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COMPOUNDED OIL

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This invention relates to new and useful compositions of matter and involves a composition comprising a hydrocarbon oil such as a mineral oil containing a polyvalent metal salt of certain types of acids, either alone or in admixture with other compounding agents of the same or different type.

The production of improved hydrocarbon oils, and particularly of lubricating oils having desired characteristics, has been the subject of extensive research and investigation. Generally speaking, the compounding of lubricating oils to obtain desired characteristics involves empirical phenomena. The present invention provides a compounded lubricating oil having one or more properties improved by the incorporation of certain metal salts. A brief discussion of significant properties of lubricating oils may serve to clarify the problems of the lubricating art.

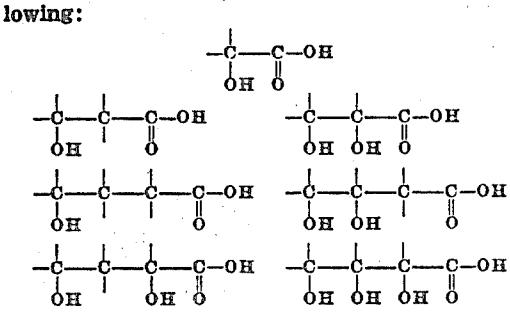
It has long been the desire of the lubricating oil compounding art to obtain an oil, particularly of petroleum origin, which alone or with the addition of relatively small amounts of compounding agents would resist deterioration or degradation when subjected for long periods of time to high temperatures and pressures in the presence of metals, air or oxygen or hydrocarbon partial combustion products. Deterioration of the character referred to manifests itself in diverse effects, depending upon the nature and degree of refinement of the hydrocarbon oil and upon the environment to which it is subjected. In Diesel engines, the effect is manifested by piston ring sticking. In these engines, the exposure of a lubricating oil to such temperatures as 425° to 650° F. in the presence of oxidizing combustion gases at pressures as high as 750 to 1150 lbs. per square inch causes the deposition of oil degradation products of such a cementitious character as to effectively take piston rings out of service. In automobile engines the deposition of sludge in the crankcase oils and the formation of "varnish" on the cylinder walls of the engine are observed to be the result of oxidation and/or polymerization phenomena occurring in the degradation process. The corrosion of hard metal bearing surfaces of the type represented by cadmium-silver and copper-lead alloys also is a difficulty encountered from the deterioration of lubricating oils in internal combustion engines or other services. The adverse effect of deterioration of hydrocarbon oils at elevated temperatures is aggravated by the fact that improvements in the mechanical arts have brought about increasing severity in the conditions to which the oils are subjected.

It has also been the practice in the lubricating oil art to improve other properties of lubricants by adding ingredients to mineral oil fractions for enhancing the oiliness characteristics, the wear reducing action, the film strength, the color stability, and the viscosity index of lubricating oils.

It is an object of the present invention to improve one or more of the above discussed properties of lubricating oils (i. e., stability against piston ring sticking, "varnish" formation, sludging, corrosivity to metal bearing surfaces, oiliness, wear reduction, film strength, color stability, or viscosity index) by incorporating in hydrocarbon oils a polyvalent metal salt of certain types of organic acids.

The lubricating oils of this invention are characterized by the presence therein of a polyvalent metal carboxylate having an alkyl hydroxy substituent near a carbonyl group of the carboxylate. The alkyl hydroxy group is preferably no more than about three carbon atoms removed from a carboxyl group of the compound. By "alkyl hydroxy group" or "alkyl hydroxy substituent" it is intended to designate a compound in which an hydroxyl radical is directly connected to an alkyl portion of the molecule. By "no more than three carbon atoms removed from a carboxyl group of the compound" it is intended to designate compounds having at least one hydroxyl group in at least one of the positions alpha, beta or gamma with respect to a carboxyl group of the compound. Exemplary compounding agents of this invention are polyvalent metal salts of acids characterized by the pres-

ence therein of chemical groups such as the following:



The various unsatisfied valences shown on the carbon atoms in the formulae may be attached to hydrogen, a carbon atom, or to an acyclic organic radical.

The addition to a lubricating oil of a small amount of polyvalent metal carboxylates having an alkyl hydroxy substituent near a carboxyl group effects an improved stability in the oil when the same is subjected to high temperatures and/or pressures in the presence of oxygen and metals. This appears to be true when the hydroxy radical is in the delta or even epsilon position, as well as when it is in the alpha, beta or gamma position, with respect to a carbonyl group. However, improvements in the properties of lubricating oil are obtained when a hydroxyl group is in an alpha, beta or gamma position, which are not obtainable with the hydroxyl group more than about three carbon atoms removed from the carbonyl group. The effectiveness of the OH constituent decreases in the order of the positions recited.

Examples of hydroxy carboxylic acids from which the oil-improving agents of this invention may be formed are: alpha hydroxy propionic acid (lactic acid), beta hydroxy propionic acid; alpha hydroxy butyric acid, beta hydroxy butyric acid, gamma hydroxy butyric acid; alpha hydroxy valeric acid, beta hydroxy valeric acid, gamma hydroxy valeric acid; alpha hydroxy caproic acid, beta hydroxy caproic acid, gamma hydroxy caproic acid; alpha hydroxy enanthic acid, beta hydroxy enanthic acid, gamma hydroxy enanthic acid; alpha hydroxy caprylic acid, beta hydroxy caprylic acid, gamma hydroxy caprylic acid; alpha hydroxy capric acid, beta hydroxy capric acid, gamma hydroxy capric acid; alpha hydroxy lauric acid, beta hydroxy lauric acid, gamma hydroxy lauric acid; alpha hydroxy myristic acid, beta hydroxy myristic acid, gamma hydroxy myristic acid; alpha hydroxy palmitic acid, beta hydroxy palmitic acid, gamma hydroxy palmitic acid; alpha hydroxy stearic acid, beta hydroxy stearic acid, gamma hydroxy stearic acid; alpha hydroxy arachidic acid, beta hydroxy arachidic acid, gamma hydroxy arachidic acid; tartronic or hydroxy malonic acid and the several alkylic tartronic acids, such as methyl tartronic or isomalic acid, ethyl tartronic, propyl and isopropyl tartronic; the gamma hydroxyalkylic malonic acids; malic acid and its homologues, for example, alpha hydroxy-pyrotartaric acid, beta methyl malic acid, alpha beta methyl ethyl malic acid, isopropyl malic acid and the paraconic acids; alpha hydroxy-glutaric acid, beta hydroxyglutaric acid; alpha hydroxy adipic acid; alpha hydroxy sebacic acid; tartaric acid and its isomers; citric acid, dihydroxytartaric acid; mucic acid; and hydroxy acids produced by the oxidation of petroleum hydrocarbons, such as paraffin wax, petrolatum, naphthenic base lubricating oils, selective solvent extracted naphthenic base lubricating oils, mixed base (e. g., Mid-Continent) lubricating oils, solvent extracted mixed base lubricating oils, paraffinic base (e. g., Pennsylvania) lubricating oils, solvent extracted paraffinic lubricating oils, where the oxidation process is controlled so as to produce at least one hydroxyl group near the carboxyl group of said acids.

