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(54) Power transmission fluids

(57) A fluid composition for all-wheel drive wet multidisk brakes and/or differentials having improved characteristics, additive concentrates for all-wheel drive vehicles and methods for improving fluid characteristics for all-wheel drive vehicles. The fluid composition is a base oil having therein an extreme pressure/antiwear additive package and a limited slip/antiwear additive package. The additive composition is substantially devoid of dithiophosphate components and has from about 1000 to about 2000 ppm phosphorous from phosphorous-containing components based on a total weight of the fluid composition.

Description

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RELATED APPLICATIONS

5 [0001] This application claims the benefit of priority of U.S. Application No. 60/802,202, filed on May 19, 2006.

TECHNICAL FIELD

[0002] The present disclosure relates to an additive concentrate and lubricant composition that provides balanced performance for lubricating wet multi-disk brakes and/or differentials suitable for off-road vehicles while providing bearing and gear pitting protections with relatively low gear wear. The combination of additives in the concentrate provides relatively low static friction for limited slip performance and relatively high dynamic friction for enhanced braking performance

BACKGROUND AND SUMMARY

[0003] Gear fluids incorporate various additives in an effort to improve and control friction and wear properties of the fluid. However, conventional gear fluids and additives therefore are not suited for all applications. In particular, all-wheel drives (AWD) and off-road vehicles having wet multi-disk brakes and/or differentials require lubricants that must meet other criteria such as ZF TE-ML 05 specifications.

[0004] AWD performance criteria were originally used to improve the off-road capacity of military and other off-road vehicles. In the early eighties, a new market for all-wheel drive performance vehicles emerged. Since then a number of studies have shown the benefits to vehicle dynamics of all-wheel drive vehicles compared to two-wheel drive vehicles. [0005] In traditional all-wheel drive systems, a viscous coupling is commonly installed on the propeller shaft in order to transmit torque while still allowing some difference in rotational speeds between front and rear axle. The disadvantage of a viscous coupling is that it is not controllable during operation and therefore does not work well in combination with electronic driving aid systems such as electronic stability programs and traction control systems. Accordingly, improved traction control systems have been developed that include an active-on-demand AWD system for vehicles with short system activation and deactivation times.

[0006] One such AWD system features a multiple disc wet clutch with clutch plates covered with a sintered friction material. The clutch pack distributes drive torque to the rear axle of the vehicle. By using a wet clutch, torque transfer control is enhanced which makes it possible to electronically control the drive torque distribution between the front and rear axle in order to optimize vehicle dynamics. When a speed difference occurs between the front and rear axle, a cam on the rear axle causes a pumping action on a hydraulic piston pump. The hydraulic pressure generated is applied to the clutch pack in order to reduce the speed difference between the shafts, thus engaging the all-wheel drive. The torque transmitted by the coupling is controlled by a throttle valve.

[0007] Fluids suitable for use in AWD vehicle wet disk brakes and/or differentials include one or more base oils and one or more additives. Such fluids must provide adequate friction performance and at the same time have good shear and oxidation stability, anti-wear performance and corrosion resistance. The concentration of each additive in the fluids, and the balance between them, is important when formulating such fluids.

[0008] Accordingly, there continues to be a need for improved fluids for all-wheel drive and/or off road vehicles that provide balanced performance characteristics for lubricating wet multi-disk brakes and/or differentials without adversely affecting other important properties of the lubricant or oil. In exemplary embodiments described herein there is provided a fluid composition for all-wheel drive wet multi-disk brakes and/or differentials having improved characteristics, additive concentrates for all-wheel drive vehicles and methods for improving fluid characteristics for all-wheel drive vehicles. The fluid composition is a base oil containing an extreme pressure/antiwear additive package, and a limited slip/antiwear additive package. The composition is substantially devoid of zinc containing additives and is substantially devoid of dithiophosphate components and includes from about 1000 to about 2000 ppm phosphorous from phosphorous-containing components based on a total weight of the fluid composition.

[0009] In one exemplary embodiment, the disclosure provides an additive concentrate for an all-wheel drive vehicle fluid. The additive concentrate includes an extreme pressure/antiwear additive package and a limited slip/antiwear additive package. The fluid containing the additive concentrate is substantially devoid of zinc containing components and is substantially devoid of dithiophosphate containing components.

[0010] Yet another exemplary embodiment of the disclosure provides a lubricant composition having an extreme pressure/antiwear package and a limited slip/antiwear additive package. The limited slip/antiwear additive package contains a dialkyl hydrogen phosphite, and provides improved high temperature performance for the lubricant composition.

[0011] As described in more detail below, the additive combination described herein may provide balanced performance

for lubricating wet multi-disk brakes and/or differentials for all-wheel drive or off-road vehicles while providing bearing and gear pitting protection with low gear wear. Specifically, a unique mixture of phosphite, rust inhibitor, and static and dynamic friction modifiers in effective amounts may provide balanced performance needs for off-road axles with multidisk brakes and/or differentials. "Balanced performance," as used herein, means that the additive may provide both low static friction for limited slip performance and high dynamic friction for brake performance. Unlike conventional limited slip additives, the limited slip/antiwear additive package described herein may enable a lubricant composition to maintain its API GL-5 performance characteristics. The limited slip/antiwear additive package may also enable a lubricant composition to possess high temperature, load bearing characteristics according to L-37 specifications.

[0012] The foregoing general description and the following detailed description are exemplary and explanatory only and are intended to provide further explanation of the disclosed embodiments.

DETAILED DESCRIPTION OF EXEMPLARY EMBODIMENTS

[0013] As used herein, the term "hydrocarbyl substituent" or "hydrocarbyl group" is used in its ordinary sense, which is well-known to those skilled in the art. Specifically, it refers to a group having a carbon atom directly attached to the remainder of a molecule and having a predominantly hydrocarbon character. Examples of hydrocarbyl groups include:

- (1) hydrocarbon substituents, that is, aliphatic (e.g., alkyl or alkenyl), alicyclic (e.g., cycloalkyl, cycloalkenyl) substituents, and aromatic-, aliphatic-, and alicyclic-substituted aromatic substituents, as well as cyclic substituents wherein the ring is completed through another portion of the molecule (e.g., two substituents together form an alicyclic radical);
- (2) substituted hydrocarbon substituents, that is, substituents containing non-hydrocarbon groups which, in the context of the description herein, do not alter the predominantly hydrocarbon substituent (e.g., halo (especially chloro and fluoro), hydroxy, alkoxy, mercapto, alkylmercapto, nitro, nitroso, and sulfoxy);
- (3) hetero-substituents, that is, substituents which, while having a predominantly hydrocarbon character, in the context of this description, contain other than carbon in a ring or chain otherwise composed of carbon atoms. Heteroatoms include sulfur, oxygen, nitrogen, and encompass substituents such as pyridyl, furyl, thienyl and imidazolyl. In general, no more than two, preferably no more than one, non-hydrocarbon substituent will be present for every ten carbon atoms in the hydrocarbyl group; typically, there will be no non-hydrocarbon substituent in the hydrocarbyl group.

