

## UNITED STATES PATENT OFFICE

2,363,516

## COMPOUNDED HYDROCARBON OILS

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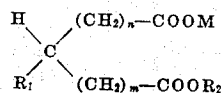
5 Claims. (Cl. 252—39)

This invention relates to new and useful com-  
positions of matter and to methods of preparing  
the same. In particular, it relates to composi-  
tions 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, particular-  
ly of petroleum origin, which alone or with the  
addition of relatively small amounts of com-  
pounding 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 hydrocar-  
bon 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 pis-  
ton 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 prod-  
ucts of such a cementitious character as to effec-  
tively take piston rings out of service; to the  
deposition of "sludge" from automobile crank-  
case 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 for-  
mation of organic acidic products. This situa-  
tion is aggravated by the fact that improvements  
in the mechanical arts have brought about in-  
creasing severity in the conditions to which hy-  
drocarbon oils are subjected, and by the fact  
that oil compounding designed to effect a sta-  
bility in one direction often brings about a  
marked instability in another.

It has been found that the addition to a lubri-  
cating oil of small amounts of a metal salt of  
an aliphatic polycarboxylic corresponding to the  
formula—



in which  $n$  and  $m$  are zero or whole numbers,

$M$  is a metal, including the hydrogen equivalent  
of a polyvalent metal,  $R_1$  is an oil-solubilizing  
group of essentially hydrocarbon structure con-  
taining at least 10 carbon atoms, and  $R_2$  is hy-  
drogen, a metal or other basic radical or an  
organic group, brings about an improved sta-  
bility in hydrocarbon oils when the same are sub-  
jected to high temperatures and/or pressures in  
the presence of oxygen and metals. One or more  
of the hydrogens of the indicated methylene  
groups and of the group



may be replaced by other groups, such as alkyl,  
aryl, aralkyl or aliphatic carbocyclic groups, and  
it has further been found that still greater im-  
provement of the desired sort is brought about  
when certain polar substitution is effected in a  
position alpha, beta, gamma, delta or even epsilon  
to the carbon atom of a salt-forming carboxylic  
acid group, the effectiveness for the desired pur-  
pose decreasing in the order of positions as rec-  
ited.

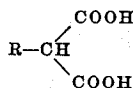
Examples of polar substituents which may be  
used in the polar substitution just referred to  
are as follows:

| Name                              | Formula               |
|-----------------------------------|-----------------------|
| Carboxylic acid.....              | —COOH                 |
| Metallo-carboxyl.....             | —COOM,                |
| Esterified carboxyl.....          | —COOR                 |
| Hydroxyl.....                     | —OH                   |
| Vinylene.....                     | —CH=CH—               |
| Amino.....                        | —NH <sub>2</sub>      |
| Ethynylene.....                   | —C≡C—                 |
| Alkoxy or aryloxy.....            | —OR                   |
| Metallo-oxy.....                  | —OM                   |
| Oxo or keto.....                  | =O                    |
| Carbamyl.....                     | —CO(NH <sub>2</sub> ) |
| Alkyl or aryl thiolcarboxyl.....  | —COSR                 |
| Alkyl or aryl thionocarboxyl..... | —CSOR                 |
| Mercapto.....                     | —SH                   |
| Alkyl or arylthio.....            | —SR                   |
| Thiono.....                       | =S                    |
| Dithio.....                       | —SS—                  |
| Sulfinyl.....                     | =SO                   |
| Sulfonyl.....                     | =SO <sub>2</sub>      |
| Imino.....                        | =NH                   |
| Alkylamino or arylamino.....      | —NHR                  |
| Dialkylamino or diarylamino.....  | —NR <sub>2</sub>      |
| Azo.....                          | —N=N—                 |
| Hydrazo.....                      | —NNH—                 |
| Hydrazono.....                    | —N=NH <sub>2</sub>    |
| Triazeno.....                     | —NNNH <sub>2</sub>    |
| Triazo.....                       | —NNN                  |
| Cyano.....                        | —CN                   |
| Isocyano.....                     | —NC                   |
| Cyanate.....                      | —OCN                  |
| Alkyl or aryl sulfino.....        | —SO <sub>2</sub> R    |
| Alkyl or aryl sulfo.....          | —SO <sub>2</sub> R    |
| Alkyl or aryl sulfamino.....      | —NHSO <sub>2</sub> R  |

