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COMPOUNDED OIL

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15 Claims. (Cl. 252—39)

This invention relates to the improvement of hydrocarbon oils and the like, in particular, mineral lubricating oils.

This application is a continuation-in-part of our copending application Serial No. 322,946, filed March 8, 1940.

Hydrocarbon oils undergo deterioration during use or exposure to the atmosphere. Mere exposure to the air at relatively low temperatures, as in the case of transformer oils and switch oils, results in the gradual formation of acidic oxidation products and the deposition of sludge. Use of a lubricating oil in the ordinary gasoline engine, as in motor cars, results in a more rapid deterioration of the oil with deposition of sludge and the formation of "varnish" on cylinder walls. Use of a lubricating oil in Diesel engines, which operate at higher temperatures and pressures, than ordinary gasoline engines, results in even more rapid deterioration with resultant greater disadvantages. The temperatures and pressures involved in Diesel engine operation, around 400–650° F. and 750–1200 pounds per square inch, cause deposition from ordinary lubricating oils on the moving parts of the engine, such as pistons, piston rings and piston ring slots, of carbonaceous matter of such a cementitious character as to cause sticking of piston rings and greatly to reduce the efficiency of the engine.

It has been found heretofore that some improvement of hydrocarbon oils, especially lubricating oils, can be effected by incorporating therein a small amount of a soap of a fatty acid, such as a sodium, calcium or magnesium soap of butyric, capric, palmitic, stearic or oleic acid. Such soaps, among other things, reduce piston ring sticking in internal combustion engines, especially Diesel engines, apparently by loosening the cementitious deposits described above, or by inhibiting the formation of such deposits, or both. The action of the added soaps, by virtue of the analogy to the common cleansing or detergent action of soaps, came to be known as a "detergent" action and the soap additives came to be known as "detergents."

The use of these soaps or detergents is not, however, without disadvantage. Among other things they are corrosive to certain alloy bearings, such as copper-lead and cadmium-silver alloy bearings, which are commonly used in internal combustion engines. So destructive are certain of the soaps to these alloy bearings that they cannot be used satisfactorily in lubricating oils for internal combustion engines.

It is an object achieved by the present invention to provide a valuable class of additives for lubricating oils, transformer and switch oils, and the like.

It is a further object achieved by the present invention to improve the use of soap-like or metal alkyl carboxylate additives in viscous hydrocarbon oils.

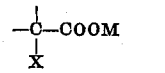
It is a still further and a particular object achieved by the present invention to provide a class of soap-like or metal alkyl carboxylate additives for lubricating oils which are non-corrosive, or substantially less corrosive than prior soap additives, such as calcium stearate, toward alloy bearings.

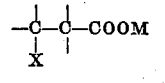
Other objects achieved by the invention will be apparent from the description and the claims.

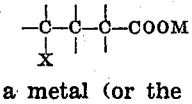
We have discovered that substantial advantages result from incorporating in a hydrocarbon oil or the like, especially a hydrocarbon lubricating oil, a polar substituted metal alkyl carboxylate wherein the polar substituent is of a certain class and is in an alpha, beta or gamma position with respect to a metal alkyl carboxylate group.

It has been found that certain phosphorus substituted metal alkyl carboxylates, more especially those in which phosphorus is directly bonded to the alkyl group of the metal alkyl carboxylate, are more highly effective or produce fewer undesirable effects than the corresponding unsubstituted metal alkyl carboxylates, when added to hydrocarbon oils or the like. In particular, it has been found that pentavalent phosphorus, especially if directly bonded to the alkyl group of the metal alkyl carboxylate, produces highly desirable results.

