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ANTI-WEAR LUBRICANT

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This invention relates to mineral oil compositions and more particularly to improved lubricating oils containing both nickel and zinc dithiophosphates and preferably other additives such as detergents and anti-wear agents.

With the advent of higher compression internal combustion engines and increases in horsepower, much difficulty has been experienced in formulating a suitable lubricating oil composition capable of operating under severe conditions to protect effectively metal surfaces which come in contact with the oil. In an effort to overcome this problem, a wide variety of additive agents such as detergents, anti-oxidants, anti-wear agents, E.P. agents and the like have been proposed for the improvement of lubricating oils. Generally, each additive agent is employed to impart a particular characteristic to the base oil so as to afford a finished lubricating composition which is oxidation resistant, stable and non-corrosive to bearing metals, and which effectively reduces varnish and sludge forming tendencies and minimizes frictional and corrosive wear.

Unfortunately, however, while many of the proposed additive agents improve mineral lubricating oils, quite frequently these lubricating oil compositions have not proved to be entirely satisfactory for commercial use since apparently an additive agent which imparts a beneficial effect may impart unpredictable and undesirable wear of a given engine part. For example, a small amount of zinc dithiophosphate displays satisfactory oxidation and bearing corrosion inhibiting properties in a mineral lubricating oil. This additve is particularly active in reducing the corrosion of copper-lead bearings subjected to severe operating conditions of temperature and pressure. However, a lubricating oil containing a zinc dithiophosphate and a detergent type agent, such as, for example, basic barium mahogany sulfonate, was found to allow excessive wear of parts such as wrist pins, valve lifters and rocker arm shafts in recent models of valve-in-head engines. Elimination of the zinc dithiophosphate reduced wrist pin and rocker arm shaft wear but, of course, the resulting composition was subject to oxidative deterioration and the bad effects derived therefrom. The subsequent addition of an anti-wear agent, i.e. sulfurized sperm oil, to the composition containing the zinc dithiophosphate for practical purposes eliminated wrist pin wear and reduced valve lifter wear but did not solve the rocker arm shaft wear problems. In fact, the anti-wear agent increased rocker arm shaft wear of the base mineral oil. Thus, both the zinc dithiophosphate and the anti-wear agent caused excessive wear of the rocker arm shaft and as a result this compounded oil had undesirable properties. Such has been the case when using many additive agents and hence much difficulty has been experienced in formulating an engine lubricating oil of satisfactory anti-wear and anti-oxidant properties.

In accordance with the present invention, I have dis-

covered that an improved mineral oil base lubricating composition can be prepared by adding both nickel and zinc dithiophosphates to the base oil and these agents cooperate in a unique and unexpected manner to inhibit oxidation and deterioration of the oil without causing undue wear of any engine part, e.g. the rocker arm shaft of a valve-in-head engine. Other additive agents such as detergents and anti-wear type agents can also be with advantage included in the lubricating composition.

By the present invention, I have discovered that severe surface wear of engine parts can be substantially prevented and oxidation of the lubricating oil inhibited through the use of both the zinc and nickel dithiophosphates in mineral lubricating oil compositions. Neither the use of the zinc salt nor the nickel salt alone will provide the same results. Thus, although each salt inhibits oxidation of the base oil, each promotes or allows wear of a different part of the valve-in-head engine, e.g. the zinc salt causes rocker arm shaft wear while the nickel salt allows the spalling of valve lifters. Surprisingly, when these salts are used together, wear of the rocker arms and the valve lifters is minimized.

