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LUBRICATING OIL

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7 Claims. (Cl. 252—39)

This invention relates to improved oils, particularly lubricating oil 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, airplane, marine and Diesel engines operating 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 lubricating oil containing a diaryloxyalkyl dithiophosphoric acid 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 sludge when the engine cools or when fresh oil is added to the engine. These precipitated sludges become caked on heated metal sufaces and cut down the effective life of the engine.

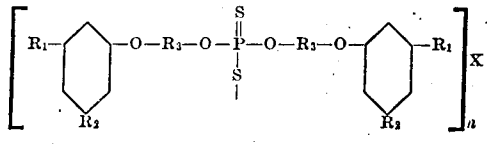
A number of oil soluble detergents of the type of metal soaps, phenolates and alcoholates have been proposed and used in crankcase oils to dissolve or disperse the sludge and prevent lacquer deposits and stuck piston rings. Unfortunately, however, the great majority of these substances increase the rate 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 function in lubricating oils the two separate additives 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.

The diaryloxyalkyl dithiophosphoric acids and salts thereof avoid the above described difficulties by possessing not only excellent corrosion-inhibiting properties, but also detergent characteristics, thus enabling us to provide a lubricating oil having a single additive effective to inhibit corrosion, sludge and varnish formation, ring sticking and other difficulties experienced with lubricating oil serving in a heavy duty capacity. These dithiophosphoric acid esters and their salts are surprisingly soluble in 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 greases 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.

The various diaryloxyalkyl dithiophosphates which we have found useful in improving lubricating oils and which may be employed to ad-

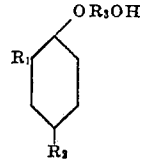
vantage therein are new compounds having the general formula:



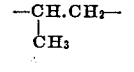
in which R_1 and R_2 are members of the group consisting of hydrogen and alkyl radicals at least one R being an alkyl radical the total carbon atoms in R_1 and R_2 being eight or more, R_3 is an alkylene radical containing 2–4 carbon atoms inclusive, X is hydrogen or a salt-forming radical and n is the valence of X.

These compounds are prepared by heating approximately 4 moles of an alkyl substituted phenoxyalkylol with 1 mole of P_2S_5 at temperatures between 90–110° C. until most of the P_2S_5 has dissolved and the evolution of H_2S has subsided. The crude bi(alkyl substituted phenoxyalkyl) dithiophosphoric acid resulting from the reaction may be employed as such in our new lubricating oils or may be first neutralized and added to the oil in the form of a salt.

As will appear from the general formula above we may react P_2S_5 with substituted aryloxyalkylol compounds having the general formula:



in which R_3 is an alkylene group of 2–4 carbon atoms such as CH_2CH_2—,



—$CH_2CH_2CH_2$—, etc. As stated before R_1 or R_2 may be hydrogen or alkyl radicals at least one of the R's being an alkyl radical the total carbon atoms in both R_1 and R_2, or in one of the R's alone when the other R is hydrogen, being at least eight. More specifically, when R_1 is a propyl radical R_2 should be an alkyl radical at least as long as an amyl radical; R_1 and R_2 may be both butyl radicals or R_2 may be a hexyl radical and R_1 an ethyl radical. When R_1 is hydrogen then R_2 should be a radical of at least eight carbon atoms such as octyl, dodecyl, tetradecyl, octadecyl, or the like. When the alkyl chains are of shorter length the dithiophosphates become less oil soluble and difficulty may be experienced in blending the compounds in mineral oil. Specific compounds of this group include 2,4-di-tertiary butyl phenoxyethanol, 4-octyl phenoxyethanol, 4-amyl-2-isopropyl phenoxyethanol, 4-octyl phenoxypropanol, 2,4-diamyl phenoxyisopropanol, 2,4-diethyl hexyl phenoxyethanol, and others of similar character.

Metal salts of the alkyl substituted phenoxyalkyl dithiophosphoric acids may be prepared by simple neutralization of the bi(alkyl substituted phenoxyalkyl) dithiophosphoric acid with a suitable salt-forming base or by double decomposition. A wide variety of metal radicals including those such as nickel, aluminum, mercury, cadmium, tin, zinc, magnesium, lithium, strontium, calcium, and barium may be introduced by neutralizing the acids with a suitable hydroxide, carbonate and in some cases sulfide or by double decomposition of their Na salts with a desired metal salt. Salts of other metals may, of course, be prepared. The alkaline-earth salts of the bi(alkyl phenoxyalkyl) dithiophosphoric acids are preferred as lubricating oil additives.