[0014] As used herein, the term "percent by weight", unless expressly stated otherwise, means the percentage the recited component represents to the weight of the entire composition.

Base Oils

[0015] Typically, the fluid compositions described herein will contain from about 80 to about 98 percent by weight of a base oil. Hence, fluid compositions as provided herein, may be based on natural or synthetic oils, or blends thereof, provided the base oil has a suitable viscosity for use in the applications described. Thus, the base oils will normally have a viscosity in the range of SAE 50 to SAE 250, and more usually will range from SAE 70W to SAE 140. Suitable base oils may also include cross-grades such as 75W-140, 80W-90, 85W-140, 85W-90, and the like.

[0016] Base oils suitable for use herein may be made using a variety of different processes including but not limited to distillation, solvent refining, hydrogen processing, oligomerization, esterification, and re-refining. API 1509 "Engine Oil Licensing and Certification System" Fourteenth Edition, December 1996 states that all base oils are divided into five general categories:

- (1) Group I contain less than 90% saturates and/or greater than 0.03% sulfur and have a viscosity index greater than or equal to 80 and less than 120;
- (2) Group II contain greater than or equal to 90% saturates and less than or equal to 0.03% sulfur and have a viscosity index greater than or equal to 80 and less than 120;
- (3) Group III contain greater than or equal to 90% saturates and less than or equal to 0.03% sulfur and have a viscosity index greater than or equal to 120;
- (4) Group IV are polyalphaolefins (PAO); and
- (5) Group V include all other base oils not included in Group I, II, III or IV.

[0017] The test methods used in defining the above groups are ASTM D2007 for saturates; ASTM D2270 for viscosity index; and one of ASTM D2622, 4294, 4927 and 3120 for sulfur.

[0018] Group IV base oils, i.e. polyalphaolefins (PAO) include hydrogenated oligomers of an alpha-olefin, the most important methods of oligomerization being free radical processes, Ziegler catalysis, and cationic, Friedel-Crafts catalysis.

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[0019] The polyalphaolefins typically have viscosities in the range of 2 to 100 cSt at 100° C., preferably 4 to 8 cSt at 100° C. They may, for example, be oligomers of branched or straight chain alphaolefins having from 2 to 16 carbon atoms, specific examples being polypropenes, polyisobutenes, poly-1-butenes, poly-1-hexenes, poly-1-octenes and poly-1-decene. Included are homopolymers, interpolymers and mixtures.

[0020] A base oil referred to above as a "Group I base oil" may include a major amount of Group I base oil and a minor amount of base oil(s) from one or more other groups, provided that the resulting admixture has characteristics falling within those specified above for Group I base oils.

[0021] Preferred base oils include Group I base oils and mixtures of Group II base oils with Group I base oils.

Use Limited Slip/Antiwear Additive Package

[0022] Fluid compositions and additive concentrates described herein include a limited slip additive package containing one or more dispersants, a detergent, a friction modifier, a rust inhibitor, and a limited slip agent.

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[0023] The limited slip/antiwear additive package of the present disclosure may contain at least one dispersant. The dispersant may comprise an ashless dispersant having basic nitrogen and/or at least one hydroxyl group in the molecule, such as a succinimide dispersant, succinic ester dispersant, succinic ester-amide dispersant, Mannich base dispersant, hydrocarbyl polyamine dispersant, or polymeric polyamine dispersants. The dispersants suitable for use also include non-phosphorus-containing dispersants, the phosphorus-containing dispersants described above as well as mixtures of phosphorus and non-phosphorus-containing, dispersants.

[0024] Polyamine succinimides in which the succinic group contains a hydrocarbyl substituent containing at least 30 carbon atoms are described for example in U.S. Pat. Nos. 3,972,892; 3,202,678; 3,216,936; 3,219,666; 3,254,025; 3,272,746; and 4,234,435. The alkenyl succinimides may be formed by conventional methods such as by heating an alkenyl succinic anhydride, acid, acid-ester, acid halide, or lower alkyl ester with a polyamine containing at least one primary amino group. The alkenyl succinic anhydride may be made readily by heating a mixture of olefin and maleic anhydride to, for example, about 180-220° C. The olefin may be a polymer or copolymer of a lower monoolefin such as ethylene, propylene, 1-butene, isobutene and the like and mixtures thereof. In one example, the source of alkenyl group is from polyisobutene having a gel permeation chromatography (GPC) number average molecular weight of up to about 10,000 or higher, or alternatively in the range of about 500 to about 2,500, or further alternatively in the range of about 800 to about 1,200.

[0025] As used herein the term "succinimide" is meant to encompass the completed reaction product from a reaction between one or more polyamine reactants and a hydrocarbon-substituted succinic acid or anhydride (or like succinic acylating agent), and is intended to encompass compounds wherein the product may have amide, amidine, and/or salt linkages in addition to the imide linkage of the type that results from the reaction of a primary amino group and an anhydride moiety.

[0026] Alkenyl succinic acid esters and diesters of polyhydric alcohols containing about 2 to about 20 carbon atoms and about 2 to about 6 hydroxyl groups can be used in forming ashless dispersants. Representative examples are described in U.S. Pat. Nos. 3,339,776; 3,381,022; and 3,522,179. The alkenyl succinic portion of these esters corresponds to the alkenyl succinic portion of the succinimides described above.

[0027] Suitable alkenyl succinic ester-amides for forming the phosphorylated ashless dispersant are described for example in U.S. Pat. Nos. 3,184,474; 3,576,743; 3,632,511; 3,804,763; 3,836,471; 3,852,981; 3,936,480; 3,950,341; 3,957,854; 3,957,855; 3,991,098; 4,071,548; and 4,173,540.

