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LUBRICATING OILS AND THE LIKE

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This invention relates to new and useful compositions of matter and to methods of preparing the same. In particular, it relates to compositions comprising hydrocarbons of the lubricating oil class, in major part, in which are dissolved or suspended minor amounts of certain metal salts of organic aliphatic carboxylic acids, either alone or in admixture with other compounding agents of the same or different type.

This application is a continuation-in-part of our copending application Serial No. 322,946, filed March 8, 1940, now Patent No. 2,349,817.

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 here manifests itself in diverse effects, dependent upon the nature and degree of refinement of the hydrocarbon oil and upon the environment to which it is subjected, but reference may be made to Diesel engine piston ring sticking, in which the exposure of a lubricating oil to such temperatures as 425°–650° F., in the presence of oxidizing combustion gases at pressures as high as 750–1150 lbs./sq. in., causes the deposition of oil degradation products of such a cementitious character as to effectively take piston rings out of service; to the deposition of "sludge" from automobile crankcase oils, apparently as the result of oxidation and/or polymerization phenomena; and to the corrosion of metal bearing surfaces, apparently as a result of phenomena which cause the formation of organic acidic products. This situation is aggravated by the fact that improvements in the mechanical arts have brought about increasing severity in the conditions to which hydrocarbon oils are subjected, and by the fact that oil compounding designed to effect a stability in one direction often brings about a marked instability in another.

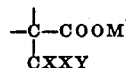
It has been found that the addition to a lubricating oil of small amounts of a metal salt of an aliphatic carboxylic acid, carrying in addition to the salt-forming carboxylic acid group a car-

boxylic or dithiocarboxylic group, which is free or is neutralized by a basic atom or group of atoms, brings about an improved stability in hydrocarbon oils when the same are subjected to high temperatures and/or pressures in the presence of oxygen and metals. Such salts may be viewed as salts of acids of the type



or $\text{HSSC}-(\text{CH}_2)_n-\text{COOH}$, in which n may be zero or a whole number, preferably not greater than three; in which there may or may not be alkyl, aryl, aralkyl or aliphatic carbocyclic substitution to increase oil solubility; in which the right-hand COOH group is converted into a metal carboxylate group and the left-hand COOH or CSSH group is a free or neutralized carboxylic or dithiocarboxylic group. It has been further found that still greater improvement of the desired sort is brought about when in such metal salts certain polar substitution is effected in a position alpha, beta, gamma, delta or even epsilon to the carbon atoms of a salt-forming carboxylic acid group, the effectiveness for the desired purpose decreasing in the order of positions as recited.

Viewed from another standpoint, the salts of this invention are metal salts of substituted aliphatic carboxylic acids capable of representation by the partial formula—



in which M is a metal, including the hydrogen equivalent of a polyvalent metal, the group COOM is attached to an aliphatic carbon atom, the carbon atom to which the group CXXY is attached is an aliphatic carbon atom (preferably alpha, beta or gamma in respect to the COOM group), X is oxygen or its analogue sulfur and Y is hydrogen or a basic atom or radical. The salts of the invention are, therefore, metal aliphatic carboxylates substituted, preferably in the alpha, beta or gamma position, by a free or neutralized carboxyl or dithiocarboxyl group.

Referring to additional polar substitution of the salts of the invention, the following polar radi-

cals will illustrate those which may be substituted in the salts of the invention as indicated:

Name	Formula
Carboxylic acid	-COOH
Metallo-carboxyl	-COOM
Esterified carboxyl	-COOR
Hydroxyl	-OH
Vinylene	-CH=CH-
Amino	-NH ₂
Ethynylene	-C≡C-
Alkoxy or aryloxy	-OR
Metallo-oxy	-OM
Oxo or keto	=O
Carbamyl	-CO(NH ₂)
Alkyl or aryl thiolcarboxyl	-COSR
Alkyl or aryl thionocarboxyl	-CSOR
Mercapto	-SH
Alkyl or arylthio	-SR
Thiono	=S
Dithio	=SS-
Sulfinyl	=SO
Sulfonyl	=SO ₂
Imino	=NH
Alkalamino or arylalamino	-NHR
Dialkalamino or diarylamino	-NR ₂
Azo	-N=N-
Hydrazo	-NHNH-
Hydrazono	-N=NH-
Triazeno	-NNNH-
Triazo	-NNN-
Cyano	-CN
Isocyano	-NC
Cyanate	-OCN
Isocyanate	-NCO
Thiocyanate	-SCN
Isothiocyanate	-SNC
Nitroso	-NO
Nitro	-NO ₂
Isonitroso	=NOH
Hydroxalamino	-NHOH
Azoxy	-NON-
Isonitro	-NOOH
Phosphino	-PH ₂ or =PH
Phosphoroso	-PO
Phospho	-PO ₂
Alkyl or aryl phosphate	-OPO(OR) ₂
Alkyl or aryl phosphite	-OP(OR) ₂
Silicyl	-SiH ₃
Silicylene	=SiH ₂
Alkyl or aryl silicone	-SiOOR
Alkyl or aryl sulfino	-SO ₂ R
Alkyl or aryl sulfo	-SO ₃ R
Alkyl or aryl sulfamino	-NHSO ₂ R
Sulfamyl	-SO ₂ NH ₂
Sulfonamido	-SO ₂ NH-
Selenyl	-SeH
Alkyl or aryl selenyl	-SeR
Seleno	=Se
Seleninyl	=SeO
Selenonyl	=SeO ₂
Alkyl or aryl selenino	-SeO(OR)
Alkyl or aryl selenono	-SeO ₂ (OR)
Selenocyno	-SeCN
Telluryl	-TeH ₃
Alkyl or aryl telluryl	-TeR
Telluro	=Te
Alkyl or aryl phosphonite	-P(OR) ₂
Alkyl or aryl phosphonate	-PO(OR) ₂
Alkyl or aryl phosphinite	-POR
Alkyl or aryl phosphinate	-POOR
Phosphazo	-PN-
Phosphoro	-PP-
Phosphoarseno	-PAs-
Arsino	-AsH ₃ or =AsH
Arseno	-AsO
Alkyl or aryl arsenate	-OAsO(OR) ₂
Alkyl or aryl arsenite	-OAs(OR) ₂
Alkyl or aryl arseno	-AsO(OR) ₂
Alkyl or aryl arsinico	-AsOOR
Arseno	-AsAs-
Stibino	-SbH ₃ or =SbH
Stiboso	-SbO
Stibo	-SbO ₂
Alkyl or aryl antimonate	-OSbO(OR) ₂
Alkyl or aryl stibono	-SbO(OR) ₂
Alkyl or aryl stibinico	-SbOOR
Antimono	-SbSb-
Stibarseno	-SbAs-
Bismuthino	-BiH ₃ or =BiH
Boryl	-BO
Alkyl or aryl borate	-OB(OR) ₂
Alkyl or aryl silicate	-OSi(OR) ₂
Iodoso	-IO
Stannyl	-SnH
Iodoxy	-IO ₂

The metals whose substituted carboxylic acid salts are useful for the purposes of the invention may have valences from one to four, inclusive, and the salts of potassium, calcium, magnesium, aluminum, chromium, cobalt, lead, manganese, tin and zinc have been found of particular utility.

Among the aliphatic carboxylic acids whose

metal salts are suitable in the practice of the invention and which correspond to the structure