The additives of our invention may also be characterized by the following formulae:

I 

II 

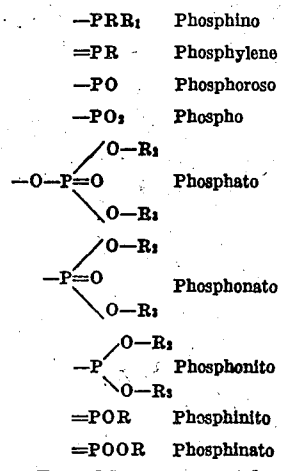
III 

wherein M is a metal (or the hydrogen equivalent of a polyvalent metal), the carbon atoms shown attached to COOM are aliphatic carbon atoms, and X is a substituent containing phosphorus, the phosphorus preferably being directly bonded to the designated aliphatic carbon atom. The unsatisfied carbon valencies shown may be satisfied by hydrogen or hydrocarbon groups (e. g. alkyl groups), by polar groups (including polar groups of the type represented by X, and/or other polar groups), etc.

It will be apparent that three principal constitutional factors may be varied in the additives of this invention: (1) the nature and amount of the substituent X; (2) the nature of the alkyl carboxylic acid which is substituted and whose salt is formed; and (3) the nature of the metal

M. These factors are discussed in more detail immediately below.

(1) *The substituent X.*—The following substituents are illustrative:



In the above R and R_1 represent hydrogen, hydrocarbon (e. g., alkyl, aryl, aralkyl and cycloalkyl), or other atoms or groups, and R_2 and R_3 represent hydrogen, hydrocarbon (e. g., alkyl, aryl, aralkyl and cycloalkyl), metal or other atoms or groups. A single atom of polyvalent metal may take the place of R_2 and R_3. In any of the above phosphorus- and oxygen-containing substiuents, sulfur may replace any or all of the oxygen atoms. More than one of the above or other like substituents may be present in the molecule, and at least one such substituent is present in the alpha, beta, or gamma position, as indicated, first preference being given to the alpha position, second to the beta position and third to the gamma position. As stated, other substituents, including polar substituents, may be present in the alkyl chain of the metal alkyl carboxylate, either in the indicated alpha, beta or gamma position or in positions further removed from the metal alkyl carboxylate group.

Those substituents are preferred which do not hydrolyze readily to produce corrosive acids. However, insofar as certain of the advantages of the metal alkyl carboxylates of the invention are concerned, even those polar substituents which hydrolyze readily to produce corrosive acids are effective; for example, as long as the hydrolyzable polar group remains attached to the metal alkyl carboxylate, it inhibits corrosion.

(2) *The alkyl carboxylic acid.*—For simplicity's sake, reference is made to the free, unsubstituted acids, and it is to be understood that in the practice of the invention a substituent will be included and a metal salt formed, as indicated hereinabove.

Mono- and polybasic acids may be employed, and although open chain acids are preferred, cycloaliphatic acids and aliphatic acids having an aromatic substituent attached to the alkyl chain (preferaby removed by three or more carbon atoms from the alkyl carboxyl group) are comprehended by the invention. In all cases, however, the acid contans at least one carboxyl group attached to one alkyl or aliphatic carbon atom. By the term "alkyl carboxylic acid" is meant a carboxylic acid in which a COOH group is attached to an aliphatic carbon atom, and by the term "metal alkyl carboxylate" is meant the metal salt of such an acid.

Illustrative of suitable acids are the following: *Acids of the acetic series,* such as propionic, butyric, isobutyric, valeric, isovaleric, alpha-methylbutyric, pivalic, caproic; alpha, alpha-dimethylbutyric; alpha, beta-dimethylbutyric, alpha-ethylbutyric; alpha-ethyl, alpha-methylbutyric, capric, lauric, myristic, palmitic, stearic, etc.; also, unsaturated and/or hydroxy and other substituted members of the same series such as oleic, linoleic, linolenic, licanic, lactic and ricinoleic acids.

Acids of the oxalic acid series, such as malonic, succinic, isosuccinic, glutaric, adipic, etc.; also unsaturated dibasic acids, such as maleic and fumaric; also hydroxy dibasic acids, such as malic, mucic, and tartaric.

Tribasic acids, such as citric and agaric acids.

Preference is given to those acids, generally the longer chain alkyl carboxylic acids, whose salts are oil soluble, although the lower acids, even acetic, when properly substituted and used in the form of appropriate metal salts, greatly improve the stability of hydrocarbon oils and inhibit ring sticking and associated phenomena. C_{10} and higher acids provide adequate oil solubility.