From the above it is to be understood that in its broader aspects the invention embraces metal monocarboxylates having only one alkyl hydroxy substituent near the carbonyl group of the compound or having a plurality of alkyl hydroxy substituents, some or all of which are near the carbonyl group of the compound, and that the invention also embraces metal polycarboxylates having only one alkyl hydroxy substituent near a carbonyl group of the compound or having a plurality of alkyl hydroxy substituents, some or all of which are near a carbonyl group of the compound. In the metal polycarboxylate compounds all or only part of the carboxyl groups may be neutralized with metal, and when only part is so neutralized the remaining ones may be neutralized by esterification, by amino groups or the like.

The compounds utilized in this invention may be prepared by methods known in the art; for example, by direct reaction of a suitable polyvalent metal compound with the corresponding free acid or by double decomposition of the sodium or potassium carboxylates with a suitable compound of the polyvalent metal. Also, the compounds may be prepared by first forming a metal carboxylate of an unsubstituted acid and then introducing an hydroxyl group in an alkyl portion of the molecule at a point near a carbonyl group thereof. Suitable methods of introducing hydroxy groups into alkyl chains are known in the art.

The metals whose alkyl hydroxy substituted carboxylates are useful for the purposes of this invention preferably have valences from two to four inclusive, and the salts of calcium, barium, magnesium, aluminum, chromium, cobalt, lead, manganese, tin and zinc are of particular utility. Although the alkali metals, sodium and potassium, are not precluded from the broadest aspects of the invention the carboxylates of these latter metals tend to cause the compounded oil to form emulsions with water and, where the lubricating service to be encountered is the lubrication of internal combustion engines, such a tendency is undesirable. Further, the alkali metal carboxylates are frequently more corrosive to bearing metals than one would desire.

Among the compounds which may be incorporated in lubricating oils according to the principles of this invention are the following: calcium, barium, magnesium, aluminum, chromium, cobalt, lead, manganese, tin and zinc salts of alpha, beta, and gamma hydroxy substituted lactic, butyric, valeric, caproic, heptanoic, caprylic, capric, lauric, myristic, palmitic, stearic, and arachidic acids; also salts of the foregoing metals and tartronic, methyl tartronic, ethyl tartronic, propyl tartronic, isopropyl tartronic, gamma hydroxy-alkylic malonic, alpha hydroxy pyrotartaric, beta methyl malic, alpha beta methyl ethyl malic, isopropyl malic, paraconic, alpha hydroxy glutaric, beta hydroxy glutaric, alpha hydroxy adipic, alpha hydroxy sebacic, tartaric, citric, dihydroxy-tartaric, and mucic acids.

It should be understood that basic as well as

neutral carboxylates may be utilized. By "basic carboxylates" is meant compounds in which the carboxylic acid groups are present in an amount insufficient to wholly satisfy the normal valence of the metal, thereby leaving an unsatisfied metal valence which may be attached to an hydroxyl group. By "a neutral salt" is meant compounds in which the carboxylic acid groups and the metal are present in stoichiometrical proportions so that the normal valence of each is fully satisfied. The invention likewise does not preclude carboxylates containing unsaturated carbon-to-carbon bonds, but compounds which do not polymerize are preferred.

This invention also embraces lubricating oils containing, in combination with polyvalent metal carboxylates having an alkyl hydroxy substituent near a carbonyl group of the compound, that is, in combination with each and every one of the salts hereinbefore disclosed, one or more of the following types of compounds:

1. Carboxylate esters having an alkyl hydroxy substituent near a carbonyl group of the compound;

2. Metal salts of organic acids, such as—

(a) Polyvalent metal salts of higher fatty or aliphatic acids;

(b) Metal salts of naphthenic acids;

(c) Metal salts of oil-soluble substituted phenols;

(d) Metal salts of carboxylic acids containing an aryl substituent;

3. Corrosion inhibitors and anti-oxidants, such as—

(a) Polyhydroxy phenols, condensed ring phenols, alkyl substituted phenols, and naturally-occurring inhibitors which may be extracted from fats and petroleum oils;

(b) Nitrogen compounds comprising aryl amines (diamines, diaryl amines), nitroso amines, cyclo-aliphatic amines, and condensation products of aldehydes or ketones with aromatic amines;

(c) Oxygenated organic compounds comprising aryl ethers, aryl ketones and alkyl ketones;

(d) Esters of polycarboxylic acids having two carboxyl groups no more than two carbon atoms apart, and esters of carboxylic acids having an unsaturated carbon-to-carbon bond conjugated with the carboxyl group;

(e) Oil-soluble organo-metallic compounds of metals selected from Groups II, III, IV and V of Mendeleeff's Periodic Table;

(f) Sulfur, selenium and tellurium compounds, such as aryl mercaptans, aryl sulfides, aryl disulfides, aryl polysulfides, aryl thioesters, alkyl thioesters, alkyl mercaptans, alkyl monosulfides, alkyl disulfides, alkyl polysulfides, alkali metal sulfonates and alkaline earth metal salts of sulfonic acids;

(g) Miscellaneous ring compounds comprising mercapto benzo-thiazole, oxazines, phenthiazine, indane and acridane;

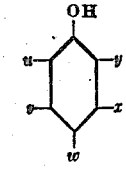
(h) Organic phosphorus compounds comprising oil-soluble phosphines, esters of phosphorous acid, and esters of phosphoric acid;

4. Polyvalent metal salts of acids of phosphorus containing an organic substituent, such as salts of partially esterified phosphoric acid, partially esterified phosphorous acid, partially esterified thiophosphoric acids, and partially esterified thiophosphorous acids;

5. Polyvalent metal oxides having an alkyl or cyclo-alkyl group directly attached to the oxygen thereof.

Among the carboxylate esters having an alkyl hydroxy substituent near a carboxyl group of the compound which may be utilized in combination with each and every one of the foregoing metal carboxylates are: the methyl, ethyl, propyl, butyl, amyl, hexyl, heptyl, octyl, nonyl, lauryl, dodecyl, tetradecyl, cetyl, and octadecyl esters of alpha or beta hydroxy propionic acid, and the corresponding esters of alpha, beta, and gamma hydroxy butyric, valeric, caproic, enanthic, caprylic, capric, lauric, myristic, palmitic, stearic, and arachidic, as well as the corresponding esters of tartronic, tartaric and citric acids.

