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(71) Applicant: **Infineum International Limited**
Abingdon
Oxfordshire OX13 6BB (GB)

(72) Inventors:
- **Purmer, Pieter**
  1852KN Heiloo (NL)
- **Stephens, Christopher**
  Abingdon,
  Oxfordshire OX14 1XT (GB)
- **Watts, Raymond**
  Long Valley,
  New Jersey 07853 (US)
- **Nibert, Roger**
  Hampton,
  New Jersey 08827 (US)

(74) Representative: **Lewis, Pauline Therese et al**
Infineum UK Ltd.
Milton Hill Business and Technology Centre,
PO Box 1
Abingdon, Oxfordshire OX13 6BB (GB)

(54) Friction and/or wear reduction in manual or automated manual transmissions

(57) A method for lubricating a manual transmission or automated manual transmission apparatus having metallic synchronizers which comprises supplying to said transmission a lubricating composition comprising a major amount of an oil of lubricating viscosity containing two ZDDP's and a thiadiazole corrosion inhibitor.

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Description

[0001] This invention relates to manual transmission lubricants which will satisfy the lubrication requirements for manual transmissions as well as automated manual transmissions, which would include double clutch or dual clutch transmissions, which rely upon synchronizers to accomplish gear changes. More specifically, the invention relates to manual transmission lubricants with a certain critical combination of anti-wear and corrosion inhibitor additives which provide wear, friction and oxidation protection to the manual transmission or automated manual transmission apparatus.

[0002] Manual transmissions commonly employ small clutches, referred to as synchronizers to accomplish smooth gear changes under a wide range of conditions. The synchronizers can rely on a number of materials to generate appropriate friction characteristics. The friction materials can be paper based, carbon based or metallic. Manual transmissions having synchronizers which rely on special metallurgy, e.g. brass, molybdenum, sintered bronze, etc., to develop the necessary levels of friction pose problems for lubricant formulators because of their unique characteristics. Transmissions of this type require a number of performance attributes from the lubricant for acceptable synchronizer performance. Acceptable fluids must provide good run-in at low temperature (60°C), low wear at higher temperature (75°C), extreme pressure and anti-wear performance as measured by 4-ball testing, good anti-scuffing and pitting performance as measured by FZG testing, low gear shift forces under engagement conditions applied in automated manual transmissions and good oxidation resistance.

[0003] The manual transmission fluid needs to provide specific frictional properties to enable the synchronizers to perform smooth gear changes. To 'shift' (i.e. change) gears, the transmission must bring the driven shaft and the gear to be engaged to equal speeds. The equalization of relative speeds of the gears is accomplished by a synchronizer. When the relative velocity of the synchronizing parts (plate to plate or ring to cone) is reduced to zero the locking splines then engage. If these parts do not obtain zero relative velocity, then a phenomenon known as synchronizer clashing (sometimes referred to as crashing) occurs. Clashing of the synchronizer results when the dynamic coefficient of friction between the engaging synchronizer parts (plate to plate or ring to cone) falls below a critical minimum value. Below this critical minimum value the synchronizer parts do not attain zero relative velocity during the time allocated for the shift. When the relative velocity is not zero the lockup mechanism (e.g., spline chamfers) contacts the rotating member (e.g., cone chamfers) resulting in a ratcheting action which can produce a loud noise (clashing/crashing). During clashing it is impossible to complete the shift.

[0004] Synchronizers in manual transmissions fail, *i.e.,* do not provide smooth 'clash-free' shifts, for two reasons. The first of which is wear. Synchronizers that use soft materials, such as brass, for the friction surface often wear in use. When the amount of wear exceeds the allowed travel of the synchronizer acceptable friction cannot be developed and the synchronizer cannot bring the relative speeds of the engaging parts to zero and the shift fails. The second failure mechanism is failure to generate sufficient dynamic friction, *i.e.*, low friction coefficient. This type of failure is more common with hard metal synchronizers such as those employing molybdenum or sintered bronze friction surfaces. Once the synchronizer can no longer develop high enough friction coefficients, the relative speeds of the engaging parts cannot be brought to zero in the time allotted for the shift and clashing occurs.