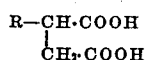
| Name                           | Formula                          |
|--------------------------------|----------------------------------|
| Sulfamyl.....                  | -SO <sub>2</sub> NH <sub>2</sub> |
| Sulfonamido.....               | -SO <sub>2</sub> NH-             |
| Selenyl.....                   | -SeH                             |
| Alkyl or aryl selenyl.....     | -SeR                             |
| Seleno.....                    | =Se                              |
| Seleninyl.....                 | =SeO                             |
| Selenonyl.....                 | =SeO <sub>2</sub>                |
| Alkyl or aryl selenino.....    | -SeO(OR)                         |
| Alkyl or aryl selenono.....    | -SeO <sub>2</sub> (OR)           |
| Selenocyno.....                | -SeCN                            |
| Telluryl.....                  | -TeH                             |
| Alkyl or aryl telluryl.....    | -TeR                             |
| Telluro.....                   | =Te                              |
| Alkyl or aryl phosphonite..... | -P(OR) <sub>2</sub>              |
| Alkyl or aryl phosphonate..... | -PO(OR) <sub>2</sub>             |
| Alkyl or aryl phosphinite..... | =POR                             |
| Alkyl or aryl phosphinate..... | =POOR                            |
| Phosphazo.....                 | -PN-                             |
| Phosphoro.....                 | -PP-                             |
| Phosphoarseno.....             | -PAs-                            |
| Arsino.....                    | -AsH <sub>3</sub> or =AsH        |
| Arsenoso.....                  | -AsO                             |
| Arso.....                      | -AsO <sub>2</sub>                |
| Alkyl or aryl arsenate.....    | -OAsO(OR) <sub>2</sub>           |
| Alkyl or aryl arsenite.....    | -OAs(OR) <sub>2</sub>            |
| Alkyl or aryl arsono.....      | -AsO(OR) <sub>2</sub>            |
| Alkyl or aryl arsinico.....    | -AsOOR                           |
| Isocyanate.....                | -NCO                             |
| Thiocyanate.....               | -SCN                             |
| Isothiocyanate.....            | -SNC                             |
| Nitroso.....                   | -NO                              |
| Nitro.....                     | -NO <sub>2</sub>                 |
| Isonitroso.....                | =NOH                             |
| Hydroxemino.....               | -NHOH                            |
| Azoxy.....                     | -NON-                            |
| Isonitro.....                  | -NOOH                            |
| Phosphino.....                 | -PH <sub>2</sub> or =PH          |
| Phosphoroso.....               | -PO                              |
| Phospho.....                   | -PO <sub>2</sub>                 |
| Alkyl or aryl phosphate.....   | -OP(OR) <sub>2</sub>             |
| Alkyl or aryl phosphite.....   | -OP(OR) <sub>2</sub>             |
| Silyl.....                     | -SiH <sub>3</sub>                |
| Silylene.....                  | =SiH <sub>2</sub>                |
| Alkyl or aryl silico.....      | -SiOOR                           |
| Arseno.....                    | -AsAs-                           |
| Stibino.....                   | -SbH <sub>3</sub> or =SbH        |
| Stiboso.....                   | -SbO                             |
| Stibo.....                     | -SbO <sub>2</sub>                |
| Alkyl or aryl antimonate.....  | -OSbO(OR) <sub>2</sub>           |
| Alkyl or aryl stibono.....     | -SbO(OR) <sub>2</sub>            |
| Alkyl or aryl stibinico.....   | =SbOOR                           |
| Antimono.....                  | -SbSb-                           |
| Stibarseno.....                | -SbAs-                           |
| Bismuthino.....                | -BiH <sub>3</sub> or =BiH        |
| Boryl.....                     | -BO                              |
| Alkyl or aryl borate.....      | -OB(OR) <sub>2</sub>             |
| Alkyl or aryl silicate.....    | -OSi(OR) <sub>2</sub>            |
| Iodoso.....                    | -IO                              |
| Stannyl.....                   | -SnH <sub>3</sub>                |
| Iodoxy.....                    | -IO <sub>2</sub>                 |

