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COMPOUNDED OIL

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24 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 an amino group preferably no more than two carbon atoms removed from a carbonyl group of said ester.

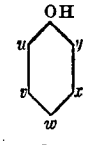
Additional objects and advantages of the invention will become apparent from the disclosure which follows.

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, 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 napthenate, cobalt naphthenate, cadmium naphthenate, tin naphthenate and manganese naphthenate. The naphthenic acid component of these salts may conveniently be obtained from petroleum.

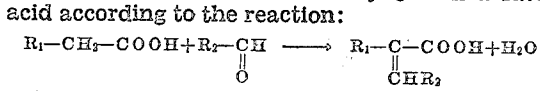
Metal phenates which may be mentioned comprise metal salts of a substituted phenol of the type formula:



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, naph-

thyl 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:

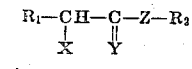


where R_1 is an alkyl and R_2 an aryl radical. Aluminum, zinc, tin, magnesium, calcium and chromium as well as other polyvalent metal salts of each of the above acids may be utilized.

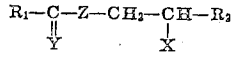
The invention also includes salts of polycarboxylic acids together with amino esters in hydrocarbon oils. Examples of such salts are the aluminum, zinc, tin, magnesium, calcium and chromium as well as other polyvalent metal salts of partially esterified acids of the oxalic acid series, including oxalic 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 an amino group preferably no more than two carbon atoms removed from a carbonyl group of the esters. These types of compounds may be represented generically by the following structural formulae:

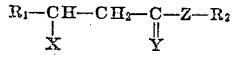
Alpha amino ester



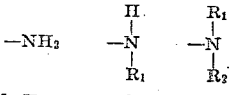
Beta amino esters



or



In these formulae R_1 and R_2 represent an alkyl, aryl, alkaryl, aralkyl or cyclic non-benzenoid group. R_1 and R_2 may contain substituents other than the amino group, which substituents may be of either the same or a different type. "X" represents an amino group which may be any one of the following:



where R_1 and R_2 may be alkyl, aryl, alkaryl, aralkyl or cyclic non-benzenoid hydrocarbon radicals; and "Y" and "Z" may be either oxygen or sulfur.

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 amino esters are esters of glycine, alanine, amino-malonic acid, aspartic acid and dimethylamino-acetic acid, such as the following: ethyl glycocollate, amyl glycocollate, octyl glycocollate, decyl glycocollate, lauryl glycocollate, tetradecyl glycocollate, cetyl glycocollate; octyl alpha amino-propionate, decyl alpha amino-propionate, lauryl alpha amino-propionate, tetradecyl alpha amino-propionate, cetyl alpha amino-propionate; diethyl amino-malonate, dioctyl amino-malonate, didecyl amino-malonate, dilauryl amino-malonate, ditetradecyl amino-malonate, dicetyl amino-malonate; diethyl aspartate, dioctyl aspartate, didecyl aspartate, dilauryl aspartate, dietetradecyl aspartate, dicetyl aspartate; octyl dimethylamino-acetic acid, decyl dimethylamino-acetic acid, lauryl dimethylamino-acetic acid tetradecyl dimethylamino-acetic acid, and cetyl dimethylamino-acetic acid.

Examples of beta amino esters comprise esters of beta alanine, beta dimethylamino-propionic acid, beta amino butyric acid, and beta amino isovaleric acid, such as the following: beta amino propionic octyl ester, beta amino propionic decyl ester, beta amino propionic lauryl ester, beta amino propionic tetradecyl ester, beta amino propionic cetyl ester; beta dimethylamino-propionic octyl ester, beta dimethylamino-propionic decyl ester, beta dimethylamino-propionic lauryl ester, beta dimethylamino-propionic tetradecyl ester, beta dimethylamino-propionic cetyl ester; beta amino butyric octyl ester, beta amino butyric decyl ester, beta amino butyric lauryl ester, beta amino butyric tetradecyl ester, beta amino butyric cetyl ester; beta amino isovaleric octyl ester, beta amino isovaleric decyl ester, beta amino isovaleric lauryl ester, beta amino isovaleric tetradecyl ester, and beta amino isovaleric cetyl ester.

The amino esters of this invention may be prepared by methods known in the art. The esters may be produced by esterification of the alpha or beta amino acids, by esterification of alpha or beta amino alcohols, or by introducing an amino group into an ester in an alpha or beta position. For example, either ethyl or amyl amino acetate may be prepared by passing dry HCl gas through a suspension of glycine hydrochloride in the corresponding alcohol, crystallizing the hydrochloride of the ester from the alcohol, decomposing the hydrochloride in a cold solution of sodium hydroxide and extracting the reaction product several times with ether. The ether solution is then agitated for several hours with potassium carbonate and then with calcium oxide, after which the ether is evaporated off and the residue fractionated. Other amino esters, including diethyl aspartate and diethyl amino-malonate may be prepared by similar methods.

It is preferred that the amino 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 an amino 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 amino 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 amino 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 amino 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 the aryl substituted or polycarboxylic acids with any one or more of the amino esters.

