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COMPOUNDED OIL

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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, now issued as Patent No. 2,349,817 of May 30, 1944.

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 can not 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.

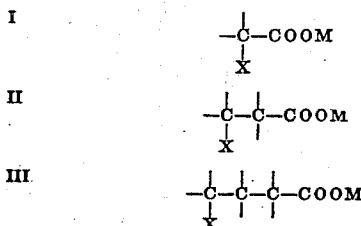
5 It is a still further and a particular object achieved by the present invention to provide a class of soap-like or metal alkyl carboxylate additives for lubricating oils which are non-corrosive, or substantially less corrosive than prior soap additives, such as calcium stearate, toward alloy bearings.

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.

The substituents that have been found to greatly improve metal alkyl carboxylates as additives for hydrocarbon oils and the like are those containing an element of group VB of the periodic table; that is, containing at least one of the elements nitrogen, phosphorus, arsenic, antimony and bismuth. Preferably, those substituents are employed in which a group VB element is directly connected to the alkyl group of the metal alkyl carboxylate, as in the case of the amino, imino, phosphino, phosphylene and analogous arsenic, antimony and bismuth substituted metal alkyl carboxylates, although substituents may be employed in which the group VB element is connected with the alkyl group of the metal alkyl carboxylate through an intervening atom, such as a carbon atom, as in the case of cyano substituted metal alkyl carboxylates.

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



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 an element of group VB of the periodic table. 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:

—NR ₁ R ₂	Amino	—AsR	Arsylene
—NR	Imino	—AsO	Arsenoso
—NO	Nitroso	—AsO ₂	Arso
—NO ₂	Nitro	—SbR ₁ R ₂	Stibino
—CN	Cyano	—SbR	Stibylene
—NC	Isoeyano	—SbO	Stiboso
—PR ₁ R ₂	Phosphino	—SbO ₂	Stibo
—PR	Phosphylene	—BiR ₁ R ₂	Bismuthino
—PO	Phosphoroso	—BiR	Bismuthylene
—PO ₂	Phospho	—BiO	Bismuthoso
—AsR ₁ R ₂	Arsino	—BiO ₂	Bismutho

In the above, R, R₁ and R₂ represent hydrogen, hydrocarbon (e. g. alkyl, aryl, aralkyl, and cycloalkyl), or other atoms or groups. 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 (preferably removed by three or more carbon atoms from the alkyl carboxyl group) are comprehended by the invention. In all cases, however, the acid contains 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.

Note.—Stable amino acids cannot be prepared from certain of the hydroxy acids except by replacement of the hydroxy group.

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. C₁₀ 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 aminobutyrate; the corresponding alpha, beta and gamma amino valerates, caproates, caprates, laurates, myristates, palmitates, stearates, acrylates, crotonates, angelates, oleates, lactates, malonates, succinates, glutarates, adipates, maleates, fumarates, malates, and citrates; also the corresponding imino, cyano, isocyno, phosphino, phosphylene, arsino, arsyleno, stibino, stibylene, bismuthino and bismuthylene substituted salts (that is, the salts formed by substituting imino, cyano, etc. for amino).

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.

Various methods of forming the metal salts may be employed, one such method being to form an alkali metal salt (as by neutralizing the acid, or saponifying the corresponding ester, with an alkali metal hydroxide) and using the alkali metal salt per se or converting it into a polyvalent metal salt by adding to an aqueous solution of the alkali metal salt, a water soluble salt of a polyvalent metal, thus producing double decomposition and precipitation of the polyvalent metal salt.

The substituted metal alkyl carboxylates of this invention improve hydrocarbon oils in sev-

eral 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 naphthe-

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 0.5% by weight based on the oil:

Table I

Oil	Additive	Cu-Pb strip			Cd-Ag strip			Fresh oil viscosity		Used oil viscosity		Neutrallization number	ASTM naphtha insolubles
		24 hrs.	48 hrs.	72 hrs.	24 hrs.	48 hrs.	72 hrs.	100° F.	210° F.	100° F.	210° F.		
Western SAE 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	1,442	76.6	4.97	189
Do.	Ca 2-ethyl butyrate	2.5	44.0	117.0	0.0	17.0	47.1	632	57.0	1,148	70.1	4.49	143
Do.	Ca laurate	14.2	67.2	97.9	12.4	16.3	15.7	630	57.3	1,361	75.5	3.07	221
Do.	Ca palmitate	47.3	125.0	166.4	9.5	38.2	90.2	632	57.0	1,340	75.0	4.02	248
Do.	Ca stearate	84.4	152.5	208.1	0.6	34.8	82.0	653	57.5	832	62.8	0.39	25
Do.	Ca alpha-aminocaprylate	+0.2	3.9	4.7	0.0	0.0	0.0	635	57.2	809	61.5	0.48	18
Do.	Ca alpha-hydroxy-aminobutyrate	1.0	0.9	1.4	0.0	+0.1	+0.2	630	57.1	840	62.5	1.02	72
Do.	Ca gamma-oximino-valerate	+0.1	0.0	+0.3	0.0	0.0	0.2	630	57.0	802	61.4	0.79	10
Do.	Ca cystinate	+0.8	+1.0	+0.6	0.0	+0.1	+0.1	635	56.9	830	62.0	0.13	20
Do.	Ca cyanoacetate	2.0	2.8	2.9	0.2	0.2	0.0	640	57.1	918	64.1	2.06	70
Do.	Ca alpha-nitratopropionate	0.3	0.5	1.0	0.1	0.3	0.4	635	57.3	1,111	69.1	3.61	201
Do.	Ca beta-nitratopropionate	1.0	4.0	1.5	0.0	0.0	+0.2	631	57.2	844	62.4	0.44	26
Do.	Ba beta-phosphonatoisobutyrate	+0.4	+0.8	+0.5	0.1	0.2	0.3	634	56.9	1,007	67.0	0.19	134
Do.	Ca beta-phosphatopropionate	0.6	1.1	1.4	0.0	0.1	0.0	640	57.2	809	61.6	2.85	14
Do.	Ba succinamate	0.2	0.2	0.3	0.0	0.0	0.0	630	57.0	878	63.6	3.05	39
Do.	Ca alpha-thiocyanatopropionate	0.5	0.7	0.6	0.0	0.0	0.1	631	57.0				

nate, are used. Also, used oil inspections (such as increase in viscosity, increase in neutralization number, and increase in naphtha 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 SAE 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, $1\frac{1}{8}'' \times 1\frac{1}{4}'' \times \frac{1}{16}''$; cadmium-silver, $\frac{1}{2}'' \times 1\frac{1}{8}'' \times \frac{1}{16}''$), and these strips were immersed in the exemplified oils carried in $2'' \times 20''$ glass test tubes; these test tubes were carried in an oil bath maintained at $300^\circ \text{F.} \pm 1^\circ \text{F.}$ 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.

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 ASTM color numbers, and from this the readings of the bridge could be converted into ASTM color numbers (Method D155-34T).

A base oil (Western paraffinic SAE 30) and the same base oil plus 0.5% by weight of inhibitor were tested, various substituted metal alkyl carboxylates being used as the inhibitor. The results are set forth in Table II below:

Table II

Base oil	Additive	Temperature	ASTM color increase
Western paraffinic SAE 30	None	$^\circ \text{F.}$ 356	8
Do.	Ca alpha-aminocaprylate	351	2
Do.	Ca alpha-hydroxyaminobutyrate	356	5—
Do.	Ca gamma-oximinovaleate	357	7—
Do.	Ca cystinate	350	5
Do.	Ca cyanoacetate	350	6
Do.	Ba beta-phosphonatoisobutyrate	356	5
Do.	Ca hydantoate	356	5
Do.	Ba succinamate	360	7—
Do.	Ca alpha-thiocyanatopropionate	356	6+

Example III.—Calcium cetyl alpha-aminosuccinate was submitted to various tests in mineral oil, with results as shown in Table III below:

Table III

Oil	Additive	Engine test			Bearing corrosion, weight loss in mgms. in 72 hrs.		Color stability, color increase (ASTM)	Oxygen absorption, cc./100 gms. oil in—		
		Hours to cause ring sticking	Relative ring slot cleanliness	Relative piston cleanliness	Cu-Pb	Cd-Ag		1 hr.	2 hrs.	2½ hrs.
Western SAE 30.	Nil.	30	Poor	Poor	13.9	0.4	6	200	330	390
Do.....	0.4% Ca cetyl alpha-aminosuccinate..	60+	Very good	Very good						
Do.....	0.5% Ca cetylphenate + 0.5% Ca cetyl alpha-aminosuccinate.	60+	do.	do.						
Do.....	1% Ca cetyl phenate.				126	12.1				
Do.....	0.61% Ca cetyl alpha-aminosuccinate.				6.3	0.0	½	20	50	60
Do.....	0.5% Ca cetyl phenate + 0.5% Ca cetyl alpha-aminosuccinate.				11.8	6.0				
Penn. SAE 30.	Nil				24.5	1.6				
Do.....	0.5% Ca cetyl phenate.				63.5	47.6				
Do.....	0.5% Ca cetyl alpha-aminosuccinate..				7.1	0.0				