- 5 or HSSC-(CH₂)_n-COOH (n=0-8 or a higher whole number, and the methylene groups being in some cases substituted by oil-solubilizing groups and/or polar groups as hereinabove indicated) there may be mentioned: the oxalic series (including oxalic acid itself and malonic, succinic, glutaric, adipic, pimelic, suberic and sebacic acids; the various alkyl homologues of these acids, especially the higher alkyl homologues, such as pentylmalonic, cetylmalonic, isopropylsuccinic, methylisopropylsuccinic, cetenylsuccinic and eicosenylsuccinic acids); and the sulfur analogues of these acids in which one of the COOH groups is replaced by a CSSH group. Representative of the tricarboxylic acids (acids in which a carboxylic group is the polar radical referred to as desirable) are the paraffin tricarboxylic acids such as isobutane- α,α,β -tricarboxylic acid, tricarballic acid and α,α,β -trimethyltricarballic or camphoronic acid, and the alkylic homologues thereof, and the olefin tricarboxylic acids such as aconitic acid and its isomers aceconitic and citracetic acids; also the sulfur analogues of these acids in which one or two of the COOH groups is replaced by a CSSH group. Representative of hydroxy substituted polycarboxylic acids (acids in which one or more hydroxy groups are the polar groups referred to as especially beneficial) are tartronic or oxymalonic acid and the several alkylic tartronic acids such as methyl, ethyl, propyl and isopropyl tartronic acids, malic acid and its homologues, such as isopropylmalic acid and the paraconic acids, the α - and β -oxyglutaric acids, the α -hydroxy adipic and sebacic acids, the tartaric acids; citric acid, and dioxytartaric acid; also the sulfur analogues of these acids in which one or more (but not all) of the COOH groups are replaced by a CSSH group. Representative of unsaturated polycarboxylic acids (acids in which one or more vinylene or ethynylene groups are the polar group referred to) are the alkylene malonic acids such as methylene malonic acid, CH₂:C(COOH)₂, isopropylene malonic acid and allylmalonic acid, 50 CH₂:CH.CH₂.CH(COOH)₂, fumaric and maleic acids, mesaconic, citraconic, itaconic and glutaric acids and their alkylic and dialkylic homologues, diallylmalonic acid, muconic acid, glutinic acid and diacetylenedicarboxylic acid; also the sulfur analogues of these acids in which one or more (but not all) of the COOH groups is replaced by a CSSH group.

The following specific examples will illustrate the practice and advantages of the invention:

EXAMPLES, SET I

- Among the beneficial effects which flow from the incorporation of a metal salt or a mixture of metal salts of the above described aliphatic 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, 2 3/4 inch bore and 2 1/2 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 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. 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°, 622 seconds and 56.6 seconds, respectively, Saybolt Universal. To this base oil were added the various salts in the amounts indicated, by 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; the losses reported, however, represent the averages of at least two and sometimes more duplicate or check corrosion tests under these conditions. In connection with the results reported in Table II, attention is directed to those oils compounded by the addition of agents other than those of the invention (oils A, B, C, etc.), in which the compounding, while perhaps of benefit in respect to some property of the oil, is of definitely deleterious effect in respect to the corrosivity of the oil toward bearing metals.

TABLE I
Prevention or postponement of piston ring sticking

Example	Oil	Hours to cause ring sticking	Relative ring slot cleanliness	Relative piston cleanliness
10	Western 30	30	Poor	Poor
15	+0.63% Ca α-eicosyltartrate	60+	Fair+	Good
16	+0.50% Ca α-cetylmalonate	75	Fair	Poor
17	+0.50% Ca α-cetenylsuccinate	90	Fair+	Do.
36	+0.34% Ca α-eicosenylsuccinate	120+	Good	Fair
42	+0.50% Ca cetylphenate + 0.50% Ca α-eicosyltartrate	120+	Very good	Very good
	+0.50% Ca cetylphenate + 0.50% Ca α-eicosenylsuccinate	60	Fair	Fair

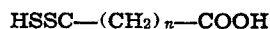
Note: A plus sign (+) following a stated number of hours in the antepenultimate column indicates free rings at the conclusion of a test of the stated hours' duration.

EXAMPLES, SET II

Among the further benefits to be derived from the addition of the metal salts of the invention to hydrocarbon lubricating oils is a decreased corrosivity toward bearing metals, particularly those of the cadmium-silver and copper-lead types. This diminution in corrosivity is particularly marked upon the incorporation in the hydrocarbon oils of metal salts of those aliphatic carboxylic acids corresponding to the type



or



($n=0-8$ or a higher whole number) in which a polar group or radical as above exemplified is substituted for a hydrogen atom attached to a carbon atom in close proximity to the carbon atom of the salt-forming carboxylic acid radical, preferably in the alpha position, less preferably in the beta position and of decreasing desirability and effectiveness in the gamma, delta, epsilon, etc., positions, in the order named.