The oil-soluble nickel dithiophosphates employed in the lubricating compositions of the present invention can be obtained from a wide variety of diester dithiophosphoric acids conventionally prepared by reacting a sulfide of phosphorus, such as phosphorus pentasulfide, with an alcohol, phenol or mercaptan. The organic groups in the acid esters may be aryl, alkyl, aralkyl or cycloalkyl groups which contain from about 4 to 20 carbon atoms, preferably about 6 to 14 carbon atoms, and may be further substituted in the organic portion. Suitable alcohols which may be employed in preparing the acid esters include primary and secondary alcohols such as 2-methylamyl alcohol, 4-methylpentanol-2, 2-methylpentanol-1, 2-ethylhexanol, di-isopropyl carbinol, cyclohexanol, butanol-1 and octadecanol-1, or mixtures of high and low molecular weight alcohols. Other hydroxyl-containing materials which can be reacted with phosphorus sulfide include phenols and alkylated phenols such as dioctylphenol, tri-isobutylphenol and the like.

A particularly suitable nickel dithiophosphate which can be employed with advantage is that prepared from a di-2-ethylhexyl dithiophosphate obtained by reacting a technical mixture of 2-ethylhexanol with phosphorus pentasulfide. The nickel dithiophosphate is employed in my improved lubricating compositions in a small or minor amount sufficient to inhibit oxidation and bearing corrosion and in most instances the amount used provides about 0.03 to 0.2% by weight of phosphorus on the basis of mineral oil in which it is incorporated.

The zinc dithiophosphates which may be incorporated in the lubricating compositions of my invention are the oil-soluble zinc salts derived from the various diester dithiophosphoric acids mentioned above. As hereinbefore set forth, the organic portion in the acid diesters may be an aryl, alkyl, aralkyl or cycloalkyl group which contains from about 4 to 20 carbon atoms, preferably 6 to 14 carbons, and may, if desired, be further substituted. More specifically, the preferred compounds of this group include the zinc salts of dialkyl dithiophosphates such as dihexyl dithiophosphate, diheptyl dithiophosphate, dilauryl dithiophosphate, di-2-methylamyl dithiophosphate, di-2-ethylhexyl dithiophosphate, and the like.

A particularly suitable zinc dithiophosphate which may be employed is the zinc salt obtained from a mixed dithiophosphate prepared by reacting a technical mixture of C_7 secondary and C_6 primary alcohols, mainly the former, with phosphorus pentasulfide. The zinc dithiophosphate is employed in my improved lubricating composition in a minor amount sufficient to inhibit oxidation and bearing corrosion and, in most instances, the amount used provides about 0.03 to 0.2 percent by weight of phosphorus on the basis of the mineral oil in which it is incorporated.

A wide variety of compounds utilized as detergents in lubricating oils to effect engine cleanliness and anti-sludging properties may be employed in the compounded lubricating compositions of this invention. Among the preferred detergents are the oil-soluble metal salts of petroleum sulfonic acids, commonly known as mahogany sulfonates, which may be obtained by neutralization of sulfonic acids prepared, for instance, by sulfonating a suitable petroleum distillate with fuming sulfuric acid, or sulfur trioxide. Preferably, the neutralization is carried out by treating the acids with a theoretical excess of an oxide or hydroxide of an alkaline earth metal, such as calcium or barium oxide, so as to obtain a metal sulfonate which is alkaline and of higher metal content than the normal salt. Advantageously, if desired, the sulfonate can be carbonated by treating with carbon dioxide at atmospheric or slightly elevated pressure until the initial pH is reduced from about 14 to about 7 to 8. In the practice of this invention the preferred basic barium sulfonate is prepared by reacting a sulfonated mineral oil fraction with at least about 1.5 times the theoretical amount of barium oxide required. The basic barium sulfonate obtained is conveniently employed as a concentrate in the oil from which it was derived. Other suitable detergent type additives which can be used in place of the mahogany sulfonate include metal soaps, metal phenates, metal alcoholates, metal alkyl phenol sulfides, metal alkyl salicylates, and the like. Specific agents of these types are barium amyl phenol sulfide, calcium cetyl phenate, basic calcium octyl salicylate and the like.

The amount of detergent type agent added to the mineral oil base will depend upon the nature of the base stock employed and its service application, and in general ranges from about 0.5% to 10% by weight on a dry soap basis. In the preferred lubricating compositions of this invention a basic barium mahogany sulfonate is added in a sufficient amount to effect a barium content of about 0.2 to 2.0% by weight.

