Patented June 15, 1943 2,321,575

UNITED STATES PATENT OFFICE

2,321,575

COMPOUNDED HYDROCARBON OIL

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20 Claims. (Cl. 252—32)

This invention relates to a new and useful composition of matter comprising a compounded hydrocarbon oil. More particularly, it involves the provision of a lubricating oil containing metal salts of organic acids and an addition agent which inhibits undesirable effects of such compounds, as set forth hereinafter.

Metal salts of organic acids are known as compounding ingredients for lubricating oils and have been added thereto for various purposes. For example, aluminum oleate is disclosed as a dispersing agent for graphite in the United States patent to Burke No. 1,732,221, various soaps have been disclosed as pour point depressing agents, and the patent to Parker No. 2,001,108 is directed to metal naphthenates as stabilizing agents for lubricating oils. In its broader aspects this invention is applicable to compounded oils containing metal salts of organic acids of the above known types, as well as to oils containing novel types of salts hereinafter disclosed. The present invention, in its more specific aspects, is concerned with oils compounded with certain metal salts among which are polyvalent metal salts, such as salts of aluminum, zinc, tin, magnesium, calcium and chromium.

One important property of lubricating oils is low corrosivity, especially with respect to modern bearing metals such as copper-lead or cadmium-silver alloys. Some lubricating oils which have been entirely satisfactory from the standpoint of corrosivity to high grade Babbitt bearing metals show a corrosion rate which is greater than is desirable with bearing metals of a type represented by cadmium-silver and copper-lead bearings. Lubricating oils containing metal salt compounding ingredients have been found, in general, to show undesirable corrosive effects on such bearing materials. However, these metal salt compounding ingredients are highly desirable or even necessary for other purposes, such as for inhibiting piston ring sticking in internal combustion engines such as Diesel engines.

Accordingly, it is an object of the invention to solve the above difficulties by providing an improved compounded mineral oil containing metal salts of organic acids.

Another object of the invention is to inhibit corrosive effects of compounded lubricating oils containing metal salts of organic acids.

A further object of the invention is to increase the stability of lubricating oils with respect to oxidation or discoloration or gum formation.

A still further object is to improve the properties of lubricating oils containing metal salts of organic acids by incorporating therein an ester containing a divalent sulfur group preferably no more than two carbon atoms removed from a carbonyl group of said ester.

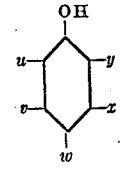
Additional objects and advantages of the invention will become apparent from the disclosure which follows.

Examples of metal salts of organic acids which may be incorporated in lubricating oils according to the principles of this invention are metal salts of higher fatty or aliphatic acids, metal salts of naphthenic acids, metals salts of oil-soluble substituted phenols, and metal salts of carboxylic acids containing an aryl substituent.

Among the metal salts of higher fatty acids may be mentioned: aluminum laurate, aluminum oleate, aluminum stearate, aluminum ricinoleate; zinc laurate, zinc oleate, zinc stearate, zinc ricinoleate; tin laurate, tin oleate, tin stearate, tin ricinoleate; magnesium laurate, magnesium oleate, magnesium stearate, magnesium ricinoleate; calcium laurate, calcium oleate, calcium stearate; calcium ricinoleate; chromium laurate, chromium oleate, chromium stearate, and chromium ricinoleate.

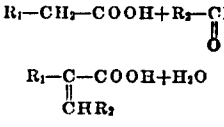
Examples of metal naphthenates are: aluminum naphthenate, zinc naphthenate, magnesium naphthenate, cobalt naphthenate, cadmium naphthenate, tin naphthenate and manganese naphthenate. The naphthenic acid component of these salts may conveniently be obtained from petroleum.

Metal phenates which may be mentioned comprise metal salts of a substituted phenol of the type formula:



in which u, v, w, x and y are selected from the group consisting of hydrogen, alkyl, aryl, alkaryl, aralkyl and cyclic non-benzenoid hydrocarbon radicals. Specific illustrations of such phenates are the aluminum, zinc, tin, magnesium, calcium and chromium as well as other polyvalent metal salts of cetyl phenol. The phenolic radical of the salts preferably contains more than about ten carbon atoms and also should preferably have an alkyl substituent substituted in the benzene ring to which the hydroxyl group of the phenol is directly attached.