(3) *The metal M.*—Any mono- or polyvalent metal capable of forming a sufficiently stable salt with the acid chosen may be used. Metals which do not exhibit adverse catalytic activity (such as promoting oxidation) and whose use does not result in excessive wear are preferred. Examples of metals whose salts may be formed and used in accordance with this invention are lithium, sodium, potassium, calcium, barium, strontium, beryllium, magnesium, aluminum, zinc, cadmium, tin, lead, chromium, molybdenum, tungsten, manganese, iron, cobalt, nickel, vanadium and bismuth. Basic and mixed, as well as normal simple salts may be employed.

Examples of substituted metal alkyl carboxylates contemplated by this invention are sodium, potassium, calcium, barium, aluminum, magnesium, zinc and nickel alpha, beta and gamma phosphato butyrates; the corresponding alpha, beta and gamma phosphato valerates, caproates, caprates, laurates, myristates, palmitates, stearates, acrylates, crotonates, angelates, oleates, lactates, malonates, succinates, glutarates, adipates, maleates, fumarates, malates, and citrates; also the corresponding phosphino, phosphylene, phosphoroso, phosphoto, phosphonato, phosphonito, phosphinato and phosphinito substituted salts (that is, the salts formed by substituting phosphino, phosphylene, etc., for phosphato).

It will be apparent to one skilled in the art that all of the possible substituents X cannot be introduced into each of the positions alpha, beta and gamma of every alkyl carboxylic acid. Thus the presence in an alkyl carboxylic acid of an alpha, beta or gamma substituent, for example an hydroxyl substituent, may hinder the further substitution of the alpha, beta or gamma position by a certain substituent X of the present invention. In such case, a different substituent X within the scope of the invention, or a different position in the alkyl carboxylic acid, or a different alkyl carboxylic acid may be chosen for substitution; or the hindering alpha, beta or gamma group, such as an hydroxyl group, may be replaced by the desired substituent.

The substituted metal alkyl carboxylates of this invention improve hydrocarbon oils in several respects. One of the most important improvements resulting from the use of these carboxylates in mineral oil lubricants is their marked detergent effect, unaccompanied by corrosion or

accompanied by relatively little corrosion of hard alloy bearings. This contrasts with excessive corrosion of similar bearings when prior art soaps, such as calcium stearate and calcium naphthenate, are used. Also, used oil inspections (such as increase in viscosity, increase in neutralization number, and increase in naptha insoluble matter in the used oil) are benefited by the presence of small amounts of the substituted metal alkyl carboxylates of the invention, or at least are not as adversely affected as by the commoner soaps and unsubstituted metal alkyl carboxylates. Moreover, the metal alkyl carboxylates of the invention render oils more stable toward oxidation than the ordinary soaps, and they produce still other advantageous effects.

The following specific examples will show how a number of properties of hydrocarbon oils are benefited by, and will provide a comparison for judging the relative utility of, the substituted metal alkyl carboxylates of the invention.

Example I.—A base oil (an S. A. E. 30 blend of 70% Western acid treated naphthenic base oil and 30% Western paraffinic base oil) was tested, with and without the presence of metal alkyl carboxylate additives, to determine its corrosiveness to various alloys of the type used in bearings of internal combustion engines. The "Strip corrosion test" was employed in these determinations, this test being as follows:

Thin sheets of the indicated bearing metals were cut into strips (copper-lead, $\frac{9}{16}$" x 1¾" x $\frac{3}{32}$"; cadmium-silver, ½" x 1⅜" x $\frac{1}{16}$"), and these strips were immersed in the exemplified oils carried in 2" x 20" glass test tubes; these test tubes were carried in an oil bath maintained at 300° F.±1° F. Each test tube contained approximately 300 cc. of oil, and air was bubbled through each tube at the rate of 10 liters per hour. At the end of each of three 24-hour periods, the strips were removed from the oils, washed with petroleum ether and carefully wiped with a soft cotton cloth; weight losses of the strips were measured in connection with the weight of each individual strip. The duration of the tests was 72 hours, and the weight losses tabulated below are those found at the end of each 24-hour period.

