

[54] **ALL-PURPOSE LUBRICATING OIL COMPOSITION WITH ANTI-CHATTER CHARACTERISTICS FOR WET DISC BRAKES**

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[58] Field of Search 252/32.7 E, 33, 33.4, 75

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[57] **ABSTRACT**

Lubricating oil compositions are provided which comprise (A) a major amount of oil of lubricating viscosity, and (B) an effective amount of each of: (1) an oil-soluble substantially neutral Group II metal salt of a hydrocarbyl sulfonic acid; (2) an oil-soluble overbased Group II metal salt of a hydrocarbyl sulfonic acid; (3) an oil-soluble Group II metal salt of a dihydrocarbyl dithiophosphoric acid; (4) tricresyl phosphate; and (5) a sulfurized mixture of C¹⁰⁻²⁵ olefins and fatty acid esters of C¹⁰⁻²⁵ fatty acids and C¹⁻²⁵ alkyl or alkenyl alcohols, in an olefin-to-ester mol ratio of about 1-2:1 wherein the fatty acid and/or alcohol is unsaturated. These lubricating oil compositions are useful as functional fluids in a variety of systems. They are particularly useful in the hydraulic and gear box systems of large industrial and farm tractors providing excellent lubrication, increased braking capacity and reduced chatter of wet-type disc brakes.

6 Claims, No Drawings

ALL-PURPOSE LUBRICATING OIL COMPOSITION WITH ANTI-CHATTER CHARACTERISTICS FOR WET DISC BRAKES

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to lubricating oil compositions, particularly to lubricating oil compositions useful as functional fluids in systems requiring fluid coupling, hydraulic fluid, and/or lubrication of relatively moving parts. More particularly this invention relates to lubricating oil compositions useful both as hydraulic fluids and as lubricants in the transmissions and differentials of heavy machinery such as high-power output tractors. This lubricating oil composition is particularly useful in machinery using wet-type disc brakes physically located within the housing containing the lubricating oil composition.

The trend today in the field of heavy machinery is toward increasing power and introducing devices which not only make the machinery more efficient but reduce operator fatigue. Some of these labor-saving devices include double-acting hydraulic systems, power steering, and power brakes. Power brakes can either be of the drum type or disc type. The disc brake is favored since it offers more braking capacity than the drum-type brake. The wet type of disc brake is preferred because it can be installed inside the differential housing where it is isolated from the dirt and grime of day-to-day operations.

The wet-type brake is in contact with the lubricating oil. A special oil is required which lubricates all the relatively moving parts such as the differential gears, transmission gears, etc. At the same time, the lubricating oil must not prevent proper braking action. Furthermore, it must not promote brake chatter. Chatter is caused by slip-stick operation of the brakes when they are in contact with certain types of fluids.

Equipment manufacturers would like to use one lubricating functional fluid in all systems of the machinery except for the motor crankcase. Thus, an all-purpose lubricating functional fluid must provide proper lubrication of the relatively moving parts in the transmission and differential as well as allow proper braking action. It must also not prevent proper clutch lock-up in wet-clutch power take-off (pto) units and must provide proper lubrication for the power steering pump and the hydraulic system pump.

Furthermore, the fluid should be able to take up a certain amount of free water which may accidentally enter the system, for example, during a rainstorm. This prevents damage to relatively moving parts by preventing their coming into contact with a large mass of free water, thereby temporarily losing lubrication. It is generally assumed that small amounts of water, generally one-half to one weight percent of the lubricating oil composition, will be vaporized as the system warms up to operating temperatures.

Lubricating functional fluids generally become quite hot when the systems containing them have been in operation for awhile. These fluids must therefore exhibit long-term thermal stability and anti-oxidation properties in order for the fluids to have a reasonably long useful life. The fluids of this invention are designed to meet the above criteria.

SUMMARY OF THE INVENTION

The lubricating oil compositions of this invention comprise (A) a major amount of an oil of lubricating viscosity, and (B) an effective amount of each of the following: (1) a neutral Group II metal salt of a hydrocarbyl sulfonic acid; (2) an overbased Group II metal salt of a hydrocarbyl sulfonic acid; (3) a Group II metal salt of a dihydrocarbyl dithiophosphoric acid; (4) tricresyl phosphate; and (5) a sulfurized mixture of olefins and fatty acid esters. These fluids are particularly valuable since they provide excellent lubrication between relatively moving parts, are fully satisfactory as hydraulic fluids and greatly reduced chatter in wet-type disc brakes.

