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LUBRICATING OIL

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This invention relates to improved oils, particularly lubricating oils of the crankcase type. Although lubricating oils of the present invention are highly desirable for use in crankcases of passenger automobiles they are especially valuable for heavy duty use in truck, bus, aeroplane, marine and Diesel engines which operate for long periods of time at high temperatures.

The principal objects of the invention are to provide a lubricating oil of the heavy duty type which is resistant to oxidation and sludge formation, being non-corrosive to alloy bearings and other metal parts and free from varnish formation and ring sticking tendencies under the severe conditions of heavy duty service. These objects, and others which will appear hereinafter, are accomplished by us by providing a hydrocarbon oil containing a dithiophosphoric acid ester of hydrogenated abietyl alcohol, such as di-(dihydro-abietyl) dithiophosphate or di-(tetrahydro-abietyl) dithiophosphate or a salt thereof. These compounds and their preparation will be described in greater detail hereinafter.

When conventional lubricating oils are subjected to high operating temperatures for long periods of time, as in heavy duty service, they tend to decompose with the formation of complex and objectionable oxidation and decomposition products. Under the high temperature conditions prevailing in the engine 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 readily precipitated to form a sludge when the engine cools or when fresh oil is added to the engine. These precipitated sludges become caked on heated metal surfaces and cut down the effective life of the engine.

A number of oil-soluble detergents of the type of metal soaps, phenolates and alcoholates have been proposed and used in crankcase oils to dissolve or disperse the sludge and prevent lacquer deposits and stuck piston rings. Unfortunately, however, the great majority of these substances increase the rate of oxidation and their presence results in an increased concentration of acidic oxidation products in the oil. Increased quantities of these acidic oxidation products in the oil create in turn an even more serious difficulty for they attack and corrode alloy bearings commonly employed in internal combustion engines. Alloys composed of copper-lead, silver-cadmium, nickel-cadmium, etc. are widely used and are subject to attack by the acidic oxidation products formed in the oil.

Certain anti-corrosion agents which have no detergent properties have been added to lubricating oils in order to counteract the corrosive effect of the oxidation products of the oil. Although many of the detergents and anti-corrosion agents which have been previously mentioned perform their individual functions in lubricating oils the two separate chemicals do not cooperate to produce a satisfactory anti-corrosion and detergent action when used together. The function of a corrosion inhibitor is to cover the bearing surfaces and other corrodable parts of the engine with a passivating film that prevents corrosion of the metal by the organic acids and other corrosive products of the oil. A detergent, as its name implies, operates to remove adhering solids in the metal parts of the engine and thus produce a clean metal surface. Consequently mixtures of detergent with a corrosion inhibitor have proven to be ineffective over any extensive period of time since the detergent action of the sludge inhibitor tends to remove the corrosion inhibitor from the metal surface thus rendering it ineffective for the purpose intended.

We have also found that compounds of aliphatic or alicyclic structure having conjugated double bonds also fail to stand up under the severe conditions found in the crankcase of heavy duty engines. As is understood in the drying oil art compounds having conjugated double bonds tend to polymerize to form oil-insoluble resin-like bodies particularly when heated in the presence of air. The crankcase of an engine provides almost ideal conditions for such polymerization. Accordingly, lubricating oil additives containing systems of conjugated double bonds are unsatisfactory. One such type of compound is the abietyl alcohol ester of dithiophosphoric acid. As known, abietyl alcohol has a structure with two double bonds in conjugation. As a result the dithiophosphoric acid ester of this alcohol is not stable in lubricating oil when used under conditions of heavy duty service. In the first instance it is of a dark color and lacks the necessary oil solubility for a satisfactory additive. It is not stable to heat and tends to form dark colored sludge in the oil in the crankcase of the engine. It easily polymerizes with itself, or with other decomposition products developed in the oil, to form oil-insoluble resin-like bodies which tend to interfere seriously with the satisfactory operation of the engine.

The hydrogenated abietyl alcohol esters of dithiophosphoric acids and salts thereof which we employ avoid the above-described defects by being heat stable and possessing anti-sludging, detergent and anti-oxidant action. These esters and their salts are surprisingly soluble in hydrocarbon lubricating oils and are very stable at high temperatures. Being polar in character they have strong film-forming characteristics and may also be advantageously employed in hypoid gear lubricants and other high pressure lubricants. This film-forming tendency also makes these compounds of value in the preparation of slushing oils, their water-insolubility further making them highly efficient in these preparations. A still further advantage of the use of the hydrogenated abietyl esters of dithiophosphoric acids lies in the soft porous character of the carbon deposits formed upon decomposition of the oils containing them.

As the hydrogenated abietyl alcohol esters of dithiophosphoric acids and salts thereof are highly effective as detergents and anti-corrosion agents it is necessary to employ but very small amounts of these compounds in crankcase oils. In lubricating oils intended for ordinary service where higher temperatures occur only occasionally, from 0.1 to 1% of the additive is sufficient. In oils intended for heavy duty service it is generally advisable to use a little more, as for example, 0.5 to 5% of the ester in the oil.