[0005] The manual transmission fluids of this invention provide a high dynamic coefficient of friction and low wear between the synchronizer ring and the steel cone. These ideal conditions also exist under fast synchronizer engagement conditions as used in automated manual gear boxes.

[0006] In accordance with the present invention there has been discovered a method for lubricating a manual transmission or automated manual transmission (including a double clutch or dual clutch transmission) apparatus having metallic synchronizers which comprises supplying to said transmission a lubricating composition comprising a major amount of an oil of lubricating viscosity containing effective amounts of:

(a) a ZDDP (zinc dialkyldithiophosphate) derived from primary alcohols,
(b) a ZDDP derived from 50 wt.% or more secondary alcohols,
(c) a thiadiazole corrosion inhibitor being 2,5-dimercapto-1,3,4-thiadiazole or a derivative thereof, and optionally but preferably,
(d) a fatty acid primary amide friction modifier active at low temperatures,
(e) at least one supplemental anti-wear agent,
(f) at least one lubricating oil dispersant,
(g) at least one antioxidant, and
(h) at least one metal detergent.

[0007] A further embodiment of this invention is a manual transmission or automated manual transmission apparatus, including a double clutch or dual clutch transmission apparatus, which has metallic synchronizers and which contains the lubricating composition described above.

[0008] Lubricating oils useful in this invention are those of lubricating viscosity derived from natural lubricating oils, synthetic lubricating oils, and mixtures thereof. In general, both the natural and synthetic lubricating oil will each have a kinematic viscosity ranging from about 1 to about 100 mm^2/s (cSt) at 100°C, although typical applications will require the lubricating oil or lubricating oil mixture to have a viscosity ranging from about 2 to about 18 mm^2/s (cSt) at 100°C.

[0009] Natural lubricating oils include animal oils, vegetable oils (e.g., castor oil and lard oil), petroleum oils, mineral oils, and oils derived from coal or shale. The preferred natural lubricating oil is mineral oil.

[0010] Suitable mineral oils include all common mineral oil basestocks. This includes oils that are naphthenic or paraffinic in chemical structure. Oils that are refined by conventional methodology using acid, alkali, and clay or other agents such as aluminum chloride, or they may be extracted oils produced, for example, by solvent extraction with solvents such as phenol, sulfur dioxide, furfural, dichlorodiethyl ether, etc. They may be hydrotreated or hydrofined, dewaxed by chilling or catalytic dewaxing processes, or hydrocracked. The mineral oil may be produced from natural crude sources or be composed of isomerized wax materials or residues of other refining processes.

[0011] Typically the mineral oils will have Kinematic viscosities of from 2.0 mm^2/s (cSt) to 18.0 mm^2/s (cSt) at 100°C. The preferred mineral oils have Kinematic viscosities of from 2 to 6 mm^2/s (cSt), and most preferred are those mineral oils with viscosities of 3 to 5 mm^2/s (cSt) at 100°C.

[0012] Synthetic lubricating oils include hydrocarbon oils and halo-substituted hydrocarbon oils such as oligomerized, polymerized, and interpolymerized olefins [e.g., polybutylenes, polypropylenes, propylene, isobutylene copolymers, chlorinated polylactenes, poly(1-hexenes), poly(1-octenes), poly-(1-decenes), etc., and mixtures thereof]; alkylbenzenes [e.g., dodecyl-benzenes, tetradecylbenzenes, dinonylbenzenes, di(2-ethylhexyl)benzene, etc.]; polyphenyls [e.g., biphenyls, terphenyls, alkylated polyphenyls, etc.]; and alkylated diphenyl ethers, alkylated diphenyl sulfides, as well as their derivatives, analogs, and homologs thereof, and the like. The preferred oils from this class of synthetic oils are oligomers of α-olefins, particularly oligomers of 1-decene.

