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(54) **Antiwear hydraulic fluid composition with useful emulsifying and rust prevention properties**

(57) Disclosed are antiwear hydraulic fluid compositions comprising (a) a major amount of a base oil of lubricating viscosity and (b) a minor amount of at least one oil soluble detergent additive comprising a salt of an alkyl-substituted hydroxybenzoic acid or a sulfurized derivative thereof, wherein said salt is selected from the group consisting of alkali metal salts, alkaline earth metal salts, ammonium salts or substituted ammonium salts, and further wherein said antiwear hydraulic fluid compositions have a Carboxylate Index of greater than levels disclosed herein.

EP 2 669 355 A1

Description

Field of the Invention

[0001] The present invention relates to detergents utilized in antiwear hydraulic fluid compositions. In particular, the present invention relates to antiwear hydraulic fluid compositions which can be useful for certain mobile equipment applications (e.g., hydraulic fluids for construction equipment).

Background of the Invention

[0002] Hydraulic fluids need to protect equipment from rust. To achieve this they are formulated with rust inhibitors. Typical rust inhibitors are metal sulfonates or succinic acid derivatives. Hydraulic fluids are also typically designed to separate readily from water (demulsify). Often, metallic rust inhibitors act to improve the demulsifying characteristics of the fluids.

[0003] Japanese Patent Publication No. JP1999311187A describes a composition containing (A) a base fluid of a sulfur content of up to 100 ppm, (B) 0.2-1 wt. % of zinc dithiophosphate, (C) 0.2-1 wt. % of an alkaline earth metal salt of salicylic acid and (D) 0.001-0.5 wt. % of a water-separating agent.

[0004] International Application No. WO0063325 describes a hydraulic fluid comprising lubricant base fluid, 0.001-5 wt.% of magnesium salicylate and 0.01-8 wt.% of zinc dithiophosphate. The hydraulic fluid composition also comprises a rust inhibitor. This publication also discloses the combination of a calcium salicylate, zinc dithiophosphate, and a rust inhibitor.

[0005] The above publications describe compositions incorporating a metal salt of an alkyl salicylate, zinc dithiophosphate, and a rust inhibitor. Typically such compositions also include demulsifiers to facilitate the separation of water from the fluid. However, there is a need in some cases to have hydraulic fluids which emulsify, rather than demulsify, water.. These include fluids with enhanced detergent and dispersant characteristics (e.g., so called HLPD and HVLPD fluids as defined by the German DIN 51 502 standard) and hydraulic fluids for certain mobile equipment applications (e.g., hydraulic fluids for Caterpillar equipment, building machinery, excavators, hydraulic hoists, lifting platforms, presses, and the like), wherein water separated from the fluid may not be adequately removed from the equipment leading to poor lubrication. Engine fluids, which are typically formulated with large amounts of dispersants, are a way to provide these emulsifying characteristics. Hydraulic fluids with certain sulfonate detergents can also have these characteristics.

Summary of the Invention

[0006] One aspect of this invention is an antiwear hydraulic fluid composition comprising a major amount of a base fluid of lubricating viscosity and a minor amount of at least one oil soluble detergent additive. This detergent additive comprises a salt of an alkyl-substituted hydroxybenzoic acid or a sulfurized derivative thereof, wherein said salt is selected from the group consisting of alkali metal salts, alkaline earth metal salts, ammonium salts or substituted ammonium salts, and wherein at least 90% of the alkyl groups of said alkyl-substituted hydroxybenzoic acid are C_{14} or greater. Furthermore, the antiwear hydraulic fluid composition is able to able to achieve an emulsion of 0 ml of fluid, 0 ml of water and 80 ml of emulsion (abbreviated 0-0-80) for 30 minutes or more, preferably 40 minutes or more in the ASTM D 1401 water separability test method, and the antiwear hydraulic fluid composition has a Carboxylate Index of greater than 0.084.

[0007] Another aspect of this invention is an antiwear hydraulic fluid composition comprising a major amount of a base fluid of lubricating viscosity and a minor amount of at least one oil soluble detergent additive. This detergent additive comprises a salt of an alkyl-substituted hydroxybenzoic acid or a sulfurized derivative thereof, wherein said salt is selected from the group consisting of alkali metal salts, alkaline earth metal salts, ammonium salts or substituted ammonium salts, and wherein at least 90% of the alkyl groups of said alkyl-substituted hydroxybenzoic acid are C_{14} or greater. Furthermore, the hydraulic fluid composition is able to achieve a "pass" result in the ASTM D 665 rust inhibition test method, and the antiwear hydraulic fluid composition has a Carboxylate Index of greater than 0.034.

[0008] Surprisingly, we have found that salts as described above exhibit excellent emulsifying and rust inhibition characteristics. This combined performance is unexpected when compared to other detergents. One advantage of the present invention is the reduction or removal of conventional rust inhibitors, such as metallic naphthalene sulfonic acid salts, (e.g., NA-SUL® from King Industries).