[0028] Hydrocarbyl polyamine dispersants that may be phosphorylated are generally produced by reacting an aliphatic or alicyclic halide (or mixture thereof) containing an average of at least about 40 carbon atoms with one or more amines, preferably polyalkylene polyamines. Examples of such hydrocarbyl polyamine dispersants are described in U.S. Pat. Nos. 3,275,554; 3,394,576; 3,438,757; 3,454,555; 3,565,804; 3,671,511; and 8,821,302.

[0029] In general, the hydrocarbyl-substituted polyamines are high molecular weight hydrocarbyl-N-substituted polyamines containing basic nitrogen in the molecule. The hydrocarbyl group typically has a number average molecular weight in the range of about 750 to about 10,000 as determined by GPC, more usually in the range of about 1,000 to about 5,000, and is derived from a suitable polyolefin. Some hydrocarbyl-substituted amines or polyamines are prepared from polyisobutenyl chlorides and polyamines having from about 2 to about 12 amine nitrogen atoms and from about 2 to about 40 carbon atoms.

[0030] Mannich polyamine dispersants which may be used to form phosphorylated ashless dispersant are a reaction product of an alkyl phenol, typically having a long chain alkyl substituent on the ring, with one or more aliphatic aldehydes containing from about 1 to about 7 carbon atoms (especially formaldehyde and derivatives thereof, and polyamines (especially polyalkylene polyamines). Examples of Mannich condensation products, and methods for their production

are described in numerous U.S. Patents.

[0031] For example, hydrocarbon sources for preparation of the Mannich polyamine dispersants are those derived from substantially saturated petroleum fractions and olefin polymers, preferably polymers of mono-olefins having from about 2 to about 6 carbon atoms. The hydrocarbon source generally contains at least about 40 and preferably at least about 50 carbon atoms to provide substantial oil solubility to the dispersant. The olefin polymers having a GPC number average molecular weight between about 600 and about 5,000 are preferred for reasons of easy reactivity and low cost. However, polymers of higher molecular weight can also be used. Especially suitable hydrocarbon sources are isobutylene polymers.

[0032] Mannich base dispersants that may be used are Mannich base ashless dispersants formed by condensing about one molar proportion of long chain hydrocarbon-substituted phenol with from about 1 to about 2.5 moles of formaldehyde and from about 0.5 to about 2 moles of polyalkylene polyamine.

[0033] Polymeric polyamine dispersants suitable for preparing phosphorylated ashless dispersants are polymers containing basic amine groups and oil solubilizing groups (for example, pendant alkyl groups having at least about 8 carbon atoms). Such materials are illustrated by interpolymers formed from various monomers such as decyl methacrylate, vinyl decyl ether or relatively high molecular weight olefins, with aminoalkyl acrylates and aminoalkyl acrylamides. Examples of polymeric polyamine dispersants are set forth in U.S. Pat. Nos. 3,329,658; 3,449,250; 3,493,520; 3,519,565; 3,666,730; 3,687,849; and 3,702,300.

[0034] The formulation of a limited slip/antiwear additive composition may include from about 1 wt. % to about 20 wt. % of one or more dispersants based on the total weight of the additive composition. The formulation of a finished fluid composition for wet multi-disk brakes and/or differentials may include about 0.05 wt. % to about 5 wt. % of the one or more dispersants. A mixture of a 900 to 2000 MW by GPC hydrocarbyl succinimide with a 1500 to 3000 MW by GPC borated phosphorylated hydrocarbyl succinimide in a ratio of about 2.0 to 2.5: 1 may be particularly useful in the additive described herein.

Detergents

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[0035] Metal-containing or ash-forming detergents function both as detergents to reduce or remove deposits and as acid neutralizers or rust inhibitors, thereby reducing wear and corrosion. Detergents generally comprise a polar head with a long hydrophobic tail where the polar head comprises a metal salt of an acidic organic compound. The salts may contain a substantially stoichiometric amount of the metal, in which case they are usually described as normal or neutral salts, and would typically have a total base number or TBN (as measured by ASTM D2896) of from 0 to less than 200. Large amounts of a metal base may be included by reacting an excess of a metal compound such as an oxide or hydroxide with an acidic gas such as carbon dioxide. The resulting overbased detergent comprises micelles of neutralized detergent surrounding a core of inorganic metal base (e.g., hydrated carbonates). Such overbased detergents may have a TBN of 150 or greater, and typically ranging from 250 to 450 or more.

[0036] Detergents that may be used include oil-soluble neutral and overbased sulfonates, phenates, sulfurized phenates, and salicylates of a metal, particularly the alkali or alkaline earth metals, e.g., sodium, potassium, lithium, calcium, and magnesium. The most commonly used metals are calcium and magnesium, which may both be present. Mixtures of calcium and/or magnesium with sodium are also useful. Particularly convenient metal detergents are neutral and overbased calcium or magnesium sulfonates having a TBN of from 20 to 450 TBN, neutral and overbased calcium or magnesium phenates and sulfurized phenates having a TBN of from 50 to 450, and neutral or overbased calcium or magnesium salicylates having a TBN of from 130 to 350. Mixtures of such salts may also be used.

[0037] The amount of detergent in the limited slip/antiwear additive package may range from about 1 wt. % to about 5 wt.%. A finished lubricant composition according to the disclosed embodiments may include from about 0.05 to about 1.5 percent by weight detergent based on the total weight of the finished lubricant composition.

Friction Modifier

[0038] In addition to the other additive components described above, embodiments of the present disclosure may comprise a succinimide prepared from an alkenyl succinic acid or anhydride and ammonia. For example, the friction modifier may comprise the reaction product of a succinic anhydride and ammonia. The alkenyl group of the alkenyl succinic acid may be a short chain alkenyl group, for example, the alkenyl group may comprise about 12 to about 36 carbon atoms. Further, the friction modifier may comprise a C_{12} to C_{36} aliphatic hydrocarbyl succinimide. As an even further example, the friction modifier may comprise a C_{16} to C_{28} aliphatic hydrocarbyl succinimide. As an even further example, the friction modifier may comprise a C_{18} to about C_{24} aliphatic hydrocarbyl succinimide.