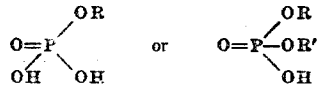
Among the metal salts of organic acids which may be utilized in combination with each and every one of the foregoing metal carboxylates having an alkyl hydroxy substituent near a carboxyl group of the compound are: aluminum laurate, aluminum oleate, aluminum stearate, aluminum ricinoleate; zinc laurate, zinc oleate, zinc stearate, zinc ricinoleate; tin laurate, tin oleate, tin stearate, tin ricinoleate; magnesium laurate, magnesium oleate, magnesium stearate, magnesium ricinoleate; calcium laurate, calcium oleate, calcium stearate, calcium ricinoleate; chromium laurate, chromium oleate, chromium stearate, chromium ricinoleate; aluminum naphthenate, zinc naphthenate, magnesium naphthenate, cobalt naphthenate, cadmium naphthenate, tin naphthenate, manganese naphthenate; aluminum, zinc, tin, magnesium, calcium and chromium salts of substituted phenols of the type formula:



in which u, v, w, x and y are selected from the group consisting of hydrogen, alkyl, aryl alkaryl, aralkyl and cyclic non-benzenoid radicals which may or may not be pure hydrocarbon substituents; aluminum phenyl stearate, zinc phenyl stearate, tin phenyl stearate, magnesium phenyl stearate, calcium phenyl stearate, chromium phenyl stearate; aluminum naphthyl stearate, zinc naphthyl stearate, tin naphthyl stearate, magnesium naphthyl stearate, calcium naphthyl stearate, chromium naphthyl stearate; aluminum phenyl laurate, zinc phenyl laurate, tin phenyl laurate, magnesium phenyl laurate, calcium phenyl laurate, chromium phenyl laurate; aluminum alpha benzal stearate, zinc alpha benzal stearate, tin alpha benzal stearate, magnesium alpha benzal stearate, calcium alpha benzal stearate, chromium alpha benzal stearate; aluminum alpha benzal laurate, zinc alpha benzal laurate, tin alpha benzal laurate, magnesium al-

pha benzal laurate, calcium alpha benzal laurate, chromium alpha benzal laurate.

Among the polyvalent metal salts of acids of phosphorus containing an organic substituent which may be utilized in combination with each and every one of the foregoing metal carboxylates are the aluminum, calcium, barium, strontium, chromium, and magnesium salts of substituted acids of pentavalent phosphorus of the following formulae:



where R and R' may be alkyl, aryl, alkaryl, aralkyl or cyclic non-benzenoid radicals which may or may not be pure hydrocarbon constituents.

Among the polyvalent metal oxides having an alkyl or cyclo-alkyl group directly attached to the oxygen thereof which may be utilized in combination with each and every one of the foregoing metal alkyl hydroxy carboxylates are: calcium amylate, calcium hexylate, calcium heptylate, calcium octylate, calcium decylate, calcium dodecylate, calcium tetradecylate, calcium cetylate; magnesium amylate, magnesium hexylate, magnesium heptylate, magnesium octylate, magnesium decylate, magnesium dodecylate, magnesium tetradecylate, magnesium cetylate; aluminum amylate, aluminum hexylate, aluminum heptylate, aluminum octylate, aluminum decylate, aluminum dodecylate, aluminum tetradecylate, aluminum cetylate; barium amylate, barium hexylate, barium heptylate, barium octylate, barium decylate, barium dodecylate, barium tetradecylate, barium cetylate; zinc amylate, zinc hexylate, zinc heptylate, zinc octylate, zinc decylate, zinc dodecylate, zinc tetradecylate, zinc cetylate.

Among the beneficial effects which flow from the incorporation of a metal salt or a mixture of metal salts of the above described alkyl hydroxy acids in a hydrocarbon oil of the lubricating oil class is the prevention of piston ring sticking, or its marked postponement, under very severe motor conditions, as for example, in Diesel engine or in aircraft spark or compression ignition engine operations.

In the tests whose results are summarized in Table I, a single cylinder Lauson gasoline spark-ignition engine, 2⅝ inch bore and 2½ inch stroke, loaded with fan dynamometers, was operated under extremely severe conditions, designed to develop fully the tendency of the crankcase lubricant to deteriorate with gum formation and piston ring sticking: operation was at 1600 R. P. M.; engine jacket temperature was maintained at 375° F.; crankcase oil temperature was maintained at 220° F.; at periods of 15 hours the operations were interrupted and the condition of the piston rings determined. In Table I, the base oil referred to as "Western 30" was an acid-refined lube stock of California origin; A. P. I. gravity 21.4°; viscosities at 100° and 210°, 662 seconds and 56.6 seconds, respectively, Saybolt Universal. To this base oil were added the various salts in the amounts indicated, by weight. The base or uncompounded oil referred to as "Pennsylvania 30" was a solvent refined stock of Pennsylvania origin, A. P. I. gravity 28.6°; viscosities at 100° and 210° F. of 519 and 66 seconds, respectively, Saybolt Universal.

TABLE I

Prevention or postponement of piston ring sticking

Oil	Hours to cause ring sticking	Relative ring slot cleanliness	Relative piston cleanliness
Western 30	30	Poor	Poor.
+0.28% potassium cetyl tartrate.	60+	Good	Good.
+0.42% magnesium cetyl tartrate.	60+	Fair—	Fair.
+0.57% aluminum cetyl tartrate.	60+	Poor	Poor.
+0.50% calcium cetyl tartrate.	120+	Very good	Very good.
+0.20% calcium cetyl mucate.	60+	Poor	Poor.
+0.34% potassium cetyl citrate.	120	Good	Fair.
+0.23% magnesium cetyl citrate.	60+	Fair	Poor.
+0.52% aluminum cetyl citrate.	60+	Good	Fair.
+0.50% calcium dicetyl citrate.	120+	do	Good.
+0.63% calcium alpha-eicosyltartrate.	60+	Fair+	Do.
+0.50% calcium cetyl malate.	105+	Good	Do.
+0.50% calcium cetyl phenate+0.50% calcium cetyl tartrate.	60+	Very good	Very good.
+0.50% calcium cetyl phenate+0.50% calcium dicetyl citrate.	60+	do	Do.
+0.50% calcium cetyl phenate+0.25% calcium dicetyl citrate.	90+	do	Do.
+0.50% calcium cetyl phenate+0.50% calcium alpha-eicosyltartrate.	120+	do	Do.
+0.63% calcium alpha hydroxy stearate.	60+	Fair	Fair.
Pennsylvania 30	30	Poor	Poor.
+0.50% calcium cetyl tartrate.	60+	Good	Do.
+0.50% calcium cetyl phenate+0.50% calcium dicetyl citrate.	60+	Very good	Very good.
+0.63% calcium alpha hydroxy stearate.	60+	Fair	Fair.

NOTE.—A plus sign (+) following a stated number of hours in the antepenultimate column indicates free rings at the conclusion of a test of the stated hours' duration.