Examples of carboxylic acids containing an aryl substituent are: phenyl stearic acid, naphthyl stearic acid, phenyl lauric acid, alpha benzal stearic acid, alpha benzal lauric acid, and analogous homologues of these acids formed by condensation of an aromatic aldehyde with a fatty acid according to the reaction:

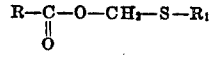


where R_1 is an alkyl and R_2 an aryl radical. Aluminum, zinc, tin, magnesium, calcium and chromium as well as other polyvalent metal salts of each of the above acids may be utilized.

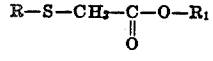
The invention also includes salts of polycarboxylic acids together with esters containing a divalent sulfur group, in hydrocarbon oils. Examples of such salts are the aluminum, zinc, tin, magnesium, calcium and chromium as well as other polyvalent metal salts of partially esterified acids of the oxalic acid series, including oxalic acid itself, malonic acid, isosuccinic or methyl malonic acid and its alkyl homologues, as well as the corresponding salts of partially esterified alkyl tartronic acid, partially esterified malic acid and its homologues, partially esterified oxyglutaric acid, partially esterified hydroxy adipic acid, partially esterified tartaric acid, partially esterified citric acid and the like.

The second component of the composition of this invention comprises oil-soluble esters containing a divalent sulfur atom preferably no more than two carbon atoms removed from a carbonyl group of the ester. Examples of these types of compounds comprise esters containing a thioether group in the alpha or beta position, esters containing a mercapto group in the alpha or beta position, and esters containing a thioketo group in the alpha or beta position. These types of compounds may be represented generically by the following structural formulae:

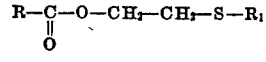
Alpha thioether substituted esters



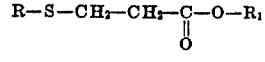
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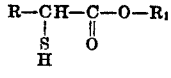
Beta thioether substituted esters



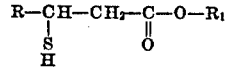
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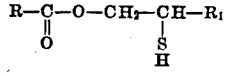
Alpha mercapto substituted ester



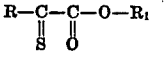
Beta mercapto substituted esters



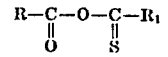
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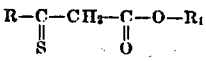
Alpha thioketo substituted esters



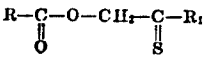
or



Beta thioketo substituted esters



or



In these formulae R and R_1 represent an alkyl, aryl, alkaryl, aralkyl or cyclic non-benzenoid group. R and R_1 may contain substituents other than the divalent sulfur group, which substituents may be of either the same or a different type. It is to be understood that the corresponding esters of monothio- or dithio-carboxylic acids fall within the broader scope of the invention.

In the type formulae herein given, frequent reference is made to alkyl, aryl, alkaryl, aralkyl or cyclic non-benzenoid radicals. Examples of alkyl radicals are: methyl, ethyl, propyl, butyl, amyl, hexyl, heptyl, ortyl, nonyl, decyl, dodecyl (lauryl), tetradecyl and cetyl. Examples of aryl radicals are phenyl and naphthyl. Examples of alkaryl radicals are radicals in which a benzene ring is attached directly to the molecule being substituted, and the benzene ring contains an alkyl substituent. Examples of aralkyl radicals are radicals in which an alkyl group is attached directly to the molecule being substituted, and the alkyl group contains an aryl substituent, for instance, an ester of phenyl methyl alcohol. Examples of cyclic non-benzenoid radicals are cyclo pentyl, cyclo hexyl and cylo heptyl.

