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[72] Inventor William H. Chandler
Wood River, Ill.
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[73] Assignee Shell Oil Company
New York, N.Y.

[54] LUBRICANT COMPOSITIONS

6 Claims, No Drawings

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[50] Field of Search ..... 252/32.7 E, 33, 389, 75, 400

[56] References Cited

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Primary Examiner—Daniel E. Wyman
Assistant Examiner—I. Vaughn
Attorney—Harold L. Denkler

ABSTRACT: The corrosivity toward copper of lubricating oils containing a polyvalent metal salt of a diester of dithiophosphoric acid is substantially reduced by incorporating therewith a zinc dialkyl naphthalene sulfonate and a basic alkaline earth metal petroleum sulfonate.

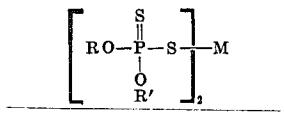
LUBRICANT COMPOSITIONS

This invention relates to lubricant compositions possessing good oxidation properties and which are noncorrosive to copper. More particularly it relates to lubricating oils containing polyvalent metal salts of diesters of dithiophosphoric acids, zinc dialkyl naphthalene sulfonates and basic alkaline earth metal petroleum sulfonates.

Hydraulic fluids employed, for example, in transmission, differentials, power steering mechanisms, etc., of tractors and other motorized farm equipment, must not only have good oxidation stability and antiwear properties, but must also be noncorrosive to metals found in such systems, e.g. aluminum, steel and copper. To impart the requisite antioxidation and load-carrying properties to such multipurpose hydraulic fluids, a natural choice of extreme pressure additives would be the metal salts of the esters of dithiophosphoric acids which are recognized in the art to perform these functions. Unfortunately, however, this class of additives has the disadvantage of being extremely corrosive to certain metals, particularly to copper, and therefore would not be suitable for use in the above application unless this deficiency could be corrected. A considerable number of additives have been proposed for use in conjunction with various dithiophosphates to reduce or overcome this problem. By and large, however, the results obtained have not been satisfactory. Frequently it has been found that those additives which are somewhat effective in reducing the corrosivity of dithiophosphates to copper, adversely affect the antioxidation and antiwear properties of these salts. The present invention provides a novel additive combination, which substantially reduces the corrosivity of dithiophosphate-containing lubricants toward copper without adversely effecting the beneficial qualities of such lubricants.

It has now been found that the copper corrosivity of lubricating oil compositions containing polyvalent metal salts of diesters of dithiophosphoric acids can be substantially reduced by incorporating therein minor amounts each of a zinc dialkyl naphthalene sulfonate and a basic alkaline earth metal petroleum sulfonate. Thus, by practice of the invention, lubricating oil compositions are obtained which not only have excellent oxidation stability and antiwear properties, but are also substantially noncorrosive to copper thus permitting their use in systems wherein exposure to copper is likely. The reduced tendency of the present compositions to attack copper is attributed to the presence of both the zinc dialkyl naphthalene sulfonate and the basic metal petroleum sulfonate. The use of either of these additives alone in the dithiophosphate-containing lubricating oil does not significantly inhibit copper corrosion, but in fact, in the case of zinc dinonyl naphthalene sulfonate, actually increases corrosion. The significant advantages of the present additive combination, therefore, is not the result of the contribution of these additives individually, but rather to the complementary interaction between the additives which results in a composition having properties superior to those predictable from the individual properties of the additives.

Metal dithiophosphates which form effective combinations with zinc dialkyl naphthalene sulfonates and basic metal petroleum sulfonates are those having the formula



wherein R and R′ may be alkyl, aryl, alkaryl or aralkyl, hydrocarbon radicals containing a total of from seven to 50 carbon atoms and M is a divalent metal. Preferably the R radical contains from one to 25 carbon atoms and R′ contains from five to 25 carbon atoms. R and R′ may be alike or dissimilar. Examples of suitable R and R′ groups include methyl, propyl, hexyl, octyl, decyl, dodecyl, tetradecyl, hexadecyl, octadecyl, hexylphenyl, octylphenyl, decylphenyl, dodecylphenyl, hexadecylphenyl, octadecylphenyl and the like.