The combinations disclosed herein cooperate to give new results in hydrocarbon lubricating oils. In general, the alpha or beta amino esters reduce the corrosive effects of hydrocarbon lubricating oils on modern 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 amino esters apparently cooperate to enhance the stability of the oil against discoloration, gum formation, piston ring sticking and the like.

Examples of specific combinations and proportions in lubricating oils are as follows: 1% of aluminum oleate with 1% of amyl glycocollate in an S. A. E. 30 acid refined naphthenic base lubricating oil; 1% of aluminum naphthenate with 1% of amyl glycocollate in the same type oil; 0.5% of calcium cetyl phenate with 0.25% amyl glycocollate in the same type oil; 1% of calcium lauryl phenate with 0.25% amyl glycocollate; 1% of calcium phenyl stearate with 0.25% amyl glycocollate; and 1% of a calcium salt of alpha benzal stearic acid with 1% amyl glycocollate—all in the same type oil.

The proportions of addition agents utilized will depend upon the particular compounds 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 amino 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 amino 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 amino 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 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 in imparting other properties to the oil, e. g., reducing wear and 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 liquid 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 containing an amino substituent.

2. A liquid 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 selected from the group consisting of alpha and beta amino substituted esters.

3. A liquid compounded hydrocarbon oil containing a metal salt of a higher aliphatic acid in an amount sufficient substantially to increase the corrosivity of said oil, and a corrosion inhibitor comprising an ester containing an amino substituent.

4. A liquid compounded hydrocarbon oil containing a metal salt of a higher aliphatic acid in an amount sufficient substantially to increase the corrosivity of said oil, and a corrosion inhibitor comprising an ester selected from the group consisting of alpha and beta amino substituted esters.

5. A compounded hydrocarbon oil containing a metal salt of a carboxylic acid having an aryl substituent in an amount sufficient substantially to increase the corrosivity of said oil, and a corrosion inhibitor comprising an ester containing an amino substituent.

6. A compounded hydrocarbon oil containing a metal salt of a carboxylic acid having an aryl substituent in an amount sufficient substantially to increase the corrosivity of said oil, and a corrosion inhibitor comprising an ester selected from the group consisting of alpha and beta amino substituted esters.

7. A compounded hydrocarbon oil containing a metal salt of a high molecular weight phenol in an amount sufficient substantially to increase the corrosivity of said oil, and a corrosion inhibitor comprising an ester containing an amino substituent.

8. A compounded hydrocarbon oil containing a metal salt of a high molecular weight phenol in an amount sufficient substantially to increase the corrosivity of said oil, and a corrosion inhibitor comprising an ester selected from the group consisting of alpha and beta amino substituted esters.

9. A liquid compounded hydrocarbon oil containing a small amount of a metal salt of an organic acid in an amount sufficient substantially

to increase the corrosivity of said oil, and from approximately 0.1% to 10% of an ester containing an amino substituent.

10. A liquid compounded hydrocarbon oil containing a small amount of a metal salt of an organic acid in an amount sufficient substantially to increase the corrosivity of said oil, and from approximately 0.1% to 10% of an ester selected from the group consisting of alpha and beta amino substituted esters.

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 containing an amino substituent.

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 selected from the group consisting of alpha and beta amino substituted esters.

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 containing an amino substituent.

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 cadimum-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 selected from the group consisting of alpha and beta amino substituted esters.

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 a higher aliphatic 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 containing an amino substituent.

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 a higher aliphatic 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 selected from the group consisting of alpha and beta amino substituted esters.

17. 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 a carboxylic acid having an aryl substituent 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 containing an amino substituent.

18. 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 a carboxylic acid having an aryl substituent 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 selected from the group consisting of alpha and beta amino substituted esters.

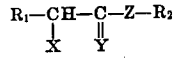
19. In a method of lubricating bearing surfaces which comprises maintaining between the bearing surfaces, one of which is a bearing metal of the type represented by cadmium-silver and copper-lead alloys, a film of a compounded lubricating oil containing a metal salt of a high molecular weight phenol 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 containing an amino substituent.

20. 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 a high molecular weight phenol 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 selected from the group consisting of alpha and beta amino substituted esters.

21. A liquid 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 an amino substituent near a carbonyl group thereof.

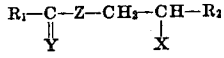
22. A compounded lubricant comprising a hydrocarbon oil containing from approximately 0.1% to 5% of a metal salt of an organic acid and from approximately 0.1% to 10% of a cor-

rosion inhibitor comprising an ester of the type formula:



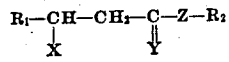
in which R_1 and R_2 are radicals of hydrocarbon structure; Y and Z are selected from the group consisting of oxygen and sulfur; and X represents an amino group.

23. 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_1 and R_2 are radicals of hydrocarbon structure; Y and Z are selected from the group consisting of oxygen and sulfur; and X represents an amino group.

24. 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_1 and R_2 are radicals of hydrocarbon structure; Y and Z are selected from the group consisting of oxygen and sulfur; and X represents an amino group.

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