[0039] The succinimide may be prepared from a succinic anhydride and ammonia as described in European Patent 0 020 037, herein incorporated by reference. In some embodiments, no metallic or non-metallic friction modifier other than the succinimide disclosed herein is included.

[0040] The fully formulated lubricant may comprise a friction-modifying amount of the succinimide friction modifier. Further, for example, the lubricant may comprise about 0.05 wt% to about 1.5 wt% of the succinimide friction modifier.

Amine Rust Inhibitors

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[0041] Another component of the limited slip/antiwear additive package provided herein is a tertiary alkyl primary amine useful as a rust inhibitor. Usually the tertiary aliphatic primary amines are monoamines represented by the formula

$$\begin{array}{c} \mathrm{CH_3} \\ \mathrm{R-C-NH_2} \\ \mathrm{CH_3} \end{array}$$

wherein R is a hydrocarbyl group containing from one to about 30 carbon atoms. Such amines may be illustrated by tertiary-butyl amine, tertiary-hexyl primary amine, 1-methyl-1-amino-cyclohexane, tertiary-octyl primary amine, tertiary-decyl primary amine, tertiary-tetradecyl primary amine, tertiary-hexadecyl primary amine, tertiary-octadecyl primary amine, tertiary-tetracosanyl primary amine, tertiary-octacosanyl primary amine.

[0042] Mixtures of amines are also useful for the purposes of the disclosed embodiments. Illustrative of amine mixtures of this type are mixtures of C_{11} - C_{14} tertiary alkyl primary amines and mixtures of C_{18} - C_{22} tertiary alkyl primary amines. The tertiary alkyl primary amines and methods for their preparation are well known to those of ordinary skill in the art and, therefore, further discussion is unnecessary. The tertiary alkyl primary amine useful for the purposes described herein and methods for their preparation are described in U.S. Pat. No. 2,945,749 which is hereby incorporated by reference for its teaching in this regard.

Limited Slip Agent

[0043] According to an embodiment of the disclosure, the limited slip/antiwear additive package includes a limited slip agent such as a dihydrocarbyl hydrogen phosphite. Suitable dihydrocarbyl hydrogen phosphites (acid phosphite esters) may be selected from the group consisting of dibutyl hydrogen phosphite, dipentyl hydrogen phosphite, di-2-ethylhexyl hydrogen phosphite, dipalmityl hydrogen phosphite, dialuryl hydrogen phosphite, distearyl hydrogen phosphite, dioleyl hydrogen phosphite, and other C_3 - C_{30} alkyl or alkenyl acid phosphites, dicresyl hydrogen phosphite, and other C_6 - C_{30} aryl acid phosphites, and mixtures thereof. More generally, the dihydrocarbyl hydrogen phosphites have hydrocarbyl groups that may independently vary from about 10 to about 30 carbon atoms arranged linearly or in branched or isoalkyl isomeric forms.

[0044] The dihydrocarbyl hydrogen phosphite may be added to a fully formulated fluid composition or may be included in an additive concentrate package. The formulation of an additive concentrate package may include about 40 wt. % to about 75 wt. % of dihydrocarbyl hydrogen phosphite. The fully formulated fluid composition may include from about 1.0 wt. % to about 10 wt. % of dihydrocarbyl hydrogen phosphite sufficient to provide from about 1000 to about 200 parts per million by weight of phosphorus in the fully formulated fluid composition.

Diluent Oil

[0045] The limited slip/antiwear additive package provided herein may contain a suitable diluent oil. The diluent oil typically is present in the additive concentrates in a major amount. A useful diluent is an oleaginous diluent of suitable viscosity. Such a diluent may be derived from natural or synthetic sources, or blends thereof. Use of mineral oils as the diluent for the additive concentrate are particularly suitable. Among the mineral (hydrocarbonaceous) oils are paraffin base, naphthenic base, asphaltic base, and mixed base oils. Synthetic oils include polyolefin *oils* (*especially hydrogenated* α -olefin oligomers), alkylated aromatics, polyalkylene oxides, aromatic ethers, and carboxylate esters (especially diesters), among others. The diluents may be light hydrocarbon base oils, both natural and (per a) synthetic.

[0046] Generally, the diluent oil has a viscosity in the range of about 1 to about 40 cSt at 100° C., and typically about 2 to about 15 cSt at 100° C. In one particular embodiment, the diluent oil is a 150 Neutral mineral oil having a viscosity of about 6 cSt at 100° C. The amount of diluent oil in the limited slip/antiwear additive package may range from about 30 to about 60 % by weight based on a total weight of the additive package.

Extreme Pressure/Antiwear Additive Package

[0047] The limited slip/antiwear additive component described above may be included in an extreme pressure/antiwear additive package concentrate or may be added to a lubricant containing an extreme pressure/antiwear additive package to provide the limited slip performance characteristics. An extreme pressure/antiwear additive package that may be used with the limited slip/antiwear additive component may include extreme pressure agents, antiwear components, corrosion and/or rust inhibitors, antifoam agents, and a diluent oil.

Extreme Pressure/Antiwear Agents

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[0048] Of the components of the additive package, the most prevalent is a sulfur-containing extreme pressure agent. Typical sulfur-containing extreme pressure agents include, but are not limited to, dihydrocarbyl polysulfides, sulfurized olefins, sulfurized fatty acid esters of both natural (e.g. sperm oil) and synthetic origins, sulfurized terpenes, sulfurized oligomers of C₂-C₈ monoolefins, and sulfurized Diels-Alder adducts such as those disclosed in reissue U.S. Pat. No. 21,331, the disclosure of which is incorporated herein by reference. Specific examples include sulfurized polyisobutene, sulfurized isobutylene, sulfurized triisobutene, dicyclohexyl polysulfide, diphenyl and dibenzyl polysulfide, di-tert-butyl polysulfide, and dinonyl polysulfide, among others.

[0049] In one embodiment, the sulfur-containing extreme pressure agent is at least one dimercaptothiadiazole or an oil-soluble derivative thereof. Such materials provide extreme pressure and/or antiwear properties to exemplary fluid compositions described herein.

[0050] Dimercaptothiadiazoles which may be used in the fluid compositions include, but are not limited to, 2,5-dimercapto-1,3,4-thiadlazoles (DMTD) of the following formula:

$$R^{1}-S_{a}-C \setminus C-S_{b}-R^{2}$$

wherein R1 and R2 are selected from hydrogen and straight and branched chain alkyl groups having from 1 to 30 carbon atoms, and a and b are independently selected from integers ranging from 1 to 3. DMTD may be prepared by reacting of one mole of hydrazine, or a hydrazine salt, with two moles of carbon disulfide in an alkaline medium, followed by acidification.