Divalent metals suitable for forming salts with diesters of dithiophosphoric acids include zinc and alkaline earth metals such as calcium, barium and strontium. Zinc salts of dithiophosphate esters have been found to be particularly effective in the lubricant compositions of the invention. An especially advantageous salt of this type is zinc bis (octylphenyl)dithiophosphate. Methods of preparing the afore-described metal dithiophosphates are well known to the art.

Zinc dialkyl naphthalene sulfonates which may be used in accordance with the invention are those having two alike or dissimilar alkyl substituents on the naphthalene ring, said alkyl substitutents having from four to 12 carbon atoms. A particularly advantageous compound of this type is zinc dinonyl naphthalene sulfonate which is commercially available under the trade name Na-Sul ZS.

Basic alkaline earth metal petroleum sulfonates suitable for use in the present compositions include those derived from petroleum sulfonic acids having a molecular weight of between 350 to 1,500, preferably between 400 and 800. By basic sulfonate is meant that the end product contains excess base and has a basicity from 20 percent or more to 1,000 percent, preferably from 40 to 800 percent, in excess of that normally required to neutralize the acid to produce a neutral salt. The term "basic" therefore includes highly basic petroleum sulfonates such as those described in U.S. Pat. No. 2,865,956 which are also very suitable for the purposes of the invention. Alkaline earth metal sulfonates which are particularly advantageous for use in the present compositions are basic calcium petroleum sulfonates.

The additive combination of the invention can be incorporated into mineral lubricating oils obtained from paraffinic, naphthenic, asphaltic or mixed base crudes and/or mixtures thereof, for example, neutral oils having viscosities which vary over a wide range such as from 100 to 6,500 SSU at 100° F. In addition to mineral lubricating oils, the additive combination can be used in synthetic lubricating oils such as polymerized olefins, alkylene oxide polymers, and synthetic esters and ethers. Mixtures of natural and synthetic oils can also be used.

The metal salts of diesters of dithiophophoric acids are employed in the present compositions in amounts sufficient to inhibit oxidation and impart antiwear properties to the lubricating oil. Concentrations of from 0.1 to 10 percent by composition weight are generally satisfactory for these purposes, preferably from 0.2 to 5 percent by weight. Zinc dialkylnaphthalene sulfonates can be incorporated into the present lubricating oils in amounts of from 0.1 to 5 percent by weight of the total composition. However, concentrations of from 0.5 to 2.5 percent by weight will generally be sufficient to impart the desired properties to lubricating oils. Basic alkaline earth metal petroleum sulfonates are normally employed in concentrations of from 1 to 20 percent by weight, preferably from 4 to 15 percent by weight.

In addition to the additive combination of the invention, any other additives recognized in the art to perform a particular function or functions may also be incorporated into the present compositions. These include pour point depressants, viscosity index improvers such as acrylate and methacrylate polymers, dispersants, additional antioxidants, antifoam agents, antirust agents and the like.

The invention will be further described by means of the following examples. These examples are given, however, for illustrative purposes only and the invention in its broader aspects should not be limited thereto.

EXAMPLE I

To demonstrate the effectiveness of the zinc dialkyl naphthalene sulfonate and basic metal petroleum sulfonate combination in inhibiting copper corrosion caused by metal

dithiophosphates, a series of fluids were prepared and tested in accordance with the BT-10 Oxidation and Corrosion test as hereinafter described. The composition of the fluids and test results are shown in table I.

TABLE I

	Fluid				
	1	2	3	4	5
Composition, wt. percent:					
Zinc bis(octylphenyl)dithiophosphate		1.0	1.0	1.0	1.0
Zinc dinonyl naphthalene sulfonate				2.0	2.0
Basic calcium petroleum sulfonate (100% excess basicity)			10.0		10.0
Mineral oil	Balance	Balance	Balance	Balance	Balance
BT-10 oxidation and corrosion test [1] mg.:					
Aluminum, deposit/corrosion	2.1/1.1	2.9/1.0	0.6/0.4	2.8/0.8	0.2/0.3
Copper, deposit/corrosion	5.6/4.0	34.8/27.2	30.1/24.7	47.1/53.4	14.2/12.7
Brass, deposit/corrosion	3.7/1.6	2.6/1.5	1.6/1.1	3.5/1.7	1.3/1.3
Steel, deposit/corrosion	1.9/0.0	1.6/0.2	0.5/0.3	2.1/0.3	0.4/0.4

[1] This test is described in International Harvester Engineering Materials Specification B-6, June 1966 revision. The test procedure is designed to evaluate the oxidation stability of fluids and their corrosive attack on metals. The test essentially comprises immersing clean weighed metal strips, i.e. aluminum, copper, brass and steel, in the test fluid which is maintained at a temperature of 275° F. and through which air is bubbled at the rate of 3.0 liters per hour. At the end of the 100-hour test period, the strips are removed from the fluid and a determination made of the weight of residue on the strips, i.e. milligrams of deposit, and the weight loss of metal, i.e. milligrams of corrosion.