An additional benefit to be derived from this invention is a decreased corrosivity toward bearing metals, particularly those of the cadmium-silver and copper-lead type. This diminution in corrosivity is particularly marked if the corrosivity of oils compounded with unsubstituted polyvalent metal carboxylates is compared with the corrosivity of the same oil compounded with the same amount of the corresponding polyvalent metal carboxylate having an alkyl hydroxy substituent therein according to the principles of this invention. This decrease in corrosivity is so extensive in many instances that the compounding agents of this invention not only are themselves non-corrosive in lubricating oils but actually reduce the corrosivity of uncompounded oils which normally become corrosive during use, e. g., highly paraffinic lubricating oils or highly refined oils, such as selective solvent extracted lubricating oils. As has been previously indicated herein, where reduction in corrosivity is a significant factor the alkyl hydroxy substituent should preferably be in the alpha position with respect to a carboxyl group of the compound, less preferably in the beta position, and of decreasing desirability and effectiveness in the gamma, delta and epsilon positions in the order named.

In the corrosion tests whose results are summarized hereinafter, thin sheets of the indicated bearing metals were cut into strips (copper-lead, ⅛" x 1¾" x 3 3/32"; cadmium-silver, ½" x 1⅜" x 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 the 72-hour period, except as indicated.

To illustrate the pronounced reduction in corrosion effect by the compounds of this invention as compared with various unsubstituted carboxylates, the following data are given:

TABLE II

Oil	Weight loss in mgms.—72 hrs.	
	Cu-Pb	Cd-Ag
Western oil S. A. E. 30 (naphthenic base)	13.9	0.4
+0.5% calcium stearate	131.9	180.5
+1% aluminum dinaphthenate	67	113
+1% magnesium naphthenate	139	119
+1% calcium cetyl phenate	126	12.1
+0.63% calcium alpha-hydroxy stearate	19.0	2.1
+0.34% potassium cetyl citrate	8.5	0.4
+0.52% aluminum cetyl citrate	5.5	0.5
+0.5% calcium dicetyl citrate	2.6	1.4
+0.63% calcium alpha-eicosyl tartrate	5.0	0.9
Pennsylvania oil S. A. E. 30 (paraffinic base)	24.5	1.6
+1% aluminum dinaphthenate (24 hrs.)	42.8	28.6
+0.10% calcium ricinoleate	135.2	222
+0.5% calcium cetyl phenate	63.5	47.6
+0.75% calcium cetyl phenate	166.6	215.4
+0.5% calcium cetyl tartrate	1.3	0.2
+0.5% calcium cetyl citrate	18.7	14.2

Attention is directed to the fact that each of the salts in the above table having an alkyl hydroxy group near a carbonyl group (i. e., the alpha hydroxy stearate, the citrates, and the tartrates) is characterized by extremely low corrosivity as compared with the unsubstituted carboxylates.

The following additional data establish the relative non-corrosiveness and, in some instances, the actual corrosion inhibiting properties of the compounds of this invention:

TABLE III

Reduction of corrosivity to bearing metals

Oil	Weight loss in mgms.—75 hrs.	
	Cu-Pb	Cd-Ag
Western 30	13.9	0.4
+0.28% potassium cetyl tartrate	1.3	0.1
+0.42% magnesium cetyl tartrate	2.0	0.3
+0.50% calcium cetyl tartrate	1.3	0.5
+0.20% calcium cetyl mucate	1.6	0
+0.28% magnesium cetyl citrate	2.1	0
+0.50% calcium cetyl malate	3.7	0.1
+0.50% calcium cetyl phenate+0.50% calcium cetyl tartrate	2.0	0.3
+0.50% calcium cetyl phenate+0.50% calcium dicetyl citrate	9.6	1.3
+0.50% calcium cetyl phenate+0.25% calcium dicetyl citrate	6.1	0.1
+0.25% calcium cetyl phosphate+0.50% calcium dicetyl tartrate	1.3	0.2
+1.0% calcium cetyl phenate	126	12.1

A still further benefit derived from the addition of the metal salts of this invention to hydrocarbon oils is a marked lessening of color instability upon exposure of the compounded oils to heat in the absence of metals.

In the tests whose results are summarized in Table IV, samples of the compounded oils were held in glass at 300° F. for six hours. The oils were cooled at the end of this period of time and their colors measured for comparison with the uncompounded base oil stocks; A. S. T. M. colors, Method D155–34T were recorded in all cases.

TABLE IV

Color stability

Oil	Color increase
Western 30	6
+0.28% potassium cetyl tartrate	½
+0.42% magnesium cetyl tartrate	2+
+0.57% aluminum cetyl tartrate	1½
+0.50% calcium cetyl tartrate	1−
+0.20% calcium cetyl mucate	4
+0.34% potassium cetyl citrate	1½−
+0.28% magnesium cetyl citrate	1½+
+0.52% aluminum cetyl citrate	½
+0.50% calcium dicetyl citrate	1
+0.63% calcium alpha-eicosyltartrate	1−
+0.50% calcium cetyl malate	1
+0.50% calcium cetyl phenate +0.40% calcium cetyl tartrate	1+
+0.50% calcium cetyl phenate +0.50% calcium dicetyl citrate	2½+
+0.50% calcium cetyl phenate +0.50% calcium cetyl malate	1
+0.25% calcium cetyl phosphate +0.40% calcium cetyl tartrate	2½
+0.25% calcium cetyl phosphate +0.50% calcium dicetyl citrate	1+
+0.25% calcium cetyl phosphate +0.50% calcium cetyl malate	1
+0.50% calcium cetyl phenate +0.25% calcium cetyl phosphate +0.40% calcium cetyl tartrate	2+
+0.50% calcium cetyl phenate +0.25% calcium cetyl phosphate +0.50% calcium dicetyl citrate	1½
+0.50% calcium cetyl phenate +0.25% calcium cetyl phosphate +0.50% calcium cetyl malate	1−
+1.0% di-isoamyl tartrate +0.50% calcium dicetyl citrate	1
+1.0% di-isoamyl tartrate +0.18% calcium cetyl oxalate	4
+1.0% di-isoamyl tartrate +0.50% calcium cetyl succinate	3½−
+1.0% di-isoamyl tartrate +0.50% calcium cetyl malate	1
+1.0% di-isoamyl tartrate +0.50% calcium cetyl maleate	½
+1.0% di-isoamyl tartrate +0.10% calcium alpha cetenylsuccinate	1
+1.0% di-isoamyl tartrate +0.50% calcium alpha-eicosenylsuccinate	½
+1.0% di-isoamyl tartrate +0.15% calcium cetyl sebacate	4½+
+0.63% calcium alpha-hydroxy stearate	1−

In many cases still further benefits may be derived from the incorporation of the metal salts of the invention in hydrocarbon oils, by reason of an enhanced "oiliness" and/or an increased load carrying capacity of the oils so compounded.