Preparation of the bi(alkyl substituted phenoxyalkyl) dithiophosphoric acids and their salts will now be described in detail by means of the following example in which the preparation of barium bi(2,4-diamyl phenoxyethyl) dithiophosphate is illustrated. Since other alkyl substituted phenoxyalkylols may be reacted with P_2S_5 in the same way using similar proportions of materials further description of the preparation of these products is not thought necessary.

100 parts by weight of 2,4-diamyl phenoxyethanol was stirred and heated for 3.5 hours at 95–105° C. with 22 parts by weight of finely ground P_2S_5. At the end of this time practically all of the P_2S_5 had dissolved and the evolution of the H_2S subsided. The product, crude bi(2,4-diamyl phenoxyethyl) dithiophosphoric acid, a light brown liquid, was recovered by decantation from the small amount of unreacted P_2S_5.

The barium salt of the above product was prepared by dissolving 90 parts by weight thereof in 30 parts by weight of toluene and 20 parts by weight of ethanol. 12 parts of finely powdered barium oxide was added and the mixture was warmed at 40–50° C. for 30 minutes at the end of which time the dithiophosphoric acid was neutralized. After filtration of traces of inorganic barium salts the solvent was evaporated, the last of the solvent being removed under reduced pressure. A barium bi(2,4-diamyl phenoxyethyl) dithiophosphate remained as a yellow liquid that was practically insoluble in water but easily soluble in both gasoline and 10–W lubricating oil.

The products prepared as thus described may be added directly to lubricating oils in which they act as detergents, sludge dispersants and corrosion inhibitors. Since they are highly effective it is necessary to employ only small amounts of the dithiophosphate in the lubricating oil. Ordinarily from 0.1–3.0% of the bi(alkyl substituted phenoxyalkyl) dithiophosphate is sufficient for oils employed in heavy duty capacity. Although the compounds described are for the most part easily soluble in lubricating oils and may be easily blended therewith it is ordinarily more convenient to first dissolve the dithiophosphate in a lubricating oil in amounts of about 50%. Solutions of the dithiophosphate of this strength in lubricating oils are easily prepared by adding a suitable hydrocarbon lubricating oil to the preparation before all of the solvent has been removed by evaporation. This product may be stored, sold and shipped in this form and need only to be blended in mineral oils of suitable grade and in desired proportions to produce a lubricating oil of greatly improved properties.

The bi(alkyl substituted phenoxyalkyl) dithiophosphates may constitute the sole additive in our lubricating oil or it may be used in conjunction with other materials added for special purposes. For example, when blended with alkyl phenyl sulfides, such as barium 2,4-diamyl phenol monosulfide, they tend to increase the detergency and heat stability of these products in lubricating oils. They also exert solubilizing effects on the less soluble alkyl esters of dithiophosphoric acid such as barium diamyl dithiophosphate.

The effectivness of the above described barium salt of bi(2,4-diamyl phenoxyethyl) dithiophosphoric acid in lubricating oils as a detergent and anti-corrosive constituent may be demonstrated by the following results obtained by subjecting a 10–W grade solvent refined Pennsylvania oil containing 0.4% of the above named barium salt to the standard Underwood oxidation test. In this test 1500 cc. of the oil was heated for 5 hours at 325° F. while continuously spraying portions of the oil against a 2 inch by 10 inch freshly sanded copper strip and 2 freshly sanded alloy bearings while permitting free circulation of the air during the operation. Samples of the oxidized oil were then examined for A. P. I. gravity, neutralization number, naphtha insolubles and bearing loss due to the effects of corrosion. The percent of naphtha insolubles formed in the oil indicated the amount of sludge formed during the test and the neutralization number indicated the formation of acids resulting from oxidation of the oil. The A. P. I. gravity also indicated decomposition in the oil during the test, a lower value indicating a greater degree of decomposition. The oil samples contained 0.116% of iron naphthenate equivalent to 0.01 of Fe_2O_3. The results of the test were as follows:

TABLE 1

UNDERWOOD OXIDATION TEST

5 hours at 325° F.

	A. P. I. gravity		Bearing loss, mg.		Naphtha insolubles	Neutralization No.
	Start	End	Cu-Pb	Ag-Cd		
Oil—control, no additive	31.1	21.4	71	885	0.42	9.41
Oil+0.4% Ba bi(2,4-diamyl phenoxyethyl) dithiophosphate	31.1	29.8	2	40	0.3	1.66

These results show the very great effectiveness of the bi(2,4-dialkyl phenoxyalkyl) dithiophosphates in reducing the oxidation of the oil, the formation of the sludge therein and the reduction in the corrosiveness of the oil to alloy bearings.