DESCRIPTION OF THE INVENTION

As described above, the lubricating functional fluid compositions of this invention comprise a major amount of oil of lubricating viscosity and an effective amount of each of a substantially neutral Group II metal salt of the hydrocarbyl sulfonic acids; an overbased Group II metal salt of a hydrocarbyl sulfonic acid, a Group II metal salt of a dihydrocarbyl dithiophosphoric acid, tricresyl phosphate, and a sulfurized mixture of olefins and fatty acid esters.

The Neutral Sulfonate

The substantially neutral Group II metal salt of a hydrocarbyl sulfonic acid is present to improve, among other things, the water tolerance of the lubricating oil composition. This means that the lubricating oil composition will absorb a certain amount, generally one-half to one weight percent, of free water rather than allow it to accumulate in the bottom of the housing containing these lubricating oil compositions. This prevents damage to the lubricated parts by preventing these parts from coming into contact with a large mass of free water, thereby temporarily losing lubrication. Generally, the neutral Group II metal sulfonate disperses the water in the lubricating oil composition. The water is then generally vaporized and expelled the next time the system is warmed up and operated.

The neutral Group II metal salts of hydrocarbyl sulfonic acids also function as detergents and dispersants. They prevent the deposit of contaminants formed during high temperature operation of the system containing the functional fluid.

The Group II metal salts of hydrocarbyl sulfonic acids are well known. Many of these salts have been used as additives for lubricating oil compositions. These salts comprise the neutralization product obtained by reacting a Group II metal base with a hydrocarbyl sulfonic acid. The hydrocarbyl portion of the sulfonate can be derived from a hydrocarbon oil stock or synthetic organic moiety.

Several processes for preparing the sulfonates are briefly outlined in U.S. Pat. No. 2,398,713. Other processes are also discussed in U.S. Pat. No. 2,388,677.

The oil-derived hydrocarbyl moiety is a mixture of different hydrocarbyl groups, the specific composition of which depends upon the particular oil stock which was used as a starting material. The fraction of the oil stock which is sulfonated is predominantly an aliphatic-substituted carbocyclic ring. The sulfonic acid group generally attaches to the carbocyclic ring. The carbocyclic ring is predominantly aromatic in nature, although a certain amount of the cycloaliphatic content

of the oil stock will also be sulfonated. The aliphatic substituent of the carbocyclic ring affects the oil solubility and detergent properties of the sulfonate. Suitably, the aliphatic substituent contains from about 12 to about 30 carbon atoms and preferably from about 15 to 25 carbon atoms. The aliphatic substituent can be straight or branched chain and can contain a limited number of olefinic linkages; preferably less than 5% of the total carbon-to-carbon bonds are unsaturated.

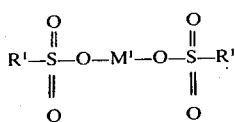
Synthetic organic moieties suitable for conversion to hydrocarbyl sulfonic acids include alkylated aromatics. A particularly suitable alkylated aromatic is known as synthetic heavy alkylate. This material is obtained as a by-product from the preparation of hard detergent alkylate (C¹²-C¹⁵ alkyl benzenes prepared by alkylating benzene with propylene tetramer and pentamer in the presence of hydrofluoric acid). During alkylation, some fragmentation of the alkyl polymer occurs, yielding light, hard benzenes (mostly C⁴-C⁶ monosubstituted benzenes). These light materials are alkylated a second time with C¹⁸-²⁰ straight-chain cracked wax olefin to yield the synthetic heavy alkylates. The sulfonic acid can be obtained by sulfonating the alkylate with 26% sulfuric acid. The Group II metal salts can be obtained by neutralizing the sulfonic acid with sodium hydroxide and converting the salt thus obtained to the Group II metal salt by metathesis.

Both the oil-derived and synthetic hydrocarbyl moieties are predominately hydrocarbyl in nature. However, they may contain small, sometimes adventitious, amounts of atoms other than carbon and hydrogen. The functional groups containing these other atoms (such as nitrogen, oxygen and sulfur) should not cause any substantial degradation of the properties of the neutral sulfonate as discussed above.

The neutral sulfonates are preferably substantially neutral, i.e., they have very little alkalinity value as discussed below. Any alkalinity value which these neutral sulfonates may have is generally caused by a slight excess of the Group II metal base used to neutralize the sulfonic acid.

