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(54) Friction modification of synthetic gear oils

Modifizierung der Reibung synthetischer Getriebeöle

Modification de la friction d'huiles synthétiques pour engrenages

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Description

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 dialkydithiophosphates, 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 by 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 alkylaryl 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.

The components of the compositions according to the claims of the present patent are disclosed in WO-A-88 05 810. It proposed numerous alternatives for component B and the base oil, but it fails to disclose the particular combination of components required by the claims of the present patent.

Further information concerning such dispersed potassium borate additive systems may be found in C.G. Salentine, SAE Technical Paper 880609 (1988) entitled "New Gear Lubricant Technology Using a Solid Lubricant Dispersion", and G.E. Callis and G.Y. Suh, SAE Technical Paper 831731 (1983) entitled "Durability Testing of Low Viscosity Borate Gear Lubricants". See also US-A-3,313,727; 3,565,802; 3,819,521; 3,846,313; 3,853,772; 3,912,639; 3,912,644; 3,929,650; 3,997,454; 4,089,790; and 4,163,729.

Thus in accordance with one 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 $mm^2.s^{-1}$ (cSt), and preferably in the range of 8 to 20 $mm^2.s^{-1}$ (cSt), and comprising:

a) a base oil comprising at least 25%, preferably at least 50%, more preferably 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 GL4 service; and
c) 0.01 to 2 wt % based on the total weight of the lubricant of an alkali or alkaline earth metal salt of an oil-soluble sulfonic acid, the amount of metal salt used being sufficient to improve the friction properties of the lubricant for use in manual transmissions, particularly those of the synchronizer type; the lubricant being essentially free of any metal additive component (i.e., the lubricant contains no more than 100 ppm and preferably no more than 50 ppm of metal as one or more additive components other than the 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 complement 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 not 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 syn-chronizer 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 in the literature. See for example US-A-Nos. 3,763,244; 3,780,128; 4,172,855; 4,218,330; and 4,950,822. Additionally, suitable hydrogenated 1-alkene oligomers of this type are available as articles of commerce, for example, from Ethyl Corporation and its affiliates under the trade mark ETHYLFLO.

Synthetic ester oils are also well known and widely available in the marketplace. Typical synthetic ester oils include such materials as the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol). Specific examples of these esters include dibutyl adipate, di(1-ethylpropyl) adipate, di(1,3-dimethylbutyl) adipate, di(2-ethylhexyl) adipate, didodecyl adipate, di(tridecyl) adipate, di(2-ethylhexyl) sebacate, dilauryl sebacate, di-n-hexylfumarate, dioctyl sebacate, di(1-methylpropyl) azelate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, mixed C_9 and C_{11} dialkyl phthalate, dibutyl sebacate, di(1-ethylpropyl) sebacate, di(eicosyl) sebacate, the 2-ethylhexyl diester of linoleic acid dimer, and the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid. Other synthetic esters which may be used as synthetic oils include those made from C_3-C_{12} monocarboxylic acids and polyols and polyol ethers such as neopentyl glycol, trimethylolpropane, pentaerythritol and dipentaerythritol. Trimethylol propane tripelargonate and pentaerythritol tetracaproate serve as examples.

Suitable commercially available products include Emkarate 911P (ICI, plc.), and KETJENLUBE synthetic oil (Akzo Chemicals).

The base oils may contain up to 75%, preferably no more than 50%, and more preferably no more than 25% by weight of a mineral oil or other suitable oleaginous liquid of lubricating viscosity, provided the overall base lubricant is suitable for use in forming a finished gear lubricant that satisfies or exceeds the specifications for API-GL4 service, and provided further that the resultant finished oil remains amenable to friction improvement pursuant to this invention. It will be understood that most gear oil packages contain diluent oils or solvents for certain active ingredients or components. However, since such diluent oils or solvents are added to the base oil along with the additive package or with one or more additive components blended separately or individually into the base oil, such diluent oils or solvents are to be omitted from consideration when assessing the makeup of the base oil of the compositions of this invention. Thus the finished gear oil lubricant may contain up to 75% by weight of a mineral oil or the like, plus an additional amount of diluent oil or solvent emanating from the additives or additive package used in formulating the finished lubricant.