In the tests whose results are summarized in Table II, thin sheets of the indicated bearing metals were cut into strips (copper-lead, $\frac{1}{16}'' \times \frac{1}{4}'' \times \frac{3}{32}''$; cadmium-silver, $\frac{1}{2}'' \times \frac{1}{8}'' \times \frac{1}{16}''$), and these strips were immersed in the exemplified oils carried in 2'' x 20'' glass test tubes; these test tubes were carried in an oil bath maintained at 300° F. $\pm 1^\circ$ 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

TABLE II
Reduction of corrosivity to bearing metals

Ex-ample	Oil	Weight loss in mgms., 72 hrs.	
		Cu-Pb	Cd-Ag
10	Western 30	13.9	0.4
15	+0.63% Ca α-eicosyltartrate	5.0	0.9
16	+0.50% Ca α-cetylmalonate	9.8	0.3
17	+0.50% Ca α-cetenylsuccinate	1.1	0.3
42	+0.34% Ca α-eicosenylsuccinate	1.6	0.1
	+0.50% Ca cetylphenate + 0.50% Ca α-eicosenylsuccinate	40.7	6.0
A	+0.50% Ca stearate	131.9	180.5
B	+1.0% Al dinaphthenate	67	113
C	+1.0% Mg naphthenate	139	119
D	+1.0% Ca cetylphenate	126	12.1

EXAMPLES, SET III

A still further benefit to be derived from the addition of the metal salts of the invention to hydrocarbon oils, particularly noticeable in the case of salts of those acids carrying polar substituents as described, is a marked lessening of color instability upon exposure of the oils of the invention to heat, in the absence of air or metals.

In the tests whose results are summarized in Table III, samples of the exemplified oils were held, in glass, at 300° F. for 6 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 III
Color stability

Ex- ample	Oil	Color after heating	Color in- crease
10	Western 30	3½ DIL.	6
17	+0.63% Ca α-eicosyltartrate	4-	1-
24	+0.34% Ca α-eicosenylsuccinate	4-	1½
29	+0.18% Ca α-cetenylsuccinate	4-	1-
41	+0.50% K α-cetylmalonate	4½	1½
42	+0.50% Ca cetylphenate+0.10% Ca α-cetenylsuccinate	6	1½
53	+0.50% Ca cetylphenate+0.50% Ca α-eicosenylsuccinate	7	2½+
54	+0.25% Ca cetylphosphate+ 0.10% Ca α-cetenylsuccinate	4	½
63	+0.25% Ca cetylphosphate+ 0.50% Ca α-eicosenylsuccinate	4-	1-
64	+0.50% Ca cetylphenate+0.25% Ca cetylphosphate+0.20% Ca α-cetenylsuccinate	5-	½
71	+0.30% Ca cetylphenate+0.25% Ca cetylphosphate+0.50% Ca α-eicosenylsuccinate	7	2½
72	+1.0% diisamyl tartrate+0.10% Ca α-cetenylsuccinate	4½	1
	+1.0% diisamyl tartrate+0.50% Ca α-eicosenylsuccinate	3½	½

EXAMPLES, SET IV

In many cases still further benefits may be derived from the incorporation of the metal salts of the invention to 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 IV, 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 1¾ inch steel cylinder which is rotated at 600 revolutions per minute 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 Timken machine as described in the S. A. E. Journal, volume 28, page 53, 1928; the results are reported in pounds at failure.

TABLE IV

Wear resistance and film strength

Ex- ample	Oil	Weeks wear	Film strength
15	Western 30	288	120
17	+0.50% Ca α-cetylmalonate	143	160
25	+0.34% Ca α-eicosenylsuccinate	106	230
B	+0.20% Ca α-cetenylsuccinate	163	120
D	+1.0% Al dinaphthenate	639	120
	+0.50% Ca cetylphenate	105	120

EXAMPLES, SET V

Still further, the capability of hydrocarbon oils to absorb oxygen, when exposed thereto at super-atmospheric temperatures and pressures, is in many cases reduced or postponed by the incorporation in the oils of the metal salts of the invention, particularly those carrying a polar group of the character and in the position referred to repeatedly hereinabove.

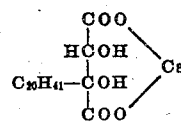
In the tests whose results are reported in Table V, the oils referred to were subjected to the "oxidator test" particularly described in the Journal of Industrial and Engineering Chemistry, volume 28, page 26, 1936, at 340° F., which conditions may be noted as extremely severe. The results of the tests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

TABLE V
Reduction of oxygen absorption

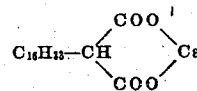
Ex- ample	Oil	Oxygen absorption		
		1 hr.	2 hrs.	2½ hrs.
10	Western 30	200	330	390
15	+0.63% Ca α-eicosyltartrate	65	105	122
17	+0.50% Ca α-cetylmalonate	40	95	150
26	+0.34% Ca α-eicosenylsuccinate	23	50	65
31	+0.25% Ca α-cetenylsuccinate	8	30	47
	+0.10% Ca α-eicosylaminosuccinate	100	240	290