Examples of alpha and beta thioether substituted esters are: methyl, ethyl, propyl, butyl, amyl, hexyl, heptyl, octyl, nonyl, decyl, lauryl, tetradecyl and cetyl esters of amylthio acetic acid; methyl, ethyl, propyl, butyl, amyl, hexyl, heptyl, octyl, nonyl, decyl, lauryl, tetradecyl and cetyl esters of methylthio propionic acid; methyl, ethyl, propyl, butyl, amyl, hexyl, heptyl, octyl, nonyl, decyl, lauryl, tetradecyl and cetyl esters of S-phenyl-monothiotartaric acid; and methyl, ethyl, propyl, butyl, amyl, hexyl, heptyl, octyl, nonyl, decyl, lauryl, tetradecyl and cetyl esters of benzylthio-succinic acid.

Examples of alpha and beta mercapto substituted esters are: methyl, ethyl, propyl, butyl, amyl, hexyl, heptyl, octyl, nonyl, decyl, lauryl; tetradecyl and cetyl esters of thiolactic acid; methyl, ethyl, propyl, butyl, amyl, hexyl, heptyl, octyl, nonyl, decyl, lauryl, tetradecyl and cetyl esters of thiohydracrylic acid; methyl, ethyl, propyl, butyl, amyl, hexyl, heptyl, octyl, nonyl, decyl, lauryl, tetradecyl and cetyl esters of thiomalic acid; methyl, ethyl, propyl, butyl, amyl, hexyl, heptyl, octyl, nonyl, decyl, lauryl, tetradecyl, and cetyl esters of dithiotartaric acid.

Examples of alpha and beta thioketo substituted esters are: methyl, ethyl, propyl, butyl, amyl, hexyl, heptyl, octyl, nonyl, decyl, lauryl, tetradecyl and cetyl esters of amyl thioketo-acetic acid; methyl, ethyl, propyl, butyl, amyl, hexyl, heptyl, octyl, nonyl, decyl, lauryl, tetradecyl and cetyl esters of methyl thioketo-propionic acid.

The esters of this invention may be prepared by methods known in the art. The esters may be prepared by esterification of the alpha or beta substituted acids, by esterification of the alpha or beta substituted alcohols, or by introducing the divalent sulfur group into an ester in an alpha or beta position. For example, ethyl thiolactate

may be prepared by warming thiolactic acid with alcohol and a little sulfuric acid, then dissolving in ether and removing the sulfuric acid with water. Diethyl thiomalate may be prepared by saturating an alcoholic solution of thiomalic acid with hydrochloric acid and fractionally distilling under vacuum. The ethyl ester of S-amyl-thioglycolic acid may be prepared by heating ethyl chloro-acetate and sodium amylmercaptide, dissolving in ether, washing out sodium chloride with water, and then fractionating.

It will be understood from the foregoing discussion that the invention embraces the addition of both a metal salt of an organic acid and the substituted ester as addition agents for liquid lubricating oils. Each and every one of the foregoing metal salts of organic acids may be utilized in hydrocarbon oils with each and every one of the foregoing substituted esters to impart improved properties to the oil; e. g. lubricating oils containing any one or more of the metal salts of fatty acids with any one or more of the alpha or beta divalent sulfur substituted esters will be found useful. Likewise, oils containing any one or more of the metal naphthenates in combination with any one or more of the alpha or beta divalent sulfur substituted esters possess advantageous properties. The same is true of combinations of any one or more of the metal salts of phenols or of the metal salts of the aryl substituted or polycarboxylic acids with any one or more of the divalent sulfur substituted esters.

The combinations disclosed herein cooperate to give new results in hydrocarbon lubricating oils. In general, the alpha or beta divalent sulfur substituted esters reduce the corrosive effects of hydrocarbon oils on modern bearing metals, such as copper-lead or cadmium-silver alloys. These esters will reduce corrosiveness of oils containing metal salts of organic acids as much as 50% or more. Various of the metal salts of organic acids and the substituted esters apparently cooperate to enhance the stability of the oil against discoloration, gum formation, piston ring sticking and the like.