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 polycarboxylic acids whose metal salts are suitable in the practice of the invention are the alpha-alkyl and alpha-alkenyl malonic acids represented by the formula



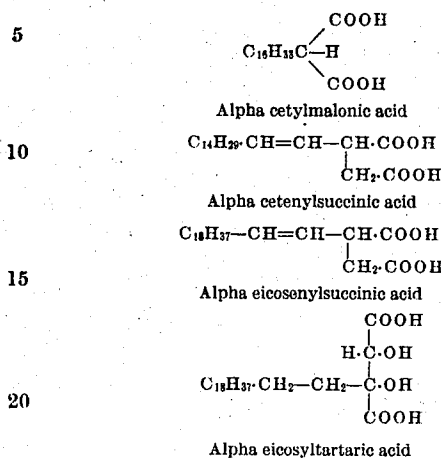
in which R represents an alkyl (C<sub>n</sub>H<sub>2n+1</sub>) or alkenyl (C<sub>n</sub>H<sub>2n-1</sub>, C<sub>n</sub>H<sub>2n-3</sub>, etc.) group of ten or more carbon atoms; the alpha-alkyl and alpha-alkenyl succinic acids—



in which R has the same significance as in the above formula for alkyl and alkenyl malonic acids; and the analogous alpha-, beta- and gamma-alkyl and alkenyl glutaric, adipic, pimelic, suberic, maleic, fumaric and tricarballic acids.

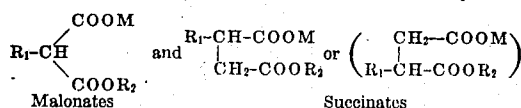
Specifically, acid and normal salts and salts of partial esters of the following acids may be used in accordance with the invention: alpha-cetyl-

malonic acid, alpha-cetenylsuccinic acid, alpha-eicosenylsuccinic acid, and alpha-eicosyl tartaric acid, these acids having the following structures—



For the purposes of the invention, these or other acids are converted into metal salts, preferably polyvalent metal salts. One manner of so doing comprises forming an aqueous or alcohol-water solution or suspension of an alkali metal salt of the acid and adding to this solution or suspension a water soluble salt of the desired polyvalent metal, e. g. calcium chloride, thereby precipitating the desired poly-valent metal salt. The acid salt or the normal salt may be formed, or one or more but not all of the free carboxyl groups may be esterified and the metal salt of the partial ester formed. Normal salts, acid salts and salts of partial esters thus formed are used in hydrocarbon oil in accordance with the invention.

With further reference to the structure and mode of preparation of the salts of the invention, we have found that malonic acid and succinic acid salts corresponding to the formulae



wherein M is a metal, R<sub>1</sub> is a C<sub>10</sub> or higher oil-solubilizing group and R<sub>2</sub> is hydrogen, a metal or other basic (salt-forming) radical, or an organic group, are especially valuable lubricant additives and that the malonates more particularly are desirable lubricant additives and the like. These salts may be exemplified by calcium alpha-cetylmalonate, calcium alpha-cetenylsuccinate, calcium alpha-eicosenylsuccinate and calcium alpha-eicosyl tartrate, the cetyl, centenyl, eicosenyl and eicosyl groups typifying the oil-solubilizing group R<sub>1</sub> and calcium typifying the metal M as well as the radical R<sub>2</sub>. (The designation "alpha" with regard to malonic and succinic acids substituted on a methylene carbon atom by an alkyl or alkenyl group is used throughout to avoid confusion with the alkyl and alkenyl esters of the same acids, wherein the alkyl or alkenyl group is present in a carboxy ester group COOR. These esters are often referred to as alkyl and alkenyl malonic acid and succinic acid, and their salts as metal alkyl (or alkenyl) malonates and succinates.) Detailed examples of the preparation of these salts are given below:

#### The alpha-alkyl malonates

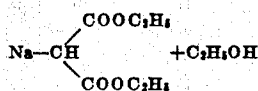
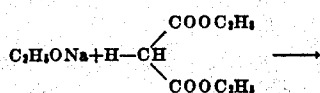
Diethyl malonate (the diethyl ester of malonic acid), is converted to sodium diethyl malonate by adding 80 grams of diethyl malonate to sodium

ethylate (prepared by dissolving 12 grams of metallic sodium in 100 cc. of absolute ethyl alcohol). Sodium diethyl malonate is precipitated from solution. It is recovered by filtration and diethyl alpha-cetylmalonate is formed by adding to the precipitate of sodium diethyl malonate 190 grams of cetyl iodide and maintaining the reaction mixture at 212° F. Sodium iodide is removed from the product by washing with water. The diethyl alpha-cetylmalonate is hydrolyzed by heating at 212° F. for 24 hours with 520 cc. of 10% aqueous potassium hydroxide solution. The resulting potassium salt is "salted out" by adding potassium chloride to the aqueous solution. Excess cetyl iodide is removed from the potassium salt by extraction with ether. The potassium salt of alpha-cetylmaleic acid is then suspended in a 50-50 alcohol-water solution and heated to 190° F. and an excess of aqueous calcium chloride solution is added. Calcium alpha-cetylmalonate is thus precipitated and is washed with water and dried.

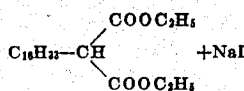
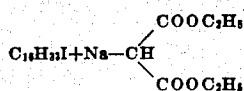
The reactions involved in this preparation are as follows:



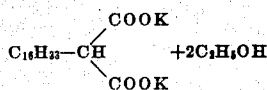
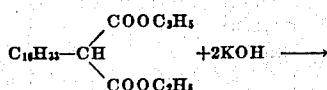
Production of sodium ethylate



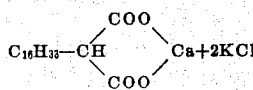
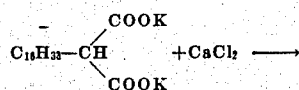
Production of sodium diethyl malonate



Production of diethyl alpha-cetylmalonate



Hydrolysis of diethyl alpha-cetylmalonate

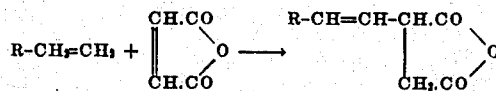


Production of calcium alpha-cetylmalonate

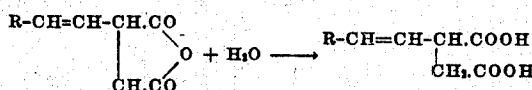
*The alpha-alkylene succinates*

One molecular proportion of maleic anhydride and 1.25 molecular proportions of olefin polymer, such as an olefinic mixture having an average carbon content of C<sub>14</sub>, C<sub>16</sub> or C<sub>20</sub> produced by polymerization of petroleum refinery olefins, are reacted in an iron pressure vessel, without agitation, at 400°-450° F. for 4 to 6 hours. The product, an alkenyl succinic anhydride, is distilled under vacuum to remove unreacted polymers and maleic anhydride, the theoretical quantity of wa-