The Group II metal cation of the sulfonate suitably is magnesium, calcium, strontium, barium, or zinc, and preferably is magnesium, calcium or barium. Most preferably the Group II metal is calcium.

Preferably, the Group II metal salt of the hydrocarbyl sulfonic acid has the following formula:



wherein: (a) each R' represents a hydrocarbyl group as described above, and (b) M' represents a Group II metal cation as described above.

The oil-soluble substantially neutral Group II metal salts of hydrocarbyl sulfonic acids are present in the lubricating oil compositions of the invention in an amount effective to prevent deposit of contaminants formed in the oil during severe high temperature operation of the system and to impart water tolerance to the composition. This effective amount can vary widely and typically ranges from 1 to about 6 weight percent, preferably from about 1.4 to about 4 weight percent of the total lubricating oil composition.

The Overbased Sulfonate

The oil-soluble overbased Group II metal salt of a hydrocarbyl sulfonic acid is present to impart, among other things, thermal stability, oxidation inhibition, and rust inhibition.

These oil-soluble overbased Group II metal salts of hydrocarbyl sulfonic acids are well known. Many of these salts have been used as additives for lubricating oil compositions.

These overbased sulfonates are obtained by "overbasing" the neutral Group II metal hydrocarbyl sulfonates discussed above and illustrated in formula I.

These overbased materials are characterized by metal content in excess of that which would be present according to the stoichiometry of the metal cation and the sulfonic acid compound which is overbased. Thus, a monosulfonic acid, when neutralized with a Group II metal basic compound, e.g., a calcium compound will produce a normal or neutral sulfonate containing one equivalent of calcium for each equivalent of acid. In other words, the normal metal sulfonate will contain 1 mol of calcium for each 2 mols of the monosulfonic acid.

By using well-known procedures, "overbased" or "basic" complexes of the sulfonic acid can be obtained. These overbased materials can contain amounts of metals many times in excess of that required to neutralize the acid. The stoichiometric excess can vary considerably, e.g., from about 0.1 to about 30 or more equivalents depending upon the reaction, the process, the conditions, etc.

The degree of overbasing can be expressed several ways. One method is to describe the "metal ratio". This method describes the ratio of the total chemical equivalents of metal in the product to the chemical equivalents of compound that is overbased, based on the known chemical reactivity and stoichiometry of the two reactants. Thus, in a normal (neutral) calcium sulfonate, such as that discussed above and exemplified in formula I, the metal ratio is one (1) and in an overbased sulfonate, the metal ratio can range from about 1.1 to 30 or more generally from about 5 to about 25.

Another method of expressing the degree of overbasing is to describe the "base ratio". This method describes the ratio of chemical equivalents of basic metal to the chemical equivalents of neutral metal. The neutral metal is the metal which would be expected to react with the compound to be overbased, i.e., the metal required to neutralize the sulfonate. The basic metal is the metal in excess of the neutral metal, i.e., it is the metal available to neutralize acidic materials present in the lubricating oil composition. Thus, a normal (neutral) calcium sulfonate has a base ratio of zero (0) and an overbase sulfonate can have a base ratio ranging from about 0.1 to about 30 or more generally from about 4 to about 24.

Another method of specifying the degree of overbasing is by stating the alkalinity value (AV) of the composition. The method for determining the alkalinity value of an overbased composition is set forth in ASTM method D-2896. Briefly, the alkalinity value is stated as the number of milligrams of potassium hydroxide per gram of composition to which the overbasing is equal. For example, if the composition is overbased to the extent that it has the same acid-neutralizing capacity per gram as 10 milligrams of potassium hydroxide, the composition is given an alkalinity value of 10. Alkalinity

ity values can range up to about 600. Of course, the lower limit is zero for a neutral sulfonate, with values of 10 to 50 being common for slightly overbased sulfonates. Highly overbased sulfonates have values ranging from about 275 to about 450.

A discussion of the general method of preparing overbased sulfonates and other overbased products is disclosed in Le Suer, U.S. Pat. No. 3,496,105 issued Feb. 17, 1970, particularly at columns 3 and 4.

The oil-soluble overbased Group II metal salts of hydrocarbyl sulfonic acids are present in the lubricating oil composition of the invention in an amount effective to impart thermal stability, oxidation inhibition, and/or rust inhibition. The effective amount can vary widely and typically ranges from about 1 to about 6 weight percent, preferably from about 1.4 to about 4 weight percent of the total lubricating oil composition.