Detailed Description of the Invention

[0009] Antiwear hydraulic fluids are used in hydraulic systems to prevent wear in mechanical equipment in hydraulic systems, for example, to prevent wear on moving metal on metal surfaces, such as steel on steel surfaces. Antiwear hydraulic fluids are useful, for example, in preventing wear in a variety of pumps, including but not limited to, vane pumps,

piston pumps, and gear pumps, commonly used in hydraulic systems. Antiwear hydraulic fluids also provide protection for other parts of the hydraulic system such as motors, actuators, and pistons. Antiwear hydraulic fluids typically contain antiwear additves or extreme pressure agents, such as zinc dialkyl dithiophosphate.

[0010] The antiwear hydraulic fluid of the present invention exhibits several performance features in addition to antiwear protection, in particular emulsification and rust protection. In addition, the antiwear hydraulic fluid of the present invention exhibits good oxidation stability, good filterability, good thermal stability, low internal friction, and good hydrolytic stability.

Base Oil of Lubricating Viscosity

[0011] The base oil of lubricating viscosity employed in the present invention may be mineral oil or synthetic oils. A base oil having a viscosity of at least 10 cSt (mm^2/s) at 40 C. and a pour point below 20 C., preferably at or below 0 C. is desirable. The base oils may be derived from synthetic or natural sources. Mineral oils for use as the base oil in this invention include, for example, paraffinic, naphthenic and other fluids that are ordinarily used in lubricating oil compositions. Synthetic oils include, for example, both hydrocarbon synthetic oils and synthetic esters and mixtures thereof having the desired viscosity. Hydrocarbon synthetic oils may include, for example, liquid polymers having the proper viscosity prepared from the polymerization of ethylene or higher alpha olefins (polyalphaolefin or PAO), or from hydrocarbon synthesis procedures using carbon monoxide and hydrogen gases such as in a Fisher-Tropsch process. Especially useful are the hydrogenated liquid oligomers of C_6 to C_{12} alpha olefins such as 1-decene trimer. Likewise, alkyl benzenes of proper viscosity, such as didodecyl benzene, can be used. Useful synthetic esters include the esters of monocarboxylic acids and polycarboxylic acids, as well as mono-hydroxy alkanols and polyols. Typical examples are didodecyl adipate, pentaerythritol tetracaproate, di-2-ethylhexyl adipate, dilaurylsebacate, and the like. Complex esters prepared from mixtures of mono and dicarboxylic acids and mono and dihydroxy alkanols can also be used. Blends of mineral oils with synthetic oils are also useful. For example, blends of 10 wt % to 25 wt % hydrogenated 1-decene trimer with 75 wt % to 90 wt % 150 SUS (100F.) mineral oil make excellent lubricating oil bases.

[0012] The base oil of the present invention is present in a "major amount." A "major amount" of a base oil of lubricating viscosity refers to a concentration of the oil within the hydraulic fluid composition of at least about 40 wt %. In some embodiments, "a major amount" of a base oil of lubricating viscosity refers to a concentration of the oil within the hydraulic fluid composition of at least about 50 wt %, at least about 60 wt %, at least about 70 wt %, at least about 80 wt %, or at least about 90 wt %.

Detergent additive

[0013] As discussed previously, the antiwear hydraulic fluid composition employed in the present invention comprises at least one suitable detergent additive that is oil soluble. Such detergent additives comprise any suitable carboxylate-containing detergents, including alkyl-substituted hydroxybenzoates and sulfurized derivatives thereof, wherein the Total Base Number ("TBN") of the detergent additive is typically less than 200 mg KOH/g, and preferably less than 160 mg KOH/g. The term "Total Base Number" or "TBN" refers to the equivalent number of milligrams of KOH needed to neutralize 1 gram of a product. Therefore, a high TBN reflects strongly overbased products and, as a result, a higher base reserve for neutralizing acids. The TBN of a product can be determined by ASTM Standard No. D 2896 or equivalent procedure. An overbased detergent can be any detergent in which the TBN of the additive has been increased by a process such as the addition of a base source (such as lime) and an acidic overbasing compound (such as carbon dioxide).

[0014] It is preferred that for at least 75% (such as at least 80%, at least 85%, at least 90%, at least 95%, or at least 99%) of the alkyl groups contained within the detergent (such as the alkyl groups of a carboxylate-containing detergent, or of an alkyl-substituted hydroxybenzoic acid) to be C_{14} or greater, such as C_{14}-C_{40}, C_{14}-C_{35}, C_{14}-C_{30}, or C_{14}-C_{25},. In some embodiments, at least 75% (such as at least 80%, at least 85%, at least 90%, at least 95%, or at least 99%) of the alkyl groups contained within the detergent, with the remainder (such as 25% or less, about 20% or less, 15% or less, 10% or less, 5% or less, or even 1% or less) of the alkyl groups contained within the detergent to be C_8 or greater (such as C_8-C_{14}, C_{10}-C_{14}, or even C_{12}-C_{14}). In one preferred embodiment, the detergent comprises a salt of an alkyl-substituted hydroxybenzoic acid that is derived from an alkyl-substituted hydroxybenzoic acid in which the alkyl groups are the residue of normal alpha-olefins containing at least 90% C_{20} or greater normal alpha-olefins.