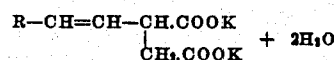
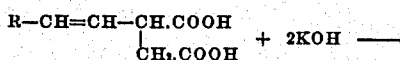
ter is added to hydrolyze the anhydride, and one water-alkenyl succinic anhydride mixture is digested under reflux for 1 hour at 195° F., thus forming the alpha-alkenyl succinic acid. A slight excess of 25% aqueous KOH solution is added and the mixture is heated at 180° F. for ½ hour, thus forming the di-potassium salt of the alkenyl succinic acid. The calcium salt is formed by adding to the aqueous solution of potassium salt as obtained above an equivalent amount of 10% aqueous CaCl<sub>2</sub> solution. The precipitate of normal calcium salt is filtered, washed free of impurities with water, and dried. The reactions involved may be represented as follows:



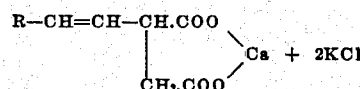
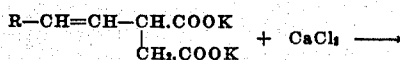
Production of alkenyl succinic anhydride



Production of alpha-alkenyl succinic acid



Production of dipotassium alpha-alkenyl succinate



Production of calcium alpha-alkenyl succinate

*Note.*—It is assumed that the olefin, which is represented as a primary olefin but which may be a secondary or tertiary olefin, adds on to maleic anhydride in the manner indicated, but it may add on in such a way as to leave intact the unsaturated bond of the maleic anhydride. Thus the final product, though called an alkenyl succinate, may be instead an alkyl maleate.

The preparation of calcium alpha cetylmalonate as given above is the familiar malonic ester synthesis (Cf. Liebig's Annalen der Chemie, vol. 204, page 121). This synthesis, based upon the reactivity of the methylene hydrogens of malonic ester (diethyl malonate), is customarily used in the synthesis of monocarboxylic aliphatic acids, since the corresponding free alpha alkyl malonic acid (produced by hydrolyzing the alpha alkyl malonic ester) is readily converted on heating, by loss of CO<sub>2</sub>, into a monocarboxylic acid. For purposes of the present invention, however, the sodium derivative of malonic ester is condensed with a C<sub>10</sub> or higher alkyl halide or the like (or a technical mixture of halides averaging C<sub>10</sub> or higher) and the resulting alpha alkyl malonic ester is converted to a metal salt in the manner shown above. Among the advantages we have found in this application of the malonic ester synthesis, there may be mentioned the fact that from cheap materials (such as malonic ester, sodium and the higher alkyl halides) there is easily prepared an oil-soluble salt of a polycarboxylic aliphatic acid, and, as shown in more detail below, such salts are exceedingly potent improvement agents for hydrocarbon oils.

The preparation of the calcium alpha-alkenyl succinate as given above is based upon the Diels and Alder reaction (Cf. Liebig's Annalen, vol. 460, page 98 and vol. 470, page 62, and Berichte der deut. Chem. Ges., vol. 62, page 554). This application of the Diels and Alder reaction is apparently based upon the reactivity of maleic anhydride with olefins; the activated ethylene



group of maleic anhydride appears to undergo a condensation reaction with the olefin, in which

cant 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.

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% calcium α-elcosyltartrate                            | 60+                          | Fair+                          | Good.                       |
| 16.     | +0.50% calcium α-cetylmalonate                              | 75                           | Fair.                          | Poor.                       |
| 17.     | +0.34% calcium α-cetenylsuccinate                           | 90                           | Fair+                          | Do.                         |
| 36.     | +0.50% calcium α-elcosenylsuccinate                         | 120+                         | Good.                          | Fair.                       |
| 42.     | +0.50% calcium cetylphenate+0.50% calcium α-elcosyltartrate | 120+                         | Very good.                     | Very good.                  |
|         | +0.50% calcium cetylphenate                                 | 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.

reaction a hydrogen of the olefin migrates to one methine



group of the maleic anhydride and the olefin residue attaches itself to the remaining methine group. However, as stated, the mechanism of the reaction and the nature of the final product may be different from that depicted above.