The Dithiophosphoric Acid Salt

As mentioned above, the lubricating functional fluid compositions of the invention contain Group I metal salts of dihydrocarbyl dithiophosphoric acids. The function of this salt is to act as an oxidation inhibitor thereby preventing the formation of a variety of oxygenated hydrocarbon products which impairs the usefulness and shortens the useful life of the lubricating oil. It also functions as an anti-wear agent.

As stated above, the temperatures to which the functional fluids of the hydraulic and transmission systems are subjected are often severe. Under these thermally severe conditions, not only is the lubricating oil quite prone to oxidation, but the anti-oxidants themselves quite often undergo thermal degradation. Accordingly, the oxidation inhibitor used must have good thermal stability at these relatively high temperatures, or its thermal degradation products must also exhibit anti-oxidation properties.

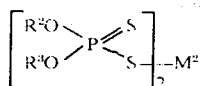
It has now been found that the above-mentioned Group II metal salts of dihydrocarbyl dithiophosphoric acids exhibit the anti-oxidant and thermal-stability properties required for the severe service proposed. Group II metal salts of phosphodithioic acids have been described previously. (See, for example, U.S. Pat. No. 3,390,080, columns 6 and 7, wherein these compounds and their preparation are described generally.)

Suitably, the Group II metal salts of the dihydrocarbyl dithiophosphoric acids useful in the lubricating oil compositions of this invention contain from about 4 to about 12 carbon atoms, preferably from about 6 to about 12 carbon atoms, more preferably from about 8 to 12 carbon atoms, and most preferably 8 carbon atoms in each of the hydrocarbyl radicals.

Examples of suitable hydrocarbyl groups include butyl, sec-butyl, iso-butyl, tert-butyl, pentyl, n-hexyl, sec-hexyl, n-octyl, mixed primary octyls, 2-ethylhexyl, decyl, dodecyl, and the like. A hydrocarbyl group which gives excellent results is dithiophosphates in the oils of this invention is n-octyl.

The metals suitable for forming these salts include barium, calcium, strontium, zinc, and cadmium, of which zinc is preferred.

Preferably the Group II metal salts of the dihydrocarbyl dithiophosphoric acids have the following formula:



wherein: (c) R^2 and R^3 each independently represent hydrocarbyl groups as described above, and (d) M^2 represents Group II metal cation as described above.

The dithiophosphoric acid salt is present in the lubricating oil compositions of this invention in an amount effective to inhibit the oxidation of the lubricating oil. This effective amount can vary widely and typically ranges from about 1 to about 4.5 weight percent, preferably from about 1.2 to about 2.25 weight percent of the total lubricating oil composition.

Tricresyl Phosphate

The lubricating oil compositions of this invention include tricresyl phosphate. This material is present in the lubricating oil compositions of this invention in order to provide the proper environment for break-in of new or "green" gears. Tricresyl phosphate provides this break-in protection by acting as an extreme pressure (EP) agent. It provides the requisite load-carrying ability of the fluid without adversely affecting the other performance characteristics of the fluid.

Tricresyl phosphate is the phosphoric acid ester of cresol. Cresol is hydroxy toluene and is available in ortho, meta and para isomers. A common source of cresol is petroleum from which the cresol (cresylic acid) is obtained by distillation and extraction. Because of its ready availability and low cost, mixed cresols obtained from petroleum are preferred for preparing the tricresyl phosphate used in the lubricating oil composition for this invention.

The tricresyl phosphate is present in the lubricating oil compositions of this invention in an amount effective to impart extreme-pressure protection properties to the oil. This effective amount can vary widely and typically ranges from about 0.5 to about 1.5 weight percent, preferably from about 0.75 to about 1.5 weight percent of the total lubricating oil composition. The Sulfurized Mixture of Olefins and Fatty Acid Esters

The lubricating oil compositions of this invention include sulfurized mixtures of olefins and fatty acid esters. These sulfurized mixtures are hereinafter referred to as "cross-sulfurized ester-olefins". These cross-sulfurized ester-olefins are present to provide extreme-pressure properties and impart additional oiliness to the lubricating oil. They usually exhibit equivalent or better oiliness and extreme-pressure properties than the sulfurized sperm whale oil materials presently available in relatively small quantities because the United States Federal Government has placed whales on the endangered species list. In addition, these crosssulfurized ester-olefins have extremely good thermal stability. (They also appear to counteract any tendency for wet disc brakes to chatter.)