To prepare the hydrogenated abietyl alcohol esters of dithiophosphoric acids we react an alcohol of the group consisting of dihydro-abietyl alcohol and tetrahydro-abietyl alcohol with phosphorous pentasulfide (P_2S_5) at temperatures of the order of 90 to 110° C.; the reaction of 1 mol of P_2S_5 with 4 mols of the hydrogenated abietyl alcohol resulting in the formation of 2 mols of a dithiophosphoric acid ester of the hydrogenated abietyl alcohol with the elimination of 1 mol of H_2S. The reaction may be brought about by merely mixing P_2S_5 preferably in a finely ground form, with the hydrogenated abietyl alcohol with heating and stirring until the evolution of H_2S has practically ceased. Should excessive foaming occur due to the evolution of H_2S the addition of a small amount of toluene to the reaction mixture will reduce the foaming to a point at which it is no longer troublesome. The dithiophosphoric acid ester is obtained in the form of a viscous liquid which may be decanted from the unreacted P_2S_5. The desired salt of the dithiophosphoric acid ester may then be prepared by simple neutralization of the compound with salt-forming bases or by double decomposition with its sodium salt.

As pointed out above the hydrogenated abietyl alcohols which may be employed by us in the preparation of our new lubrication oil additives are known products derived by the catalytic hydrogenation of a primary or secondary ester of abietic acid. The product usually contains both dihydro-abietyl alcohol and tetrahydro-abietyl alcohol in proportion depending upon the particular conditions employed in the hydrogenation. Accordingly, the recitation of dithiophosphoric acid ester of hydrogenated abietyl alcohol in the claims is intended to include esters of both dihydro- and tetrahydro-abietyl alcohol.

As stated above the dithiophosphoric acid esters may be made into salts by simple neutralization with a suitable salt-forming base or by double decomposition. A wide variety of salt-forming radicals including those such as nickel, aluminum, lead, mercury, cadmium, tin, zinc, magnesium, sodium, potassium, ammonium, copper, strontium, calcium, lithium and barium may be introduced by neutralizing the acid with their oxides, hydroxides, carbonates and in some cases sulfides. The alkaline earth salts of our hydrogenated abietyl alcohol esters of dithiophosphoric acids are preferred as lubricating oil additives, since these salts are neutral, stable and resist emulsification well.

The preparation of these hydrogenated abietyl alcohol esters of dithiophosphoric acid and salts thereof will now be described in detail by means of the following example in which the preparation of the barium salt of di-(dihydro-abietyl) dithiophosphoric acid is illustrated.

1810 parts by weight of dihydro-abietyl alcohol and 382 parts by weight of finely ground P_2S_5 were heated with stirring at 100 to 105° C. for 3 hours. At the end of this time most of the P_2S_5 had reacted and the evolution of H_2S had practically ceased. The crude di-(dihydro-abietyl) dithiophosphoric acid thus obtained was decanted from unreacted P_2S_5. The product was a viscous liquid with a light blackish-brown color.

The barium salt of di-(dihydro-abietyl) dithiophosphoric acid was prepared as follows: 2100 parts by weight of di-(dihydro-abietyl) dithiophosphoric acid as obtained above was dissolved in 550 parts by weight of ethyl alcohol (97.5%) and 1200 parts by weight of toluene. 240 parts of finely powdered barium oxide was added gradually with stirring and cooling so that the temperature of the reaction mixture was maintained below 40° C. As soon as the product was neutralized 1200 parts by weight of toluene was added and the solution filtered from traces of barium salts. The solvent was then removed by evaporation under reduced pressure with stirring. Barium di-(dihydro-abietyl) dithiophosphate was obtained as a viscous light yellow liquid.

The barium salt of di-(dihydro-abietyl) dithiophosphoric acid may also be prepared by treating the acid esters with barium sulfide. The use of barium sulfide in this preparation is advantageous in that the formation of water during the neutralization is avoided, H_2S being formed instead and is evolved from the reaction mixture during the neutralization.

The products prepared as thus described may be added directly to lubricating oils in which they act as detergents, sludge dispersants and corrosion inhibitors. A more convenient method of incorporating the dithiophosphoric acid salt in the oil is to add a suitable hydrocarbon lubricating oil such as S. A. E. 10 grade to the preparation before all of the solvent has been removed by evaporation. This step simplifies the blending of the lubricating oil with additive. It is possible to obtain a concentration of the ester in lubricating oils of as high as 50% in which form the composition may be stored, sold and shipped.

The di-(dihydro- and tetrahydro-abietyl) dithiophosphoric acids and their salts may constitute the sole additive in our improved lubricating oils or they may be used in conjunction with other materials added for special purposes. It has been found, for example, that the hydrogenated abietyl alcohol esters of dithiophosphates exert solubilizing effects on other less soluble alkyl esters of dithiophosphoric acids such as barium diamyl dithiophosphate and by blending the two types of esters it is possible to incorporate in lubricating oils substantial amounts of the less soluble but highly effective dithiophosphoric esters. When blended with alkyl phenol sulfides, such as barium 2,4-diamylphenol monosulfide, the detergency, heat stability and corrosion inhibition of the resulting mixture is unusually good.