The salt additives of the invention, as stated, comprise at least two aliphatic carboxylate groups, at least one of which is in the form of a metal carboxylate group, and a C<sub>10</sub> or higher oil-solubilizing group. The oil-solubilizing group may be substituted provided the substituent or substituents do not greatly inhibit its oil-solubilizing capacity, and while long chain alkyl and alkenyl groups are preferred, the higher alkaryl, aralkyl, aryl and cycloaliphatic groups may be used. Polyvalent metals are preferred in forming the salts of the invention, and the same atom of polyvalent metal may neutralize two or more aliphatic carboxylate groups of the polycarboxylic acid. However, the one or more carboxylate groups in addition to the essential metal carboxylate group may, as stated, be a free carboxyl group, or may be neutralized by ammonia or an amine or may be esterified.

The following specific examples will serve to illustrate the practice and the 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 $\frac{5}{8}$  inch bore and 2 $\frac{1}{2}$  inch stroke, loaded with fan dynamometers, was operated under extremely severe conditions, designed to develop fully the tendency of the crankcase lubri-

## EXAMPLES, SET II

30 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 R<sub>2</sub>OOC-(CH<sub>2</sub>)<sub>m</sub>-CH(R<sub>1</sub>)-(CH<sub>2</sub>)<sub>n</sub>-COOH 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 a salt-forming carboxylic acid—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, 1 $\frac{1}{8}$ " x 1 $\frac{3}{4}$ " x  $\frac{3}{16}$ "; cadmium-silver,

$$\frac{1}{2}" \times 1\frac{3}{8}" \times \frac{1}{16}"$$

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. ±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; 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 com-

pounding, 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. Attention is additionally directed to the compounded oils of Example No. 42 to which has been added, as a further compounding agent, calcium cetylphenate, wherein it appears that the increased corrosivity due to the original compounding has been prevented or inhibited by the agents of the invention.

TABLE II

## Reduction of corrosivity to bearing metals

| Example | Oil                                                                     | Weight loss<br>in mgms.,<br>72 hrs. |       |
|---------|-------------------------------------------------------------------------|-------------------------------------|-------|
|         |                                                                         | Cu-Pb                               | Cd-Ag |
| 10      | Western 30.                                                             | 13.9                                | 0.4   |
| 15      | +0.63% calcium $\alpha$ -eicosyltartrate.                               | 5.0                                 | 0.9   |
| 16      | +0.50% calcium $\alpha$ -cetylmalonate.                                 | 9.8                                 | 0.3   |
| 17      | +0.50% calcium $\alpha$ -cetenylsuccinate.                              | 1.1                                 | 0.3   |
| 42      | +0.34% calcium $\alpha$ -eicosenylsuccinate.                            | 1.6                                 | 0.1   |
| A       | +0.50% calcium cetylphenate+0.50% calcium $\alpha$ -eicosenylsuccinate. | 40.7                                | 6.0   |
| B       | +0.50% calcium stearate.                                                | 131.9                               | 180.5 |
| C       | +1.0% aluminum dinaphthenate.                                           | 67                                  | 113   |
| D       | +1.0% magnesium naphthenate.                                            | 139                                 | 119   |
|         | +1.0% calcium 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

| Example | Oil                                                                                                  | Color after heating | Color increase |
|---------|------------------------------------------------------------------------------------------------------|---------------------|----------------|
| 10      | Western 30.                                                                                          | 3½ Dil.             | 6              |
| 17      | +0.63% calcium $\alpha$ -eicosyltartrate.                                                            | 4-                  | 1-             |
| 24      | +0.34% calcium $\alpha$ -eicosenylsuccinate.                                                         | 4-                  | ½              |
| 29      | +0.18% calcium $\alpha$ -cetenylsuccinate.                                                           | 4-                  | 1-             |
| 41      | +0.50% potassium $\alpha$ -cetylmalonate.                                                            | 4½                  | 1½             |
| 42      | +0.50% calcium cetylphenate+0.10% calcium $\alpha$ -cetenylsuccinate.                                | 6                   | 1½             |
| 53      | +0.50% calcium cetylphenate+0.50% calcium $\alpha$ -eicosenylsuccinate.                              | 7                   | 2½+            |
| 54      | +0.25% calcium cetylphosphate+0.10% calcium $\alpha$ -cetenylsuccinate.                              | 4                   | ½              |
| 63      | +0.25% calcium cetylphosphate+0.50% calcium $\alpha$ -eicosenylsuccinate.                            | 4-                  | 1-             |
| 64      | +0.50% calcium cetylphenate+0.25% calcium cetylphosphate+0.20% calcium $\alpha$ -cetenylsuccinate.   | 5-                  | ½              |
| 71      | +0.50% calcium cetylphenate+0.25% calcium cetylphosphate+0.50% calcium $\alpha$ -eicosenylsuccinate. | 7                   | 2½             |
| 72      | +1.0% diisooamyl tartrate+0.10% calcium $\alpha$ -cetenylsuccinate.                                  | 4½                  | 1              |
|         | +1.0% diisooamyl tartrate+0.50% calcium $\alpha$ -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 1½ 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