My present compositions can have added an antiwear agent, particularly to reduce wrist pin wear. The anti-wear type agents which are preferred are the sulfurized fatty oils such as sulfurized sperm oil, sulfurized rape seed oil, sulfurized cotton seed oil and sulfurized palm oil. A particularly effective anti-wear type agent employed is sulfurized sperm oil which contains about 5 to 15 weight percent of combined sulfur. For anti-wear purposes the sulfurized sperm oil is usually employed in a small or minor amount sufficient to contribute about 0.06 to 0.2% by weight of sulfur on the basis of the mineral oil of the composition. Although the sulfurized oils combat wrist pin wear, it apparently promotes rocker arm shaft wear. Surprisingly, when this additive is used in my compositions containing both the zinc and nickel dithiophosphates rocker arm shaft wear is still not excessive. The compositions of this invention can contain other additive agents such as pour depressors, antifoam agents and viscosity index improvers.

The mineral oil base stock used in the present invention is of lubricating viscosity, e.g. 35 to 225 SUS at 210° F. and may be a solvent extracted or solvent refined oil obtained in accordance with conventional methods of treating lubricating oils. The base oil may be derived from paraffinic, naphthenic, asphaltic or mixed base crudes, and if desired, a blend of solvent-treated Mid-Continent neutrals and Mid-Continent bright stocks may be employed. A particularly suitable base oil used in the preparation of my compositions is a solvent-treated Mid-Continent neutral having a viscosity index of about 95.

The following examples, which are not to be construed as limiting, are offered to further illustrate the novel lubricating compositions of the present invention.

EXAMPLE I.—PREPARATION OF NICKEL DI-2-ETHYLHEXYL DITHIOPHOSPHATE BASE

Basic nickel carbonate (2585 g.) was added portionwise to 13,375 g. of dry di-2-ethylhexyl dithiophosphoric acid at 80 to 132° F. over a period of 3 hours. The solution was dehydrated under vacuum (20–30 mm.) at 185 to 200° F. to give, after filtration, 12,230 g. product, pH 6.8, and acid number (D–974) 20.9. The product analyzed:

	Percent
Ni	6.79
S	15.2
P	7.67

EXAMPLE II.—PREPARATION OF ZINC DITHIOPHOSPHATE

A dithiophosphoric acid was prepared by reacting a technical mixture of C_7 secondary and C_8 primary alcohols with phosphorus pentasulfide until esterification was complete. The acid ester was then reacted with a theoretical amount of zinc oxide at 120 to 170° F. for about 3 hours. The mixture was taken up to 250° F. and then held there for one hour under vacuum. Diluent oil was then added to make about a 60% concentrate which had a typical analysis of:

5.5% zinc
5.5% phosphorus

and approximately 10.5% sulfur.

Laboratory engine test

Lubricating oil blends were prepared containing each of the products prepared in Examples I and II using as a reference oil an extracted Mid-Continent paraffinic type lubricating oil of SAE 10–W grade. The reference oil in each of the compositions tested contained an anti-foam agent and a polymethacrylate viscosity index improver and pour depressor.

In all of the following tests a standardized 100 hour cycling procedure was carried out on a popular make 1955 V-8 valve-in-head engine using a particular combination of additive agents in the reference oil. Wear of the rocker arm shaft in these 100 hour tests is measured in ten thousandths of an inch. When the values are quite low a better guide is the maximum surface roughness of the loaded areas, which can be measured more accurately. A rough shaft indicates excessive wear or is a forerunner of excessive wear. The following results shown in Table I show that both the zinc dithiophosphate and the sulfurized sperm oil contribute to rough wear of the rocker arm shaft.

