Patented June 15, 1943 2,321,578

UNITED STATES PATENT OFFICE

2,321,578

COMPOUNDED LUBRICATING OIL

James O. Clayton and Bruce B. Farrington, Berkeley, Calif., assignors to Standard Oil Company of California, San Francisco, Calif., a corporation of Delaware

No Drawing. Application June 10, 1940, Serial No. 339,664

22 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 oil containing metal salts of organic acids by incorporating therein an ester containing, preferably no more than two carbon atoms removed from a carbonyl group of said ester, a nitrogen-containing substituent having at least two bonds connected to a single atom.

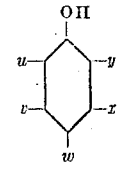
Additional objects and advantages of the invention will become apparent from the disclosure which follows.

Examples of metal salts or 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, metal 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.

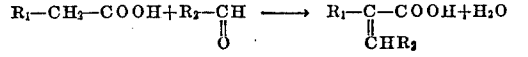
Metal phenates which may be mentioned comprise metal salts of a substituted phenol of the type formula:



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 analo-

gous homologues of these acids formed by condensation of an aromatic aldehyde with a fatty acid according to the reaction:

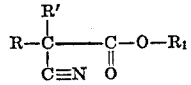


where R_1 is an alkyl and R_2 an aryl radical. Aluminum, zinc, tin, magnesium, calcium and chromium as well as other polyvalent metal salts of each of the above acids may be utilized.

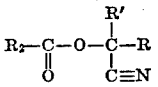
The invention also includes salts of polycarboxylic acids together with the substituted esters of this invention in hydrocarbon oils. Examples of such salts are the aluminum, zinc, tin, magnesium, calcium, and chromium as well as other polyvalent metal salts of partially esterified acids of the oxalic 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 having, preferably no more than two carbon atoms removed from a carbonyl group of the esters, a substituent comprising nitrogen having at least two bonds connected to a single atom. There are a considerable number of these types of compounds, and exemplary types may be represented generically by the following structural formulae:

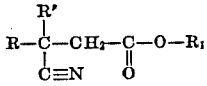
Alpha nitrile substituted esters



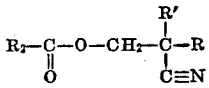
or



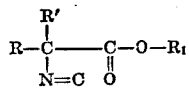
Beta nitrile substituted esters



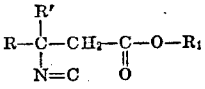
or



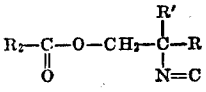
Alpha isonitrile substituted ester



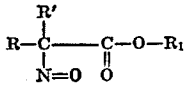
Beta isonitrile substituted esters



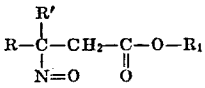
or



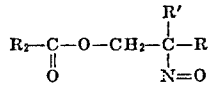
Alpha nitroso substituted ester



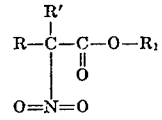
Beta nitroso substituted esters



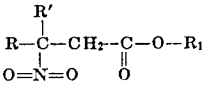
or



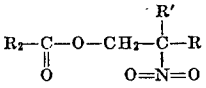
Alpha nitro substituted ester



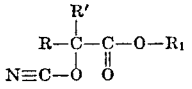
Beta nitro substituted esters



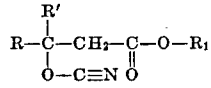
or



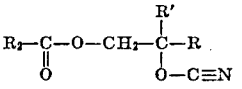
Alpha cyanate substituted ester



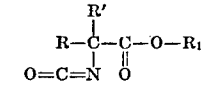
Beta cyanate substituted esters



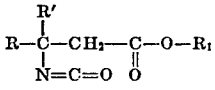
or



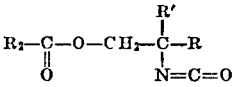
Alpha isocyanate substituted ester



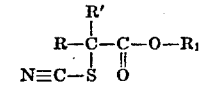
Beta isocyanate substituted esters



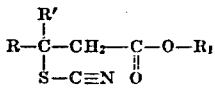
or



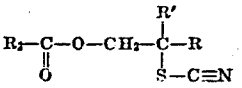
Alpha thiocyanate substituted ester



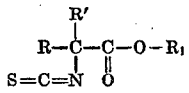
Beta thiocyanate substituted esters



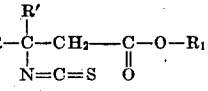
or



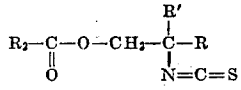
Alpha isothiocyanate substituted ester



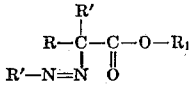
Beta isothiocyanate substituted esters



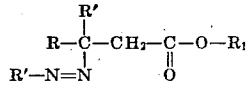
or



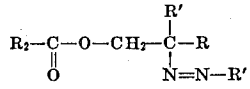
Alpha azo substituted ester



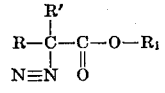
Beta azo substituted esters



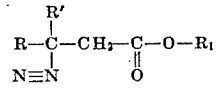
or



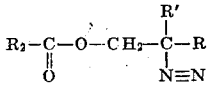
Alpha diazo substituted ester



Beta diazo substituted esters



or



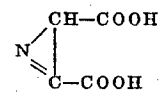
In each of the above type formulae, R and R' may be hydrogen, alkyl, aryl, alkaryl, aralkyl or cyclic non-benzenoid radicals. R_1 may be an alkyl, aralkyl or cyclic non-benzenoid radical, and R_2 may be an alkyl, aryl, alkaryl, aralkyl or cyclic non-benzenoid radical. The invention also includes the sulfur analogues of each of the above esters, that is, either mono or dithio esters corresponding to each of the above.

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, octyl, 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 cyclo heptyl.

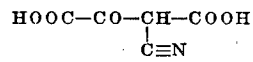
Examples of alpha nitrile substituted esters are: esters of nitrilo malonic acid—

$$N{\equiv}C{-}CH_2{-}COOH$$

such as the hexyl, heptyl, octyl, nonyl, decyl, lauryl, tetradecyl and cetyl esters of this acid; diesters of nitrilo succinic acid—

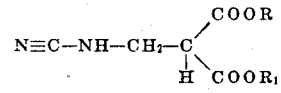


such as the dipropyl, dibutyl, diamyl, dihexyl, diheptyl, dioctyl, dinonyl, didecyl, dilauryl, ditetradecyl and dicetyl esters of this acid; diesters of α cyano α' oxo succinic acid—



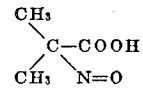
such as the diethyl, dipropyl, dibutyl, diamyl, dihexyl, diheptyl, dioctyl, dinonyl, didecyl, dilauryl, ditetradecyl and dicetyl esters of this acid.

Examples of beta nitrile esters are: beta cyanamido isosuccinic,



where R and R_1 are, for example, butyl, amyl, hexyl, heptyl, octyl, nonyl, decyl, lauryl, tetradecyl and cetyl.

Examples of suitable nitroso substituted esters are: methyl, ethyl, propyl, butyl, amyl, hexyl, heptyl, octyl, nonyl, decyl, lauryl, tetradecyl and cetyl esters of nitroso isobutyric acid,



as well as the butyl, amyl, hexyl, heptyl, octyl, nonyl, decyl, lauryl, tetradecyl and cetyl esters of isonitroso acetic acid,

$$HO{-}N{=}CH{-}COOH$$

Examples of alpha and beta nitro substituted esters are: alpha nitro-propionic esters,

$$CH_3{-}CH{-}(NO_2){-}COOR$$

alpha nitro-butyric esters,

$$C_2H_5{-}CH{-}(NO_2){-}COOR$$

alpha nitro-isobutyric esters,

$$(CH_3)_2C{-}(NO_2){-}COOR$$

where R may be ethyl, propyl, butyl, amyl, hexyl, heptyl, octyl, nonyl, decyl, lauryl, tetradecyl and cetyl; beta nitro-propionic esters,

$$NO_2{-}CH_2{-}CH_2{-}COOR$$

beta nitro-isovaleric esters,

$$(CH_3)_2C{-}(NO_2){-}CH_2{-}COOR$$

where R is selected from the group of alcoholic radicals above listed.