[0015] In another embodiment, the detergent comprises a carboxylate salt, such as a salt (e.g., an overbased salt) of an alkyl-substituted hydroxybenzoic acid, or even an alkali metal or an alkaline earth metal salt, or an ammonium and substituted ammonium salt of an alkyl-substituted hydroxybenzoic acid. In another embodiment, the detergent comprises an overbased salt (such as an overbased alkaline earth metal salt) of a mixture of alkyl-substituted hydroxybenzoic acid and alkyl-substituted phenol. In another embodiment, the detergent comprises an overbased salt of an alkyl-substituted hydroxybenzoic acid and/or an overbased salt of an alkyl-substituted phenol, in combination or mixture with a non-overbased salt of one or more of: an alkyl-substituted hydroxybenzoic acid and an alkyl-substituted phenol. In another embodiment, the antiwear hydraulic fluid composition comprises one or more detergents comprising an overbased salt

of an alkyl-substituted hydroxybenzoic acid and no other overbased salts (other than the salt of the detergent). The detergent additive, in this regard, can comprise any suitable concentration of anion (e.g., organic anion) associated with the carboxylate salt (or salt of the alkyl-substituted hydroxybenzoic acid).

[0016] Some non-limiting examples of other suitable detergents which may be used in combination with alkyl-substituted hydroxybenzoates include alkyl or alkenyl aromatic sulfonates, borated sulfonates, sulfurized or unsulfurized metal salts of multi hydroxy alkyl or alkenyl aromatic compounds, alkyl or alkenyl hydroxy aromatic sulfonates, sulfurized or unsulfurized alkyl or alkenyl naphthenates, metal salts of alkanoic acids, metal salts of an alkyl or alkenyl multiacid, and chemical and physical mixtures thereof. Other non-limiting examples of suitable detergent additives include metal sulfonates, salicylates, phosphonates, thiophosphonates and combinations thereof. The metal can be any metal suitable for making sulfonate, salicylate or phosphonate detergents. Non-limiting examples of suitable metals include alkali metals, alkaline metals and transition metals. In some embodiments, the metal is Ca, Mg, Ba, Sr, K, Na, Li or the like.

[0017] The detergent additive employed in the present invention is generally soluble in oil as characterized by the following test: A mixture of a 600N oil and the additive at a content of 10% by weight with respect to the total weight of the mixture is centrifuged at a temperature of 60 C and for 30 minutes, the centrifugation being carried out under the conditions stipulated by the standard ASTM D2273 (it should be noted that centrifugation is carried out without dilution, i.e. without adding solvent); immediately after centrifugation, the volume of the deposit which forms is determined; if the deposit is less than 0.05% v/v (volume of the deposit with respect to the volume of the mixture), the product is considered as soluble in oil.

[0018] The aforementioned oil soluble detergent additive in the antiwear hydraulic fluid composition of the present invention has a TBN typically less than 200 mg KOH/g, and preferably less than 160 mg KOH/g. In the antiwear hydraulic fluid composition of the present invention, the concentration of the oil soluble detergent additive itself will generally range from an amount of between about 0.05 wt % to about 0.3 wt%, and preferably about 0.07 wt% to about 0.25 wt %, based on the total weight of the hydraulic fluid composition. Alternatively speaking, the detergent additive of the present invention is present in a "minor amount." A "minor amount" of detergent additive refers to a concentration of the detergent additive within the hydraulic fluid composition of less than about 60 wt %. In some embodiments, a "minor amount" of detergent additive refers to a concentration of the detergent additive within the hydraulic fluid composition of less than about 50 wt%, of less than about 30 wt %, of less than about 10 wt %, of less than about 1 wt %, or of less than about 0.5 wt %.

[0019] Generally speaking, detergents help control varnish, ring zone deposits, and rust by keeping insoluble particles in colloidal suspension. Metal-containing (or ash-forming detergents) function both as detergents to control deposits, and as acid neutralizers or rust inhibitors, thereby reducing wear and corrosion and extending equipment life. Detergents generally comprise a polar head with a long hydrophobic tail; with the polar head comprising 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.

Alkyl-substituted hydroxybenzoate detergent additive component

[0020] The detergent additives in the antiwear hydraulic fluid composition of the present invention can be characterized by the amount of potassium hydroxide equivalent to the amount of alkyl-substituted hydroxybenzoate (also referred to herein as a salt of an alkyl substituted hydroxybenzoic acid), or a sulfurized derivative thereof, present in the detergent expressed as mg KOH/g detergent and referred to as the Carboxylate Index (CI). Thus, a detergent additive with 56 mg KOH equivalent hydroxyphenyl carboxylate per gram of detergent would have a CI of 56 and would be referred to as 56 CI alkyl-substituted hydroxybenzoate.

Determination of the Carboxylate Index of a Detergent Additive and of an Antiwear Hydraulic Fluid Composition

[0021] The alkyl-substituted hydroxybenzoate detergent additive is dissolved in an organic solvent and washed three times with equal volumes of a dilute, strong acid solution. The aqueous layers are collected. The combined aqueous layers are washed with an organic solvent. The aqueous layer is removed and the organic layers are combined and subsequently washed with distilled water. The aqueous layer is decanted. The acidified extract is treated with pyridine and titrated with dilute, standardized base.

[0022] The Carboxylate Index (CI) of the detergent additive can then be calculated from the following formula:

$$CI = (V_1 \times C \times MW_{KOH})/W$$

wherein

V1 is the volume required to reach the first end point in the titration curve;

C is the concentration of the dilute, standardized base;
MW_{KOH} is the molecular weight of KOH; and
W is the weight of the alkyl-substituted hydroxybenzoate detergent additive.