The effectiveness of the above-described barium salt of di-(dihydroabietyl) dithiophosphoric acid in lubricating oils as a detergent and anti-corrosive constituent is demonstrated by the following results obtained by subjecting a 30 S. A. E.

solvent refined Mid-Continent oil containing 0.5% of the above-named barium salt 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 2 inch by 10 inch freshly sanded copper strip and two freshly sanded bearings to be tested for corrosion for 5 hours while permitting free circulation of air during the operation. Samples of the oxidized oil are then examined for A. P. I. gravity, neutralization number, and bearing loss due to the effects of corrosion. The neutralization number indicates the formation of acids resulting from oxidation of the oil. The A. P. I. gravity also indicates the decomposition in the oil during the test, a lower value indicating the greater degree of decomposition. A sample of the same oil without additive to serve as a basis for comparison was also tested at the same time and under the same conditions. The oil samples contained 0.01% of Fe_2O_3 in the form of iron naphthenate as required by the test. The results were as follows:

TABLE I

Underwood oxidation test

Oil	A. P. I. gravity (used oil)	Loss in bearing, mg		Neutralization No.
		Cu-Pb	Ag-Cd	
	Degrees			
Control	21.3	42	838	8.66
With 0.5% Ba salt	26.0	1	56	1.05

These results show a very startling reduction in the corrosiveness of the oil as a result of the incorporation therein of a metal salt of a hydrogenated abietyl dithiophosphoric acid ester. The neutralization number also shows a marked decrease indicating the substantial absence of acids formed by oxidation during the test. The results of the A. P. I. gravity test also indicates very little decomposition in the oil containing the barium salt.

Another oil containing 0.5% of barium di-(dihydro-abietyl) dithiophosphate was also tested by the 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 produced in the crankcase of an engine weighed strips of a copper-lead alloy are suspended in the samples. Bearing corrosion rates are determined by weighing the strips after 70 hours immersion. The results of this test were as follows:

TABLE II

Catalytic Indiana test

[70 hours at 341° F.—Copper-lead bearing]

	Bearing loss—mg.
Control, no additive	302
Oil containing 0.5% Ba di-(dihydro-abietyl) dithiophosphate	+7 (gain)

The walls of the test tube containing oil treated with the Ba di-(dihydro-abietyl) dithiophosphate were comparatively clean after the test, thus showing the detergent action of the added salt. The results of this test not only confirm the results obtained by the previously described Underwood test but also emphasizes the detergent qualities of our improved lubricating oil compositions.

The effectiveness of calcium di-(dihydro-abietyl) dithiophosphate in lubricating oil was also tested by means of the well-known Lauson engine test. In this test a solvent refined S. A. E.-30 Mid-Continent oil containing 1.0% by weight of calcium di-(dihydro-abietyl) dithiophosphate and 0.25% of barium 2,4-diamylphenol monosulfide was used. The engine was operated at a speed of 1860 R. P. M. with a load of 2 H. P. for 25 hours with white gasoline under optimum ring-sticking conditions. The temperature of the coolant was maintained at 400° F. and the temperature of the oil at 225° F. A standard Lauson aluminum piston with a 0.0035" clearance was used in the engine. After a 25 hour run both compression rings and the oil ring as well were free and clean. The copper-lead bearings showed a loss in weight of 3 mg. for the upper half of the bearing and 1 mg. for the lower half of the bearing. The oil itself had the following analytical characteristics before and after the test.

TABLE III

	Fresh oil	25 hour oil
Naptha insolubles ...percent..	Nil	0.02
Conradson carbon ...do...	0.32	0.42
Neutralization number	0.21	0.20
Viscosity S. U. S. at 100° F	508	616

The naphtha insolubles show clearly that the formation of resin-like polymerization products in the oil was practically negligible. The neutralization number also shows the formation of extremely small amounts of acidic material through decomposition of the oil.

This is a continuation-in-part of our application Serial No. 439,400 filed April 17, 1942.

What we claim is:

1. A lubricating oil composition containing a lubricating oil and 0.1 to 5% of a di-(dihydro-abietyl) dithiophosphate.

2. A lubricating oil composition containing a lubricating oil and 0.1 to 5% of a hydrogenated abietyl alcohol ester of dithiophosphoric acid.

3. A lubricating oil composition containing a lubricating oil and an alkaline earth metal salt of a hydrogenated abietyl alcohol ester of a dithiophosphoric acid in amounts sufficient to exert detergent and anti-corrosion properties in the oil under heavy duty service.

4. A lubricating oil composition containing a lubricating oil and a salt of di-(dihydro-abietyl) dithiophosphate in amounts sufficient to exert detergent and anti-corrosion properties in the oil under heavy duty service.

5. A lubricating oil composition containing a lubricating oil and barium di-(dihydro-abietyl) dithiophosphate in amounts sufficient to exert detergent and anti-corrosion properties in the oil under heavy duty service.

6. A lubricating oil composition containing a lubricating oil and a salt of di-(tetrahydro-abietyl) dithiophosphoric acid in amounts sufficient to exert detergent and anti-corrosion properties in the oil under heavy duty service.

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