Another oil containing 0.4% of barium bi(2,4-diamyl phenoxyethyl) dithiophosphate was also tested by the Catalytic Indiana test. This test was conducted in an apparatus consisting of a constant temperature bath maintained at 341° F. in which a number of large glass test tubes were immersed. 300 cc. samples of the oil under test were poured into test tubes and air was bubbled through the oil at the rate of 10 liters per hour. Sanded strips of a copper-lead alloy were suspended in the oil and bearing corrosion determined by weighing the strips after 70 hours. The results of these tests were as follows:

TABLE 2

CATALYTIC INDIANA TEST

Solvent extracted Pennsylvania Oil 10–W Grade

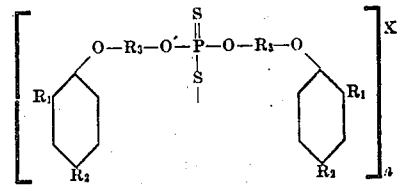
	Bearing loss in mg. (Cu-Pb)
Oil—control	215
Oil+0.4% Ba bi(2,4-diamyl phenoxyethyl) dithiophosphate	+8 (gained)

The walls of the test tube containing the oil treated with the barium bi(2,4-diamyl phenoxyethyl) dithiophosphate were comparatively clean after the test thus showing the detergent action of the additive.

The results of this test not only confirm the results of the previously described Underwood test, but also emphasize the detergent quality of our improved lubricating oil compositions.

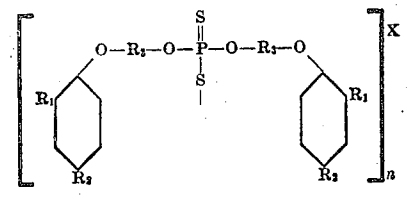
We claim:

1. A lubricating oil composition containing a major portion of a lubricating oil and 0.1–3.0 per cent of a compound having the general formula:



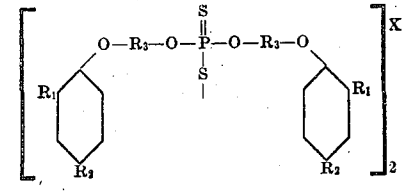
in which R_1 and R_2 are members of the group consisting of hydrogen and alkyl radicals at least one R being an alkyl radical the total carbon atoms in R_1 and R_2 being at least eight, R_3 is an alkylene radical containing 2–4 carbon atoms inclusive, X is a member of the group consisting of hydrogen and metal salt forming radicals and n is the valence of X.

2. A lubricating oil composition containing a major portion of a lubricating oil and 0.1–3.0% by weight of a compound having the general formula:



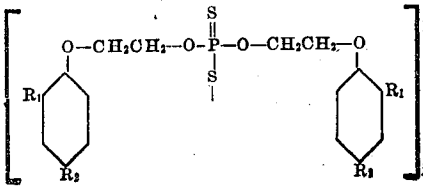
in which R_1 and R_2 are members of the group consisting of hydrogen and alkyl radicals at least one R being an alkyl radical the total carbon atoms in R_1 and R_2 being at least eight, R_3 is an alkylene radical containing 2–4 carbon atoms inclusive, X is a metal and n is the valence of X.

3. A lubricating oil composition containing a major portion of a lubricating oil and 0.1–3.0% by weight of a compound having the general formula:



in which R_1 and R_2 are alkyl radicals having a total number of carbon atoms of at least eight, R_3 is an alkylene radical containing 2–4 carbon atoms inclusive, X is an alkaline earth metal.

4. A lubricating composition containing a major portion of a lubricating oil and 0.1–3.0% by weight of a compound having the general formula:

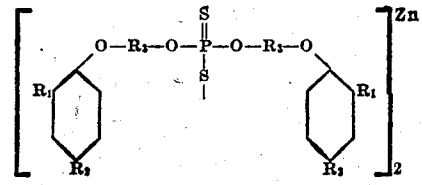


in which R_1 and R_2 are alkyl radicals having a total number of carbon atoms of at least eight and X is an alkaline earth metal.

5. A lubricating oil composition containing a major portion of hydrocarbon lubricating oil and 0.1–3.0% of barium bi(2,4-diamyl phenoxy-ethyl) dithiophosphate.

6. A lubricating oil composition containing a major portion of hydrocarbon lubricating oil and 0.1–3.0% of barium bi(2,4-dibutyl phenoxy-ethyl) dithiophosphate.

7. A lubricating oil composition containing a major portion of lubricating oil and 0.1–3.0% by weight of a compound having the general formula:



in which R_1 and R_2 are alkyl radicals having a total number of carbon atoms of at least eight, and R_3 is an alkylene radical containing 2–4 carbon atoms inclusive.

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