The various tests indicated in Table III were carried out as follows:

Engine test.—A single cylinder Lauson gasoline spark-ignition engine, 2½ inch bore and 2½ inch stroke, loaded with an induction generator, 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 revolutions per minute; 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.

Color stability.—The Deep Rock method was used, in which a 50 gram sample of oil is held in an open container at 300° F. for six hours and the color increase is determined. Results are given in the units of ASTM Method D155-34T.

Oxygen absorption.—The "Oxidator test" described in "Industrial and Engineering Chemistry," vol. 28, page 26 (1936) was used. A temperature of 340° F. was used and the results are reported in cubic centimeters of oxygen absorbed per 100 grams of oil.

Corrosion.—The Strip corrosion test in Example I was employed.

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 SSU or lower at 100° F. to 160 SSU 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 cetylphenol, cetyl chlorphenol and cetylthiophenol.

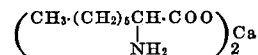
(3) Metal salts of organo substituted oxy- and thio-acids of phosphorus, such as calcium cetyl phosphate, aluminum lauryl phosphate and calcium cetylphenyl phosphate.

(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 tartaric, tartaric and citric acids.

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

Calcium alpha-aminocaprylate

The structural formula of this substance is as follows:

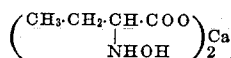


Alpha-amino caprylic acid is prepared by allowing a mixture of equal volumes of enanthaldehyde-ammonia and anhydrous hydrogen cyanide to stand for 18 hours, heating 18 hours with excess 10% hydrochloric acid, evaporating to one-third its volume and precipitating with ammonia. Fifteen grams of alpha-aminocaprylic acid are

mixed with enough ethyl alcohol to make a thin paste which is slowly added to 500 cc. of water while stirring. A 20% KOH solution is then added until the aminocaprylic acid just completely dissolves. A solution of 5.25 grams of calcium chloride in a small amount of water is added to the caustic solution of alpha-aminocaprylic acid while stirring. A curdy precipitate is formed which is filtered off and dried. This constitutes the calcium alpha-amino caprylate.

Calcium alpha-hydroxaminobutyrate

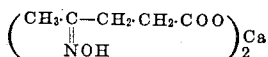
The structural formula of this substance is as follows:



14.2 grams of metallic sodium are dissolved in 200 cc. of absolute alcohol and to the resulting solution a solution of 43 grams of hydroxylamine hydrochloride in 200 cc. of absolute alcohol is added. 21.5 grams of crotonic acid are dissolved in 100 cc. of alcohol and the solution is added to the above solution and the mixture is allowed to stand for three days at room temperature. The alcohol is then evaporated off and the viscous residue is extracted with hot alcohol. The hot alcohol solution is neutralized with a slurry of lime and the solution of calcium salts is evaporated to dryness. The residue is the desired calcium alpha-hydroxaminobutyrate.

Calcium gamma-oximinovaleate

The structural formula of this substance is as follows:



25 grams of levulinic acid are dissolved in 250 cc. of water and 15 grams of hydroxylamine are added to this solution. The solution is then made slightly alkaline with NaOH and allowed to stand over night. It is then acidified with sulfuric acid and extracted with ethyl ether. The ether is evaporated and the residue of acid is dissolved in water and neutralized with calcium hydroxide and the solution of calcium gamma-oximinovaleate is evaporated to dryness to recover the desired calcium salt as residue.

Calcium cyano-acetate

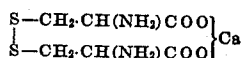
The structural formula of this substance is as follows:



20.5 grams of cyano-acetic acid are dissolved in 500 cc. of water and neutralized with a slurry of lime. The solution is then heated on a steam plate, filtered and evaporated to dryness to recover the calcium cyano-acetate as residue.