There are given below the structural formulae of a few typical salts of this invention, from which the relationship of structure (illustrated by the formulae) to performance (illustrated by the specific examples) will be made more clear:

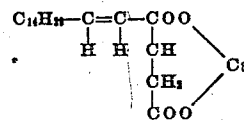
Calcium alpha-eicosyl-tartrate



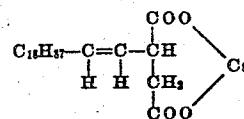
Calcium alpha-cetyl-malonate



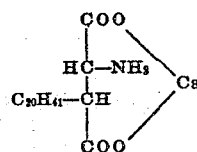
Calcium alpha-cetenyl-succinate



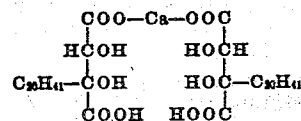
Calcium alpha-eicosenyl-succinate



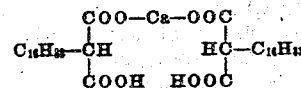
Calcium alpha-eicosyl-aminosuccinate



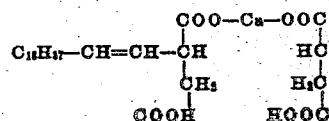
Calcium alpha-eicosyl acid tartrate



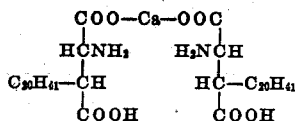
Calcium alpha-cetyl acid malonate



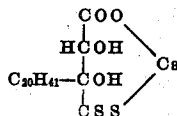
Calcium alpha-eicosenyl acid succinate



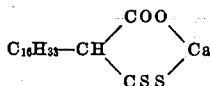
Calcium alpha-eicosyl-amino acid succinate



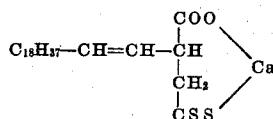
Calcium alpha-eicosyl dithiotartrate



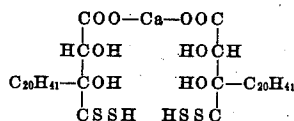
Calcium alpha-cetyl dithiomalonate



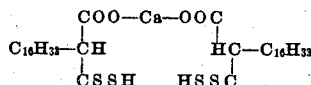
Calcium alpha-eicosenyl dithiosuccinate



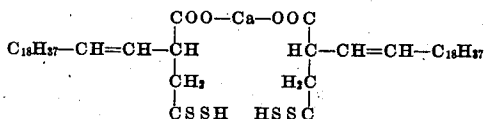
Calcium alpha, beta-dihydroxy-beta-dithiocarboxy tricosanoate



Calcium alpha-dithiocarboxy stearate



Calcium alpha-eicosenyl-beta-dithiocarboxy propionate



As exemplified by the above structural formulae, the salts of the present invention all contain a metal carboxylate group COOM attached to an aliphatic carbon atom; there is also present a free or neutralized carboxyl or dithiocarboxyl group close to the salt-forming COOM group. (In the salts just exemplified, the metal is calcium and in several of the salts the same calcium atom serves to neutralize two carboxyl groups or a carboxyl group and a dithiocarboxyl group, but other metals than calcium may be used, and in those salts having two metal carboxylate groups or a metal carboxylate group and a metal dithiocarboxylate group, two different metals may be present, one in combination with a carboxyl group and the other in combination with a second carboxyl group or with a dithiocarboxyl group.) Also, there may be present in the salt molecule an oil solubilizing group, exemplified by the eicosyl, cetyl, ceteryl and eicosenyl groups, and in certain of the salt molecules there is present in addition to the carboxyl and dithiocarboxyl groups one or more polar groups, exemplified by the hydroxyl, amino and vinylene groups, in close proximity to a metal carboxylate (COOM) group. Oil solubilizing and polar

groups, such as those exemplified, are not essential to the practice of the invention but their presence is advantageous. Alternative oil-solubilizing and polar groups are indicated hereinabove.