The metal sulfonates used in the invention are preferably overbased metal sulfonates, but the so-called neutral metal sulfonates can be used, if desired. The use of calcium salts of oil-soluble alkylbenzene sulfonates, especially overbased calcium alkylbenzene sulfonates, is particularly preferred. Methods for forming metal sulfonates are described for example in US-A-2,865,956; 2,956,018; 2,671,430; 3,779,920; 3,907,691; 4,137,184; 4,261,840; 4,326,972; 4,328,111; 5,089,155; and 5,112,506. Petroleum sulfonates are usually prepared by the sulfonation of suitable petroleum fractions with subsequent removal of acid sludge and purification followed by neutralization with the appropriate basic metal compound (e.g., oxide or hydroxide). Petroleum oxidates such as described in EP-A- 275,395 (published July 27, 1988) can be used in forming overbased sulfonates. Alkylaryl sulfonates are usually prepared by sulfonation of alkylated benzene or benzene analogs (toluene, naphthalene, phenothiazine, diphenyl oxide, or diphenyl sulfide), followed by workup and neutralization. For example alkylbenzenes suitable for producing the sulfonates can be formed by alkylating benzene with an oligomer or polymer such as tetrapropylene in the presence of an Friedel-Crafts catalyst. A number of highly suitable metal sulfonates are available as articles of commerce.

Quantities ranging from as little as 0.01 % wt % up to as much as 2 % by wt % or more of the metal sulfonate based on the total weight of the finished lubricant can be employed. Ordinarily the amount used will not be greatly in excess of that amount needed to yield the friction performance desired in the particular finished gear oil lubricant in question. Thus often the amount will not be above 1 wt %, and in some cases will not exceed 0.5 wt %. In the case of the friction-improved additive packages of this invention, the amount will be proportioned such that when the package is blended into the base oil at the recommended or desired concentration, the resultant finished oil will contain from 0.01 wt % up to 2 wt % or more, preferably up to about 1 wt %, and in some cases up to about 0.5 wt % of the metal sulfonate. It is to be noted that these proportions of the metal sulfonate are based on the active ingredient, and thus the weight of any solvent or diluent associated with the metal sulfonate as used should be subtracted from the additive weight when calculating the concentration of metal sulfonate in the finished oil or in the friction-improved additive package. However the total weight of the finished oil or of the completed additive package will include the weight of such solvent or diluent.

The specifications for API-GL4 and API-GL5 service are published in ASTM Publication STP-512A entitled "Lab-

oratory 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 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, selected from succinimide and/or a succinic ester-amide, and more preferably a Mannich base ashless dispersant;
b) an oil-soluble metal-free sulphur-containing antiwear and/or extreme pressure agent;
c) an oil-soluble metal-free phosphorus-containing antiwear and/or extreme pressure agent; and
d) at least one alkali or alkaline earth 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 comprising 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 the metal salt:

A) satisfies or exceeds the specifications for API-GL4 service;
B) contains, if any, no more than 100 ppm and preferably no more than 50 ppm of metal apart from the metal of the 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 250 ppm, preferably 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 "Synchromesh 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 pneumatic cylinder provides the actuating force which is measured by means of a load ring strain gauge. A small heater is used to control oil temperature.

Torque transmitted through the output shaft can be measured to give an indication of the coefficient of friction between the synchronizing cones. The synchromesh units used are standard commercially available steel units with a molybdenum-based plasma spray coating on the inner surface of the outer synchro-ring. The syn-chromesh units are renewed before each test. Typically, when measured at a point of relatively high torque during a gear change, the coefficient of friction for satisfactory synchronizer performance in the test is at least 0.065.

Another performance criterion which may be used when performing the test for qualification purposes is excessive vibration of the gear box casing in the axial plane, a condition symptomatic of poor gear changes. For this purpose the control and monitoring of the rig is coordinated by a process controller. During a test, which consists of 10^5 cycles, the number of poor changes is recorded. The test is terminated prematurely if this number becomes unacceptable.

Test components may be evaluated by inspecting the friction surface of the inner synchronizer cone using a Perthometer stylus device both before and after test. Polishing of the metal surface or the build up of a glaze of decomposed lubricant or additive yields an unacceptably smooth surface finish. This in turn causes low frictional values during the gear change and can lead to clash of the sleeve and gear clutch teeth. Wear measurements are also made on the test components.