[0051] Fluid compositions described herein may include DMTD or derivatives of DMTD as set forth in the foregoing formula. For example, U.S. Pat. Nos. 2,719,125; 2,719,126; and 3,087,937 describe the preparation of various 2,5-bis (hydrocarbon dithio)-1,3,4-thiadiazoles. The total amount of sulfur in the fluid composition that is provided by the sulfur-containing additives may range from about 0.5 to about 5.0 weight percent based on the total weight of the lubricant composition containing the additive package.

[0052] Other suitable antiwear agents may include phosphorus-containing antiwear agents such as organic esters of phosphoric acid, phosphorous acid, or amine salts thereof. For example, the phosphorus-containing antiwear agent may include one or more of a monohydrocarbyl phosphate, a dihydrocarbyl phosphate, a trihydrocarbyl phosphate, any sulfur analogs thereof, and any amine salts thereof. As a further example, the phosphorus-containing antiwear agent may include at least one of 2-ethyl hexyl acid phosphate, dibutyl hydrogen phosphate, amyl acid phosphate, an amine salt of sulfurized dibutyl hydrogen phosphate, or dialkyl thiophosphoric acid.

[0053] The phosphorus-containing antiwear agent may be present in an amount sufficient to provide about 50 to about 500 parts per million by weight of phosphorus in the fully formulated lubricant composition. As a further example, the phosphorus-containing antiwear agent may be present in an amount sufficient to provide about 150 to about 350 parts per million by weight of phosphorus in the fluid composition.

Rust or Corrosion Inhibitors

[0054] Rust or corrosion inhibitors are another preferred type of inhibitor additive for use in fluid compositions described herein. Such materials include monocarboxylic acids and polycarboxylic acids. Examples of suitable monocarboxylic acids are octanoic acid, decanoic acid and dodecanoic acid. Suitable polycarboxylic acids include dimer and trimer acids such as are produced from such acids as tall oil fatty acids, oleic acid, linoleic acid, or the like. Products of this type are currently available from various commercial sources.

[0055] Another useful type of rust inhibitor for use in the compositions described herein is comprised of the alkenyl succinic acid and alkenyl succinic anhydride corrosion inhibitors such as, for example, tetrapropenylsuccinic acid, tetrap-

ropenylsuccinic anhydride, tetradecenylsuccinic acid, tetradecenylsuccinic anhydride, hexadecenylsuccinic acid, hexadecenylsuccinic anhydride, and the like. Also useful are the half esters of alkenyl succinic acids having 8 to 24 carbon atoms in the alkenyl group with alcohols such as the polyglycols. Other suitable rust or corrosion inhibitors include ether amines; acid phosphates; amines; polyethoxylated compounds such as ethoxylated amines, ethoxylated phenols, and ethoxylated alcohols; imidazolines; aminosuccinic acids or derivatives thereof, and the like. Materials of these types are available as articles of commerce. Mixtures of such rust or corrosion inhibitors may be used. The amount of corrosion inhibitor in the additive package may range from about 0.01 to about 0.5 weight percent based on the total weight of the formulation.

[0056] Yet another rust inhibitor that may be used is a tertiary alkyl primary amine. Usually the tertiary aliphatic primary amines are monoamines represented by the formula

wherein R is a hydrocarbyl group containing from one to about 30 carbon atoms. Such amines may be illustrated by tertiary-butyl amine, tertiary-hexyl primary amine, 1-methyl-1-amino-cyclohexane, tertiary-octyl primary amine, tertiary-decyl primary amine, tertiary-tetradecyl primary amine, tertiary-hexadecyl primary amine, tertiary-octadecyl primary amine, tertiary-octadecyl primary amine, tertiary-octadecyl primary amine.

[0057] Mixtures of amines are also useful for the purposes of the disclosed embodiments. Illustrative of amine mixtures of this type are mixtures of C_{11} - C_{14} tertiary alkyl primary amines and mixtures of C_{18} - C_{22} tertiary alkyl primary amines. The tertiary alkyl primary amines and methods for their preparation are well known to those of ordinary skill in the art and, therefore, further discussion is unnecessary. The tertiary alkyl primary amine useful for the purposes described herein and methods for their preparation are described in U.S. Pat. No. 2,945,749 which is hereby incorporated by reference for its teaching in this regard. The amount of tertiary alky primary amine in the additive package may range from about 0.5 to about 5.0 weight percent based on a total weight of the additive package.

Antifoam agents

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[0058] A foam inhibitor forms another component suitable for use in the compositions described herein. Foam inhibitors may be selected from silicones, polyacrylates, surfactants, and the like. The amount of antifoam agent in the additive package described herein may range from about 0.01 to about 0.1 weight percent based on the total weight of the lubricant composition.

Process Oil

[0059] The additive package provided herein may contain a suitable process oil. The process oil typically is present in the additive concentrates in a major amount. A useful process oil is an oleaginous diluent of suitable viscosity. Such an oil may be derived from natural or synthetic sources, or blends thereof. Use of mineral oils as the process oil for the additive concentrate are particularly suitable. Among the mineral (hydrocarbonaceous) oils are paraffin base, naphthenic base, asphaltic base, and mixed base oils. *Synthetic oils include polyolefin oils* (especially hydrogenated α -olefin oligomers), alkylated aromatics, polyalkylene oxides, aromatic ethers, and carboxylate esters (especially diesters), among others. The process oils may be light hydrocarbon base oils, both natural and (per a) synthetic.

[0060] Generally, the process oil has a viscosity in the range of about 1 to about 40 cSt at 100° C., and typically about 2 to about 15 cSt at 100° C. In one particular embodiment, the process oil is a 150 Neutral mineral oil having a viscosity of about 6 cSt at 100° C. The amount of process oil in the additive package may range from about 1 to about 10 percent by weight based on a total weight of the additive package.