[0023] Once the CI of the detergent additive has been calculated, the CI of the antiwear hydraulic fluid composition can be readily determined from the amount of the alkyl-substituted hydroxybenzoate detergent additive present in the composition. This is expressed by the following formula:

CI of antiwear hydraulic fluid composition = (CI of alkyl-substituted hydroxybenzoate detergent) x (wt. % alkyl-substituted hydroxybenzoate detergent in fluid)

[0024] In one embodiment of the invention, the CI of the antiwear hydraulic fluid composition is greater than 0.084, preferably greater than 0.10, and more preferably greater than 0.12. In another embodiment of the invention, the CI of the antiwear hydraulic fluid composition is greater than 0.034, and more preferably greater than 0.04.

Concentrate Formulation

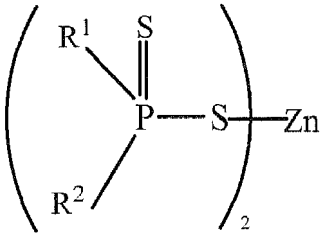
[0025] The oil soluble detergent additive of the present invention can be employed as a concentrate which will typically contain a sufficient amount of an organic liquid diluent and the oil soluble detergent additive employed in the present invention. The concentrates contain sufficient organic liquid diluent to make them easy to handle during shipping and storage. Typically, the concentrate will contain from about 10 wt % to 90 wt %; preferably, from about 20 wt % to 70 wt %; and more preferably, from about 20 wt % to 35 wt %, of a compatible organic liquid diluent. Suitable organic liquid diluents which can be used include, for example, paraffinic base oils such as solvent refined 100N, e.g., Cit-Con 100N, and hydrotreated 100N, e.g., Chevron 100N, and the like. The organic liquid diluent preferably has a viscosity of from about 1 to 20 cSt at 100C. From about 10 wt % to 90 wt %; preferably, from about 30 wt % to 80 wt % of the concentrate is the oil soluble additive employed in the present invention.

Other Additive Components

[0026] The following additive components are examples of some of the components that can be favorably employed in the present invention. These examples of additives are provided to illustrate the present invention, but they are not intended to limit it:

1. Dispersants: Alkenyl succinimides, alkenyl succinate esters, alkenyl succinimides modified with other organic compounds, alkenyl succinimides modified by posttreatment with ethylene carbonate or boric acid, pentaerythritols, phenate-salicylates and their post-treated analogs, alkali metal or mixed alkali metal, alkaline earth metal borates, dispersions of hydrated alkali metal borates, dispersions of alkaline-earth metal borates, polyamide ashless dispersants and the like or mixtures of such dispersants.
2. Anti-oxidants: Anti-oxidants reduce the tendency of mineral oils to deteriorate in service which deterioration is evidenced by the products of oxidation such as sludge and varnish-like deposits on the metal surfaces and by an increase in viscosity. Examples of anti-oxidants useful in the present invention include, but are not limited to, phenol type (phenolic) oxidation inhibitors, such as 4,4'-methylene-bis(2,6-di-tert-butylphenol), 4,4'-bis(2,6-di-tert-butylphenol), 4,4'-bis(2-methyl-6-tert-butylphenol), 2,2'-methylene-bis(4-methyl-6-tert-butyl-phenol), 4,4'-butylidene-bis(3-methyl-6-tert-butylphenol), 4,4'-isopropylidene-bis(2,6-di-tert-butylphenol), 2,2'-methylene-bis(4-me- thyl-6-nonylphenol), 2,2'-isobutylidene-bis(4,6-dimethylphenol), 2,2'-methylene-bis(4-methyl-6-cyclohexylphenol), 2,6-di-tert-butyl-4-methylphenol, 2,6-di-tert-butyl-4-ethylphenol, 2,6-di-tert-butylphenol, 2,4-dimethyl-6-tert-butyl-phenol, 2,6-di-tert-l-dimethylamino-p-cresol, 2,6-di-tert-4-(N,N'-dimethylamino- methylphenol), 4,4'-thiobis(2-methyl-6-tert-butylphenol), 2,2'-thiobis(4-methyl-6-tert-butylphenol), bis(3-methyl-4-hydroxy-5-tert--butylbenzyl)-sulfide, and bis (3,5-di-tert-butyl-4-hydroxybenzyl). Other types of oxidation inhibitors include alkylated diphenylamines (e.g., Irganox L-57 from Ciba-Geigy), metal dithiocarbamate (e.g., zinc dithiocarbamate), and methylenebis(dibutyldithiocarbamate).
3. Antiwear agents: As their name implies, these agents reduce wear of moving metallic parts. Examples of such agents include, but are not limited to, phosphates, phosphites, carbamates, esters, sulfur containing compounds, and molybdenum complexes.
4. Emulsifiers: Linear alcohol ethoxylates, including TERGITOL® 15-S-3 available from the Dow Chemical Company.
5. Demulsifiers: addition product of alkylphenol and ethylene oxide, polyoxyethylene alkyl ether, and polyoxyethylene sorbitan ester.