[0013] Synthetic lubricating oils also include alkylene oxide polymers, interpolymers, copolymers, and derivatives thereof where the terminal hydroxyl groups have been modified by esterification, etherification, etc. This class of synthetic oils is exemplified by: polyoxyalkylene polymers prepared by polymerization of ethylene oxide or propylene oxide; the alkyl and aryl ethers of these polyoxyalkylene polymers (e.g., methyl-polyisopropylene glycol ether having an average molecular weight of 1000, diphenyl ether of polypropylene glycol having a molecular weight of 1000 to 1500); and mono- and poly-carboxylic esters thereof (e.g., the acetic acid esters, mixed C_3-C_8 fatty acid esters, and C_{12} oxo acid diester of tetraethylene glycol).

[0014] Another suitable class of synthetic lubricating oils comprises the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, alkyl succinic acids and alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, sebasic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkylmalonic acids, alkenyl malonic acids, etc.) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoethers, propylene glycol, etc.). Specific examples of these esters include dibutyl adipate, di(2-ethylhexyl) sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, and the complex ester formed by reacting one mole of sebasic acid with two moles of tetraethylene glycol and two moles of 2-ethyl-hexanoic acid, and the like. A preferred type of oil from this class of synthetic oils are adipates of C_4 to C_{12} alcohols.

[0015] Esters useful as synthetic lubricating oils also include those made from C_5 to C_{12} monocarboxylic acids and polyols and polyol ethers such as neopentyl glycol, trimethylolpropane pentaerythritol, dipentaerythritol, tripentaerythritol, and the like.

[0016] Silicon-based oils (such as the polyalkyl-, polyaryl-, polyalkoxy-, or polyaryloxy-siloxane oils and silicate oils) comprise another useful class of synthetic lubricating oils. These oils include tetraethyl silicate, tetraisopropyl silicate, tetra-(2-ethylhexyl) silicate, tetra-(4-methyl-2-ethylhexyl) silicate, tetra-(p-tert-butylphenyl) silicate, hexa-(4-methyl-2-pentoxy)-disiloxane, poly(methyl)-siloxanes and poly(methylphenyl) siloxanes, and the like. Other synthetic lubricating oils include liquid esters of phosphorus-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, and diethyl ester of decylphosphonic acid), polymeric tetrahydrofurans, poly-α-olefins, and the like.

[0017] The lubricating oils may be derived from refined, rerefined oils, or mixtures thereof. Unrefined oils are obtained directly from a natural source or synthetic source (e.g., coal, shale, or tar sands bitumen) without further purification or treatment. Examples of unrefined oils include a shale oil obtained directly from a retorting operation, a petroleum oil obtained directly from distillation, or an ester oil obtained directly from an esterification process, each of which is then used without further treatment. Refined oils are similar to the unrefined oils except that refined oils have been treated in one or more purification steps to improve one or more properties. Suitable purification techniques include distillation, hydrotreating, dewaxing, solvent extraction, acid or base extraction, filtration, and percolation, all of which are known to those skilled in the art.

[0018] Two types of oil soluble zinc dihydrocarbyldithiophosphates (ZDDP) are required in the lubricating composition of this invention, a ZDDP derived from primary alcohols and a ZDDP derived from 50 wt.%, preferably 80 wt.%, or more secondary alcohols. These components provide antioxidant and anti-wear properties to the lubricating composition. Such compounds may be prepared in accordance with known techniques by first forming a dithiophosphoric acid, usually by reaction of an alcohol or a phenol with P_2S_5 and then neutralizing the dithiophosphoric acid with a suitable zinc compound. Mixtures of alcohols may be used including mixtures of primary and secondary alkyl alcohols. Examples of such alcohols include, but are not restricted to the following list: iso-propanol, iso-octanol, 2-butanol, methyl isobutyl carbinol (4-methyl-1-pentane-2-ol), 1-pentanol, 2-methyl butanol, and 2-methyl-1-propanol. The alkyl groups can have 1 to 25 carbons, preferably 3 to 12 carbons. Zinc dithiophosphates derived from primary or secondary alcohols have certain advantages over other types of zinc dithiophosphates Primary alcohol-derived zinc dithiophosphates are more thermally stable than secondary alcohol-derived zinc dithiophosphates, but the latter are more effective anti-wear agents.