Examples of other types of compounds disclosed herein will be apparent to those skilled in the art. It should be observed that in some instances, for example in the case of azo and diazo substituted esters, the substituents are reactive and appear to combine with constituents in the oil to yield a modified compound of unknown constitution.

The substituted esters of this invention may be prepared by methods known in the art. Established methods of preparing substituted esters involve esterification of the substituted acids, esterification of the substituted alcohols, or introducing the substituent into the ester by suitable known types of reactions. For example, ethyl cyano acetate may be prepared by heating ethyl chloro acetate and potassium cyanide in methyl

alcohol under a reflux condenser and filtering off the potassium chloride. Likewise, the isocyanate ester, $O{=}C{=}N{-}CH_2{-}COOC_2H_5$, may be prepared by passing $COCl_2$ in large excess through a suspension of the hydrochloride of ethyl amino acetate in boiling toluene. Each of the above reaction products may be fractionated to obtain the ester. The former ester boils at 208 to 208.5° C., and the latter boils at 115 to 120° C. at 15 mm.

It is preferred that the substituted esters be of the non-polymerizable type since polymerized esters having molecular weights over 800 increase the viscosity of the oil, which is not desired in many instances.

It will be understood from the foregoing discussion that the invention embraces the addition of both a metal salt of an organic acid and a substituted ester of the type disclosed 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 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 substituted esters possess advantageous properties. The same is true of combinations of any one or more of the metal salts of the phenols or of the metal salts of the aryl substituted or polycarboxylic acids with any one or more of the aforesaid substituted esters.

The combinations disclosed herein cooperate to give new results in hydrocarbon lubricating oils. In general, the alpha or beta substituted esters disclosed herein reduce the corrosive effects of hydrocarbon lubricating oils on bearing metals, such as copper-lead or cadmium-silver alloys. Such 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 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 or beta 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 the substituted 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. 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 compounded 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, said ester having a substituent comprising nitrogen with at least two bonds connected to a single atom, said substituent being directly attached to an alkyl carbon atom and no more than two carbon atoms removed from a carbonyl group of the ester.

2. A compounded 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 of a carboxylic acid, said ester having a substituent comprising nitrogen with at least two bonds connected to a single atom, said nitrogen atom being no more than two carbon atoms removed from a carbonyl group of said ester, and said substituent being directly attached to an alkyl carbon atom of said ester.

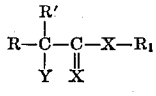
3. A compounded hydrocarbon oil containing a metal salt of an organic acid in an amount sufficient substantially to increase the corrosivity of said oil, and a corrosion inhibitor comprising an ester of a carboxylic acid, said ester having a nitrile group attached to an alkyl carbon atom and no more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

4. A compounded 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 of a carboxylic acid, said ester having a cyanate group 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 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 of a carboxylic acid, said ester having a thiocyanate group attached to an alkyl carbon atom and no more than two carbon atoms removed from a carbonyl group of said ester.

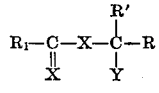
6. A compounded lubricant comprising a hydrocarbon oil containing from approximately 0.1% to 5% of a metal salt of an organic acid and from approximately 0.1% to 10% of a corrosion inhibitor comprising an ester of a carboxylic acid, said ester having no more than two carbon atoms removed from a carbonyl group thereof a substituent comprising nitrogen with at least two bonds connected to a single atom, said substituent being attached to an alkyl carbon atom.

7. 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 of the type formula:



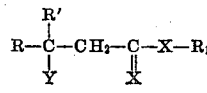
in which R and R' are selected from the group consisting of hydrogen and radicals of hydrocarbon structure; R_1 is a radical of hydrocarbon structure; X is selected from the group consisting of oxygen and sulfur; and Y is a substituent comprising nitrogen with at least two bonds connected to a single atom.

8. 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 of the type formula:



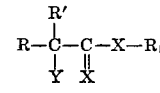
in which R and R' are selected from the group consisting of hydrogen and radicals of hydrocarbon structure; R_1 is a radical of hydrocarbon structure; X is selected from the group consisting of oxygen and sulfur; and Y is a substituent comprising nitrogen with at least two bonds connected to a single atom.