The esters are derived from fatty acids containing 10-25 carbon atoms. Examples of the fatty acids include unsaturated monoethenoid acids such as oleic acid ($\text{C}^{17}\text{H}_{33}\text{COOH}$), palmitoleic acid ($\text{C}^{14}\text{H}_{27}\text{COOH}$), petroselenic acid ($\text{C}^{17}\text{H}_{33}\text{COOH}$), urucic acid ($\text{C}^{21}\text{H}_{41}\text{COOH}$), gadoleic acid ($\text{C}^{19}\text{H}_{37}\text{COOH}$), vaccenic acid ($\text{C}^{17}\text{H}_{33}\text{COOH}$), and other naturally occurring and synthetic acids of the formula $\text{C}_n\text{H}^{2n-1}\text{COOH}$; and unsaturated polyethenoid acids such as linoleic acid ($\text{C}^{17}\text{H}_{31}\text{COOH}$). Also included are saturated acids such as n-undecanoic ($\text{C}^{10}\text{H}_{21}\text{COOH}$), lauric ($\text{C}^{11}\text{H}_{23}\text{COOH}$), myristic ($\text{C}^{13}\text{H}_{27}\text{COOH}$), palmitic ($\text{C}^{15}\text{H}_{31}\text{COOH}$), stearic ($\text{C}^{17}\text{H}_{35}\text{COOH}$), and other nat-

urally occurring and synthetic acids of the formula $C_nH^{2n+1}COOH$. Branched-chain fatty acids are also included, as well as substituted acids such as ricinoleic ($C^{17}H^{32}OHCOOH$).

Another suitable acid is tall oil. Tall oil is a byproduct of the sulfate process for the manufacture of wood pulp. It consists of about 50 percent resin acids. The resin obtained from various species of pine is called rosin, which is chiefly abietic acid, $C^{20}H^{30}O^2$. The remaining 50 percent of tall oil consists of unsaturated fatty acids, chiefly oleic and linoleic acids. Thus, "derosinified tall oil" is a convenient source of these unsaturated acids. Rosin is a source of the undesirable auxiliary properties of lube oil additives when it is present in high percentage in tall oil prior to neutralization and/or sulfurization. Derosinified tall oil is commercially available. For use in embodiments of the present invention, the derosinified tall oil contains less than five percent of rosin.

The esters are illustrated by isopropyl oleate, ethyl linoleate, pentadecyl oleate, eicosyl linoleate, decenyl stearate, eicosenyl laurate, propyl linoleate, pentadecenyl linoleate, undecyl ricinoleate, pentadecyl tallate, etc.

It is essential that either the alcohol or the fatty acid of the ester be unsaturated. This is necessary for effective cross-sulfurization. Although the usefulness of these materials as lubricating additives is independent of any particular supposition about the structure of the sulfurized products, it is believed that the sulfurization step introduces sulfur by forming linkages with $-(S)-$ between ethylenic double-bond positions. Thus it is believed that either the alcoholic or acidic portions of the ester molecule must be unsaturated to form effective linkages with the olefins.

Examples of the alcohols which find use in preparing the ester used in the present invention are methyl alcohol, propyl alcohol, butyl alcohol, hexanol, octanol, undecanol, tetradecanol, etc. Monoethenoid and polyethenoid alcohols are also included, such as 1-hydroxy-3-hexene, 2-hydroxy-5,7-dodecadiene, 1-hydroxy-4,7-pentadecadiene, 2-hydroxy-10-docosene, etc. The alcohols can be straight-chain or branched chain or partially branched and partially straight-chain alcohols. Substituted alcohols are also included, such as the 1,2-glycols, 1,3-glycols, etc.

The olefins are aliphatic alkenes. Particularly preferred are the cracked wax olefins, which are predominantly straight-chain $C^{10}-C^{25}$ alpha-olefins. Other olefins within the scope of this invention include monoethenoid and polyethenoid olefins, conjugated olefins, and partially substituted olefins. The olefins may be straight chain or branched, or they may be partially straight chain and partially branched.

An excellent cross-sulfurized ester-olefin is obtained from a mixture of the ester of oleic or linoleic acid with a $C^{10}-C^{20}$ alcohol, such as undecyl alcohol and a $C^{11}-C^{18}$ fraction of cracked wax olefins which is sulfurized to a sulfur content of about 10 percent; the ratio of olefin to ester in the mixture being about 1-2:1.