[0019] The compositions of this invention will preferably contain, on an active ingredient (a.i.) basis, about 0.10 to about 1.00, preferably about 0.25 to 0.75, wt. % of the ZDDP derived from primary alcohols and 0.01 to 0.50, preferably 0.05 to 0.25, wt.% , of the ZDDP derived from 50 wt.% or more secondary alcohols.

[0020] All percentages and proportions reported herein are on an a.i. basis, that is, without regard to solvent or carrier oil, unless otherwise indicated.

[0021] The thiadiazole corrosion inhibitor is 2,5-dimercapto-1,3,4-thiadiazole (DMTD) or a derivative thereof. Preferred amounts are 0.01 to 1.00 weight percent, preferably 0.20 to 0.50 weight percent, most preferably 0.20 to 0.35 weight percent.

[0022] Derivatives of DMTD include:

(a) 2-hydrocarbyldithio-5-mercapto-1,3,4-thiadiazole or 2,5-bis-(hydrocarbyldithio)-1,3,4-thiadiazole and mixtures thereof;
(b) carboxylic esters of DMTD;
(c) condensation products of alpha-halogenated aliphatic monocarboxylic acids with DMTD;
(d) reaction products of unsaturated cyclic hydrocarbons and unsaturated ketones with DMTD;
(e) reaction products of an aldehyde and a diaryl amine with DMTD;
(f) amine salts of DMTD;
(g) dithiocarbamate derivatives of DMTD;
(h) reaction products of an aldehyde, and an alcohol or aromatic hydroxy compound, and DMTD;
(i) reaction products of an aldehyde, a mercaptan and DMTD;
(j) 2-hydrocarbylthio-5-mercapto-1,3,4-thiadiazole; and
(k) products from combining an oil soluble dispersant with DMTD; and mixtures thereof.

[0023] DMTD derivative compositions a)-k) above are described in U.S. Pat. No. 4,612,129 and patent references cited therein.

[0024] Some preferred thiadiazoles for use in this invention are those listed in a), h), and k) above. 2,5-bis-(hydrocarbyldithio)-1,3,4-thiadiazole, wherein the hydrocarbyl is nonyl, and its mono-substituted equivalent 2-hydrocarbylthio-5-mercapto-1,3,4-thiadiazole are commercially available as a mixture of the two compounds in a ratio of about 85 percent bis-hydrocarbyl to 15 percent monohydrocarbyl from the Ethyl Corporation as " Hitec 4313".

[0025] The fatty acid primary amide friction modifier used in the compositions of this invention is an amide of a long chain carboxylic acid and is represented by the structure $RCONH_2$ wherein R is an alkyl or alkenyl group having about 12 to 24, more preferably 16 to 20 carbons. The preferred primary amide is oleamide. The primary amide is preferably present in an amount from about 0.01 to 1.00 wt. % based upon the weight percent of the fully formulated oil composition, most preferably present in an amount of 0.05 to 0.10 wt. % on an a.i. basis. This friction modifier is active at low temperatures.