In the tests whose results are summarized in Table V, the figures reported under "Weeks wear" are those obtained in the operation of a Weeks wear testing machine, in which a ½ inch steel ball is pressed against a 1⅜ inch steel cylinder which is rotated at 600 R. P. M. and which dips into the oil being tested; the duration of the test is 16 hours and the body of oil is held at 300° F.; the results are reported in inches of wear $\times 10^5$, as measured on the cylinder. The figures reported under "Film strength" are those obtained in the operation of a modified Timken machine similar to that described in the S. A. E. Journal, volume 28, page 53, 1928; the results are reported in pounds at failure.

TABLE V

Wear resistance and film strength

Oil	Weeks wear	Film strength
Western 30	283	120
+0.50% calcium cetyl tartrate	74	160
+0.50% calcium cetyl malate	83	560
+0.50% calcium cetyl phenate+0.25% calcium dicetyl citrate	103	320
+1.0% aluminum dinaphthenate	639	120
+0.50% calcium cetyl phenate	105	120

Still further, the ability of hydrocarbon oils to resist oxidation, i. e., absorption of oxygen when exposed thereto at superatmospheric temperatures and pressures, is in many cases enhanced and oxygen absorption postponed by the incorporation in the oils of the metal salts of the invention.

In the tests whose results are reported in Table VI the oils referred to were subjected to the "Oxidator test," particularly described in the Journal of Industrial and Engineering Chemistry, volume 28, page 26, 1936. These tests were carried out at 340° F., which condition may be noted as extremely severe. The results of the tests are reported in cubic centimeters of oxygen absorbed per 100 grams of the respective oils at the periods of time indicated.

TABLE VI

Reduction of oxygen absorption

Oil	Oxygen absorption		
	1 hr.	2 hrs.	2½ hrs.
Western 30	200	330	390
+0.28% potassium cetyl tartrate	135	235	280
+0.42% magnesium cetyl tartrate	80	200	270
+0.57% aluminum cetyl tartrate	87	150	175
+0.50% calcium cetyl tartrate	25	55	70
+0.20% calcium cetyl mucate	18	45	75
+0.34% potassium cetyl citrate	30	50	55
+0.28% magnesium cetyl citrate	35	135	190
+0.52% aluminum cetyl citrate	24	65	93
+0.50% calcium dicetyl citrate	20	40	50
+0.63% calcium alpha-eicosyltartrate	65	105	122
+0.50% calcium cetyl malate	22	60	90
+0.5% calcium stearate	400+	Too rapid to measure	
+0.35% calcium ricinoleate	325	400+	
+0.63% calcium alpha-hydroxy stearate	50	100	125

Study of the foregoing data will show that the compounded oils of this invention have a combination of properties which is particularly desirable and difficult to obtain. The ability to impart color stability, to inhibit oxidation, to inhibit piston ring sticking, to impart freedom from the production of increased wear, and in many instances actually decrease wear on cylinder walls and piston rings as compared with uncompounded mineral oils, and non-corrosivity as respects the chemical action of the compounded oil on bearing metals such as copper-lead and cadmium-silver alloys, together with the ability of certain compounds and combinations to actually decrease corrosivity of normally corrosive uncompounded oils, represents an array of advantageous properties which is quite rare in single compounding agents or simple combinations thereof.

Attention is particularly directed to the unpredictable excellence of the results obtained with an oil compounded with both a calcium alkyl phenate and an alpha hydroxy carboxylate, such as calcium alkyl citrate, as shown by the following data:

TABLE VII

	S. A. E. 30 Western oil	S. A. E. 30 Western oil+0.5% calcium cetyl phenate+0.5% calcium cetyl citrate
Time	30 hrs.	60 hrs.
Ring sticking	Yes	None.
Piston discoloration No.	600	20.
Oil ring slot clogging	High	None.
Copper-lead corrosion mgms.	13.9	1.

These two types of compounding agents cooperate to give results obtainable with neither alone.

A discussion and data on the preparation of exemplary compounds and lubricants of this invention may serve to guide those skilled in the art in the practice thereof.

The compounds may be prepared by a number of alternative methods which may involve, for example, (1) neutralization of an alkyl hydroxy acid with an alkali metal hydroxide, and addition of a water-soluble polyvalent metal salt to an aqueous solution of the neutralized acid whereby precipitation of the desired compound is obtained; or (2) hydrolysis and saponification of the neutral ester to form an alkali metal salt of the acid of the ester, and precipitation of the polyvalent metal salt from the saponified product. Where polycarboxylic acids are utilized as the salt-forming agent, an acid ester may first be formed or the neutral ester partially hydrolyzed and saponified to obtain compounds from which polyvalent metal alkyl hydroxy carboxylates are formed. Specific examples are as follows:

Example 1.—Preparation of calcium alpha hydroxy stearate from stearic acid. Eight hundred and fifty-two grams of commercial triple-pressed stearic acid (equivalent weight=273), which had been recrystallized from ethyl alcohol, were intimately mixed with 40 grams of acid-free red phosphorus. This mixture was heated on a water bath in a flask equipped with a dropping funnel and a reflux condenser, which was vented through an aqueous ammonia trap (to absorb bromine) to a vacuum line. When the stearic acid and phosphorus mixture had been heated sufficiently to melt the acid, 430 cc. of anhydrous liquid bromine were slowly dropped into the reaction flask. The addition of bromine was carried out over a period of 3½ hours at a temperature varying from 130° F. initially to 180° at the completion of the addition. Heating was continued at 200° F. for six hours after all the bromine had been added. The product of this reaction, impure alpha bromostearyl bromide, was slowly poured into cold water and the whole then warmed on a hot plate for about an hour to effect hydrolysis of the acid bromide to the acid. The equation describing these processes are:

$$3RCH_2COOH + P + 5\tfrac{1}{2}Br_2 = 3RCHBrCOBr + 5HBr + HPO_3$$
$$RCHBrCOBr + HOH = RCHBrCOOH + HBr$$

Alpha-bromostearic acid

The alpha-bromo acid was washed well with water and then taken up in petroleum ether. This solution was separated from the water layer, washed several times by shaking with water, and filtered. The bromo acid was crystallized from the petroleum ether in 73% yield and gave the following analysis:

	Theoretical	Observed
Percent bromine	22.8	23.5
Neutralization value	160	157

The analysis indicates the presence of about 8% of dibromostearic acid in the product.