TABLE I

Test No.	Composition	Rocker Arm Shaft Max. Roughness, Micro-inches	Average Wear, In.×10^{-4}
47	Reference oil [1] plus zinc dithiophosphate of Ex. II in an amount to provide .093% P in total composition, 1.25% sulfurized sperm oil (12% S) and basic barium mahogany sulfonate in an amount to provide .94% Ba in total composition	70	2
59	Reference Oil	15	1
70	Reference oil plus basic barium mahogany sulfonate in an amount to provide .94% Ba in total composition	15	0
55	Reference oil plus zinc dithiophosphate of Ex. II in an amount to provide .093% P in total composition	38 38	3 3
64	Reference oil plus 1.25% sulfurized sperm oil (12% S)	40	0

[1] Reference oil is a SAE 10–W base stock containing polymethacrylate VI improver and pour depressor, and an antifoam agent.

The results tabulated in Table II below show that the addition of nickel di-2-ethylhexyl dithiophosphate to a lubricating oil containing the zinc dithiophosphate of Example II together with sulfurized sperm oil and basic barium mahogany sulfonate, effectively overcomes the rough rocker arm shaft wear created by zinc dithiophosphate and anti-wear agent. The data further show that when the nickel dithiophosphate replaces the zinc dithiophosphate the resulting composition is deficient in preventing spalling of valve lifters in the LS-5 test.

The LS-5 engine test is run in a 1953 Chevrolet power glide engine with 235 cubic inch displacement. The hydraulic valve lifters are made of chilled cast iron, the camshaft of forged steel and the rocker arms of malleable iron. The valve train is 50% overloaded. The test duration is 24 hours at an engine speed of 3150 r.p.m. with a load of 30 B.H.P. In this test the faces of the 12-hydraulic valve lifters tend to spall or pit if the oil is deficient in this particular type of anti-wear property.

The base stock employed in each test was an SAE 10-W oil containing a polymethacrylate VI improver and an anti-foam agent. The base stock also contained a basic barium mahogany sulfonate detergent blended to give a barium content of 0.94% in the final composition.

zinc diester being present in an amount to provide about 0.03 to 0.2 percent of phosphorus based on the mineral oil and said nickel diester being present in an amount to provide about 0.03 to 0.2 percent of phosphorus based on the mineral oil.

2. The composition of claim 1 wherein the mineral lubricating oil is a solvent-refined Mid-Continent neutral oil.

3. A lubricating oil composition consisting essentially of a major amount of a mineral lubricating oil containing minor amounts of oil-soluble zinc and nickel dithiophosphate diesters in which the organic portions of said diesters contain from about 4 to 14 carbon atoms, said zinc diester being present in an amount to provide about 0.03 to 0.2 percent of phosphorus based on the mineral oil, said nickel diester being present in an amount to provide about 0.03 to 0.2 percent of phosphorus based on the mineral oil, a small amount of sulfurized sperm oil to impart anti-wear properties and a small amount of basic barium petroleum sulfonate sufficient to impart a barium content of about 0.2 to 2.0 percent by weight.

4. The composition of claim 3 wherein the mineral lubricating oil is a solvent-refined Mid-Continent neutral oil.

TABLE II

Test	47	67	86	X	91
Weight Percent:					
Zinc Dithiophosphate of Example II.	1.7		1.7		0.85.
Sulfurized Sperm Oil (12% Sulfur).	1.25		1.25	1.25	1.25.
Nickel di-2-ethylhexyl dithiophosphate of Example I.		1.65	0.62	1.3	0.62.
Rocker Arm Shaft Surface Finish, In.	Coarse, −70.	Smooth, −15 (Av.).	Medium, −20.		Smooth, −12.
LS-5 Test Spalled Lifters	2	12	1	7	3.

As shown in tests 91 and 86, the compositions of the present invention are especially effective in reducing rocker arm shaft wear while keeping the number of spalled valve lifters at an acceptable level.

I claim:

1. A lubricating oil composition consisting essentially of a major amount of a mineral lubricating oil containing minor amounts of oil-soluble zinc and nickel dithiophosphate diesters, in which the organic portions of said diesters contain from about 4 to 14 carbon atoms, said

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