[0026] Suitable supplemental antiwear agents include, for example, phosphates, phosphate esters, amine salts of phosphates, which are preferred, phosphites, such as dialkyl hydrogen phosphites, tricresyl phosphates, chlorinated waxes, sulphurised fats and olefins, such as thiodipropionic esters, dialkyl sulphides, dialkyl polysulphides, alkyl-mercaptans, dibenzothiophenes and 2,2'-dithiobis(benzothiazole); organic lead compounds, fatty acids, molybdenum complexes, such as molybdenum disulphide, halogen substituted organosilicon compounds, organic silicon compounds, borates and halogen- substituted phosphorus compounds. A preferred supplemental anti-wear agent is the amine phosphate made by reacting hydroxyl-substituted triesters (made by reaction of dithiophosphoric acids with epoxides) with phosphorus pentoxide and then neutralization of the resulting acids with amines. The preparation of these materials is described in US 3,197,405, incorporated herein by reference. These may each be present in amounts ranging from 0.01 to about 3.00 wt.%, preferably 0.1 to 1.00 wt.%.

[0027] Suitable lubricating oil ashless dispersants for use in this invention include hydrocarbyl succinimides, hydrocarbyl succinamides, mixed ester/amides of hydrocarbyl-substituted succinic acid, hydroxyesters of hydrocarbyl-substituted succinic acid, and Mannich condensation products of hydrocarbyl-substituted phenols, formaldehyde and polyamines. Also useful are condensation products of polyamines and hydrocarbyl substituted phenyl acids. Mixtures of these dispersants can also be used.

[0028] Basic nitrogen containing ashless dispersants are well known lubricating oil additives, and methods for their preparation are extensively described in the patent literature. For example, hydrocarbyl-substituted succinimides and succinamides and methods for their preparation are described, for example, in U.S. patent numbers: 3,018,247; 3,018,250; 3,018,291; 3,361,673 and 4,234,435. Mixed ester-amides of hydrocarbyl-substituted succinic acids are described, for example, in U.S. patents numbers: 3,576,743; 4,234,435 and 4,873,009. Mannich dispersants, which are condensation products of hydrocarbyl-substituted phenols, formaldehyde and polyamines are described, for example, in U.S. patents numbers: 3,368,972; 3,413,347; 3,539,633; 3,697,574; 3,725,277; 3,725,480; 3,726,882; 3,798,247; 3,803,039; 3,985,802; 4,231,759 and 4,142,980. Amine dispersants and methods for their production from high molecular weight aliphatic or alicyclic halides and amines are described, for example, in U.S. patent numbers: 3,275,554; 3,438,757 and 3,565,804.

[0029] The preferred dispersants are the alkenyl succinimides and succinamides. The succinimide or succinamide dispersants can be formed from amines containing basic nitrogen and additionally one or more hydroxy groups. Usually, the amines are polyamines such as polyalkylene polyamines, hydroxy-substituted polyamines and polyoxyalkylene polyamines. Examples of polyalkylene polyamines include diethylene triamine, triethylene tetramine, tetraethylene pentamine, pentaethylene hexamine. Low cost poly(ethyleneamines) (PAM's) averaging about 5 to 7 nitrogen atoms per molecule are available commercially under trade names such as "Polyamine H", "Polyamine 400", Dow Polyamine E-100", etc. Hydroxy-substituted amines include N-hydroxyalkyl-alkylene polyamines such as N-(2-hydroxyethyl)ethylene diamine, N-(2-hydroxyethyl)piperazine, and N-hydroxyalkylated alkylene diamines of the type described in U.S. 4,873,009. Polyoxyalkylene polyamines typically include polyoxyethylene and polyoxypropylene diamines and triamines having average molecular weights in the range of 200 to 2500. Products of this type are available under the Jeffamine trademark.

[0030] Use of alkenyl succinimides which have been treated with a boronating agent are also suitable for use in the compositions of this invention as they are much more compatible with elastomeric seals made from such substances as fluoro-elastomers and silicon-containing elastomers. Dispersants may be post-treated with many reagents known to those skilled in the art. (see, e.g., U.S. Pat. Nos. 3,254,025, 3,502,677 and 4,857,214).

