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LUBRICATING OIL COMPOSITION

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6 Claims. (Cl. 252—37)

This invention relates to a new and useful composition of matter; more particularly a composition comprising a lubricating oil and a zinc salt of diamyl dithiophosphate.

In our copending application Serial No. 401,960 filed July 11, 1941, of which this is a continuation-in-part, it was pointed out that conventional types of lubricating oils when subjected to high operating temperatures for long periods of time tend to decompose with the formation of complex and objectionable oxidation and decomposition products. Under the high temperature conditions obtaining in engines, particularly in bus, tractor, Diesel and aeroplane engines in heavy duty service, these decomposition products polymerize to form lacquer-like deposits on or between the moving parts causing these parts to stick. Even larger quantities of polymerization products remain dispersed in the partly oxidized crankcase oil, and are precipitated to form a sludge when the engine cools or when fresh oil is added. These precipitated sludges become caked on heated metal surfaces and cut down the effective life of the engine.

As pointed out in our copending application referred to above the lubricating oil oxidation and decomposition products are corrosive and attack modern type alloy bearings such as copper-lead, silver-cadmium, nickel-cadmium, and the like which are widely employed in internal combustion engines. To disperse the sludge, remove the deposits and prevent corrosion many different types of materials have been tried with more or less success. Compounds having a detergent action such as calcium stearate, calcium naphthenate and the like have been employed and while these compounds are effective as detergents they do not prevent corrosion of the alloy bearings. Certain anti-corrosion agents such as triphenyl phosphite and sulfurized sperm oil have been employed to combat the corrosive effects of the acidic oxidation products of the oil but have no detergent action. Ordinarily mixtures of detergents and anti-corrosion agents do not perform satisfactorily together since the function of a corrosion inhibitor is to cover the corrodible metal surfaces with a passivating film but the detergent tends to remove it thus producing a clean metal surface subject to corrosion.

In our above-mentioned copending application we disclose that certain heavy metal salts of dithiophosphate esters may be employed in lubricating oils to perform the dual function of preventing corrosion and sludge formation with its tendency to form lacquer-like deposits on the metal surfaces of the engine. In that application we stated that we prefer the alkaline earth metal salts of dialkyl dithiophosphates because of their excellent detergent properties. We also stated that we prefer those dialkyl dithiophosphates in which each alkyl group contains 8, 10, 12, 14 or more carbon atoms. The preference for these long chain dialkyl dithiophosphates was based principally upon the greater ease with which these compounds could be dissolved in lubricating oils. In fact, it has become generally recognized among chemists that organic compounds should have one or more long chain alkyl groups preferably of about 12 carbon atoms to render them sufficiently soluble in lubricating oil to be of practical value. The difficulty with which alkaline earth metal short chain dialkyl dithiophosphates dissolved in lubricating oils was illustrated in our above-mentioned case when we stated that we had succeeded in incorporating substantial amounts, even greater than 3%, of barium and other heavy metal salts of the lower dialkyl dithiophosphates by first admixing or dissolving them in metal salts of 2,4-diamylphenol sulfides which act as mutual solvents. Ordinarily barium diamyl dithiophosphate is soluble only to the extent of about 0.2–0.5% in ordinary lubricating oil.

Easy blending of lubricating oil additives with hydrocarbon lubricating oils is of considerable importance from a practical standpoint and accordingly while certain of the lower dialkyl dithiophosphates can be blended with lubricating oils by the employment of special techniques the difficulty and additional expense of doing so does not warrant their use. It is also customary in the art to prepare, ship and store these additives in the form of about 50% solutions of the additive in lubricating oil so that the blender need only pour the additive composition into the lubricating oil with suitable stirring. Additives of difficult solubility cannot be employed in this manner and consequently are under a serious handicap.

The present invention is based on our discovery that the zinc salts of diamyl dithiophosphoric acid have a very unexpected and surprisingly high solubility in lubricating oils of the hydrocarbon type. We have for example prepared a zinc diamyl dithiophosphate and dissolved in it an equal weight of 30–W lubricating oil without difficulty and the solution has remained perfectly clear and stable upon standing over a long period of time. The reason for the unexpectedly high solubility of this particular compound is not altogether clear, but the importance of this property is evident.