The increase in viscosity of the oil, the neutralization number of the oil at the conclusion of each test, and the amount of naphtha insoluble matter at the conclusion of each test, were also measured. The results of the tests are set forth in Table I below, the additives referred to having been used in the amount of .05% by weight based on the oil:

Oil	Additive	Cu-Pb strip, hours			Cd-Ag strip, hours			Fresh oil viscosity		Used oil viscosity		Neutralization number	A. S. T. M. naphtha insolubles
		24	48	72	24	48	72	100° F.	210° F.	100° F.	210° F.		
Western S. A. E. 30 blend.	None	0.8	1.6	5.5	0.0	0.0	0.0	632	57.0	1,041	66.6	2.00	109
Do	Ca butyrate	3.9	13.3	37.4	0.0	15.5	45.8	628	57.1				
Do	Ca 2-ethyl butyrate	2.5	44.0	117.0	0.0	17.0	47.1	632	57.0	1,442	76.6	4.97	189
Do	Ca laurate	14.2	67.2	97.9	12.4	16.3	15.7	630	57.3	1,148	70.1	4.49	143
Do	Ca palmitate	47.3	125.0	166.4	9.5	38.2	90.2	632	57.0	1,361	75.5	3.07	221
Do	Ca stearate	84.4	152.5	208.1	0.6	34.8	82.0	653	57.5	1,340	75.0	4.02	248
Do	Ba beta-phosphonato-isobutyrate.	+0.4	+0.8	+0.5	0.1	0.2	0.3	634	56.9	844	62.4	0.44	26
Do	Ca beta-phosphato-propionate.	0.6	1.1	1.4	0.0	0.1	0.0	640	57.2	1,007	67.0	0.19	134

Example II.—Oil was placed in a beaker in contact with air, maintained at a given temperature, and protected against drafts until darkening due to oxidation had occurred. A sample of the original oil was placed in a glass cell 50 mm. square by 7 mm. thick, and an equal sample of the exposed oil was placed in a second similar glass cell. The glass cells were placed equidistant from an electric light. The light that passed through each glass cell was caused to impinge on a photoelectric cell. The two photoelectric cells were mounted in two arms of a Wheatstone bridge. The difference in light transmissions, caused by the different colors of the oils, was thus registered on the Wheatstone bridge. The readings of the bridge were calibrated against the standard A. S. T. M. color numbers, and from this the readings of the bridge could be converted into A. S. T. M. color numbers (method D155-34T).

A base oil (Western paraffinic S. A. E. 30) and the same base oil plus 0.5% by weight of barium beta-phosphonato-isobutyrate were tested. The results are set forth in Table II below:

Table II

Base oil	Additive	Temperature	A. S. T. M. color increase
		° F.	
Western paraffinic S. A. E. 30.	None	356	8
Do	Ba beta-phosphonato-isobutyrate.	356	5

The substituted metal alkyl carboxylates of the invention may be advantageously added to any hydrocarbon oil or lubricating oil, such as the more viscous distillates and residues from petroleum oil, viscous olefin polymers, and viscous oils derived from oxides of carbon or other forms of carbon by hydrogenation, and they may be added with advantage to any of the newer synthetic lubricants, such as amyl naphthalene. The additives of our invention may be used in viscous hydrocarbon oils ranging in viscosity from about 60 S. S. U. or lower at 100° F. to 160 S. S. U. or higher at 210° F. The metal alkyl carboxylate may be used, in the finished oil, in amounts ranging from 0.1% or less to 10% or more by weight based on the finished oil, but preferably it is used in amounts of about 0.1 to 5%, usually 0.5 to 2%. Concentrates may be prepared containing more than 10% and up to 50% or more of the metal alkyl carboxylate of the invention, alone or together with another additive or other additives, and the concentrate may be diluted with more oil when it is desired to produce the finished oil.