[0061] Additives used in formulating the fluid compositions described herein may be blended into the base oil individually or in various sub-combinations. However, it is preferable to blend all of the components concurrently using an additive concentrate (i.e., additives plus a diluent, such as a hydrocarbon solvent described above). The use of an additive concentrate takes advantage of the mutual compatibility afforded by the combination of ingredients when in the form of an additive concentrate. Also, the use of a concentrate reduces blending time and lessens the possibility of blending errors. **[0062]** The fluid compositions containing the additives described above may be further characterized as having a substantial absence of zinc-containing components. Further the fluid compositions may be further characterized as

having a substantial absence of dithiophosphate-containing components.

[0063] Exemplary additive concentrates that may be combined for balanced limited slip performance and enhanced multi-disk braking for off-road vehicles according to the disclosure may be provided by the following compositions:

Table 1

Limited Slip/Antiwear Package (LS Additive)	Wt. %
1300 MW succinimide dispersant	1 to 5
Borated, phosphorylated dispersant	0.5 to 1.5
Tertiary alkyl primary amine	5 to 15
Succinimide friction modifier	1 to 5
Calcium phenate detergent	1 to 5
Dihydrocarbyl hydrogen phosphite	20 to 50
Diluent oil	20 to 50

Table 2

Extreme Pressure/Antiwear Package (EP Additive)	Wt. %
Sulfurized isobutylene	70 to 90
Tertiary alkyl primary amine	1 to 5
Fatty acid amine	0.5 to 2.5
Tolytriazole	0.05 to 1.0
Amyl acid phosphate	1 to 10
Dialkylthiadiazole	1 to 10
Acrylic copolymer antifoam agent	0.5 to 2.0
Dimer acid	0.05 to 1.0
Process oil	1.0 to 10.0

EXAMPLE 1

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[0064] In order to demonstrate aspects of the disclosed embodiments, the following non-limiting examples are provided. In the first example, an additive composition as provided in Table 1 was added to a conventional ZF TE ML05C fluid containing the additive of Table 2. A conventional oil including only the additive package of Table 2 was also tested. The results are giving in the following Table 3.

Table 3

Component Testing	Requirements	Conventional Oil (including Additive Pkg of Table 2)	Conventional Oil (Including Additive Pkg of Table 2) Plus Additive Pkg of Table 1		
ZF elastomer compatibility at 168 Hr (hardness)	-1	-2	0		
Thermal & Oxidation Stability (130°C./192 Hr, PAI increase)	84.6	57.9	78.6		
FZG Scuffing Resistance		LS 12 Pass			

(continued)

5	Component Testing	Requirements	Conventional Oil (including Additive Pkg of Table 2)	Conventional Oil (Including Additive Pkg of Table 2) Plus Additive Pkg of Table 1
	FZG Sprung (S A10/16.6R/90)	LS 9 min.	Ls 12 Pass	LS 10/9 F
10	FZG Pitting test (new oil) (PT C/9/90)	160 Hr	300/215/194 Hr	174/306 Hr
	ZF Evaluation of Relative Micropitting (rpt)	10-20%		20-30%/30-40%
15	Size of pitting	0.5 - 5.0 mm ²		0.5 - 8.0 mm ² / 8 mm ²
15	Scouring (profile deviation) < 15 μm	7 μm		9.6 μm/ 5.6μm
20	Bearing Pitting Test (3 tests) ≥ LS90 Ref Oil		Pass	Pass
20	Test duration		750 Hrs	1084/750 Hrs
	Cylinder roller thrust retainer Wt. Loss		232 mg	322/318 mg
25	Housing Disc. Wt. loss		5.5 mg	4/2 mg
	Shaft Disc. Wt. loss		6.5 mg	5/3 mg
	Surface fatigue		0%	0/0 mm ²
30	Appreciation of Disc 1	Pitting on Disc of bearing 1	Unusual Traces from Roller on disc	Unusual Traces from Roller on disc
	Appreciation of Disc 2	Traces from Rollers on the discs of bearing 2, no pitting	Traces from honing still visible	Traces from honing still visible
	Wear Behavior	30 mg Max	21 mg after 120 Hrs	17 mg after 120 Hrs
35	Wet Brake	Pass	NA	Pass
	Disk Locking Differential	Pass	NA	Pass

[0065] In the foregoing example, a conventional oil containing the additive packages of Table 1 and Table 2 exhibited a passing grade for meeting the ZF TE ML05C specifications indicated in the table including the L-37 high temperature test. Whereas, a lubricant containing only the additive package of Table 2 failed the L-37 high temperature test.

EXAMPLE 2

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[0066] In the following example, an additive composition as provided in Table 1 was added to a conventional GL-5 oil containing the additive package of Table 2 to determine if the additive has any adverse effects on the GL-5 oil. The results are giving in the following Table 4.

Table 4

Component Testing	Requirements	GL-5 Oil (Including Additive Pkg of Table 2)	GL-5 (Including Additive Pkg of Table 2) Plus Additive Pkg of Table1
Chemical & Physical Data			
Sulfur wt. %		2.1	2.03
Phosphorus wt.%		0.031	0.136

(continued)

5	Component Testing	Requirements	GL-5 Oil (Including Additive Pkg of Table 2)	GL-5 (Including Additive Pkg of Table 2) Plus Additive Pkg of Table1
3	Viscometric Requirements			
	SAE Grade	J-306	80W-90	80W-90
10	KV at 100° C. (DIN 51562) mm ² /sec	13.5 cSt min.	14.63	15.06
	KV at 40° C. (DIN 51562) mm ² /see	Report	138.3	145.5
15	Viscosity at-26° C. (DIN 51398) (cP)	SAE 80W 150,000 cP max	115,800	131,800
	Shear Stability at 20 Hrs		Pass	Pass
	KV at 100° C. 20 Hrs	13.5cSt Min.	13.77	14.25
20	GL-5 Testing			
	L-60		Pass L-60	Pass L-60
	CV	NA	4.36	5.0
25	Sludge	NA	9.19	9.1
20	% Viscosity Increase	100 % max.	30.56	19.1
	PI	3 max.	0.81	1.3
	TI	2 max.	2.0	1.3
30	L-33-1		Pass	Pass
	Overall Merit Rating	9.0 min.	9.32	10.0
	L-37 Green Pinion Merit Rating	Pass	Pass	Pass
35	Wear	5 min.	8	7
	Scoring	10 min.	10	10
	Rippling	8 min.	10	10
40	Ridging	8 min.	9	10
	Spitting (Pitting/Spalling)	9.3 min.	10	9.9
	L-37 Lubrited	Pass	Pass	Pass
45	Wear	8 min.	8	5
45	Scoring	10 min.	10	10
	Rippling	8 min.	10	8
	Ridging	8 min.	9	9
50	Spitting (Pifting/Spalling)	9.3 min.	10	10
	L-37 High Temperature	Pass	Fail	Pass
	Wear	8 min.	3	8
5.F	Scoring	10 min.	10	10
55	Rippling	8 min.	5	9
	Ridging	8 min.	3	10