From the data of table I it is evident that the addition of zinc dialkyl dithiophosphate to a mineral lubricating oil significantly increases the corrosiveness of the resulting composition to copper (results of fluid 1 compared with fluid 2). It is likewise apparent that the addition of calcium sulfonate by itself (fluid 3) does not significantly reduce the corrosiveness of the dithiophosphate compound, nor does the addition of zinc dialkyl naphthalene sulfonate by itself (fluid 4). In fact fluid 4 actually is more corrosive to copper than fluid 2 containing the dithiophosphate compound alone. However, when calcium petroleum sulfonates are used in conjunction with zinc dialkyl naphthalene sulfonate as in fluid 5, the corrosiveness of the zinc dithiophosphate-containing fluid is substantially reduced, i.e. from 34.8 mg./27.2 mg. (fluid 2) to 14.2 mg./12.7 mg. (fluid 5).

EXAMPLE II

In order to demonstrate the effectiveness of the present additive combination in a typical hydraulic fluid composition, fluid 6 not in accordance with the invention was compared to fluid 7 containing the inventive additive combination by means of the previously described BT-10 Oxidation and Corrosion test. Fluid 6 contains a dithiophosphate compound and basic petroleum sulfonates, but does not contain zinc dialkyl naphthalene sulfonate. Fluid 7 is identical to fluid 6, except that 1.5 percent of the third essential ingredient has been added. The composition of the fluids and test results are presented in table II.

Table II

BT-10 Oxidation and Corrosion Test	fluid 6	Fluid 7
Aluminum, Deposit, mg./Corrosion, mg.	<0.1/<0.1	<0.1/<0.1
Copper, Deposit, mg./Corrosion, mg.	35.9/22.7	1.0/<0.1
Brass, Deposit, mg./Corrosion, mg.	0.7/0.5	0.3/0.3
Steel, Deposit, mg./Corrosion, mg.	0.1/<0.1	0.1/0.1

Fluid 6–59% w. HVI mineral oil (100 SUS 100° F.) with 25% w. LVI mineral oil (200 SUS 100° F.) containing 1.0%w. zinc bis(octyphenyl)dithiophosphate, 12%w. calcium petroleum sulfonate 0.5%w. copolymer of methyl vinyl pyridine with alkyl methacrylates, 0.5%w. dioctyl diphenylamine, 2.0%w. sulfurized sperm oil, 0.14%w. dye and 2 p.p.m. silicone fluid. Fluid 7 –Fluid 6 plus 1.5%w. zinc dinonyl naphthalene sulfonate.

The test results shown in table II further illustrate the effectiveness of zinc dinonyl naphthalene sulfonate in reducing copper corrosivity of dithiophosphate-containing fluids when employed in conjunction with basic petroleum sulfonates.

I claim as my invention:

1. A lubricant composition consisting essentially of a major amount of mineral lubricating oil containing an oxidation inhibiting and copper corrosion inducing amount of a polyvalent metal salt of a diester of dithiophosphoric acid having seven to 50 carbon atoms, and synergistic copper corrosion inhibiting proportions of zinc di-C_{4-12} alkylnaphthalene sulfonate and a basic alkaline earth metal petroleum sulfonate having a molecular weight of from 350 to 1,500 and a basicity of from 20 to 1,000 percent in excess of that normally required for neutralization.

2. The composition of claim 1 wherein the polyvalent metal is zinc.

3. The composition of claim 1 wherein the alkaline earth metal is calcium.

4. The composition of claim 3 wherein the zinc dialkyl naphthalene sulfonate is zinc dinonyl naphthalene sulfonate.

5. The composition of claim 1 wherein the ester radicals of the dithiophosphate salt are selected from the group consisting of alkyl, aryl, alkaryl and aralkyl.

6. The composition of claim 4 wherein the dithiophosphate is zinc bis (octylphenyl)dithiophosphate.

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