[0031] The preferred ashless dispersants are polyisobutenyl succinimides formed from polyisobutenyl succinic anhydride and an alkylene polyamine such as triethylene tetramine or tetraethylene pentamine wherein the polyisobutenyl substituent is derived from polyisobutene having a number average molecular weight in the range of 300 to 2500 (preferably 400 to 2200). It has been found that selecting certain dispersants within the broad range of alkenyl succinimides produces fluids with improved frictional characteristics. The most preferred dispersants of this invention are those wherein the polyisobutene substituent group has a molecular weight of approximately 950 atomic mass units, the basic nitrogen containing moiety is polyamine (PAM) .

[0032] The ashless dispersants of the invention can be used in any effective amount. However, they are typically used from about 0.1 to 10.0 mass percent, on an a.i. basis, in the finished lubricant, preferably from about 0.5 to 7.0 percent and most preferably from about 2.0 to about 5.0 percent.

[0033] Suitable antioxidants for use in combination in the compositions of the present invention include amine-type and phenolic antioxidants. Examples of amine-type antioxidants, which are preferred in this invention include phenyl alpha naphthylamine, phenyl beta naphthylamine and bis-alkylated diphenyl amines (e.g., p,p'-bis(alkylphenyl)-amines wherein the alkyl groups each contain from 8 to 12, especially 9, carbon atoms). Phenolic antioxidants include sterically hindered phenols (e.g., 2,6-di-tert-butylphenol, 4-methyl-2,6-di-tert-butylphenol) and bis-phenols (e.g., 4,4"-methylenebis(2,6-di-tert-butylphenol). Another class of useful phenolic antioxidants are the derivatives of cinnamic acid and cinnamic acid esters (e.g., the octyl ester of 3,5-dimethyl-4-hydroxyl cinnamic acid).. In this invention, antioxidants are used in amounts ranging from 0.1 to about 3.0 wt. %, preferably about 0.15 to 1.0 wt.%.

[0034] The metal detergents which may be used in the compositions of this invention may be oil-soluble neutral or overbased alkali metal, alkaline earth metal (including magnesium) salts of one or more of the following acidic substances (or mixtures thereof): (1) sulfonic acids, (2) carboxylic acids, (3) salicylic acids, (4) alkyl phenols and (5) sulfurized alkyl phenols.

[0035] Oil-soluble neutral metal-containing detergents are those detergents that contain stoichiometrically equivalent amounts of metal in relation to the amount of acidic moieties present in the detergent. Thus, in general the neutral detergents will have a low basicity when compared to their overbased counterparts. The acidic materials utilized in forming such detergents include carboxylic acids, salicylic acids, alkylphenols, sulfonic acids, sulfurized alkylphenols and the like.

[0036] The term "overbased" in connection with metallic detergents is used to designate metal salts wherein the metal is present in stoichiometrically larger amounts than the organic radical. The commonly employed methods for preparing the overbased salts involve heating a mineral oil solution of an acid with a stoichiometric excess of a metal neutralizing agent such as the metal oxide, hydroxide, carbonate, bicarbonate, of sulfide at a temperature of about 50°C, and filtering the resultant product. The use of a "promoter" in the neutralization step to aid the incorporation of a large excess of metal likewise is known. Examples of compounds useful as the promoter include phenolic substances such as phenol, naphthol, alkyl phenol, thiophenol, sulfurized alkylphenol, and condensation products of formaldehyde with a phenolic substance; alcohols such as methanol, 2-propanol, octanol, Cellosolve alcohol, Carbitol alcohol, ethylene glycol, stearyl alcohol, and cyclohexyl alcohol; and amines such as aniline, phenylene diamine, phenothiazine, phenyl-beta-naphthylamine, and dodecylamine. A particularly effective method for preparing the basic salts comprises mixing an acid with an excess of a basic alkaline earth metal neutralizing agent and at least one alcohol promoter, and carbonating the mixture at an elevated temperature such as 60 to 200°C. Overbased detergents have a TBN (total base number, ASTM D-2896) typically of 150 or more such as 250-450.