A few typical instances of preparation of the salt additives of the invention and of the manner of compounding such salt additives with hydrocarbon oils for the purpose of preparing concentrates or finished oils will serve further to illustrate the practice of the invention.

Calcium alpha-cetylmalonate.—The malonic ester synthesis is employed (cf. Leibig's Annalen der Chemie, vol. 204, p. 121), involving forming the sodium derivative of malonic ester, reacting the sodium derivative with cetyl iodide, hydrolyzing the resulting alpha-cetyl malonic ester with aqueous KOH to produce the potassium salt, and precipitating the calcium salt by adding CaCl₂ solution to a suspension of the potassium salt in a 50-50 alcohol-water mixture.

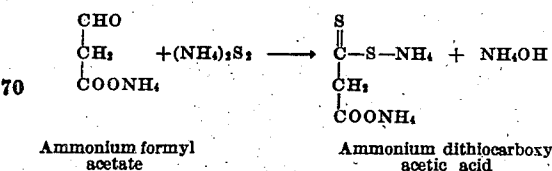
Calcium alpha-alkenyl succinates.—These alkenyl succinates, exemplified by the ceteryl and eicosenyl members, are prepared by the Diehl and Alder method (cf. Liebig's Annalen, vol. 460, page 68, and vol. 470, page 62; also Berichte der deutschen Chem. Ges., vol. 62, page 554), involving condensing an olefin (such as C₁₆ or C₂₀ olefin polymers) with maleic anhydride under pressure at an elevated temperature, hydrolyzing the resulting alkenyl succinic anhydride and forming the calcium salt of the free acid.

Calcium alpha-eicosyltartrate.—This may be prepared by oxidizing ceterylsuccinic acid, prepared as described above, with hypochlorous acid to form the corresponding chlorohydrin. The chlorine is removed from the chlorohydrin by refluxing with a 10% solution of potassium hydroxide. The resulting product is the potassium salt of a dihydroxy dicarboxylic acid.

Salts of acids of the type



can be prepared by the method given in Gilman's "Organic Chemistry," 2nd ed., page 931. See also Bruni and Levi, Atti Acad. Lincei, vol. 32, pt. 1, page 5 (1923) and Bloch, Hohn and Bugge, J. prakt. Chemie, vol. 82, page 473 (1910). By this method an aldehyde (which, for the purpose of preparing the carboxy compounds of the type referred to above, also contains a carboxyl group) is reacted with ammonium disulfide. An illustrative preparation is as follows: To an aqueous solution of ammonium formylacetate add an excess of ammonium disulfide, allow to stand several days and then heat to remove water, ammonia and ammonium sulfide, and crystallize out the ammonium salt of dithiocarboxy acetic acid, or add to the aqueous solution of ammonium salt an aqueous solution of a polyvalent metal salt to precipitate a polyvalent metal dithiocarboxy acetic acid. The equation for the reaction is as follows:



Examples of useful hydrocarbon oil composi-

tions containing the above salts, with and without other compounding agents, are as follows:

1. 99% SAE 30 Paraffinic oil	+1%	Ca α-cetylmalonate
2. Ditto	+1%	Ba α-octadecylsuccinate
3. Ditto	+1%	Zn α-dodecylglutarate
4. Ditto	+1%	Cr β-octyladipate
5. 99% SAE 30 naphthenic oil	+1%	Ca α-cetenylsuccinate
6. Ditto	+1%	Ca α-cetylmalate
7. Ditto	+1%	Zn α-octadecyltartrate
8. Ditto	+1%	Ca α-cetylaminosuccinate
9. Ditto	+1%	Ca α-dodecyltricarballate
10. 99% SAE 30 mixed base oil	+1%	Ba α-dodecylcitrate
11. Ditto	+1%	Ca agarate
12. Ditto	+1%	Zn α-cetylaconitate
13. Ditto	+1%	Ca α-cetylmersaptosuccinate
14. Ditto	+1%	Ca α-cetyldithiomalonate
15. 98% SAE 30 naphthenic oil	+1%	Ce α-cetylmalonate
16. Ditto	+1%	Ca α-cetylmalonate
17. 98% SAE 30 naphthenic oil	+1%	Ca α-cetylphosphate
18. Ditto	+1%	Ca α-cetylmalonate
19. Ditto	+1%	Ca α-cetylphenol sulfonate
	+1%	Ca α-cetylmalonate
	+1%	dicetyl sulfide
	+1%	Ca α-cetylmalonate
	+1%	dihydroxy diphenyl sulfide

Generally, measurable improvements in the properties of hydrocarbon oils are obtained by the incorporation of as little as 0.1% of the agents of the invention, but amounts between about 0.2% and 2.0% of the agents, by weight based on the oil, are preferable, dependent upon the degree of inherent tendency toward degradation of the oil itself or as otherwise compounded; amounts higher than about 5.0% are regarded as unnecessary in the best practice of the invention.