Another excellent cross-sulfurized ester-olefin is obtained when derosinified tall oil is reacted with an alkyl alcohol and mixed with cracked-wax olefin. The mixture is sulfurized to the extent of 4-10 percent of sulfur by weight. More preferably, derosinified tall oil is reacted with a $C^{10}-C^{20}$ alkyl alcohol and mixed with $C^{11}-C^{18}$ cracked wax olefin in a mol ratio of 1:1-2 and the

mixture sulfurized to the extent of 4-10 percent sulfur by weight.

Method of Preparation

Cross-sulfurized ester-olefin for use in this invention can be prepared by a variety of methods. The methods which have been utilized are designated as the 1-Step, 1½-Step, and 2-Step process, respectively.

In the 1-Step Process, a mixture of alcohol, fatty acid, olefin and sulfur is heated under an inert atmosphere for a period of from about 5 to about 25 hours and preferably from about 10 to about 20 hours. The reaction temperature is maintained at about 160°C to about 180°C, and preferably about 165°C to about 175°C. The reaction product is a crosssulfurized ester-olefin.

The 2-Step Process proceeds by acid-catalyzed esterification of the fatty acid as the first step. The ester is then mixed with the olefin and sulfur and cross-sulfurized as in the 1-Step Process. The 1½-Step Process comprises a noncatalytic esterification of the fatty acid, followed by the usual cross-sulfurization with olefin.

In the 1-Step Process, the mol ratio of olefin to acid to alcohol can vary from about 0.5:1:1 to about 4:1:1, but about 1-2:1:1 is the preferred ratio. Similar mol ratios are preferred in the other processes.

The cross-sulfurized ester-olefins are present in the lubricating oil compositions of this invention in amounts effective to provide extreme-pressure properties and to reduce chatter of the brakes. The effective amount usually ranges from about 0.5 to 1.5 weight percent, more usually from about 0.75 to about 1.25 weight percent of total lubricating oil composition.

The Lubricating Oil

The lubricating oils used for the hydraulic and transmission fluids generally have viscosities in the range from about 75 to 1,000 SUS (Saybolt Universal Seconds) at 100°F and from about 35 to 75 SUS at 210°F. The base oils for these functional fluids are generally light lubricating oils ordinarily having a viscosity in the range of about 50 to 400 SUS at 100°F and 30 to 50 SUS at 210°F. The viscosity of both the base oil and the finished lubricating oil can be chosen and tailored to meet the requirements of the individual manufacturer of the equipment in which the oil is to be used. For example, Deere and Company specify in their specification J14B that the finished oil should have a maximum viscosity at 0°F, extrapolated, of 12,000 SUS and a viscosity at 210°F of 54 to 58 SUS. Mixtures of base oils and various viscosity index improvers can be combined to provide oils having the proper viscosity.

The base stock generally is a lubricating oil fraction of petroleum, either naphthenic or paraffinic base, unrefined, acid-refined, hydrotreated, or solvent-refined, as required by the particular lubricating need.

Also, synthetic oils meeting the viscosity requirements, either with or without viscosity index improvers may be used as the base stock.

Other Additives

The functional fluids of this invention will normally contain a number of other additives. It is usually necessary to heavily compound such oils in order to meet the exacting requirements specified by the manufacturers of heavy-duty equipment.

Included among the other additives which can be used are anti-foam agents such as various silicone and fluorosilicone compounds commercially available.

Another useful functional fluid additive is a seal swell agent. A variety of compositions are useful for this function and include the bottom product from catalytic cracking units used in producing gasoline. These materials, containing a high percentage of condensed ring aromatics, are commercially available from a number of sources. One excellent seal swell agent is available from Lubrizol Corp. under the name "Lubrizol 725." Another is available from Ashland Oil Co., "ASHLAND APON".

Also generally included in functional fluids are viscosity improving agents. These are normally high-molecularweight polymers such as the acrylate polymers. Useful examples include the copolymer of alkyl methacrylate with vinyl pyrrolidine available under the trade name "Acryloid" from Rohm and Haas. Other alkyl methacrylate copolymers with nitrogencontaining substituted vinyl are also available. Terpolymers derived from styrene, alkyl acrylate and nitrogen-containing polymer precursors are available from Lubrizol Corp. under the name "Lubrizol 3,700" Series. Methacrylates are available from Texaco Inc. Other viscosity improving agents include hydrocarbon polymers such as polyisobutylene or ethylene/propylene copolymers.