6. Extreme pressure agents (EP agents): zinc dialkyldithiophosphate (primary alkyl, secondary alkyl, and aryl type), sulfurized oils, diphenyl sulfide, methyl trichlorostearate, chlorinated naphthalene, fluoroalkylpolysiloxane, and lead naphthenate. A preferred EP agent is zinc dialkyl dithiophosphate (ZnDTP) as one of the co-additive components for the antiwear hydraulic fluid composition of the present invention, and is shown by the general formula:



wherein, R_1 and R_2 are each a primary or secondary alkyl group having a carbon number of 1 to 18, and may be the same or different. The primary or secondary alkyl groups of R_1 and R_2 having a carbon number of 1 to 18, shown by the general formula, include methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, 2-ethyl hexyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, and octadecyl. However, the preferable zinc dialkyl dithiophosphate for the antiwear hydraulic fluid of the present invention has a mixed alkyl group of primary and secondary alkyl groups having a carbon number of 3 to 12. A more preferable zinc dialkyl dithiophosphate for the antiwear hydraulic fluid composition of the present invention has a primary alkyl group having a carbon number of 3 to 12. The zinc dialkyl dithiophosphates having a mixed alkyl group of primary and secondary alkyl groups may be used either individually or in combination for the antiwear hydraulic fluid composition of the present invention. The zinc dialkyl dithiophosphate is incorporated at 0.01 to 0.50 wt. % as phosphorus derived therefrom, based on the whole composition, preferably 0.02 to 0.04 wt. %.

7. Friction modifiers: fatty alcohol, fatty acid, fatty ester amine, borated ester, and other esters.

8. Multifunctional additives: sulfurized oxymolybdenum dithiocarbamate, sulfurized oxymolybdenum organo phosphorodithioate, oxymolybdenum monoglyceride, oxymolybdenum diethylate amide, amine-molybdenum complex compound, and sulfur-containing molybdenum complex compound.

9. Viscosity index improvers: polymethacrylate type polymers, ethylene-propylene copolymers, styrene-isoprene copolymers, hydrogenated styrene-isoprene copolymers, polyisobutylene, and dispersant type viscosity index improvers.

10. Pour point depressants: polymethacrylate type polymers.

11. Foam inhibitors: alkyl methacrylate polymers and dimethyl silicone polymers

Examples

Emulsification Performance

[0027] A base-line formulation was prepared and used for assessing the performance of the detergent in Example 1 in the ASTM D 1401 water separability test. The base-line formulation contained 0.31 wt. % of a zinc dialkyldithiophosphate, 0.15 wt. % of a hindered phenol antioxidant, 0.044 wt. % of a succinate ester dispersant, 0.044 wt. % of a fatty ester friction modifier, 0.013 wt. % of an arylpolyol demulsifier and 0.008 wt. % of a foam inhibitor in a base fluid containing Shell HVI basestocks. All finished fluids in these Examples are ISO VG 46 with 8 wt. % of a polyalkyl methacrylate viscosity index improver.

Example 1

[0028] An antiwear hydraulic fluid composition was prepared consisting of the baseline formulation above with the addition of 0.225 wt. % of an overbased calcium alkyl-substituted hydroxybenzoate detergent wherein at least 90% of the alkyl groups are C_{20} or greater and 0.06 wt. % of the succinate ester dispersant. The overbased calcium alkyl-substituted hydroxybenzoate detergent was prepared according to the method described in Example 1 of US Patent Application 2007/0027043 and has a calcium content of 5.35 wt. %, a TBN of 150 and a CI of 56.

Example 2

[0029] An antiwear hydraulic fluid composition was prepared in accordance with the formulation of Example 1 except that 0.01 wt. % of a linear alcohol ethoxylate emulsifier and 0.16 wt% zinc dialkyl dithiophosphate was added.

Comparative Example 1

[0030] An antiwear hydraulic fluid composition was prepared consisting of the base-line formulation above with the addition of 0.041 wt. % of an overbased, sulfurized alkyl-substituted hydroxybenzoate-containing detergent, 0.024 wt. % of an overbased calcium phenate, 0.027 wt. % of a naphthalene sulfonic acid zinc salt rust inhibitor and 0.008 wt. % of a phenolic resin demulsifier. The overbased, sulfurized carboxylate-containing detergent was prepared according to the method described in Example 16 of US Patent Number 5808145 and has a calcium content of 9.3 wt. %, a sulfur content of 2.4 wt. %, a TBN of 260 and a CI of 28.

Comparative Example 2

[0031] An antiwear hydraulic fluid composition was prepared consisting of the baseline formulation above with the addition of 0.075 wt. % of the 56 CI overbased calcium alkyl-substituted hydroxybenzoate as described in Example 1.

Comparative Example 3

[0032] An antiwear hydraulic fluid composition was prepared in accordance with the formulation of Comparative Example 2 except that 0.06 wt. % of the succinate ester dispersant was added.

Comparative Example 4

[0033] An antiwear hydraulic fluid composition was prepared consisting of the baseline formulation above with the addition of 0.15 wt. % of the 56 CI overbased calcium alkylhydroxybenzoate as described in Example 1.

Comparative Example 5

[0034] An antiwear hydraulic fluid composition was prepared in accordance with the formulation of Comparative Example 4 except that 0.06 wt. % of the succinate ester dispersant was added.