The proportions of addition agents utilized will depend upon the particular compound incorporated in the oil, upon the base oil being compounded, as well as upon the conditions which the oil is to encounter during use and the properties desired. In general, from 0.1% to 5% of the metal salts of organic acids are utilized, and more usually 0.5% to 2% thereof are found desirable. Measurable improvements in the properties of the compounded oil are obtained with as little as 0.1% of the substituted esters, but as much as 1% is preferred. More than 10% is regarded as unnecessary.

The chemical mechanism by which the results of this invention are obtained has not been established. Metal salts of organic acids appear generally to catalyze corrosive effects in hydrocarbon lubricating oils. The alpha and beta divalent sulfur substituted esters inhibit or offset this catalytic action. The present invention, in its broader aspects, is applicable to oils, such as highly refined or highly paraffinic mineral oils, which are in themselves corrosive to bearing metals in the absence of added metal salts of organic acids; i. e., the alpha and beta divalent sulfur substituted esters may, according to the broader principles of the invention, be utilized to inhibit the corrosive action of hydrocarbon lubricating oils on copper-lead and cadmium-silver bearing metals whether or not the oils contain metal salts. However, the invention appears to find its greatest utility in oils containing metal salts of organic acids in that these salts cooperate with esters to yield properties which are not obtainable with either type of component alone.

It is apparent that the particular ester and the particular metal salt must be selected with various factors in mind, such as the service to be encountered and the type of bearings or other machine elements to be lubricated, if the maximum benefits of the invention are to be obtained. In general, salts containing at least ten carbon atoms are preferred. Where reduced corrosion is desired esters containing less than ten carbon atoms are preferred. Esters containing more than ten carbon atoms are useful for imparting other properties to the oil, e. g., reducing wear or reducing friction. While specific examples and methods of preparation of the compositions of the invention have been described, this has been done by way of illustration only and with the intention that no limitation should be imposed upon the invention thereby. Numerous modifications and variations of the illustrative examples may be effected in the practice of the invention which is of the scope of the claims appended hereto.

We claim:

1. A composition of matter comprising a hydrocarbon oil containing a metal salt of an organic acid in an amount sufficient substantially to increase the corrosivity of said oil, and a corrosion inhibitor comprising an ester having a divalent sulfur substituent attached to an alkyl carbon atom and no more than two carbon atoms removed from a carbonyl group of said ester.

2. A composition of matter comprising a hydrocarbon oil containing a metal salt of an organic acid in an amount sufficient substantially to increase the corrosivity of said oil, and a corrosion inhibitor comprising an ester having a thioether substituent attached to an alkyl carbon atom and no more than two carbon atoms removed from a carbonyl group of said ester.

3. A composition of matter comprising a hydrocarbon oil containing a metal salt of an organic acid in an amount sufficient substantially to increase the corrosivity of said oil, and a corrosion inhibitor comprising an ester having a thioketo substituent no more than two carbon atoms removed from a carbonyl group of said ester.

4. A composition of matter comprising a hydrocarbon oil containing a metal salt of an organic acid in an amount sufficient substantially to increase the corrosivity of said oil, and a corrosion inhibitor comprising an ester having a mercapto substituent attached to an alkyl carbon atom and no more than two carbon atoms removed from a carbonyl group of said ester.

5. A compounded hydrocarbon oil containing a small amount of a metal salt of an organic acid sufficient substantially to increase the corrosivity of said oil, and from approximately 0.1% to 10% of an ester having a divalent sulfur substituent attached to an alkyl carbon atom and no more than two carbon atoms removed from a carbonyl group of said ester.

6. A compounded hydrocarbon oil containing a small amount of a metal salt of an organic acid sufficient substantially to increase the corrosivity of said oil, and from approximately 0.1% to 10% of an ester having a thioether substituent attached to an alkyl carbon atom and no more

than two carbon atoms removed from a carbonyl group of said ester.

7. A compounded hydrocarbon oil containing a small amount of a metal salt of an organic acid sufficient substantially to increase the corrosivity of said oil, and from approximately 0.1% to 10% of an ester having a thioketo substituent no more than two carbon atoms removed from a carbonyl group of said ester.