These additives will be present in the functional fluid in varying amounts necessary to accomplish the purpose for which they were included. For example, the antifoam agent will generally be present in from about 2 to about 50 parts per million. The viscosity index improver will normally be present in from about 0.5 to 15 weight percent of the base oil, more usually from about 2 to about 10 weight percent of the base oil. The seal swell agent will be present in an amount effective to control changes in the size of the seals with which the functional fluid comes in contact. For example, the bottoms from the catalytic cracking unit will be present in an amount ranging from about 1 to about 10 percent, more usually from about 2 to about 5 percent weight.

Quite often it is most convenient to prepare the lubricating oil additives as a concentrate package which may be then shipped to the user's location. The user then obtains the base oil from whatever source he desires and blends the finished lubricating oil compositions of this invention as needed.

Generally, to save shipping costs, the concentrate package contains the smallest amount of diluent oil possible and the maximum amount possible of each of the additives. The quantity of each additive present in the concentrate will be correspondingly higher than that found in the finished lubricating oil but the same relative proportions of each of the additives will generally be maintained in the concentrate. However, in some cases it may be found desirable to prepare an additive package containing less than all of the additives. In this case, generally two or more additive packages are combined together with the base oil to provide the finished lubricating oil. Such matters are well within those skilled in the art and need not be further discussed.

EXAMPLES

The following examples are offered by way of illustration and not by way of limitation.

EXAMPLE 1

An additive concentrate was prepared having the

composition shown in Table I. This concentrate was added to lubricating oil stocks which contained a seal swell agent and low (Oil No. 1, Table II) and high (Oil No. 2, Table II) levels of a viscosity index improver. The concentrate was added to the lube oil stocks at the rate of 8.10 weight percent. This provides a finished oil in which components 1 through 6 are at the concentration shown in Table I.

TABLE I

No.	Component	Additive Package	
		Concentration, Weight Percent Concentrate	Concentration, Weight Percent Finished Oil
1	Neutral calcium salt of a hydrocarbyl sulfonic acid prepared from a neutral lubricating oil	25.27	2.05
2	Overbased version of component No. 1, 9.3 base ratio, 11.4% calcium	26.04	2.11
3	Zinc di(n-octyl)dithiophosphate	18.60	1.51
4	Tricresyl phosphate	12.35	1.0
5	Cross-sulfurized mixture of the ester of a C ₁₂ -C ₁₃ alcohol & deroxinified tall oil & a cracked wax olefin (C ₁₅ -C ₁₈), 10.2 wt.% sulfur fluoro-silicone	12.35	1.0
6	Foam inhibitor	0.2469	20 ppm
7	Diluent oil	5.1431	

These two finished oils were tested for various physical properties including rust prevention and copper corrosion. The results of these tests are shown in Table II below.

TABLE II

	Performance Tests	
	Fluid No. 1	Fluid No. 2
Viscosity		
-20°F, (16 hr.) CP	26,800	17,200
-20°F, (64 hr.) CP	30,500	20,100
0°F, CP	4,010	3,900
0°F, CSS*, CP	2,450	2,430
100°F, SUS	269	273
210°F, SUS	52.7	54.2
Index	115	128
Compatibility with Rubber Materials (JD Method)		
Volume change, %	1.10	1.08
Durometer change	none	none
Additive separation	none	none
Oxidation Test		
Evaporation loss	0.5	0.43
Viscosity increase at 210°F, %	1.0	0.25
Sludge formation	none	none
Additive separation	none	none
Humidity Cabinet Test (ASTM-D-1748)		
Hours to rust	100+	100+
Copper Strip Corrosion Test		
3 Hrs. at 212°F (ASTM-D-130)	1A	1A
Timken Test (ASTM 2782)		
OK load, lbs	—	25
Foam Test (ASTM-D-892)		
	T S	T S
Seq. I	0 0	5 0
Seq. II	20 0	25 0
Seq. III	0 0	0 0

*CCS = Cold Cranking Simulator

The above results demonstrate that an excellent hydraulic fluid is provided by this invention.

In addition to the above tests, Oil No. 2 was tested for gear wear protection according to the FZG Gear Test (DIN-51,354). In this test, Dip-lubricated gears are

weighed and operated at a fixed speed and fixed initial oil temperature (90°C) in the gear oil under test. The load on the teeth is increased in increments. After each load stage, the weight changes are determined and recorded. For comparison, a gear oil containing a commercially available additive prepared from sulfurized sperm whale oil was tested. This additive has been the standard of the industry for the past eight years. The results of the tests are shown in Table III.

TABLE III

Load Stage	FZG Gear Test Oil No. 2	Reference oil
1-11 12	pass fail	pass fail

These results demonstrate that results are obtained comparable to the best obtained from the reference oil.