Results for emulsification performance test

[0035] The water separability of antiwear hydraulic fluids is characterized in the ASTM D 1401 test method. In this method, a 40 mL volume of the sample material was emulsified with a 40 mL volume of distilled water by stirring the combined liquids in a graduated cylinder at 54°C for 5 minutes. The separation of the emulsion into organic and aqueous layers was characterized by monitoring the relative volumes of the respective fluid, water and emulsion layers after cessation of stirring. Results are set forth below in Table 1 as the respective mL fluid-mL water-mL emulsion observed at minutes after cessation of stirring.

Table 1

	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4	Comp. Ex. 5	Ex.1	Ex.2
56 Cl Ca alkyl-substituted hydroxybenzoate detergent (wt.%)	-	0.075	0.075	0.15	0.15	0.225	0.225
28 Cl Ca alkyl-substituted hydroxybenzoate detergent (wt.%)	0.041	-	-	-	-	-	-
Cl of antiwear hydraulic fluid composition'	0.011	0.042	0.042	0.084	0.084	0.126	0.126
Dispersant	0.044	0.044	0.1	0.044	0.1	0.1	0.1

(continued)

	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4	Comp. Ex. 5	Ex.1	Ex.2
Zinc dialkyl dithiophosphate	0.31	0.31	0.31	0.31	0.31	0.31	0.47
Rust inhibitor	0.027	-	-	-	-	-	-
Demulsifier	0.008	-	-	-	-	-	-
Emulsifier	-	-	-	-	-	-	0.01
ASTM D 665B (mL fluid-mL water-mL emulsion at minutes after stirring)	40-40-0 9 min 40-40-0 9 min	44-36-0 30 min 46-34-0 35 min	40-32-8 40 min 40-38-2 40 min	42-38-0 25 min 43-37-0 27 min	0-10-70 40 min 0-16-64 40 min	0-0-80 40 min 0-0-80 40 min	0-0-80 40 min 0-0-80 40 min
[1]CI of antiwear hydraulic fluid composition = (CI of alkyl-substituted hydroxybenzoate detergent) x (wt. % alkyl-substituted hydroxybenzoate detergent in fluid)							

Rust Inhibition Performance

[0036] A base-line formulation was prepared and used for assessing the performance of various detergents in the ASTM D 665 rust prevention test. The base-line formulation contained 0.31 wt. % of a zinc dialkyldithiophosphate, 0.15 wt. % of a hindered phenol antioxidant, 0.044 wt. % of a succinate ester dispersant, 0.044 wt. % of a fatty ester friction modifier, 0.013 wt. % of an arylpolyol demulsifier, 0.008 wt. % of a phenolic resin demulsifier, 0.2 wt. % of a pour point depressant and 0.008 wt. % of a foam inhibitor in a base oil containing ExxonMobil AP/E CORE® basestocks. All finished fluids in these Examples are ISO VG 68.

Example 3

[0037] An antiwear hydraulic fluid composition was prepared consisting of the baseline formulation above with the addition of 0.075 wt. % of the 56 CI overbased calcium alkyl-substituted hydroxybenzoate detergent as described in Example 1.

Comparative Example 6

[0038] An antiwear hydraulic fluid composition was prepared consisting of the baseline formulation above with the addition of 0.041 wt. % of the 28 CI overbased, sulfurized, alkyl-substituted hydroxybenzoate-containing detergent as described in Comparative Example 1, 0.024 wt. % of an overbased calcium phenate and 0.027 wt. % of a naphthalene sulfonic acid zinc salt rust inhibitor.

Comparative Example 7

[0039] An antiwear hydraulic fluid composition was prepared consisting of the baseline formulation above with the addition of 0.067 wt. % of an overbased calcium alkyl-substituted hydroxybenzoate detergent wherein at least 90% of the alkyl groups are C_{14} - C_{18}. The detergent has a TBN of 168 and a CI of 51.

Comparative Example 8

[0040] An antiwear hydraulic fluid composition was prepared consisting of the baseline formulation above with the addition of 0.049 wt. % of an overbased calcium alkyl-substituted hydroxybenzoate detergent wherein at least 90% of the alkyl groups are C_{20} - C_{28}. The detergent has a TBN of 230 and a CI of 46.

Comparative Example 9

[0041] An antiwear hydraulic fluid composition was prepared consisting of the baseline formulation above with the addition of 0.035 wt. % of an overbased calcium alkyl-substituted hydroxybenzoate detergent wherein at least 90% of

the alkyl groups are C_{20} - C_{28}. The detergent has a TBN of 325 and a CI of 36.

Comparative Example 10

[0042] An antiwear hydraulic fluid composition was prepared consisting of the baseline formulation above with the addition of 0.032 wt. % of an overbased calcium alkyl-substituted hydroxybenzoate detergent wherein at least 90% of the alkyl groups are C_{20} or greater. The overbased calcium alkyl-substituted hydroxybenzoate detergent is prepared according to the method described in Example 1 of US Patent Application 2007/0027043 and has a calcium content of 12.5 wt. %, a TBN of 350 and a CI of 37.