A feature of the invention is in the preparation and distribution of bases or concentrates containing relatively large proportions of the additive agents in admixture with hydrocarbon oils of the lubricating or less viscous types or, if more suitable in conjunction with certain other agents, by reason of solubility relationships or the like, in admixture with aromatic hydrocarbons or with alcohols, esters, ketones or ethers, generally of the aliphatic series. Admixtures of agents and lubricating oils or other solvents or carriers containing upward of 50% of the essential agents, by weight, may be thus prepared and distributed, for later blending with the particular lubricating oil media desired to be put to use, as occasion demands. In the preparation of either the finished oils of the invention or the bases or concentrates referred to, complete or clear and homogeneous solution is not always necessary: blending agents or homogenizers may be employed if desirable, to prevent sedimentation of the more oil-insoluble of the agents, but it has been found the possible detrimental effect of the presence of filterable insoluble materials of this character, if indeed present, is determined largely by the particular conditions attending the contemplated use, and that their presence is not in all cases deleterious to the functioning of the compositions in their intended manner.

While the character of the invention has been given in detail and numerous illustrative examples of the preparation and utility of the compositions of the invention have been described, this has been done largely by way of illustration and with the intention that no limitation should be imposed upon the invention thereby. It will be obvious to those skilled in the art that numerous modifications and variations of the above illustrative examples may be effected in the practice of the invention, which is intended to be of the scope of the appended claims.

We claim:

1. A liquid hydrocarbon oil of the lubricating class, normally tending to deteriorate at operat-

ing temperatures encountered in the operation of internal combustion engines, containing dissolved in the oil a small amount, sufficient to retard said deterioration, of a metal salt of an aliphatic carboxylic acid, said metal salt carrying, on an aliphatic carbon atom not more than about two carbon atoms removed from a metal carboxylate group, a substituent selected from the class consisting of the free carboxyl group, the free dithiocarboxyl group, and neutralized carboxyl and dithiocarboxyl groups.

2. The oil of claim 1, wherein said substituent is a free carboxyl group.

3. The oil of claim 1, wherein said substituent is a neutralized carboxyl group.

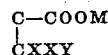
4. The oil of claim 1, wherein said substituent is a neutralized dithiocarboxyl group.

5. A liquid hydrocarbon oil of the lubricating class, normally tending to deteriorate at operating temperatures encountered in the operation of internal combustion engines containing a small amount, sufficient to retard said deterioration, of a polyvalent metal salt of an aliphatic carboxylic acid containing at least one metal carboxylate group attached to an aliphatic carbon atom, containing at least one other group also attached to an aliphatic carbon atom and selected from the class consisting of COOH, CSSH, COOM and CSSM groups, wherein M represents a metal, and containing an oil-solubilizing group.

6. The oil of claim 5, wherein said oil-solubilizing group is a long chain aliphatic group.

7. A liquid hydrocarbon oil of the lubricating class, normally tending to deteriorate at operating temperatures encountered in the operation of internal combustion engines, containing a small amount, sufficient to retard said deterioration, of an oil-soluble polyvalent metal salt of an aliphatic carboxylic acid containing a metal carboxylate group attached to an aliphatic carbon atom, containing a second group also attached to an aliphatic carbon atom and selected from the class consisting of COOH, CSSE, COOM and CSSM groups, wherein M represents a metal, and containing a third group of polar nature attached to an aliphatic carbon atom not more than about two carbon atoms removed from a metal carboxylate group.