| Example | Oil                                          | Weeks wear | Film strength |
|---------|----------------------------------------------|------------|---------------|
| 15      | Western 30.                                  | 288        | 120           |
| 17      | +0.50% calcium $\alpha$ -cetylmalonate.      | 143        | 160           |
| 25      | +0.34% calcium $\alpha$ -eicosenylsuccinate. | 106        | 220           |
| B       | +0.20% calcium $\alpha$ -cetenylsuccinate.   | 163        | 120           |
| D       | +1.0% aluminum dinaphthenate.                | 639        | 120           |
|         | +0.50% calcium cetylphenate.                 | 105        | 120           |

## EXAMPLES, SET V

Still further, the capability of hydrocarbon oils to absorb oxygen, when exposed thereto at superatmospheric 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

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

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 of the 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 the 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 lubricating oil normally tending to deteriorate and to form carbonaceous deposits on pistons at temperatures encountered in the operation of internal combustion engines, containing a small amount, sufficient to inhibit said deterioration and deposition,

of a metal salt of an alkylated phenol, and a small amount, sufficient to inhibit said deterioration and deposition and to inhibit the tendency of said salt of phenol to corrode alloy bearings of the copper-lead and cadmium-silver types, of a metal salt of an aliphatic polycarboxylic acid having as a substituent on an aliphatic carbon atom other than the carbon atom of a carboxyl group, an oil-solubilizing essentially hydrocarbon group of not less than 10 carbon atoms.

2. The oil of claim 1, wherein said metal salts are polyvalent metal salts.

3. A liquid hydrocarbon lubricating oil normally tending to deteriorate and to form carbonaceous deposits on pistons at temperatures encountered in the operation of internal combustion engines, containing a small amount, sufficient to inhibit said deterioration and deposition, of an oil-soluble polyvalent metal salt of an alkylated phenol and about 0.1 to 5% by weight based on finished oil of a polyvalent metal salt of an alpha alkyl substituted malonic acid wherein the alpha alkyl substituent contains not less than 10 carbon atoms.

4. A liquid hydrocarbon lubricating oil normally tending to deteriorate and to form carbonaceous deposits on pistons at temperatures encountered in the operation of internal combustion engines, containing a small amount, sufficient to inhibit said deterioration and deposition, of an oil-soluble polyvalent metal salt of an alkylated phenol and about 0.1 to 5% by weight based on finished oil of a polyvalent metal salt of an alpha alkaryl substituted malonic acid wherein the alpha alkaryl substituent contains not less than 10 carbon atoms.

5. A liquid hydrocarbon lubricating oil normally tending to deteriorate and to form carbonaceous deposits on pistons at temperatures encountered in the operation of internal combustion engines, containing a small amount, sufficient to inhibit said deterioration and deposition, of an oil-soluble polyvalent metal salt of an alkylated phenol and about 0.1 to 5% by weight based on finished oil of a polyvalent metal salt of the product of condensing maleic anhydride with a C<sub>10</sub> or higher olefin to produce an alpha substituted maleic anhydride.

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