8. A compounded hydrocarbon oil containing a small amount of a metal salt of an organic acid sufficient substantially to increase the corrosivity of said oil, and from approximately 0.1% to 10% of an ester having a mercapto substituent attached to an alkyl carbon atom and no more than two carbon atoms removed from a carbonyl group of said ester.

9. In a method of lubricating bearing surfaces which comprises maintaining between the bearing surfaces, one of which is a bearing metal of the type represented by cadmium-silver and copper-lead alloys, a film of a lubricating oil which initially produces an effective lubricating action but which would normally tend to corrode said bearing metal, the step of inhibiting the corrosive action of the oil on said bearing by incorporating therein from approximately 0.1% to 10% of an ester having a divalent sulfur substituent attached to an alkyl carbon atom and no more than two carbon atoms removed from a carbonyl group of said ester.

10. In a method of lubricating bearing surfaces which comprises maintaining between the bearing surfaces, one of which is a bearing metal of the type represented by cadmium-silver and copper-lead alloys, a film of a lubricating oil which initially produces an effective lubricating action but which would normally tend to corrode said bearing metal, the step of inhibiting the corrosive action of the oil on said bearing by incorporating therein from approximately 0.1% to 10% of an ester having a thioether substituent attached to an alkyl carbon atom and no more than two carbon atoms removed from a carbonyl group of said ester.

11. In a method of lubricating bearing surfaces which comprises maintaining between the bearing surfaces, one of which is a bearing metal of the type represented by cadmium-silver and copper-lead alloys, a film of a lubricating oil which initially produces an effective lubricating action but which would normally tend to corrode said bearing metal, the step of inhibiting the corrosive action of the oil on said bearing by incorporating therein from approximately 0.1% to 10% of an ester having a thioketo substituent no more than two carbon atoms removed from a carbonyl group of said ester.

12. In a method of lubricating bearing surfaces which comprises maintaining between the bearing surfaces, one of which is a bearing metal of the type represented by cadmium-silver and copper-lead alloys, a film of a lubricating oil which initially produces an effective lubricating action but which would normally tend to corrode said bearing metal, the step of inhibiting the corrosive action of the oil on said bearing by incorporating therein from approximately 0.1% to 10% of an ester having a mercapto substituent attached to an alkyl carbon atom and no more than two carbon atoms removed from a carbonyl group of said ester.

13. In a method of lubricating bearing surfaces which comprises maintaining between the bearing surfaces, one of which is a bearing metal of the type represented by cadmium-silver and copper-lead alloys, a film of a compounded lubricating oil containing a metal salt of an organic acid in an amount which would normally increase the corrosivity of said oil to said bearing metal, the step of inhibiting the corrosive action of the oil on said bearing by incorporating therein from approximately 0.1% to 10% of an ester having a divalent sulfur substituent no more than two carbon atoms removed from a carbonyl group of said ester.

14. In a method of lubricating bearing surfaces which comprises maintaining between the bearing surfaces, one of which is a bearing metal of the type represented by cadmium-silver and copper-lead alloys, a film of a compounded lubricating oil containing a metal salt of an organic acid in an amount which would normally increase the corrosivity of said oil to said bearing metal, the step of inhibiting the corrosive action of the oil on said bearing by incorporating therein from approximately 0.1% to 10% of an ester having a thioether substituent no more than two carbon atoms removed from a carbonyl group of said ester.

15. In a method of lubricating bearing surfaces which comprises maintaining between the bearing surfaces, one of which is a bearing metal of the type represented by cadmium-silver and copper-lead alloys, a film of a compounded lubricating oil containing a metal salt of an organic acid in an amount which would normally increase the corrosivity of said oil to said bearing metal, the step of inhibiting the corrosive action of the oil on said bearing by incorporating therein from approximately 0.1% to 10% of an ester having a thioketo substituent no more than two carbon atoms removed from a carbonyl group of said ester.