As those skilled in the art already know, arrangements can be made with Zahnradfabrik Friedrichshafen A.G. whereby that company will perform the ZF.Synchronizer test on formulations submitted by a party for test. It is understood that a summary report of the results of the test is provided to the submitter of the test formulation.

The following examples numbered 1 through 35 illustrate, inter alia, preferred additive concentrates and oleaginous compositions of this invention. These examples are not intended to limit, and should not be construed as limiting, this invention. In all of the examples, all percentages are by weight.

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 agitated 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 C_{12}-C_{14} 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-tert-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, parts of di-tert-nonyl polysulfide, 5.7 parts of dibutyl hydrogen phosphite, 0.1 part of tolyltriazole, and 2.9 parts of amyl 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 3.7 parts of Primene 81-R amine, 3.7 parts of C_{16} and C_{18} 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 C_{36} 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-tert-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 C_{16} and C_{18} 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-dodecyldithio-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, 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 C_{16} and C_{18} 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-dodecyldithio-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:

Additive package	6.5% wt
AMOCO 421 Magnesium Sulfonate	0.35% wt
Diisodecyladipate	25% wt
ETHYLFLO 174 PAO	58.15% wt
ETHYLFLO 168 PAO	10.0% wt

EXAMPLES 5-8

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

Additive package	3.2% wt
HiTEC® 614 Calcium Sulfonate	0.1% wt
ETHYLFLO 170 PAO	80.7% wt
ETHYLFLO 174 PAO	6.0% wt
Diisodecyladipate	10.0% wt

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:

PAO (I) is ETHYLFLO 170 PAO (Ethyl Corporation), a hydrogenerated poly-α-olefin having a kinematic viscosity at 100°C of approximately 9.6 $mm^2.s^{-1}$ (cSt);

ESTER is diisodecyl adipate;
MIN. OIL is Shell HVI 115; and
PAO (II) is ETHYLFLO 174 PAO (Ethyl Corporation), a hydrogenated poly-α-olefin having a kinematic viscosity at 100°C of approximately 40 $mm^2.s^{-1}$ (cSt).

The above Shell HVI 115 mineral oil was a solvent neutral oil having a kinematic viscosity of 9 $mm^2.s^{-1}$ (cSt) at 100°C containing 1.0 HiTEC® 623 pour point depressant. The first seven tests in Table I (i.e., Run Nos. 1-7) used SAE 80W viscosity grade formulations. Run Nos. 1-7 are comparative tests as none of these formulations contained a sulfonate additive. However, Run No. 8 used a formulation containing 0.5 wt% of HiTEC® 611 additive, an overbased calcium alkylbenzene sulfonate having a nominal TBN of 300 available commercially from Ethyl Petroleum Additives, Inc. and Ethyl Petroleum Additives, Ltd. The HiTEC 611 additive contains approximately 44% diluent oil. The formulation of Run No. 8 is an SAE 90 grade formulation useful as a total driveline fluid suitable for use in final drives such as hypoid differentials, as well as gear boxes.

TABLE I

Run No.	% HiTEC 380	% PAO (I)	% ESTER	% MIN. OIL	%PAO (II)	ZF RESULTS
1	3.2	--	--	96.8	--	PASS
2	3.2	96.8	--	--	--	FAIL
3	3.2	86.8	10	--	--	FAIL
4	6.5	86.8	10	--	--	FAIL
5	3.2	71.8	25	--	--	FAIL
6	3.2	71.8	25	--	--	FAIL
7	3.2	36.8	--	60	--	FAIL
8	6.5	32.2	10	--	50.8	PASS

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 II

Run No.	% HiTEC 380	% PAO (I)	% PAO (II)	% ESTER	ZF RESULT
9	3.2	46.8	25.0	25	FAIL
10	6.5	80.0	3.5	10	FAIL
11	3.2	78.8	6.0	10	PASS
12	3.2	79.8	6.0	10	PASS
13	3.2	80.6	6.0	10	PASS
14	3.2	80.7	6.0	10	PASS
15	3.2	79.8	6.0	10	FAIL
16	3.2	77.3	6.0	10	FAIL

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$mm^2.s^{-1}$ (cSt), and comprising:

   a) a base oil comprising 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) 0.01 to 2 wt% based on the total weight of the lubricant of an alkali or alkaline earth metal salt of an oil-soluble sulfonic acid, the amount of metal salt used being sufficient to improve the friction properties of the lubricant for use in manual transmissions, particularly those of the synchronizer type;

   the lubricant containing, if any, not more than 100 ppm of metal as one or more metal-containing additive components other than the 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 component c) is a calcium salt of an oil-soluble alkylbenzene sulfonic acid.