The substituted metal alkyl carboxylates of the invention, as is clear from the examples, are multifunctional in character, and an oil containing one or more of the additives of this invention is improved in several respects. However, the additives of the invention may be advantageously combined in hydrocarbon oils with one or more

other additives, such as other antioxidants or corrosion inhibitors, other detergents or anti-ring sticking agents, pour point inhibitors, viscosity and viscosity index improvement agents, oiliness, wear, and film strength agents, etc. Specifically, the additives of this invention may be used in mineral or hydrocarbon oils in combination with any one or more of the following:

(1) Unsubstituted or corrosive carboxylate salts such as the calcium, barium, and aluminum salts of lauric, palmitic, stearic, arachidic, naphthenic, phenyl stearic, benzal stearic, dihydroabietic, oleic, linoleic and alkylated aromatic acids; also various polar substituted metal carboxylates, such as metal salts of chloro stearic, hydroxy stearic, licanic, cetyl hydroxybenzoic, mercaptostearic, cetyl tartaric, cetyl cystine and dodecyl aminobenzoic acids.

(2) Metal phenates such as the calcium, barium and aluminum salts of cetyl phenol, cetyl chlorphenol and cetylthiophenol.

(3) Metal salts of organo-substituted oxy- and thio-acids of phosphorus, such as calcium cetyl phosphate, aluminum lauryl phosphate, and calcium cetyl phenyl phosphate.

(4) Carboxylate esters having an alkyl hydroxy substituent (an hydroxy substituent attached to an alkyl carbon atom) near a carbonyl group of the ester, such as the methyl, ethyl, propyl, butyl, amyl, hexyl, heptyl, octyl, nonyl, lauryl, dodecyl, tetradecyl, cetyl and octadecyl esters of alpha, beta or gamma hydroxy propionic acid, and the corresponding esters of alpha, beta or gamma hydroxy butyric, valeric, caproic, enanthic, caprylic, capric, lauric, myristic, palmitic, stearic, and arachidic acids, as well as the corresponding esters of tartonic, tartaric and citric acids.

The structural formulae and preparation of typical additives capable of use in accordance with this invention are given below:

Barium beta-phosphonato-isobutyrate

The structural formula of this substance is as follows:

$$\left(\begin{matrix}CH_3\cdot CH\cdot COO-\\ |\\ CH_2\cdot PO_3=\end{matrix}\right)_2 Ba_3$$

500 grams of PCl_3 are mixed in a 2-liter flask with 800 cc. of dry, alcohol-free acetone. 80 grams of aluminum chloride are added in small portions. Rapid evolution of HCl occurs, after which the flask is heated on a water bath to remove additional HCl. Diacetone phosphorus chloride is thus formed, and it is hydrolyzed by adding it to water, producing diacetone phosphinic acid which is recovered in impure form by evaporating the water. It is purified by dissolving in alcohol and precipitating the ammonium salt with ammonia. The salt is washed with alcohol, dissolved in water and filtered. The acid is then obtained by acidification with HCl followed by evaporation. The solid is extracted with alcohol, filtered, and evaporated to dryness. The purified diacetone phosphinic acid thus produced is oxidized first with nitric acid and then with fuming nitric acid. The excess nitric acid is removed by heating on a water bath. Impure beta-phosphonato-isobutyric acid is formed and it is dissolved in water and barium hydroxide is added until the solution is strongly alkaline. This solution is heated to boiling and filtered. The barium salt is only slightly soluble in hot water while the impurities dissolve. The filtrate is therefore discarded and the residue remaining on the filter is extracted with cold water in which the barium salt is soluble and the extract is evaporated to dryness to recover the purified barium beta-phosphonato-isobutyrate.

Calcium beta-phosphatopropionate

The structural formula of this substance is as follows:

$$(PO_4(CH_2\cdot CH_2\cdot COO)_3)_2Ca_3$$

13.6 grams of beta iodopropionic acid are dissolved in 200 cc. of water and 9.5 grams of silver phosphate are added. The mixture is heated for one-half hour and the silver iodide is filtered off. Calcium hydroxide is added until the solution is neutral and the solution is then evaporated to dryness.