(continued)

Component Testing	Requirements	GL-5Oil (Including Additive Pkg of Table 2)	GL-5 (Including Additive Pkg of Table 2) Plus Additive Pkg of Table1
Spitting (Pitting/Spalling)	9.3 min.	8	9.9
L-42	Pass	Pass	Pass
Candidate Ring / Pinion	Better than Ref.	13/18	13/22
Passing Reference Ring / Pinion		22/27	18/24
Discriminant oil Ring / Pinion		79/84	61/65

[0067] As shown by the foregoing example, the additive package of Table 1 provided improvement in the rust inhibitor performance (as indicated by the L-33-1 test) compared to a GL-5 oil containing only the additive package of Table 2. The additive also provided a passing L-37 high temperature grade to an otherwise failing GL-5 oil. The additive package of Table 1 also contributed no significant detrimental effects under the GL-5 testing criteria. Hence, the additive package of Table 1 may provide a balanced performance for lubricating wet multi-disk brakes and/or differentials while providing bearing and gear pitting protections with relatively low gear wear. The additive package of Table 1 may also be used as a top treat to differentials in passenger vehicles to provide improved limited slip performance.

EXAMPLE 3

[0068] In this example, lubricants containing the additive packages of Table 1 and Table 2 were compared to conventional gear oils and to oils containing conventional additive packages. In Table 5, Sample 1 is a gear oil containing a tractor hydraulic fluid additive package. Sample 2 is a conventional GL-5 gear oil. Samples 3 and 4 are the same gear oils of Sample 2 with the additive package of Table 2. Sample 3 contains a conventional limited slip package and Sample 4 contains the limited slip package of Table 1. Samples 5-8 contain are gear oils containing conventional extreme pressure and limited slip additive packages. Samples 5 and 6 were the same oils with and without the conventional limited slip additive package 1. Samples 7 and 8 were the same oils with and without the conventional limited slip additive package 2.

Table 5

	Sample 1	Sample 2	Sample 3	Sample 4
Gear Oil	94 wt.%	96 wt.%	91 wt.%	91 wt.%
LS Additive (Table 1)	None	None	None	5 wt.%
EP Additive (Table 2)	None	4 wt.%	4 wt.%	4 wt.%
Tractor Hydraulic fluid additive	6 wt.%	0	0	0
Conventional EP additive	None	None	None	None
Conventional LS additive 1	None	None	5 wt.%	None
Conventional LS additive 2	None	None	None .	None
Antiwear component	Dithiophosphate	Acid Phosphate	Acid Phosphate	Acid Phosphate
Dispersant	None	None	None	Yes
Detergent	Yes	None	None	Yes
Limited Slip additive	None	None	Phosphate/phosphite	Phosphite
Rust inhibitor	None	None	Primary Amine	Primary Amine
Static friction modifier	Yes	None	Yes	Yes
Dynamic friction modifier	Yes	None	None	Yes
Zinc (ppm)	1254	0	0	0
Phosphorus (ppm)	1029	310	1475	1335
Sulfur (wt.%)	0.4	2.03	2.03	2.03
Nitrogen (ppm)	350	220	420	1640
Mg (ppm)	100	0	0 .	0
Ca (ppm)	3348	0	0	143
B (ppm)	0	0	0	0
Other metals (ppm)	<5	<5	<5	<5
GL-5 Test	Fail	Pass	Fail	Pass
High Temp. L-37 test	Fail	Fail	Pass	Pass
Axle Brake Test	Pass	Fail	Fail	Pass
SAE #2 Dynamic Friction test	Pass	Fail	Fail	Pass
Axle LS differential test	Pass	Fail	Pass	Pass
ZF Low Speed Wear test	Pass	Pass	Pass	Pass
ZF Bearing Pitting test	Pass	Fail	Pass	Pass

Table 5 (Cont.)

	Sample 5	Sample 6	Sample 7	Sample 8
Gear Oil	93.5 wt.%	88.5 wt.%	93.5 wt.%	88.5 wt.%
LS Additive (Table 1)	None	None	None	None
EP Additive (Table 2)	None	None	None	None
Tractor Hydraulic	0	0	0	0
fluid additive				
Conventional EP additive	6.5 wt.%	6.5 wt.%	6.5 wt.%	6.5 wt.%
Conventional LS additive 1	None	5 wt.%	None	None
Conventional LS additive 2	None	None	None	5 wt.%
Antiwear component	Dithiophosphate	Dithiophosphate	Dithiophosphate	Dithiophosphate

Dispersant	None	None	None	None
Detergent	None	None	None	None
Limited Slip additive	None	Phosphate/phosphite	None	Phosphate/phosphite
Rust Inhibitor	None	Primary Amine	None	Primary Amine
Static friction modifier	None	Yes	None	Yes
Dynamic friction modifier	None	None	None	None
Zinc (ppm)	8	8	1	10
Phosphorus (ppm)	1063	2227	1092	2243
Sulfur (wt.%)	2.40	2.41	2.08	3.03
Nitrogen (ppm)	700	1246	700	1651
Mg (ppm)	0	0	1	2
Ca (ppm)	2	7	1	11
B (ppm)	4	5	1	21
Other metals (ppm)	<5	<5	<5	<5
GL-5 Test	Pass	Fail	Pass	Fail
High Temp. L-37 test	Pass	The state of the s	Pass	
Axle Brake Test	Fail	Pass	Fail	Pass
SAE #2 Dynamic Friction test	Fail	Pass	Fail	Pass
Axle LS differential test	Pass	Pass	Pass	. Pass
ZF Low Speed Wear test	Pass	Pass .	Pass	Pass
ZF Bearing Pitting test	Pass	Pass	Pass	Pass

[0069] As shown by the foregoing tables, Sample 4 containing the additives of Table 1 and Table 2 not only provided suitable TE ML 05C performance, but also passed the GL-5 test and the high temperature L-37 test. Sample 2 containing only the additive package of Table 2 passed the GL-5 test but failed most of the other tests. Sample 3 containing the additive package of Table 2 and a conventional limited slip (LS) additive failed the GL-5 test but passed some of the other tests. The other samples (5-8) containing conventional EP and LS additives were likewise inferior to Sample 4 since they either failed the GL-5 test or the axle brake test and SAE #2 dynamic friction test.