Calcium cystinate

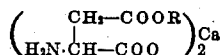
The structural formula is:



12.0 grams of cystine and 3.7 grams of calcium hydroxide are added to 500 cc. of water and the mixture is heated on a steam plate for one-half hour and is then filtered. The residue on the filter is leached several times with hot water and the washings combined with the filtrate. The combined filtrate is evaporated to dryness to recover the desired salt as residue.

Calcium cetyl alpha-aminosuccinate

The structural formula is as follows:

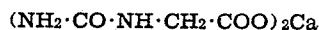


where R represents an organic radical or mixture of radicals derived from an alcohol obtained by saponifying "Cosmol" (a hydrogenated sperm oil product). It is probably a mixture of cetyl ($\text{C}_{16}\text{H}_{33}$) and higher alkyl radicals and for convenience is referred to as "cetyl."

50 grams of calcium cetyl fumarate and 50 cc. of anhydrous liquid ammonia are warmed to 120°-135° F. in a stainless steel bomb, the pressure reaching 275 pounds per square inch, and the mixture is maintained at this temperature for 9 hours. The bomb is then opened, the contents removed, and ammonia removed by evaporation. The residue constitutes the desired amino salt.

Calcium hydantoate

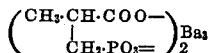
The structural formula is:



15 grams of glycine are mixed with 12 grams of urea and the mixture is heated on a steam plate over night. Excess barium hydroxide solution is then added to the mixture and it is heated further until no odor of ammonia is noticeable. The excess urea is thus destroyed and barium hydantoate is formed. The excess barium hydroxide is precipitated with carbon dioxide and the resulting barium carbonate is removed by filtration. A silver nitrate solution is added to the solution of barium hydantoate, causing precipitation of insoluble silver hydantoate. This is filtered off, washed with cold water and suspended in water. Hydrogen sulfide is passed through the suspended salt causing precipitation of silver sulfide which is then removed by filtration. The filtrate is evaporated to a syrupy consistency and allowed to crystallize. The crystals are filtered, washed and dissolved in water and neutralized with calcium hydroxide.

Barium beta-phosphonato-isobutyrate

The structural formula of this substance is as follows:



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

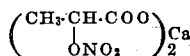
The structural formula of this substance is as follows:



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.

Calcium alpha-nitratopropionate

The structural formula of this substance is as follows:



20 grams of zinc lactate is added to a mixture of 25 grams of fuming nitric acid and 40 grams of concentrated sulfuric acid, the mixed acid being kept below 40° F. while adding the zinc lactate. The solution is then allowed to warm and most of the excess nitric acid is removed on a hot water bath. The residue is then poured into a large amount of cold water, from which a heavy oil separates. This is neutralized with calcium hydroxide solution and water is removed on a steam plate.

Calcium beta-nitropropionate

The structural formula of this substance is as follows:



15.3 grams of beta iodopropionic acid are dissolved in 400 cc. of water and the solution is cooled to 40° F. 12.23 grams of silver nitrite are added slowly to the cooled solution and the mixture is allowed to warm to room temperature. The solution is filtered to remove silver iodide and evaporated to a volume of about 100 cc. under vacuum. Excess calcium hydroxide is added and the excess removed by treating with carbon dioxide and filtering off the calcium carbonate. The filtered solution is evaporated to dryness.

Barium succinamate

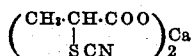
The structural formula is as follows:



19.8 grams of succinimide are dissolved in water and a solution of 31.6 grams of barium hydroxide octahydrate is added. The solution is evaporated to dryness.

Calcium alpha-thiocyanatopropionate

The structural formula is as follows:



20 grams of ethyl alpha-bromopropionate are mixed with an alcoholic solution of 10.7 grams of potassium thiocyanate. The solution is allowed to stand for several days on a steam plate after which potassium bromide is filtered off. Excess calcium hydroxide solution is then added and

the mixture is heated. Carbon dioxide is passed through to remove excess lime. The precipitate of calcium carbonate is removed by filtration and the filtrate is evaporated to dryness.

5 The phrase "group VB of the periodic table," as used in the specification and claims, refers to that form of the periodic table shown on page 411 of Partington's "Textbook of Inorganic Chemistry," 4th ed. (1933), MacMillan & Co., London. Thus group VB is the same as the right-hand subgroup of group V in the periodic tables shown in the following places: "Handbook of Chemistry and Physics," 18th ed., pages 700-701; the frontispiece of J. Newton Friend's "A Textbook of Inorganic Chemistry"; and vol. I, page 46 of "International Critical Tables." Group VB, as used herein, consists of the elements nitrogen, phosphorus, arsenic, antimony and bismuth.