Alpha-hydroxystearic acid.—One hundred and twenty-five grams of alpha-bromostearic acid were mixed with 120 grams (an excess) of freshly precipitated silver carbonate and one liter of 50% aqueous alcohol in a flask equipped with a stirrer

and a reflux condenser. The reactants were heated at refluxing temperature for ten hours. The product, impure silver alpha-hydroxystearate, was separated from the 50% alcohol and treated with 20% nitric acid to decompose the salt into the acid, which was taken up simultaneously in ethyl ether. The ether solution was washed, filtered, and evaporated. The crude acid was recrystallized from benzene and petroleum ether (1 to 3 mixture) in 30% overall yield. This product had the following analysis:

	Theoretical	Observed
Saponification number	194	194
Percent bromine	0	0
Bromine number	0	0

The equations representing the preparation of the hydroxy acid are as follows:

$$RCHBrCOOH + Ag_2CO_3 = RCHOHCOOAg + AgBr + CO_2$$
$$RCHOHCOOAg + HNO_3 = RCHOHCOOH + AgNO_3$$

Alpha-hydroxystearic acid

The calcium salt was prepared by neutralizing the alpha-hydroxy stearic acid in hot water with aqueous caustic potash and then precipitating the calcium salt by adding calcium chloride solution. The washed and dried salt was obtained in 73% overall yield. The salt had an ash of 8.6% and 0% bromine content.

Examples 2, 3 and 4.—Compounds Nos. 2, 3 and 4 in Table VIII below were prepared by sterification of the corresponding acid, partial saponification, precipitation of the calcium salt, and purification of the precipitated salt as follows:

Formation of the dicetyl ester (or tricetyl ester)—*g* grams (see Table VIII, horizontal column *g*) of cetyl alcohol of hydroxyl number *h*, and *i* grams of di- or tricarboxylic acid were mixed and heated in a suitable flask equipped with a stirrer and a trap for collecting the water produced in the esterification. The reactants were heated at an average temperature of *j* degrees Fahrenheit for *k* hours. During the last several hours of heating, nitrogen gas was bubbled through the reaction mixture in some cases to facilitate completion of the reaction and removal of any remaining water. The rapidity and degree of completeness of the reaction were followed by measuring the volume of water in the trap. The product was obtained in *l* grams yield and was checked for completeness of reaction and purity by determining a saponification number *m* and a neutralization value *n*.

No catalyst was employed in this reaction, but hydrochloric or sulfuric acids can be used for such purposes.

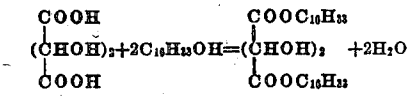
Partial saponification of the di- or tri-cetyl ester.—*o* grams of ester prepared as in the above example were washed with water to remove any unused acid (where the acid was sufficiently water-soluble). The washed ester was dissolved in 95%–100% ethyl alcohol, the solution stirred and heated to *q* degrees Fahrenheit, and *p* grams of caustic potash in an alcohol or alcohol-water solution slowly added, the rate of addition being regulated in such manner that at no time was there an appreciable excess of caustic present, as shown by phenolphthalein indicator added to the solution. The rate of saponification varies for the different esters; the total time required is given in Table VIII, horizontal column *r*.

Precipitation of the calcium salt.—The alcoholic solution from the partial saponification, containing potassium salt, unreacted ester, and cetyl alcohol produced in the reaction, was diluted with approximately an equal volume of water, the temperature brought to 150–170° F., giving a creamy suspension, and *s* grams of calcium chloride in water solution added with stirring. There may or may not be curding of the calcium salt, depending on the particular compound and the conditions of the reaction. The precipitated solid material was washed with water to remove potassium chloride and any unused calcium chloride, and was then dried.

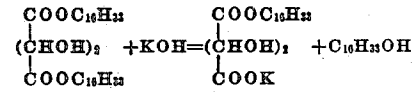
Purification of calcium salt.—The dry calcium salt was freed of cetyl alcohol (produced in the partial saponification) and any unreacted ester by extraction with ethyl ether or other suitable solvent, giving a final yield of *t* grams of the calcium alkyl hydroxy carboxylate. The cetyl alcohol extracted from the crude salt was recovered for reuse.

Equations for a representative preparation.—The following equations are for the preparation of calcium cetyl tartrate:

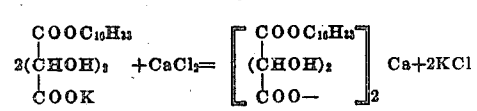
Esterification



Partial saponification



Formation of calcium salt



Example 5.—Calcium dicetyl citrate was also made by preparing a partial or acid ester directly and neutralizing as follows:

Formation of the partial ester.—384 grams of citric acid were mixed with 100 grams of cetyl alcohol and heated at 320° F. in a flask equipped with a stirrer and trap for catching the water produced in the reaction. Additional cetyl alcohol, up to a total of 547 grams, was added to the reaction mixture in approximately 100 grams increments at one hour intervals. The total time required for the reaction was eight hours. The yield was 767 grams of crude acid ester. This product was washed with water to remove excess citric acid and a dried sample had a saponification number of 229 and neutralization number of 75. These figures correspond to approximately 85% dicetyl citric acid.

Formation of calcium salt.—The washed 85% dicetyl citric acid was suspended in water at a temperature of 170° F. and slowly neutralized in the presence of an indicator with 30 grams of potassium hydroxide in aqueous solution. The calcium salt was then precipitated by adding excess aqueous calcium chloride. The salt was washed free of potassium chloride and excess calcium chloride and dried. The yield of dry calcium salt was 383 grams, or 60% of theoretical, calculated on the basis of calcium dicetyl citrate. The salt had an ash of 5.35%.

TABLE VIII

Data on preparation of compounds and their solution in oil

		Example 2	Example 3	Example 4	Example 5
		Calcium cetyl tartrate	Calcium cetyl malate	Calcium dicetyl citrate	Calcium dicetyl citrate direct method
	ESTERIFICATION PROCESS				
g	Cetyl alcohol, gm.	484	1094	1641	547
h	Hydroxyl no. of alcohol	232	205	205	205
i	Polycarboxylic acid, gm.	150	268	384	384
j	Avg. temp. of heating, °F.	310	320	340	320
k	Time of heating, hours	24	19	6	8
l	Yield of crude ester, gm.	596	1273	1780	767
l'	Yield of % of theoretical based on *l*, *m*, *n*	93	95	81	51
m	(Sapon. no. of ester	188	176	161	229
	(Theoretical value	188	193	195	195
n	Neutraliz. value of ester	12	8	8	75
	PARTIAL SAPONIFICATION PROCESS AND MAKING OF SALT				
o	Ester of saponification, gm.	400	500	216	
p	KOH for saponification, gm.	35	42	11	80
q	Avg. temp. of sapon., °F.	160	160	180	
r	Time for saponification	30 min.	30 min.	2 hrs.	
s	$CaCl_2$ to make salt, gm.	35	42	11	146
t	Yield of salt, gm.	148	75	58	383
t'	Yield in % of theoretical	60	27	46	60
	Yield in overall % of theoretical	56	26	37	31
u	Temp. during solution of salt concentrate in oil, °F.	400	400	250	250
v	Time of heating during solution in oil, minutes	10	5	5	5

Preparation of compounded oil containing the calcium salt.—The dry calcium salt was made into an oil concentrate by dissolving the salt in a small amount of lubricating oil. The concentrate may contain as much as 50% or more of the salt dissolved in the solvent. When oil is the solvent, stirring and heating to a temperature of from 300° to 400° F. is desirable. The concentrate was then added to sufficient mineral lubricating oil to dilute to the desired final concentration and the whole was heated at *u*° F. for *v* minutes (Table VIII). In the case of calcium cetyl tartrate particularly, it was necessary that the temperature *u* be high in order to destroy a false viscosity or thickening of the oil which resulted if a lower temperature was employed. For compounds of low solubility it is also necessary to aid solution by stirring at relatively high temperatures and for longer periods of time. The oil was finally filtered through a press preceded by centrifuging where necessary.