16. In a method of lubricating bearing surfaces which comprises maintaining between the bearing surfaces, one of which is a bearing metal of the type represented by cadmium-silver and copper-lead alloys, a film of a compounded lubricating oil containing a metal salt of an organic acid in an amount which would normally increase the corrosivity of said oil to said bearing metal, the step of inhibiting the corrosive action of the oil on said bearing by incorporating thereon from approximately 0.1% to 10% of an ester having a mercapto substituent no more than two carbon atoms removed from a carbonyl group of said ester.

17. The composition of claim 1, wherein said metal salt of an organic acid is a metal phenate having an oil-solubilizing substituent.

18. The composition of claim 1, wherein said metal salt of an organic acid is a metal salt of an aliphatic carboxylic acid.

19. The composition of claim 1, wherein said metal salt of an organic acid is a metal salt of a partial ester of an aliphatic polycarboxylic acid.

20. The composition of claim 1, wherein said metal salt of an organic acid is a metal salt of a carboxylic acid having an aryl substituent.

JAMES O. CLAYTON.
BRUCE B. FARRINGTON.

CERTIFICATE OF CORRECTION.

Patent No. 2,321,575. June 15, 1943

JAMES O. CLAYTON, ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 4, second column, line 1, beginning with "13. In a method" strike out all to and including the words and period "said ester." in line 57, comprising claims 13, 14, 15 and 16 and insert instead the following -

13. A compounded lubricant comprising a hydrocarbon oil containing from approximately 0.1% to 5% of a metal salt of an organic acid and from approximately 0.1% to 10% of a corrosion inhibitor comprising an ester having a divalent sulfur substituent attached to an alkyl carbon atom and no more than two carbon atoms removed from a carbonyl group of the ester.

14. A compounded lubricant comprising a hydrocarbon oil containing from approximately 0.1% to 10% of an ester of a carboxylic acid, said ester having a mercapto substituent no more than two carbon atoms removed from a carbonyl group of the ester.

15. A compounded lubricant comprising a hydrocarbon oil with the properties of such composition affecting its use as a lubricant improved by incorporating therein at least 0.1% by weight based on the oil of a metal salt of an organic acid and from approximately 0.1% to 10% by weight based on the oil of an ester having a divalent sulfur substituent attached to an alkyl carbon atom and no more than two carbon atoms removed from a carbonyl group of the ester.

16. A compounded lubricant comprising a hydrocarbon oil with the properties of such composition affecting its use as a lubricant improved by incorporating therein at least 0.1% by weight based on the oil of a metal salt of an organic acid and from approximately 0.1% to 10% by weight based on the oil of an ester having a thioether substituent attached to an alkyl carbon atom and no more than two carbon atoms removed from a carbonyl group of the ester. ;

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

Signed and sealed this 24th day of August, A. D. 1943.

Henry Van Arsdale,
Acting Commissioner of Patents.

(Seal)

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13. A compounded lubricant comprising a hydrocarbon oil containing from approximately 0.1% to 5% of a metal salt of an organic acid and from approximately 0.1% to 10% of a corrosion inhibitor comprising an ester having a divalent sulfur substituent attached to an alkyl carbon atom and no more than two carbon atoms removed from a carbonyl group of the ester.

14. A compounded lubricant comprising a hydrocarbon oil containing from approximately 0.1% to 10% of an ester of a carboxylic acid, said ester having a mercapto substituent no more than two carbon atoms removed from a carbonyl group of the ester.

15. A compounded lubricant comprising a hydrocarbon oil with the properties of such composition affecting its use as a lubricant improved by incorporating therein at least 0.1% by weight based on the oil of a metal salt of an organic acid and from approximately 0.1% to 10% by weight based on the oil of an ester having a divalent sulfur substituent attached to an alkyl carbon atom and no more than two carbon atoms removed from a carbonyl group of the ester.

16. A compounded lubricant comprising a hydrocarbon oil with the properties of such composition affecting its use as a lubricant improved by incorporating therein at least 0.1% by weight based on the oil of a metal salt of an organic acid and from approximately 0.1% to 10% by weight based on the oil of an ester having a thioether substituent attached to an alkyl carbon atom and no more than two carbon atoms removed from a carbonyl group of the ester. ;

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

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Acting Commissioner of Patents.

(Seal)