Results for rust inhibition performance test

[0043] Rust inhibition of antiwear hydraulic fluids was determined using ASTM D 665, which is incorporated herein by reference. ASTM D 665 is directed at a test for determining the ability of fluid to aid in preventing the rusting of ferrous parts should water become mixed with the fluid. For the determining the rust prevention properties in the instant invention, Procedure B of ASTM D 665 was employed. In this test, a mixture of 300 mL of the test fluid is stirred with 30 mL of synthetic sea water at a temperature of 60°C with a cylindrical steel specimen completely immersed therein for 24 hours. The rust test results are reported as either a "pass" or a "fail." The results are presented in Table 2.

Table 2

	Ex.3	Comp. Ex. 6	Comp. Ex. 7	Comp. Ex. 8	Comp. Ex. 9	Comp. Ex. 10
56 CI alkyl-substituted hydroxybenzoate detergent (wt.%)	0.075	-	-	-	-	-
28 CI alkyl-substituted hydroxybenzoate (wt.%)	-	0.041	-	-	-	-
51 CI alkyl-substituted hydroxybenzoate (wt.%)	-	-	0.067	-	-	-
46 CI alkyl-substituted hydroxybenzoate (wt.%)	-	-	-	0.049	-	-
36 CI alkyl-substituted hydroxybenzoate (wt.%)	-	-	-	-	0.035	-
37 CI alkyl-substituted hydroxybenzoate (wt.%)	-	-	-	-	-	0.032
CI of antiwear hydraulic fluid composition	0.042	0.011	0.034	0.023	0.013	0.012
Rust Inhibitor (wt. %)	-	0.027	-	-	-	-
Rust Inhibition Result (ASTM D 665B)	Pass	Pass	Fail	Fail	Fail	Fail
[1]CI of antiwear hydraulic fluid composition = [CI of alkyl-substituted hydroxybenzoate detergent] x [wt.% alkyl-substituted hydroxybenzoate detergent in fluid]						

[0044] The alkyl-substituted hydroxybenzoate from Example 3 demonstrated unexpected rust inhibiting performance when compared to other carboxylate/salicylate detergents (Comparative Examples 2-5) and also demonstrated unexpected rust inhibiting performance when compared to a formulation containing a rust inhibitor (Comparative Example 6). The formulation of Example 3 advantageously does not require the addition of a rust inhibitor in order to pass this test.

[0045] As discussed previously, it is advantageous in certain hydraulic fluid applications, such as hydraulic fluids for

certain mobile equipment applications and HLPD and HLVPD fluids, to emulsify water, rather than to demulsify water. Since the alkyl-substituted hydroxybenzoate from Example 1 also demonstrated good rust inhibition without the need for a metal sulfonate rust inhibitor and since metal sulfonate rust inhibitors are known to demulsify water, the alkyl-substituted hydroxybenzoate used in Example 1 provides additional performance advantages for such emulsifying hydraulic fluids.

[0046] For the avoidance of doubt, the subject-matter of the present invention includes subject-matter as defined in the following numbered paragraphs (hereafter "para."):

1. An antiwear hydraulic fluid composition comprising (a) a major amount of a base oil of lubricating viscosity and (b) a minor amount of at least one oil soluble detergent additive comprising a salt of an alkyl-substituted hydroxybenzoic acid or a sulfurized derivative thereof, wherein said salt is selected from the group consisting of alkali metal salts, alkaline earth metal salts, ammonium salts or substituted ammonium salts, and further wherein said antiwear hydraulic fluid composition has a Carboxylate Index of greater than 0.084.

2. The antiwear hydraulic fluid composition according to para. 1, wherein said alkyl-substituted hydroxybenzoic acid comprises a linear or branched alkyl group or a mixture of linear and branched alkyl groups.

3. The antiwear hydraulic fluid composition according to para. 1 wherein at least 90% of the alkyl groups of said alkyl-substituted hydroxybenzoic acid are C_{14} or greater.

4. The antiwear hydraulic fluid composition according to para. 1 wherein said antiwear hydraulic fluid composition is able to achieve an emulsion of 0-0-80 at 40 minutes in the ASTM D 1401 water separability test method.

5. The antiwear hydraulic fluid composition according to para. 1, wherein said salt comprises a calcium salt.

6. The antiwear hydraulic fluid composition according to para. 1, wherein said hydraulic fluid composition comprises no added rust inhibitors.

7. The antiwear hydraulic fluid composition according to para. 1, wherein said oil soluble detergent additive comprises a TBN of less than 200 mg KOH/g.

8. The antiwear hydraulic fluid composition according to para. 1, wherein said oil soluble detergent additive comprises a TBN of less than 160 mg KOH/g.

9. The antiwear hydraulic fluid composition according to para. 1, wherein said oil soluble detergent additive comprises greater than 0.1 weight percent of the total weight of said antiwear hydraulic fluid composition.

10.The antiwear hydraulic fluid composition according to para. 1, wherein said oil soluble detergent additive comprises greater than 0.2 weight percent of the total weight of said antiwear hydraulic fluid composition.

11.The antiwear hydraulic fluid composition of para. 1 further comprising at least one of these co-additives: (a) an ashless dispersant; (b) an oxidation inhibitor; (d) a demulsifier; (e) an extreme pressure agent; (f) a friction modifier; (g) a multifunctional additive; (h) a viscosity index improver; (i) a pour point depressant; (j) a foam inhibitor; and (k) an emulsifier..