20 We claim:

1. A composition of matter, comprising a major proportion of a hydrocarbon oil and a small amount, sufficient to stabilize the 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 an element of group VB of the periodic table, said element being directly connected to the said alkyl carbon atom.

2. A composition of matter, comprising a major proportion of an oil of lubricating viscosity and a small amount, sufficient to improve properties of the oil affecting its use as a lubricant, 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 an element of group VB of the periodic table, said element being directly connected to the said alkyl carbon atom.

3. The composition of claim 2, wherein said substituent contains nitrogen.

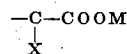
4. The composition of claim 2, wherein said substituent contains phosphorus.

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

6. A composition of matter, comprising a major proportion of a hydrocarbon oil of lubricating viscosity and a small amount, sufficient to improve the oil, of a polyvalent metal alkyl carboxylate substituted on an alpha, beta or gamma alkyl carbon atom with respect to a metal alkyl carboxylate group by an amino substituent, including substituted amino substituents.

7. A composition of matter, comprising a major proportion of a hydrocarbon oil of lubricating viscosity and a small amount, sufficient to improve the oil, of a polyvalent metal alkyl carboxylate substituted on an alpha, beta or gamma alkyl carbon atom with respect to a metal alkyl carboxylate group by a phosphino substituent, including substituted phosphino substituents.

8. A composition of matter, comprising a major proportion of a hydrocarbon oil of lubricating viscosity and a small amount, not less than about 0.1% by weight based on finished oil, of a polyvalent metal alkyl carboxylate having in its molecule the structure



wherein M is a polyvalent metal, X is a group containing an element of group VB of the peri-

odic table, said element being directly connected to the alkyl group of said metal alkyl carboxylate, and the alkyl carbon atom to which said group X is attached is not more than two carbon atoms removed from the group COOM.

9. The composition of claim 8, wherein said element of group VB is nitrogen.

10. The composition of claim 8, wherein said element of group VB is phosphorus.

11. The composition of claim 8, wherein said metal alkyl carboxylate is an alkaline earth metal alkyl carboxylate.

12. A petroleum lubricating oil containing dissolved therein about 0.1 to 5% by weight based on finished oil of a polyvalent metal salt of an aliphatic carboxylic acid substituted on an alpha, beta or gamma aliphatic carbon atom with respect to an aliphatic metal carboxylate group by trivalent nitrogen.

13. A petroleum lubricating oil containing dissolved therein about 0.1 to 5% by weight based on finished oil of a polyvalent metal salt of an aliphatic carboxylic acid substituted on an alpha, beta or gamma aliphatic carbon atom with respect to an aliphatic metal carboxylate group by trivalent phosphorus.

14. A petroleum lubricating oil containing dissolved therein about 0.1 to 5% by weight based on finished oil of a polyvalent metal salt of an aliphatic carboxylic acid substituted on an alpha, beta or gamma aliphatic carbon atom with respect to an aliphatic metal carboxylate group by trivalent arsenic.

15. 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 sub-

stituent containing an element of group VB of the periodic table, said element being directly connected to the said alkyl carbon atom.

16. A petroleum lubricating oil containing dissolved therein about 0.1 to 5% by weight based on finished oil of an oil-soluble metal salt of an aliphatic polycarboxylic acid substituted on an alpha, beta or gamma aliphatic carbon atom with respect to an aliphatic metal carboxylate group by an element of group VB of the periodic table.

17. A petroleum lubricating oil containing dissolved therein about 0.1 to 5% by weight based on finished oil of an oil-soluble polyvalent metal salt of a partial ester of succinic acid substituted on an alpha carbon atom of the acid by an amino group.

18. A petroleum lubricating oil containing dissolved therein about 0.1 to 5% by weight based on finished oil of an alkaline earth metal salt of a monoalkyl ester of a higher aliphatic alcohol and alpha amino succinic acid.

19. The oil of claim 18, wherein said salt is the calcium salt of the monocetyl ester of alpha amino succinic acid.

20. A hydrocarbon lubricating oil containing a small amount each, sufficient to improve the oil as a crankcase lubricant, of an oil-soluble metal salt of an alkylated phenol and an oil-soluble metal salt of an aliphatic carboxylic acid substituted on an alpha, beta or gamma carbon atom with respect to a metal alkyl carboxylate group by a polar substituent containing an element of group VB of the periodic table.

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