[0037] Examples of suitable metal-containing detergents include, but are not limited to, neutral and overbased salts of such substances as calcium or magnesium phenates, sulfurized magnesium or calcium phenates, wherein each aromatic group has one or more aliphatic groups to impart hydrocarbon solubility; calcium or magnesium sulfonates, wherein each sulfonic acid moiety is attached to an aromatic nucleus which in turn usually contains one or more aliphatic substituents to impart hydrocarbon solubility; calcium or magnesium salicylates wherein the aromatic moiety is usually substituted by one or more aliphatic substituents to impart hydrocarbon solubility, salts of hydrolyzed phosphosulfurized olefins having 10 to 2,000 carbon atoms or of hydrolyzed phosphosulfurized alcohols and/or aliphatic-substituted phenolic compounds having 10 to 2,000 carbon atoms; calcium or magnesium salts of aliphatic carboxylic acids and aliphatic substituted cycloaliphatic carboxylic acids; and many other salts of oil-soluble organic acids. Mixtures of neutral or over-based salts of two or more different alkali and/or alkaline earth metals can be used. Likewise, neutral and/or overbased salts of mixtures of two or more different acids (e.g. one or more overbased calcium phenates with one or more overbased calcium sulfonates) can also be used.

[0038] As is well known, overbased metal detergents are generally regarded as containing overbasing quantities of inorganic bases, probably in the form of micro dispersions or colloidal suspensions. Thus the term "oil soluble" as applied to metallic detergents is intended to include metal detergents wherein inorganic bases are present that are not necessarily completely or truly oil-soluble in the strict sense of the term, inasmuch as such detergents when mixed into base oils behave much the same way as if they were fully and totally dissolved in the oil.

[0039] Methods for the production of oil-soluble neutral and overbased metallic detergents and alkaline earth metal-containing detergents are well known to those skilled in the art, and extensively reported in the patent literature. See for example, the disclosures of U.S. Pat. Nos. 2,001,108; 2,081,075; 2,095,538; 2,144,078; 2,163,622.

[0040] Preferred calcium detergents for use with this invention are overbased calcium sulfonates and phenates and overbased sulfurized calcium phenates.

[0041] While any effective amount of the metal overbased detergent may be used in this invention, typically effective amounts will be from 0.01 to 5.0 mass percent in the finished fluid on an a.i. basis. Preferably, the treat rate in the fluid will be from 0.05 to 3.0 mass percent, and most preferred is 1.0 to 2.0 mass percent.

[0042] The following examples are given as specific illustrations of the claimed invention. It should be understood, however, that the invention is not limited to the specific details set forth in the examples. All parts and percentages are by weight unless otherwise specified.

EXAMPLE

[0043] For the purpose of exemplifying the benefits of this invention a fluid was prepared which fully meets the requirements of the claimed invention. The composition of this fluid, Fluid A, is given in the table below:

Table 1 Fluid A Composition

Components		a.i. wt.% in Oil
(a)	Zinc Dialkyldithiophosphate derived from primary alcohols	0.45
(b)	Zinc Dialkyldithiophosphate derived from secondary alcohols	0.08
(c)	Alkyl Thiadiazole	0.25
(d)	Oleamide	0.09
(e)	Amine Phosphate Anti-wear agent	0.68
(f)	PIBSA/PAM Dispersant	1.04
(g)	Diphenyl Amine- Antioxidant	0.25
(h)	Ca Sulfonate TBN 300	1.65
(i)	Mineral Base Stock, Viscosity Modifier and < 1% other conventional additives	Balance

[0044] Fluid A was tested with two types of metallic synchronizers. Both tests were run on a conventional Hurth type synchronizer test apparatus with test conditions appropriate for the synchronizers used.