3. A lubricant composition according to claim 1 or 2 wherein component c) is an overbased salt of the sulfonic acid.

4. A lubricant composition according to any one of claims 1 to 3 wherein component a) comprises at least 50% by weight of hydrogenated poly-alpha-olefin oligomer oil.

5. A gear oil additive concentrate which comprises:

   a) an oil-soluble ashless dispersant, selected from succinimide, succinic ester-amide and Mannich base ashless dispersants;
   b) an oil-soluble metal-free sulfur-containing antiwear and/or extreme pressure agent;
   c) an oil-soluble metal-free phosphorus-containing antiwear and/or extreme pressure agent; and
   d) at least one alkali or alkaline earth 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 comprising 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 the metal salt, provides a lubricant composition that:

      A) satisfies or exceeds the specifications for API-GL4 service;
      B) contains, if any, not more than 100 ppm of metal apart from the metal of the metal salt; and
      C) has a boron content, if any, of not more than 1,000 ppm.

6. A concentrate according to claim 5 wherein in d) the metal salt is as defined in claim 2 or 3.

7. A concentrate according to claim 5 or 6 having a total halogen content, if any, of not more than 1000 ppm on a weight basis.

8. A concentrate according to claim 7 wherein the total halogen content, if any, is not more than 250 ppm on a weight basis.

9. A method of improving the frictional characteristics of a low-friction synthetic lubricant composition which contains

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, which contains, if any, not more than 100 ppm metal as one or more metal-containing additives and which has a boron content, if any, of not more than 1,000ppm but which does not exhibit satisfactory friction properties for use in manual transmissions, particularly those of the synchronizer type, the method comprising including in such lubricant composition 0.01 to 2 wt% based on the total weight of the lubricant of an alkali or alkaline earth metal salt of an oil-soluble sulfonic acid.

Patentansprüche

1. Getriebeölschmiermittel mit einer kinematischen Viskosität bei 100°C im Bereich von 4 bis 32 $mm^2 \cdot s^{-1}$ (cSt), welches umfaßt:

   a) ein Basisöl, das mindestens 25 Gew.-% (i) eines hydrierten poly-α-Olefinoligomeröls oder (ii) eines synthetischen Esteröls oder (iii) einer Kombination von (i) und (ii) enthält,
   b) eine derartige Menge einer Getriebeölzusatzzubereitung, daß das Getriebeölschmiermittel den Spezifikationen für GL4-Service genügt oder diese übersteigt, und
   c) 0,01 bis 2 Gew.-%, bezogen auf das Gesamtgewicht des Schmiermittels, eines Alkali- oder Erdalkalimetallsalzes einer öllöslichen Sulfonsäure, wobei die Menge des verwendeten Metallsalzes ausreichend ist, um die Reibungseigenschaften des Schmiermittels zur Verwendung in manuellen Schaltungen, insbesondere solchen vom synchronisierenden Typ, zu verbessern,

   wobei das Schmiermittel, wenn überhaupt, nicht mehr als 100 ppm Metall in Form einer oder mehrerer metallenthaltender Additiv-Komponenten, die nicht das Metallsalz sind, und, bezogen auf das Gewicht, gegebenenfalls einen Borgehalt von nicht mehr als 1000 ppm aufweist.

2. Schmiermittelzusammensetzung nach Anspruch 1, wobei die Komponente c) ein Calciumsalz einer öllöslichen Alkylbenzolsulfonsäure ist.

3. Schmiermittelzusammensetzung nach Anspruch 1 oder 2, wobei die Komponente c) ein überbasisches Salz der Sulfonsäure ist.