8. A composition of matter, comprising a major proportion of a hydrocarbon oil of lubricating viscosity and, dissolved in the oil, about 0.1 to 5 per cent by weight based on finished oil of a compound represented by the partial formula



wherein M is a metal, the group COOM is attached to an aliphatic carbon atom, the carbon atom to which CXXY is attached is an aliphatic carbon atom situated not more than about two carbon atoms removed from said COOM group, X represents a member of the class consisting of oxygen and sulfur, and Y represents a member of the class consisting of hydrogen, metals and basic nitrogenous radicals.

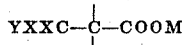
9. A composition of matter, comprising a major proportion of a hydrocarbon oil of lubricating viscosity and about 0.1 to 5 per cent by weight based on finished oil of a compound of the structure



wherein M represents a polyvalent metal, X represents a member of the class consisting of oxy-

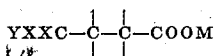
gen and sulfur, and Y represents a member of the class consisting of hydrogen, metals and basic nitrogenous radicals.

10. A composition of matter, comprising a major proportion of a hydrocarbon oil of lubricating viscosity and about 0.1 to 5 per cent by weight based on finished oil of a compound of the structure



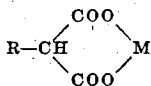
wherein M represents a polyvalent metal, X represents a member of the class consisting of oxygen and sulfur, and Y represents a member of the group consisting of hydrogen, metals and basic nitrogenous radicals, said compound containing an oil-solubilizing substituent.

11. A composition of matter, comprising a major proportion of a hydrocarbon oil of lubricating viscosity and about 0.1 to 5 per cent by weight based on finished oil of a compound of the structure



wherein M represents a polyvalent metal, X represents a member of the class consisting of oxygen and sulfur, and Y represents a member of the group consisting of hydrogen, metals and basic nitrogenous radicals, said compound containing an oil solubilizing substituent.

12. A petroleum lubricating oil containing about 0.1 to 5 per cent by weight based on finished oil of a compound having the structure

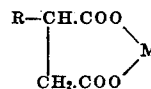


wherein M represents a polyvalent metal and R represents an oil-solubilizing group.

13. The composition of claim 12, wherein M is an alkaline earth metal and R is a long chain alkyl group.

14. The composition of claim 12, wherein M is calcium and R is a long chain alkyl group.

15. A petroleum lubricating oil containing about 0.1 to 5 per cent by weight based on finished oil of a compound having the structure



16. The composition of claim 15, wherein M is an alkaline earth metal and R is a long chain alkylene group.

17. The composition of claim 15, wherein M is calcium and R is a long chain alkylene group.

18. A petroleum lubricating oil tending normally to deteriorate and form carbonaceous deposits on pistons when used as the crankcase lubricant of an internal combustion engine and a small amount each, sufficient to retard said deterioration and deposition, of a polyvalent metal salt of an alkylated phenol and a polyvalent metal salt of an aliphatic carboxylic acid, said

polyvalent metal salt of an aliphatic carboxylic acid carrying, on an aliphatic carbon atom not more than about two carbon atoms removed from a metal carboxylate group, a substituent selected from the class consisting of the free carboxyl group, the free dithiocarboxyl group, and neutralized carboxyl and dithiocarboxyl groups.

19. A concentrated dispersion in hydrocarbon lubricating oil of a metal salt of an aliphatic carboxylic acid, said metal salt carrying, on an aliphatic carbon atom not more than about two carbon atoms removed from a metal carboxylate group, a substituent selected from the class consisting of COOH, CSSH, COOM and CSSM groups, wherein M represents a metal.

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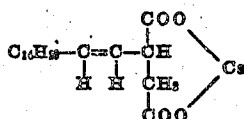
Certificate of Correction

Patent No. 2,363,514.

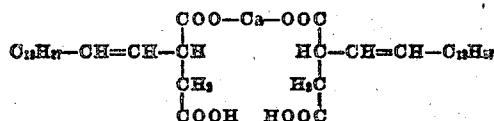
November 28, 1944.

BRUCE B. FARRINGTON ET AL

It is hereby certified that errors appear in the printed specification of the above numbered patent requiring correction as follows: Page 2, first column, line 67, for the formula " $-\text{SnH}$ " read $-\text{SnH}_2$; page 4, second column, lines 36 to 40 inclusive, strike out the formula and insert instead the following—



lines 71 to 75 inclusive, strike out the formula and insert instead the following—



and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 5th day of June, A. D. 1945.

[SEAL]

LESLIE FRAZER,
Acting Commissioner of Patents.