9. 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 of the type formula:



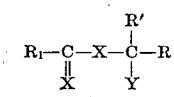
in which R and R' are selected from the group consisting of hydrogen and radicals of hydrocarbon structure; R_1 is a radical of hydrocarbon structure; X is selected from the group consisting of oxygen and sulfur; and Y is a substituent comprising nitrogen with at least two bonds connected to a single atom.

10. A compounded lubricant comprising a hydrocarbon oil containing an ester of the type formula:



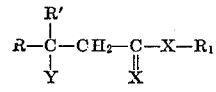
in which R and R' are selected from the group consisting of hydrogen and radicals of hydrocarbon structure; R_1 is a radical of hydrocarbon structure; X is selected from the group consisting of oxygen and sulfur; and Y is a substituent comprising nitrogen with at least two bonds connected to a single atom.

11. A compounded lubricant comprising a hydrocarbon oil containing an ester of the type formula:



in which R and R' are selected from the group consisting of hydrogen and radicals of hydrocarbon structure; R_1 is a radical of hydrocarbon structure; X is selected from the group consisting of oxygen and sulfur; and Y is a substituent comprising nitrogen with at least two bonds connected to a single atom.

12. A compounded lubricant comprising a hydrocarbon oil containing an ester of the type formula:



in which R and R' are selected from the group consisting of hydrogen and radicals of hydrocarbon structure; R_1 is a radical of hydrocarbon structure; X is selected from the group consisting of oxygen and sulfur; and Y is a substituent comprising nitrogen with at least two bonds connected to a single atom.

13. 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 a carboxylic acid and from approximately 0.1% to 10% by weight based on the oil of an ester having a substituent comprising nitrogen with at least two bonds connected to a single atom, said substituent being directly 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 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 aliphatic carboxylic acid and from approximately 0.1% to 10% by weight based on the oil of an ester having a substituent comprising nitrogen with at least two bonds connected to a single atom, said substituent being directly attached to an alkyl carbon atom and 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 a carboxylic acid containing an aryl substituent and from approximately 0.1% to 10% by weight based on the oil of an ester having a substituent comprising nitrogen with at least two bonds connected to a single atom, said substituent being directly 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 a phenol containing an oil-solubilizing substituent and from approximately 0.1% to 10% by weight based on

the oil of an ester having a substituent comprising nitrogen with at least two bonds connected to a single atom, said substituent being directly attached to an alkyl carbon atom and no more than two carbon atoms removed from a carbonyl group of the ester.

17. A compounded lubricant comprising a hydrocarbon oil and from approximately 0.1% to 10% by weight based on the oil of an organic ester of a carboxylic acid, said ester having a thiocyanate group attached to an alkyl carbon atom and no more than two carbon atoms removed from a carbonyl group of said ester.

18. A compounded lubricant comprising a hydrocarbon oil and from approximately 0.1% to 10% by weight based on the oil of an organic ester of a carboxylic acid, said ester having a cyanate group attached to an alkyl carbon atom and no more than two carbon atoms removed from a carbonyl group of said ester.

19. A compounded lubricant comprising a hydrocarbon oil and from approximately 0.1% to 10% by weight based on the oil of an organic ester of a carboxylic acid, said ester having a nitrile group attached to an alkyl carbon atom and no more than two carbon atoms removed from a carbonyl group of said ester.

20. A compounded 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 of a carboxylic acid, said ester having a substituent represented by the group (OCN) attached to an alkyl carbon atom and no more than two carbon atoms removed from a carbonyl group of said ester.

21. A compounded 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 of a carboxylic acid, said ester having a substituent represented by the group (SCN) attached to an alkyl carbon atom and no more than two carbon atoms removed from a carbonyl group of said ester.

22. The compounded lubricant of claim 14, wherein said metal salt of an aliphatic carboxylic acid is a salt of a partial ester of an aliphatic polycarboxylic acid.

JAMES O. CLAYTON.
BRUCE B. FARRINGTON.