Brass Synchronizers

[0045] One evaluation was run using brass synchronizers (designated J63D) as fitted in Renault manual transmissions under conditions as specified by Renault. The evaluation under Renault conditions was run for 100,000 engagements. At the end of the 100,000 engagements the synchronizers were still providing adequate friction for the engagement. Total wear of the brass cone was less than 0.4 mm. This illustrates the ability of the claimed composition, Fluid A, to control wear on brass synchronizers.

Sintered Bronze Synchronizers

[0046] A second evaluation was run using sintered bronze synchronizers coated with a sintered material designated as HS45 by Hoerbiger. These synchronizers (designated BK 117) are fitted in manual transmissions manufactured by ZF and were tested under conditions as specified by ZF (ZF Friedrichshafen AG). The evaluation under ZF conditions using Fluid A was run for 150,000 engagements. At the end of the 150,000 engagements the synchronizers were in good condition and still providing acceptable engagements. The friction level was 0.097, well above the required minimum of 0.07. This illustrates the ability of the claimed composition to provide adequate friction levels on sintered bronze synchronizers.

Claims

1. A method for lubricating a manual transmission or automated manual transmission apparatus having metallic synchronizers, which method comprises supplying to said transmission a lubricating composition comprising a major amount of an oil of lubricating viscosity,

(a) a zinc dialkyldithiophosphate derived from primary alkyl alcohols,
(b) a zinc dialkyldithiophosphate derived from 50 wt.% or more secondary alkyl alcohols, and
(c) a thiadiazole corrosion inhibitor which is a 2,5-dimercapto-1,3,4-thiadiazole or derivative thereof.

2. The method of claim 1, wherein the lubricating composition further includes at least one of the following:

(d) a fatty acid primary amide friction modifier,
(e) at least one supplemental anti-wear agent,
(f) at least one lubricating oil dispersant,
(g) at least one antioxidant, or
(h) at least one metal detergent.

3. The method of any one of the preceding claims, wherein the synchronizers are brass or sintered bronze.

4. The method of any one of the preceding claims, wherein there is present 0.1 to 1.0 wt. % of the (a) component.

5. The method of any one of the preceding claims, wherein there is present 0.01 to 0.5 wt. % of the (b) component.

6. The method of any one of the preceding claims, wherein the alkyl groups of the (a) and (b) components have 3 to 12 carbon atoms.

7. The method of any one of the preceding claims, wherein there is present 0.01 to 1.0 wt. % of the (c) component.

8. The method of any one of the preceding claims, wherein the (c) component is 2,5-bis-(nonyldithio)-1 ,3,4-thiadiazole.

9. The method of any one of the preceding claims, wherein there is present 0.01 to 1.0 wt. % of the (d) component; component (d) preferably being oleamide.

10. Use to reduce friction and/or wear in a manual transmission or an automated manual transmission apparatus having metallic synchronizers of a lubricating composition comprising a major amount of an oil of lubricating viscosity,

(a) a zinc dialkyldithiophosphate derived from primary alkyl alcohols,
(b) a zinc dialkyldithiophosphate derived from 50 wt.% or more secondary alkyl alcohols, and
(c) a thiadiazole corrosion inhibitor which is a 2,5-dimercapto-1,3,4-thiadiazole or derivative thereof.

European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 05 27 0044

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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A	EP 0 725 129 A (THE LUBRIZOL CORPORATION) 7 August 1996 (1996-08-07) * example 2 * * page 10, line 53 - page 11, line 33 * * page 11, line 49 - page 12, line 7 * -----	1-10	
A	US 6 521 570 B2 (OSTYN MARCEL ALPHONSE ET AL) 18 February 2003 (2003-02-18) * abstract * * claims 1,6,7 * * column 1, lines 3-5,39-53 * * column 2, line 61 - column 3, line 19 * * column 3, lines 41-52 * -----	1-10	TECHNICAL FIELDS SEARCHED (IPC) C10M
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	24 January 2006	Perakis, N

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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L : document cited for other reasons
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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 05 27 0044

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
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24-01-2006

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