The proportion of the metal alkyl hydroxy carboxylates added to mineral lubricating oils may vary widely, depending upon the uses involved and the properties desired. As little as 0.1% by weight of the metal alkyl hydroxy carboxylate gives measurable improvements, although from approximately 0.25% to approximately 2% is preferred where the compounded oil is to be used as a crankcase lubricant for internal combustion engines. Similarly, the proportion of the carboxylate esters having an alkyl hydroxy substituent near a carbonyl group of the ester may vary widely but in general from 0.1% to 5% of the ester is utilized in combination with the metal alkyl hydroxy carboxylates, and more usually 0.5% to 2% thereof is found desirable. More than 10% is regarded as unnecessary, except when a concentrate is being prepared for subsequent dilution with mineral oil to produce the finished lubricant. The proportion of metal salts of other organic acids, such as the aliphatic acids, naphthenic acids, phenolic acids, and aryl carboxylic, likewise may vary from 0.1% to 5% and, more usually, from 0.5% to 2% when utilized in combination with metal alkyl hydroxy carboxylates. The corrosion inhibitors and anti-oxidants represented by the various types listed above under the heading "3 Corrosion inhibitors and anti-oxidants such as—" may be present with the metal alkyl hydroxy carboxylates in an amount of from about 0.05% to 2%, or more. The polyvalent metal salts of acids of phosphorus containing an organic substituent when utilized in combination with the polyvalent metal alkyl hydroxy carboxylates may be added in amounts from 0.05% to about 2%, or more. Usually 1% or less is found adequate. The polyvalent metal oxides having an alkyl or cycloalkyl group attached to the oxygen thereof may be added in amounts of from 0.05%, or less, to 5% and preferably 0.1% to 2% when used in combination with the metal alkyl hydroxy carboxylates. In each of the above instances the proportions of ingredients may be very materially increased when a concentrate is being prepared for subsequent dilution with lubricating oil. Proportions are given throughout this specification in per cent by weight based on the oil unless otherwise indicated.

In general, metal alkyl hydroxy carboxylates containing at least about ten carbon atoms are preferred. Where the organic alkyl hydroxy pure esters are utilized in combination with the metal carboxylates and reduced corrosion is desired, the ester should preferably contain less than ten carbon atoms; where reduced friction at low rubbing speeds is a paramount factor, more than ten carbon atoms in the ester are preferred; cooperation with the metal alkyl hydroxy carboxylates to give increased stability against oxidation may be obtained with esters containing either ten or less carbon atoms, or more than ten carbon atoms; more than 75 carbon atoms are regarded as unnecessary.

The concentrates previously referred to may be prepared and distributed as a hydrocarbon oil or

ıer organic solution containing relatively large oportions of the additive agents. The solvent ay be hydrocarbon oils of the lubricating or less ıcous type or, if more suitable, an admixture th oil of certain other agents, such as aromatic drocarbons, alcohols, esters, ketones or ethers, ıich are generally of low molecular weight and the aliphatic series. These latter blending ents may serve to improve the solubility relaınships or the like of the compounds. Admixres of the addition agents and lubricating oils other solvents or carriers containing 50% or ore of the essential agents by weight may be us prepared and distributed for later blending th the particular lubricating oil media to be it to use as occasion demands. In the preparaın of either the finished oils of the invention or the bases or concentrates referred to, complete clear and homogeneous solution is not always cessary. Stabilizing or blending agents may be nployed to prevent sedimentation of the more l-insoluble addition agents. The possible detrimental effect of the presence of filterable insolue materials of this character, if they be present, determined largely by the particular conditions tending the contemplated use and their presıce is not in all cases deleterious to the functiong of the composition in its intended manner.

The compounded lubricant herein disclosed ay have one or more advantages depending upon ıe particular compounds selected, the proporons utilized, and the environment which the ibricating oil is to encounter. It should be oberved, for example, that even though a compounded oil may not be entirely non-corrosive to ppper-lead or cadmium-silver alloys, other bearıg metals may be little if at all affected by such orrosive action. Hence, compounding agents or ombinations thereof which may not be particuırly desirable for one service, where corrosion at igh temperatures becomes a factor of imporance, may nevertheless be highly useful and exremely advantageous in other services. Likerise, a compounding agent which may not be ufficiently powerful to adequately stabilize a paricular oil stock against deterioration under the ıost severe conditions may be highly advanageous in such an oil where the environment to e encountered is not so severe, as for example in urbine oils, cable oils, electric switch oils, transormer oils and the like. Further, the same comounding agent may cooperate with other agents, s disclosed hereinbefore, to adequately stabilize he oil even for the most severe service. The resent invention in its broader aspects is thereore not limited to the particular compounding ngredients having the greatest stability or havng all of the advantages of the preferred agents r combinations of agents. The invention emraces various of the less advantageous compounding agents or combinations thereof which nay find utility in particular applications where ll possible improvements in properties of the oil may not be required or where the standard of performance may not be so high.

The compounding ingredients of this invention are not limited in their applicability to any particular base oil stock. The advantages herein disclosed may be obtained with various oil stocks, the selection of which will be determined by conditions and services which the compounded lubricant is to encounter. The compounding ingredients are useful not only in Pennsylvania oils or highly refined naphthenic base oils, but also in moderately refined naphthenic base oils or in lubricating oils from Mid-Continent stocks, as wall as in synthetic hydrocarbon oils, such as hydrogenated polymers of olefin hydrocarbons, or condensation products of chlorinated alkyl hydrocarbons with aryl compounds.

The compounding ingredients of this invention may be utilized in hydrocarbon oils containing other compounding agents, such as pure point depressants, extreme pressure addition agents, blooming agents and the like. Also the compounds are useful in greases, e. g. a grease comprising a mineral oil and a sodium soap.