4. Schmiermittelzusammensetzung nach einem der Ansprüche 1 bis 3, wobei die Komponente a) mindestens 50 Gew.-% eines hydrierten poly-α-Olefinoligomeröls enthält.

5. Getriebeölzusatzkonzentrat, das umfaßt:

   a) ein öllösliches, aschefreies Dispergiermittel, ausgewählt unter Succinimid, Bernsteinsäureesteramid und aschefreien Mannichbasen-Dispergiermitteln,
   b) ein öllösliches, metallfreies, Schwefel enthaltendes Mittel gegen Verschleiß und/oder für extremen Druck,
   c) ein öllösliches, metallfreies, Phosphor-enthaltendes Mittel gegen Verschleiß und/oder für extremen Druck, und
   d) mindestens ein Alkali- oder Erdalkalimetallsalz einer öllöslichen Sulfonsäure in einer derartigen Menge, daß eine durch Einmischen der Zusatzzubereitung in ein Basisöl gebildete Schmiermittelzusammensetzung eine kinematische Viskosität im Bereich von 4 bis 32 cSt bei 100°C aufweist und mindestens 25 Gew.-% (i) eines hydrierten poly-α-Olefinoligomeröls oder (ii) synthetischen Esteröls oder (iii) einer Kombination von (i) und (ii) enthält, um ein Schmiermittel zu bilden, das 0,01 bis 2 Gew.-% des Metallsalzes enthält, und eine Schmiermittelzusammensetzung liefert, welche

      A) den Spezifikationen für API-GL4-Service genügt oder diese übersteigt,
      B) wenn überhaupt, nicht mehr als 100 ppm Metall neben dem Metall im Metallsalz enthält, und
      C) einen Borgehalt, wenn überhaupt, von nicht mehr als 1000 ppm aufweist.

6. Konzentrat nach Anspruch 5 , wobei in d) das Metallsalz wie in Anspruch 2 oder 3 definiert ist.

7. Konzentrat nach Anspruch 5 oder 6, wobei der Gesamthalogengehalt, wenn überhaupt, nicht mehr als 1000 ppm, bezogen auf das Gewicht, beträgt.

8. Konzentrat nach Anspruch 7, wobei der Gesamthalogengehalt, wenn überhaupt, nicht mehr als 250 ppm, bezogen auf das Gewicht, beträgt.

9. Verfahren zur Verbesserung der Reibungseigenschaften einer synthetischen Schmiermittelzusammensetzung mit geringer Reibung, welche zu mindestens 25 Gew.-% (i) hydriertes poly-α-Olefinoligomeröl oder (ii) synthetisches Esteröl oder (iii) eine Kombination von (i) und (ii) enthält, und eine Getriebeölzusatzzubereitung, damit das Getriebeölschmiermittel den Spezifikationen des API-GL4-Service genügt oder diese übersteigt, welche, wenn überhaupt, nicht mehr als 100 ppm Metall in Form eines oder mehrerer metallenthaltender Zusätze und einen Borgehalt aufweist, der, wenn überhaupt, nicht mehr als 1000 ppm beträgt, die jedoch keine ausreichende Reibungseigenschaften zur Verwendung in manuellen Schaltungen, insbesondere solchen von synchronisierenden Typ aufweist, wobei das Verfahren das Einbringen von 0,01 bis 2 Gew.-%, bezogen auf das Gesamtgewicht des Schmiermittels eines Alkali- oder Erdalkalimetallsalzes einer öllöslichen Sulfonsäure umfaßt.

Revendications

1. Lubrifiant servant d'huile pour engrenages, ayant une viscosité cinématique à 100°C comprise dans l'intervalle de 4 à 32 $mm^2.s^{-1}$ (cSt) et comprenant :

   a) une huile de base comprenant au moins 25 % en poids (i) d'une huile oligomère de poly-alpha-oléfine hydrogénée, ou (ii) une huile du type ester synthétique, ou (iii) d'une association des huiles (i) et (ii) ;
   b) une quantité d'une formulation d'additifs pour huile pour engrenages telle que le lubrifiant servant d'huile pour engrenages satisfasse ou dépasse les normes pour un fonctionnement GL4 ; et
   c) 0,01 à 2 % en poids, sur la base du poids total du lubrifiant, d'un sel de métal alcalin ou de métal alcalino-terreux d'un acide sulfonique soluble dans l'huile, la quantité de sel métallique utilisée étant suffisante pour améliorer les propriétés de frottement du lubrifiant destiné à être utilisé dans des transmissions manuelles, en particulier celles du type à synchronisation ;

   ledit lubrifiant contenant une quantité, s'il en existe une quelconque, non supérieure à 100 ppm de métal sous forme d'un ou plusieurs constituants additifs contenant un métal autre que le sel métallique, et ayant, sur base pondérale, une teneur en bore, s'il en existe une quelconque, non supérieure à 1000 ppm.