We claim:

1. A composition of matter, comprising a major proportion of a hydrocarbon oil and a small amount, sufficient to improve the oil, of a metal alkyl carboxylate substituted on an alpha, beta or gamma alkyl carbon atom with respect to a metal alkyl carboxylate group by a substituent containing pentavalent phosphorus.

2. A composition of matter, comprising a major proportion of a mineral oil of lubricating viscosity and a small amount, sufficient to improve the oil, of a metal alkyl carboxylate substituted on an alpha, beta or gamma alkyl carbon atom with respect to a metal alkyl carboxylate group by a substituent containing pentavalent phosphorus, said substituent being attached to said alkyl carbon atom through an element selected from the group consisting of phosphorus, oxygen and sulfur.

3. The composition of claim 2, wherein pentavalent phosphorus is directly bonded to the alkyl group of the metal alkyl carboxylate.

4. The composition of claim 2, wherein said metal is a polyvalent metal.

5. The composition of claim 2, wherein said metal is an alkaline earth metal.

6. A hydrocarbon lubricating oil containing about 0.1 to 5 per cent by weight based on finished oil of an oil-soluble polyvalent metal alkyl carboxylate substituted on an alpha, beta or gamma alkyl carbon atom with respect to a metal alkyl carboxylate group by a substituent containing pentavalent phosphorus and oxygen, said substituent being attached to said alkyl carbon atom through one of the elements phosphorus and oxygen.

7. A hydrocarbon lubricating oil containing about 0.1 to 5 per cent by weight based on finished oil of an oil-soluble polyvalent metal alkyl carboxylate substituted on an alpha, beta or gamma alkyl carbon atom with respect to a metal alkyl carboxylate group by a radical of an oxy acid of pentavalent phosphorus.

8. A hydrocarbon lubricating oil containing about 0.1 to 5 per cent by weight based on finished oil of an oil-soluble polyvalent metal alkyl carboxylate substituted on an alpha, beta or gamma alkyl carbon atom with respect to a metal alkyl carboxylate group by a radical of a thio acid of pentavalent phosphorus.

9. The composition of claim 7, wherein the pentavalent phosphorus atom is directly bonded to the alkyl group of the metal alkyl carboxylate.

10. The composition of claim 8, wherein the pentavalent phosphorus atom is directly bonded to the alkyl group of the metal alkyl carboxylate.

11. A petroleum lubricating oil containing a small amount, not less than about 0.1 per cent by weight based on finished oil, of a polyvalent

metal salt of a fatty acid containing not less than 10 carbon atoms and substituted on an alpha, beta or gamma alkyl carbon atom with respect to the metal alkyl carboxylate group by a substituent containing pentavalent phosphorus, said substituent being attached to said alkyl carbon atom through one of the elements phosphorus, oxygen and sulfur.

12. The composition of claim 11, wherein said polyvalent metal is an alkaline earth metal.

13. A composition of matter, comprising a concentrated solution in viscous mineral oil of a metal alkyl carboxylate substituted on an alpha, beta or gamma alkyl carbon atom with respect to a metal alkyl carboxylate group by a substituent containing pentavalent phosphorus.

14. A petroleum lubricating oil comprising a small amount each of an oil-soluble polyvalent metal salt of an alkylated phenol and an oil-soluble polyvalent metal alkyl carboxylate substituted on an alpha, beta or gamma alkyl carbon atom with respect to a metal alkyl carboxylate group by a substituent containing pentavalent phosphorus, said salt of phenol and said carboxylate being present in respective amounts and in relative proportions sufficient to provide a lubricant of enhanced detergency and low corrosivity in the crankcase of an internal combustion engine.

15. A petroleum lubricating oil comprising a small amount each of an oil-soluble alkaline earth metal salt of an alkylated phenol and an oil-soluble alkaline earth metal alkyl carboxylate substituted on an alpha, beta or gamma alkyl carbon atom by a radical of an acid of pentavalent phosphorus, said salt of phenol and said carboxylate being present in respective amounts and in relative proportions sufficient to provide a lubricant of enhanced detergency and low corrosivity in the crankcase of an internal combustion engine.

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