It is to be understood that the invention in its broader aspects does not preclude the use of substituted alkyl hydroxy carboxylates and that the term "alkyl hydroxy" is intended to define a compound in which the hydroxy group retains the essential characteristics of a hydroxyl group attached to a pure alkyl radical. However, substituents may be present in the polyvalent metal alkyl hydroxy carboxylates in a position which is so far removed from the hydroxy group as not to substantially destroy the essential alkyl hydroxy characteristics of the hydroxy radical. The invention therefore includes polyvalent metal salts of substituted alkyl hydroxy carboxylic acids when the substituent present is not so close to the alpha, beta or gamma hydroxy radical as to substantially destroy its essential alkyl hydroxy characteristics. Thus functional groups, such as an aromatic ring positioned on an alkyl chain relatively remote (for example, ten or twelve carbon atoms removed) from the alpha, beta or gamma hydroxy radical, are regarded as falling within the scope of the invention in its broader aspects.

The term "carbonyl group" is used through out the specification and claims to include an esterified or neutralized carboxyl group, i. e. the group

$$-\overset{\overset{O}{\|}}{C}-O-X$$

where X may be either a metal or an organic radical.

Our copending application Serial No. 322,946, filed March 8, 1940, is directed to those aspects of the present disclosure pertaining to salts of polycarboxylic acids.

While the character of the invention has been described in detail and numerous examples given, this has been done by way of illustration only and with the intention that no limitation should be imposed upon the invention thereby. Numerous modifications and illustrations of the illustrative examples may be effected in the practice of the invention which is of the scope of the claims appended hereto.

We claim:

1. A composition comprising a major proportion of a hydrocarbon lubricating oil subject to deterioration, and from about 0.1% to 2% by weight of a metal alkyl monocarboxylate having an alkyl hydroxy group no more than about three carbon atoms removed from a carbonyl group of the carboxylate.

2. A composition comprising a major proportion of a hydrocarbon lubricating oil subject to deterioration, and from about 0.1% to 2% by weight of a polyvalent metal alkyl monocarboxylate having an alkyl hydroxy group no more than about three carbon atoms removed from a carbonxyl group of the carboxylate.

3. A composition comprising a major proportion of a hydrocarbon lubricating oil subject to deterioration, and from about 0.1% to 2% by

weight of an alkaline earth metal alkyl monocarboxylate having an alkyl hydroxy group no more than about three carbon atoms removed from a carbonyl group of the carboxylate.

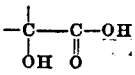
4. A composition comprising a major proportion of a hydrocarbon lubricating oil subject to deterioration, and from about 0.1% to 2% by weight of a calcium alkyl monocarboxylate having an alkyl hydroxy group no more than about three carbon atoms removed from a carbonyl group of the carboxylate.

5. A composition comprising a major proportion of a hydrocarbon lubricating oil subject to deterioration, and from about 0.1% to 2% by weight of an aluminum alkyl monocarboxylate having an alkyl hydroxy group no more than about three carbon atoms removed from a carbonyl group of the carboxylate.

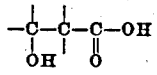
6. A composition comprising a major proportion of a hydrocarbon lubricating oil subject to deterioration, and from about 0.1% to 2% by weight of a chromium alkyl monocarboxylate having an alkyl hydroxy group no more than about three carbon atoms removed from a carbonyl group of the carboxylate.

7. A compounded lubricant subject to deterioration at elevated temperatures comprising a hydrocarbon oil and a small amount of a metal alkyl monocarboxylate sufficient substantially to inhibit said deterioration, said carboxylate being characterized by the presence of an alkyl hydroxy group not more than about three carbon atoms from a carbonyl group of said carboxylate to reduce the corrosivity of said carboxylate to bearing metals of the class represented by metals selected from the group consisting of cadmium-silver and copper-lead alloys.

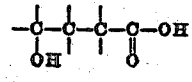
8. A compounded lubricant subject to deterioration at elevated temperatures comprising a hydrocarbon oil and a small amout of a metal alkyl carboxylate sufficient substantially to inhibit said deterioration, said carboxylate being a polyvalent metal salt of an acid characterized by the presence of the group



9. A compounded lubricant subject to deterioration at elevated temperatures comprising a hydrocarbon oil and a small amount of a metal alkyl monocarboxylate sufficient substantially to inhibit said deterioration, said carboxylate being a polyvalent metal salt of an acid characterized by the presence of the group



10. A compounded lubricant subject to deterioration at elevated temperatures comprising a hydrocarbon oil and a small amount of a metal alkyl carboxylate sufficient substantially to inhibit said deterioration, said carboxylate being a polyvalent metal salt of an acid characterized by the presence of the group



11. A composition comprising a hydrocarbon lubricating oil subject to deterioration, from about 0.1% to 2.0% by weight of a metal alkyl carboxylate having an alkyl hydroxy substituent no more than about three carbon atoms removed from a carbonyl group of the metal carboxylate, and from about 0.1% to 5% by weight of an oil soluble metal phenate.

12. A composition comprising a hydrocarbon lubricating oil subject to deterioration, from about 0.1% to 2.0% by weight of a metal alkyl carboxylate having an alkyl hydroxy substituent no more than about three carbon atoms removed from a carbonyl group of the metal carboxylate, and from about 0.05% to 2.0% by weight of an alkyl thio ether.

13. A composition comprising a hydrocarbon lubricating oil subject to deterioration, from about 0.1% to 2.0% by weight of a metal alkyl carboxylate having an alkyl hydroxy substituent no more than about three carbon atoms removed from a carbonyl group of the metal carboxylate, and from about 0.05% to 2.0% by weight of a polyvalent metal salt of an acid of phosphorus containing an organic substituent.

14. A composition comprising a major proportion of a hydrocarbon lubricating oil and from about 0.1% to 2.0% by weight of a metal salt of an alkyl carboxylic acid characterized by the presence of the group

R(OH)B—COOH

where R is a radical of alkyl structure, B is an alkyl group of no more than three carbon atoms, said acid containing at least ten carbon atoms.

15. A composition comprising a major proportion of a hydrocarbon lubricating oil and from about 0.1% to 2.0% by weight of a polyvalent metal salt of an alkyl carboxylic acid characterized by the presence of the group

R(OH)B—COOH

where R is a radical of alkyl structure, B is an alkyl group of no more than three carbon atoms, said acid containing at least ten carbon atoms.

16. A compounding agent for lubricating oils which is miscible with hydrocarbon lubricating oil and adapted to be diluted therewith comprising a concentrated solution in an organic solvent of a polyvalent metal monocarboxylate having an alkyl hydroxy group no more than about three carbon atoms from a carbonyl group of the carboxylate.

17. A compounding agent for lubricating oils which is miscible with hydrocarbon lubricating oil and adapted to be diluted therewith comprising a concentrated solution in a hydrocarbon oil of a polyvalent metal monocarboxylate having an alkyl hydroxy group no more than about three carbon atoms from a carbonyl group of the carboxylate.

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