What is claimed is:

1. A lubricating oil composition comprising:

A. a major amount of an oil of lubricating viscosity, and

B. an effective amount of each of:

1. an oil-soluble substantially neutral Group II metal salt of a hydrocarbyl sulfonic acid;

2. an oil-soluble overbased Group II metal salt of a hydrocarbyl sulfonic acid;

3. an oil-soluble Group II metal salt of a dihydrocarbyl dithiophosphoric acid;

4. tricresyl phosphate; and

5. a sulfurized mixture of C¹⁰⁻²⁵ olefins and fatty acid esters of C¹⁰⁻²⁵ fatty acids and C¹⁻²⁵ alkyl or alkenyl alcohols, in an olefin-to-ester mol ratio of about 1-2:1 wherein the fatty acid and/or alcohol is unsaturated.

2. A lubricating oil composition of claim 1 wherein:

A. said Group II metal of said Group II metal salt of a hydrocarbyl sulfonic acid is magnesium, calcium or barium,

B. said Group II metal of said Group II metal salt of a dihydrocarbyl dithiophosphoric acid is zinc, and

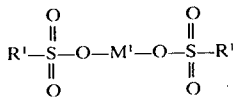
C. said fatty acid esters are derosinified tall oil esters of a C¹⁻²⁵ alkyl or alkenyl alcohol.

3. A lubricating oil composition comprising:

A. a major amount of an oil of lubricating viscosity, and

B. an effective amount of each of:

1. an oil-soluble neutral Group II metal salt of a hydrocarbyl sulfonic acid of the following formula:

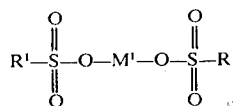


wherein

a. each R¹ represents a hydrocarbyl group, and

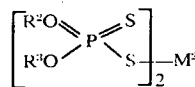
b. M¹ represents a Group II metal cation;

2. an oil-soluble overbased Group II metal salt of a hydrocarbyl sulfonic acid of the following formula:



wherein R¹ and M¹ are as defined above;

3. an oil-soluble Group II metal salt of a dihydrocarbyl dithiophosphoric acid of the following formula:



wherein:

c. R² and R³ each independently represent hydrocarbyl groups, and

d. M² represents a Group II metal cation;

4. tricresyl phosphate; and

5. a sulfurized mixture of C¹⁰⁻²⁵ olefins and fatty acid esters of C¹⁰⁻²⁵ fatty acids and C¹⁻²⁵ alkyl or alkenyl alcohol, in an olefin-to-ester mol ratio of about 1-2:1 wherein the fatty acid and/or alcohol is unsaturated.

4. A lubricating oil composition of claim 3 wherein:

a. M¹ represents calcium, magnesium or barium,

b. R² and R³ each represent a hydrocarbyl group containing from 8 to 12 carbon atoms,

c. M² represents zinc,

d. said olefin is a C¹¹-C¹⁸ alpha-olefin and said fatty acid ester is a derosinified tall oil ester of a C¹⁰⁻²⁰ alcohol.

5. A lubricating oil composition of claim 4 wherein:

a. said neutral Group II metal salt of a hydrocarbyl sulfonic acid is present in from 1 to 6 weight percent of said composition;

b. said overbased Group II metal salt of a hydrocarbyl sulfonic acid is present in from 1 to 6 weight percent of said composition;

c. said Group II metal salt of a dihydrocarbyl dithiophosphoric acid is present in from 1 to 4.5 weight percent of said composition;

d. said tricresyl phosphate is present in from 0.5 to 1.5 weight percent of said composition; and

3. said sulfurized mixture of said olefins and said fatty acid esters is present in from 0.5 to 1.5 weight percent of said composition.

6. A lubricating oil composition of claim 4 wherein:

a. said neutral Group II metal salt of a hydrocarbyl sulfonic acid is present in from 1.4 to 4 weight percent of said composition;

b. said overbased Group II metal salt of a hydrocarbyl sulfonic acid is present in from 1.4 to 4 weight percent of said composition;

c. said Group II metal salt of a dihydrocarbyl dithiophosphoric acid is present in from 1.2 to 2.25 weight percent of said composition;

d. said tricresyl phosphate is present in from 0.75 to 1.25 weight percent of said composition; and

e. said sulfurized mixture of said olefins and said fatty acid esters is present in from 0.75 to 1.25 weight percent of said composition.

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