[0070] At numerous places throughout this specification, reference has been made to a number of U.S. Patents. All such cited documents are expressly incorporated in full into this disclosure as if fully set forth herein.

[0071] Other embodiments of the present invention will be apparent to those skilled in the art from consideration of the specification and practice of the invention disclosed herein. As used throughout the specification and claims, "a" and/or "an" may refer to one or more than one. Unless otherwise indicated, all numbers expressing quantities of ingredients, properties such as molecular weight, percent, ratio, reaction conditions, and so forth used in the specification and claims are to be understood as being modified in all instances by the term "about." Accordingly, unless indicated to the contrary, the numerical parameters set forth in the specification and claims are approximations that may vary depending upon the desired properties sought to be obtained by the present invention. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques. Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the invention are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical value, however, inherently contains certain errors necessarily resulting from the standard deviation found in their respective testing measurements. It is intended that the specification and examples be considered as exemplary only, with a true scope and spirit of the invention being indicated by the following claims.

Claims

1. A fluid composition far all-wheel drive wet multi-disk brakes and/or differentials, comprising a base oil, an extreme pressure/antiwear additive package, and a limited slip/antiwear additive package, wherein the composition is substantially devoid of zinc containing additives and is substantially devoid of dithiophosphate components and comprises from about 1000 to about 2000 ppm phosphorous from phosphorous-containing components based an a

total weight of the fluid composition.

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- 2. The fluid composition of claim 1, wherein the base oil comprises one or more of a natural oil, a mixture of natural oils, a synthetic oil, a mixture of synthetic oils, and a mixture of natural and synthetic oils.
- 3. The fluid composition of claim 2, wherein the natural oil comprises one or more of a mineral oil, a vegetable oil, and a mixture of mineral oil and vegetable oil.
- **4.** The fluid composition of claim 2 or 3, wherein the synthetic oil comprises one or more of an oligomer of an alphaolefin, an ester, an oil derived from a Fischer-Tropsch process, a gas-to-liquid stock, and a mixture thereof.
 - 5. The fluid composition of any one of claims 1 to 4, wherein the extreme pressure/antiwear additive package and the limited slip antiwear additive package comprises an amin antiwear agent comprising a mixture of C₁₂-C₁₄ tertiary alkyl primary amines.
 - **6.** The fluid composition of any one of claims 1 to 5, wherein the composition comprises from about 0.5 to about 5 wt. % of the dialkyl hydrogen phosphite based on a total weight of the fluid composition.
- 7. The fluid composition of any one of claims 1 to 6, wherein the extreme pressure/antiwear additive package comprises from about 70 to about 90 weight percent of a sulfur-containing extreme pressure agent based an a total weight of the additive package.
 - **8.** The fluid composition of any one of claims 1 to 7, wherein the composition comprises from about 0.5 to about 5.0 weight percent sulfur based on a total weight of the fluid composition.
 - **9.** The fluid composition of any one of claims 1 to 8, wherein the composition comprises a phosphate other than a dithiophosphate.
- **10.** The fluid composition of any one of claims 1 to 9, wherein the fluid composition comprises from about 0.5:1 to about 1:1 extreme pressure/antiwear additive package to limited slip/antiwear additive package in the fluid composition.
 - 11. An all-wheel drive differential comprising the fluid composition of any one of claims 1 to 10.
 - 12. A multi-disk brake for an all-wheel drive vehicle comprising the fluid composition of any one of claims I to 10.
 - 13. A vehicle comprising the multi-disk brake of claim 12.
 - 14. An additive concentrate for an all-wheel drive vehicle fluid comprising:
- an extreme pressure/antiwear additive package; and a limited slip/antiwear additive package,
 - wherein the fluid containing the additive concentrate is substantially devoid of zinc containing components and is substantially devoid of dithiophosphate containing components.
 - **15.** The additive concentrate of claim 14, wherein the extreme pressure/antiwear additive package and the limited slip/antiwear additive package comprises an amine antiwear agent comprising a mixture of C₁₂-C₁₄ tertiary alkyl primary amines.
- **16.** The additive concentrate of claim 14 or 15, wherein the concentrate comprises from about 0.5 to about 5.0 wt.% of the dialkyl hydrogen phosphite based on a total weight of the concentrate.
 - 17. The additive concentrate of any one of claims 14 to 16, wherein the extreme pressure/antiwear additive package comprises from about 70 to about 90 weight percent of a sulfur-containing extreme pressure agent based on a total weight of the extreme pressure/antiwear additive package.
 - **18.** The additive concentrate of any one of claims 14 to 17, wherein the extreme pressure/antiwear additive package comprises a fatty acid phosphate.

- **19.** The additive concentrate of any one of claims 14 to 18, wherein the concentrate comprises from about 0.5:1 to about 1:1 extreme pressure/antiwear additive package to limited slip/antiwear additive package.
- 20. A fluid composition comprising from about 0.5 to about 15 wt. \(^{1}/0\) of the additive concentrate of claim 14.

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- 21. A method for lubricating wet multi-disk brakes and/or differentials comprising providing a lubricant composition comprising an extreme pressure/antiwear package and a limited slip/antiwear additive package, wherein the limited slip/antiwear additive package comprises a dialkyl hydrogen phosphite, and wherein the limited slip/antiwear additive package provides improved high temperature performance for the lubricant composition.
- **22.** The method of Claim 21 wherein the lubricant composition containing the limited slip/antiwear additive package maintains API GL-5 performance characteristics.
- **23.** The method of any one of claim 21 or 22, wherein the lubricant composition is substantially devoid of zinc and dithiophosphate components.
 - **24.** The method of any one of claims 21 to 23, wherein the lubricant composition comprises from about 0.5 to about 5.0 weight percent sulfur from sulfur components based an a total weight of the lubricant composition.
 - **25.** The method of any one of claims 21 to 24, wherein the lubricant composition comprises from about 1000 to about 2000 ppm total phosphorous from phosphorous-containing components.



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