2. Composition de lubrifiant suivant la revendication 1, dans laquelle le constituant c) est un sel de calcium d'un acide alkylbenzènesulfonique soluble dans l'huile.

3. Composition de lubrifiant suivant la revendication 1 ou 2, dans laquelle le constituant c) est un sel surbasique de l'acide sulfonique.

4. Composition de lubrifiant suivant l'une quelconque des revendications 1 à 3, dans laquelle le constituant a) comprend au moins 50 % en poids d'une huile oligomère poly-alpha-oléfinique hydrogénée.

5. Concentré d'addition pour huile pour engrenages, qui comprend :

   a) un dispersant sans cendres soluble dans l'huile, choisi parmi des dispersants sans cendres du type succinimide, du type ester-amide succinique et du type base de Mannich ;
   b) un agent anti-usure et/ou extrême-pression contenant du soufre, dépourvu de métaux, soluble dans l'huile ;
   c) un agent anti-usure et/ou extrême-pression contenant du phosphore, dépourvu de métaux, soluble dans l'huile ; et
   d) au moins un sel de métal alcalin ou de métal alcalino-terreux d'un acide sulfonique soluble dans l'huile, en une quantité telle qu'une composition de lubrifiant formée en mélangeant la formation d'additifs à une huile de base ayant une viscosité cinématique comprise dans l'intervalle de 4 à 32 cSt à 100°C et comprenant au moins 25 % en poids (i) d'une huile oligomère poly-alpha-oléfinique hydrogénée ou (ii) d'une huile du type ester synthétique ou bien (iii) d'une association des huiles (i) et (ii) pour former un lubrifiant contenant 0,01 à 2 % en poids du sel métallique, donne une composition de lubrifiant qui :

      A) satisfait ou dépasse les normes pour un fonctionnement API-GL4 ;
      B) contient une quantité, s'il en existe une quelconque, non supérieure à 100 ppm de métal à l'exception du métal du sel métallique ; et

C) a une teneur en bore, s'il en existe une quelconque, non supérieure à 1000 ppm.

6. Concentré suivant la revendication 5, dans lequel, en d) le sel métallique répond à la définition suivant la revendication 2 ou 3.

7. Concentré suivant la revendication 5 ou 6, ayant une teneur totale en halogènes, s'il en existe une quelconque, non supérieure à 1000 ppm sur base pondérale.

8. Concentré suivant la revendication 7, dans lequel la teneur totale en halogènes, s'il en existe une quelconque, est non supérieure à 250 ppm sur base pondérale.

9. Procédé pour améliorer les caractéristiques de frottement d'une composition de lubrifiant synthétique à faible frottement qui contient au moins 25 % en poids (i) d'une huile oligomère poly-alpha-oléfinique hydrogénée ou (ii) une huile du type ester synthétique ou bien (iii) d'une association des huiles (i) et (ii) et une formulation d'additifs pour huile pour engrenages de telle sorte que la composition de lubrifiant satisfasse ou dépasse les normes pour un fonctionnement API-GL4, qui contient, s'il en existe une quelconque, pas plus de 100 ppm de métal provenant d'un ou plusieurs additifs contenant des métaux et qui a une teneur en bore, s'il en existe une quelconque, non supérieure à 1000 ppm, mais qui ne présente pas de propriétés de frottement satisfaisantes pour une utilisation dans des transmissions manuelles, en particulier celles du type à synchronisation, procédé qui comprend l'incorporation à une telle composition de lubrifiant d'une quantité de 0,01 à 2 % en poids, sur la base du poids total du lubrifiant, d'un sel de métal alcalin ou de métal alcalino-terreux d'un acide sulfonique soluble dans l'huile.