12. An antiwear hydraulic fluid composition comprising (a) a major amount of a base oil of lubricating viscosity and (b) a minor amount of at least one oil soluble detergent additive comprising a salt of an alkyl-substituted hydroxybenzoic acid or a sulfurized derivative thereof, wherein said salt is selected from the group consisting of alkali metal salts, alkaline earth metal salts, ammonium salts or substituted ammonium salts, and further wherein said antiwear hydraulic fluid composition has a Carboxylate Index of greater than 0.034.

13.The antiwear hydraulic fluid composition according to para. 12, wherein said alkyl-substituted hydroxybenzoic acid comprises a linear or branched alkyl group or a mixture of linear and branched alkyl groups.

14.The antiwear hydraulic fluid composition according to para. 12 wherein at least 90% of the alkyl groups of said alkyl-substituted hydroxybenzoic acid are C_{14} or greater.

15.The antiwear hydraulic fluid composition according to para. 12 wherein said antiwear hydraulic fluid composition is able to achieve a pass result in the ASTM D 665 rust inhibition method.

16.The antiwear hydraulic fluid composition according to para. 12, wherein said salt comprises a calcium salt.

17.The antiwear hydraulic fluid composition according to para. 12, wherein said hydraulic fluid composition comprises no added rust inhibitors.

18.The antiwear hydraulic fluid composition according to para. 12, wherein said oil soluble detergent additive comprises a TBN of less than 200 mg KOH/g.

19.The antiwear hydraulic fluid composition according to para. 12, wherein said oil soluble detergent additive comprises a TBN of less than 160 mg KOH/g.

20. The antiwear hydraulic fluid composition according to para. 12, wherein said oil soluble detergent additive comprises greater than 0.05 weight percent of the total weight of said antiwear hydraulic fluid composition.

21.The antiwear hydraulic fluid composition according to para. 12, wherein said oil soluble detergent additive comprises greater than 0.07 weight percent of the total weight of said antiwear hydraulic fluid composition.

22.The antiwear hydraulic fluid composition of para. 12 further comprising at least one of these co-additives: (a) an ashless dispersant; (b) an oxidation inhibitor; (d) a demulsifier; (e) an extreme pressure agent; (f) a friction modifier;

(g) a multifunctional additive; (h) a viscosity index improver; (i) a pour point depressant; (j) a foam inhibitor; and (k) an emulsifier.

Claims

1. An antiwear hydraulic fluid composition comprising (a) a major amount of a base oil of lubricating viscosity and (b) a minor amount of at least one oil soluble detergent additive comprising a salt of an alkyl-substituted hydroxybenzoic acid or a sulfurized derivative thereof, wherein said salt is selected from the group consisting of alkali metal salts, alkaline earth metal salts, ammonium salts or substituted ammonium salts, and further wherein said antiwear hydraulic fluid composition has a Carboxylate Index of greater than 0.034.

2. The antiwear hydraulic fluid composition according to claim 1, wherein said alkyl-substituted hydroxybenzoic acid comprises a linear or branched alkyl group or a mixture of linear and branched alkyl groups.

3. The antiwear hydraulic fluid composition according to claim 1 wherein at least 90% of the alkyl groups of said alkyl-substituted hydroxybenzoic acid are C_{14} or greater.

4. The antiwear hydraulic fluid composition according to claim 1 wherein said antiwear hydraulic fluid composition is able to achieve a pass result in the ASTM D 665 rust inhibition method.

5. The antiwear hydraulic fluid composition according to claim 1, wherein said salt comprises a calcium salt.

6. The antiwear hydraulic fluid composition according to claim 1, wherein said hydraulic fluid composition comprises no added rust inhibitors.

7. The antiwear hydraulic fluid composition according to claim 1, wherein said oil soluble detergent additive comprises a TBN of less than 200 mg KOH/g.

8. The antiwear hydraulic fluid composition according to claim 1, wherein said oil soluble detergent additive comprises a TBN of less than 160 mg KOH/g.

9. The antiwear hydraulic fluid composition according to claim 1, wherein said oil soluble detergent additive comprises greater than 0.05 weight percent of the total weight of said antiwear hydraulic fluid composition.

10. The antiwear hydraulic fluid composition according to claim 1, wherein said oil soluble detergent additive comprises greater than 0.07 weight percent of the total weight of said antiwear hydraulic fluid composition.

11. The antiwear hydraulic fluid composition of claim 1 further comprising at least one of these co-additives: (a) an ashless dispersant; (b) an oxidation inhibitor; (d) a demulsifier; (e) an extreme pressure agent; (f) a friction modifier; (g) a multifunctional additive; (h) a viscosity index improver; (i) a pour point depressant; (j) a foam inhibitor; and (k) an emulsifier.

12. The use of an oil soluble detergent additive comprising a salt of an alkyl-substituted hydroxybenzoic acid or a sulfurized derivative thereof, wherein said salt is selected from the group consisting of alkali metal salts, alkaline earth metal salts, ammonium salts or substituted ammonium salts, as a rust inhibitor in an antiwear hydraulic fluid composition comprising a major amount of a base oil of lubricating viscosity and which has a Carboxylate Index of greater than 0.034.

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EUROPEAN SEARCH REPORT

Application Number
EP 13 18 0664

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Place of search	Date of completion of the search	Examiner
Munich	21 October 2013	Greß, Tobias

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