79.8</td>
<td>6.0</td>
<td>10</td>
<td>PASS</td>
</tr>
<tr>
<td>13</td>
<td>3.2</td>
<td>80.6</td>
<td>6.0</td>
<td>10</td>
<td>PASS</td>
</tr>
<tr>
<td>14</td>
<td>3.2</td>
<td>80.7</td>
<td>6.0</td>
<td>10</td>
<td>PASS</td>
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<tr>
<td>15</td>
<td>3.2</td>
<td>79.8</td>
<td>6.0</td>
<td>10</td>
<td>FAIL</td>
</tr>
<tr>
<td>16</td>
<td>3.2</td>
<td>77.3</td>
<td>6.0</td>
<td>10</td>
<td>FAIL</td>
</tr>
</tbody>
</table>

As used in the foregoing description, the term "oil-soluble" is used in the sense that the component in question has sufficient solubility in the selected base oil in order to dissolve therein at ordinary temperatures to a concentration at least equivalent to the minimum concentration specified herein for use of such component. Preferably, however, the solubility of such component in the selected base oil will be in excess of such minimum concentration, although there is no requirement that the component be soluble in the base oil in all proportions. As is well known to those skilled in the art, certain useful additives do not completely dissolve in base oils but rather are used in the form of stable suspensions or dispersions. Additives of this type can be employed in the compositions of this invention, provided they do not significantly interfere with the performance or usefulness of the composition in which they are employed.

Claims

1. A gear oil lubricant having a kinematic viscosity at 100°C in the range of 4 to 32 mm².s⁻¹ (cSt), and comprising:
   a) a base oil having at least 25% by weight of (i) hydrogenated poly-alpha-olefin oligomer oil or (ii) synthetic ester oil, or (iii) a combination of (i) and (ii);
   b) an amount of a gear oil additive package such that the gear oil lubricant satisfies or exceeds the specifications for GL4 service; and
   c) an amount in the range of 0.01 to 2 wt % based on the total weight of the lubricant of at least one alkali or alkaline earth metal salt of an oil-soluble sulfonic acid, the amount of said metal salt used being sufficient to improve the friction properties of the lubricant for use in manual transmissions, particularly those of the synchronizer type;
   said lubricant containing at most, if any, 100 ppm of metal as one or more metal-containing additive components other than said metal salt, and having on a weight basis a boron content, if any, of not more than 1,000 ppm.

2. A lubricant composition according to Claim 1 wherein said component c) is a calcium salt of an oil-soluble alkylbenzene sulfonic acid.

3. A lubricant composition according to Claim 1 wherein said component c) is an overbased salt of the sulfonic
4. A lubricant composition according to Claim 1 wherein said component a) is at least 50% by weight of hydrogenated poly-alpha-olefin oligomer oil.

5. A gear oil additive package (concentrate) which comprises:
   a) at least one oil-soluble ashless dispersant, selected from succinimide ashless dispersants and/or succinic ester-amide ashless dispersants, and Mannich base ashless dispersants;
   b) at least one oil-soluble metal-free sulfur-containing antiwear and/or extreme pressure agent;
   c) at least one oil-soluble metal-free phosphorus-containing antiwear and/or extreme pressure agent; and
   d) at least one alkali or alkaline metal salt of an oil-soluble sulfonic acid in an amount such that a lubricant composition formed by blending the additive package in a base oil having a kinematic viscosity in the range of 4 to 32 cSt at 100°C and composed of at least 25% by weight of (i) hydrogenated poly-alpha-olefin oligomer oil or (ii) synthetic ester oil, or (iii) a combination of (i) and (ii) to form a lubricant containing from 0.01 to 2 wt % of said metal salt, provides a lubricant composition that:
      A) satisfies or exceeds the specifications for API GL4 service;
      B) contains at most 100 ppm, if any, of metal apart from the metal of said metal salt; and
      C) has a boron content, if any, of not more than 1,000 ppm.

6. A gear oil additive package according to Claim 5 wherein said metal salt is a calcium salt of an oil-soluble alkylbenzene sulfonic acid.

7. A gear oil additive package according to Claim 5 wherein said metal salt is an overbased salt of the sulfonic acid.

8. A gear oil additive package according to Claim 5 further characterized by having a total halogen content, if any, of not more than 1000 ppm on a weight basis.

9. A gear oil additive package according to Claim 8 wherein said total halogen content, if any, does not exceed 250 ppm on a weight basis.

10. A method of beneficially modifying the frictional characteristics of a low-friction synthetic lubricant composition containing at least 25% by weight of (i) hydrogenated poly-alpha-olefin oligomer oil or (ii) synthetic ester oil or (iii) a combination of (i) and (ii) and a gear oil additive package such that the lubricant composition satisfies or exceeds the specifications for API-GL4 service, but does not exhibit satisfactory friction properties for use in manual transmissions, particularly those of the synchronizer type, said method comprising including in such lubricant composition an amount in the range of 0.01 to 2 wt % based on the total weight of the lubricant of at least one alkali or alkaline earth metal salt of an oil-soluble sulfonic acid such that the friction properties of said lubricant are improved for use in manual transmissions of the synchronizer type.
<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document with indication, where appropriate, of relevant passages</th>
<th>Relevant to claim</th>
<th>CLASSIFICATION OF THE APPLICATION (Int. Cl.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>WO-A-8 805 810 (THE LUBRIZOL CORPORATION) * page 37, line 22 * * page 38, line 9 - line 10 * * page 40, line 6 - line 11 * * page 42, line 14 - line 15 * * claims 17, 20, 21 * ---</td>
<td>1-10</td>
<td>C10M169/04 //C10M169/04, 105:32, 107:02, 133:56, 135:00, 137:00, 159:16, 159:24)</td>
</tr>
<tr>
<td>Y</td>
<td>EP-A-0 399 764 (ETHYL PETROLEUM ADDITIVES) * page 2, line 1 * * page 3, line 2 - line 9 * * page 3, line 15 - line 17 * * page 4, line 7 - line 10 * * page 4, line 50 - line 51 * ---</td>
<td>1-10</td>
<td>(C10N10:02)</td>
</tr>
<tr>
<td>Y</td>
<td>EP-A-0 407 124 (TONEN CORPORATION) * page 6, line 3 - line 25 * * page 6, line 37 - line 53 * * page 7, line 2 - line 5 * ---</td>
<td>1-10</td>
<td>(C10N10:04)</td>
</tr>
<tr>
<td>X</td>
<td>EP-A-0 237 804 (NIPPON OIL COMPANY) * page 3, line 6 - line 21 * * page 4; examples III, IV * ---</td>
<td>1-4</td>
<td>C10M</td>
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<tr>
<td>A</td>
<td>EP-A-0 480 644 (ETHYL PETROLEUM ADDITIVES) * page 2, line 13 - line 18 * * page 9, line 21 - line 23 * * claims 3, 4 * ---</td>
<td>1,4,5</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>FR-A-2 442 265 (EXXON RESEARCH AND ENGINEERING COMPANY) * claim 1 * * page 9, line 20 - line 22 * ---</td>
<td>1-3</td>
<td></td>
</tr>
<tr>
<td>P,A</td>
<td>EP-A-0 531 585 (ETHYL PETROLEUM ADDITIVES) * page 4, line 16 - line 24 * * page 4, line 41 - line 43 * * claim 1 * ---</td>
<td>1-3</td>
<td></td>
</tr>
</tbody>
</table>

The present search report has been drawn up for all claims

Place of search
THE HAGUE
Date of completion of the search
15 OCTOBER 1993
Examiner
HILGENGA