Although it has been heretofore believed that the most advantageous dithiophosphoric acid esters for use as constituents of lubricating oil additives are those containing the alkaline earth metals, we have found that equally good and in some cases better results are obtained with the zinc salt of diamyl dithiophosphoric acid. This is true because alkyl groups of only 5 carbon

atoms will serve to impart an equal degree of oil solubility to the zinc salts whereas alkyl groups of 8–12 or more carbon atoms are necessary to impart the requisite oil solubility to the alkaline earth metal dialkyl dithiophosphates.

The net result of our discovery is, therefore, that a given weight of our new lubricating oil additive contains a higher percentage of phosphorus and sulfur, which are the active anti-corrosion agents, and also a larger molecular proportion of the metal, i. e. zinc, than is present in the alkaline earth metal salts of higher molecular weight. Detergent and anti-corrosion effects comparable with those obtained by the use of an alkaline earth metal such as barium are therefore obtained by the compounds of our present invention.

Although we may prepare our lubricating oil additives by reacting P_2S_5 with any straight or branched chain primary, secondary or tertiary amyl alcohol we prefer to use a commercially obtainable mixture of amyl alcohols known in the trade as "Pentasol." This mixture of amyl alcohols is prepared by chlorinating a mixture of normal and isopentane which product is then hydrolyzed to the corresponding amyl alcohols. The various amyl alcohols present in this mixture are as follows:

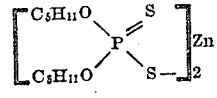
$CH_3CH_2CH_2CH_2CH_2OH$
$(CH_3)_2CHCH_2CH_2OH$
$CH_3CH_2CH(CH_3)_2CH_2OH$
$CH_3CH_2CH_2CHOHCH_3$

and

$CH_3CH_2CHOHCH_2CH_3$

The three primary alcohols predominate. The mixture has an initial boiling point of 112° C. and a final boiling point of about 140° C., a refractive index at 20° C. of 1.4092 and a specific gravity of 0.810 to 0.820. Where the word "amyl" is recited in the appended claims this is intended to include any of the amyl alcohols or mixtures thereof described herein.

The preparation of our zinc diamyl dithiophosphates will now be described: 745 grams of the "Pentasol" mixture described above and 516 grams of finely ground P_2S_5 (10% excess) were heated for two hours at 85–100° C. with stirring at which time almost all of the P_2S_5 had disappeared and evolution of H_2S from the reaction mixture had practically stopped. The reaction mixture was cooled and the unreacted P_2S_5 allowed to settle. 1039 g. of the di-Pentasol dithiophosphate, decanted from the unreacted P_2S_5, 343 cc. of 95% ethyl alcohol and 701 cc. of toluene were mixed and 135 g. of zinc oxide added in 30 g. portions with stirring while maintaining the temperature between 35° and 45° C. until the reaction mixture was neutral to Congo red paper. The solution was then filtered and evaporated under a vacuum until about 75% of the solvent had been removed. 1135 g. of a 30–W grade lubricating oil was then blended with the zinc diamyl dithiophosphate while continuing the vacuum evaporation to remove the remainder of the solvent. A yield of 2268 g. of a clear blend containing about 50% of zinc diamyl dithiophosphate,



was obtained.

The effectiveness of the above-described zinc salt of diamyl dithiophosphoric acid in lubricating oils as a detergent and anti-corrosion constituent is demonstrated by the following results obtained by subjecting a #30–W grade Mid-Continent solvent extracted oil containing 0.25% of zinc diamyl dithiophosphate to the standard Underwood oxidation test. This test consists in heating 1500 cc. of the oil to 325° C. and continuously spraying a portion of the heated oil against a 3 inch by 10 inch freshly sanded copper baffle, a freshly sanded copper-lead alloy bearing and a freshly sanded silver-cadmium alloy bearing, for five hours while permitting free circulation of air. Samples of the oil are then examined for A. P. I. gravity, neutralization number, naphtha insolubles and bearing loss due to the effects of corrosion. The neutralization number indicates the formation of acids resulting from oxidation of the oil and the A. P. I. gravity also indicates the decomposition of the oil during the test, the lower value indicating the greater degree of decomposition. The particular oil employed in these tests, being of the solvent refined type, was particularly resistant to sludge formation. A sample of the same oil to serve as a basis of comparison was also tested at the same time and under the same conditions. The samples contained 0.116% of iron naphthenate as required by the test. The results were as follows:

TABLE I

Underwood oxidation test

Oil	A. P. I. grav. used oil	Bearing loss, mg.		Naphtha insol.	Neutralization No.
		Cu-Pb	Ag-Cd		
	Degrees			*Percent*	
Control (A. P. I. grav. 28.1°)	22.2	66	722	0.02	9.00
+0.25% zinc di-Pentasol dithiophosphate	26.1	5	10	Nil	0.60

These results show the very great effectiveness of zinc diamyl dithiophosphates in preventing oxidation and decomposition of the oil and corrosion of alloy bearings under the extremely drastic conditions of the Underwood test.

Zinc diamyl dithiophosphate was also tested by the well known Catalytic Indiana test. This test is conducted in an apparatus consisting of a constant temperature bath maintained at 341° F. in which a number of large glass test tubes are immersed. 300 cc. samples of the oil under test are poured into these tubes and air is bubbled through the oil at the rate of 10 liters per hour. In order to reproduce the conditions prevailing in the crankcase of an engine, weighed strips of a copper-lead alloy are suspended in the samples. Bearing corrosion tests are determined by weighing the strips after 70 hours immersion. The results of this test were as follows:

TABLE II

Catalytic Indiana test

Oil	Bearing loss, mg. Cu-Pb
Control	275
+0.4% zinc di-Pentasol dithiophosphate	[1] +14

[1] Gained.

Results obtained from this test were unusual in that the bearing showed no loss whatever in weight and in fact gained slightly. The walls of

the test tube containing the oil treated with zinc diamyl dithiophosphate were clean after the test thus showing the detergent action of the added salt. The results of this test confirm the results obtained by the previously described Underwood test.

Because of the very high effectiveness of these zinc diamyl dithiophosphates as detergents and anti-corrosion agents it is necessary to employ but very small amounts of them in the oil. In lubricating oils intended for an ordinary service where extremely high temperatures occur only occasionally 0.1–0.8% of the zinc diamyl dithiophosphate is sufficient. In heavy duty service it is generally advisable to use a little more as for example 0.5–3% in the oil. They may, of course, be used with other materials added to the oil for specific purposes and form particularly heat-stable lubricating oils in combination with 10% or more of their weight of an alkaline earth salt of 2,4-dialkyl diphenol monosulfide, such as barium 2,4-diamyl diphenol monosulfide.

Although as pointed out before one of the advantageous features of our new lubricating oil additive is its high solubility in lubricating oils enable us to prepare solutions for distribution to the trade containing from 30–60% or more by weight of the zinc diamyl dithiophosphate. However, because of the ease with which they may be dissolved in lubricating oils it is a simple matter for the blender to disperse them directly in the oil without previous treatment and without the aid of mutual solvents, etc. Accordingly the appended claims are intended to cover both the improved lubricating oil composition containing our zinc diamyl dithiophosphates as well as blends of the same containing as high as 50% or more of the salt in conventional type lubricating oils.

What we claim is:

1. A lubricating oil composition comprising at least 0.1% by weight of a zinc salt of diamyl dithiophosphoric acid and a lubricating oil.

2. A lubricating oil composition comprising at least 0.1% by weight of a zinc di-Pentasol dithiophosphate and lubricating oil.

3. A lubricating oil composition containing zinc diamyl dithiophosphate in amounts of from 0.1–3.0% and a hydrocarbon lubricating oil.

4. A composition adapted to be blended with hydrocarbon lubricating oils which comprises a 50% solution of zinc diamyl dithiophosphate in lubricating oil.

5. A lubricating oil composition comprising at least 0.1% by weight of zinc diamyl dithiophosphate, an alkaline earth salt of 2,4-dialkyl diphenol monosulfide, and a lubricating oil.

6. A lubricating oil composition comprising at least 0.1% by weight of zinc diamyl dithiophosphate and a barium salt of 2,4-diamyl diphenol monosulfide and a major proportion of a lubricating oil.

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