

UNITED STATES PATENT OFFICE

2,369,908

MINERAL OIL COMPOSITION

Rush F. McCleary, Beacon, N. Y., assignor to The Texas Company, New York, N. Y., a corporation of Delaware

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12 Claims. (Cl. 252-46)

This invention relates to an improved lubricating oil adapted for use in internal combustion engines and particularly to lubricating oil having a combination of additive ingredients incorporated therein.

It is generally recognized that in the recent development of internal combustion engines, and particularly engines designed for heavy duty service, the increase in operating temperatures and engine speeds, together with the reduction of clearances and the use of hard bearing alloys such as copper-lead, cadmium-silver, etc., has set up such severe operating conditions as to necessitate improvement in the highly refined mineral oils refined for use as lubricants. These rigorous operating conditions which are most prevalent in Diesel and gasoline engines used in heavy duty bus and tractor service where the piston temperatures range from approximately 425° F. to 650° F. and pressures from the oxidizing combustion gases are as high as 750 to 1150 pounds per square inch, have seriously accentuated such problems of corrosion, oxidation and varnish and lacquer formation in the refined mineral lubricating oils with the resultant deleterious effect on the efficiency of the engines. The nature and extent of these problems depend upon the conditions of operation of the particular engine type and upon the type and extent of refining of the base oil used, and numerous other factors.

The tendency of mineral lubricating oils to deposit carbonaceous materials which are commonly referred to as varnish and lacquer deposits about the valves, rings, pistons, cylinders and other engine parts, can be largely overcome by the addition of certain types of additive ingredients which possess detergent qualities when dissolved or dispersed in lubricating oils. By detergent properties is meant not only that property which aids in dispersing, removing or purging foreign materials which accumulate on the surface of the engine parts, but also that property which prevents the accumulation or deposition of such materials, as distinguished from solvent action upon the accumulations or deposits.

In addition thereto, the tendency of these oils to become oxidized and to corrode the metal surfaces with which the lubricating oil comes in contact may be overcome or reduced by the addition of additive components which possess anti-oxidant and/or anti-corrosive properties when dissolved or dispersed in mineral lubricating oils. These anti-oxidant or anti-corrosive properties are meant to include all such properties which effect a reduction of the oxidation products in

the body of the oil and effect a reduction or elimination of weight loss of the lubricated surfaces, particularly bearing surfaces.

It is the object of the present invention to provide a mineral oil composition possessing combined detergent, anti-oxidant and anti-corrosive properties by incorporating in a mineral lubricating oil an additive ingredient possessing predominant detergent properties with an additive ingredient possessing predominant anti-oxidant and anti-corrosive properties.

According to the present invention, a class of compounds has been found which when incorporated in a mineral lubricating oil possess exceptional detergent properties.

These compounds may be broadly described as oil-soluble alicycloxy aliphatic alcohols, ether alcohols and their corresponding metal alcoholates. These compounds possess an alicyclic or cycloaliphatic nucleus bound to an aliphatic alcohol radical through an ether linkage. The aliphatic alcohol radical may be subdivided by ether linkages into similar or dissimilar aliphatic radicals and the alcohol radical may be retained as such or in the form of its corresponding metal alcoholates.

When describing the compounds of the present invention throughout the specification and claims, it is to be understood that when reference is made to an ether linkage or an alcohol or an alcoholate radical, the corresponding thio ethers, thio alcohols and thio alcoholates are meant to be included. This class of compounds may be illustrated by the following structural formula



in which C is a cycloaliphatic nucleus; R may be a hydrogen, alkyl, aryl, aralkyl, cycloalkyl or naphthenyl radical together with substituted derivatives thereof; R₁ is an aliphatic radical which may contain oxygen or sulfur substituents or both in the form of ether and thio ether linkages together with further substituents in the form of halogen, oxygen, sulfur, or nitrogen derivatives; X may be either oxygen or sulfur; Y may be an hydroxyl radical (OH), a sulfhydryl radical (SH) or metal salts thereof; and y and z are integers of one or more. The cycloaliphatic nucleus designated by C in the formula includes cycloaliphatic radicals containing one or more cyclic nuclei together with hydrogenated aromatic radicals possessing varying degrees of hydrogenation. The monocyclic nuclei may be derived from such cycloaliphatic compounds as cyclopentane, cyclohexane, cycloheptane, cyclooctane etc.

In illustrating the methods of preparing the afore-mentioned class of compounds and the resultant effect of these compounds when incorporated in a mineral lubricating oil, one compound—namely, calcium diamyl cyclohexoxy ethylate—is presented as being representative of the general class of additives. It is to be understood that the method of preparing these compounds, which is illustrated in the subsequent example, is merely one of the numerous classical methods of synthesis which may be used.

EXAMPLE I

A mixture of 450 grams of 2-4 diamyl cyclohexanol, 45 grams of sodium, 1000 cc. benzene and 50 cc. alcohol, were stirred together until the sodium was dissolved. To the resulting solution, 175 grams of ethylene chlorohydrin was added during a period of two hours. During this addition, the temperature was maintained at 35 to 50° C. after which the reaction mass was heated to 75-80° C. for approximately two hours. The resulting salt was filtered out and the solvent and excess ethylene chlorohydrin were removed by distillation in vacuo. The residual oily liquid which consisted of diamyl cyclohexoxy ethanol weighed 440 grams and had a hydroxyl number of 189.

EXAMPLE II

Four hundred grams of diamyl cyclohexoxy ethanol prepared in accordance with Example I was added to a solution of 400 grams of calcium dissolved in 1000 cc. of liquid ammonia with substantial agitation. Two liters of toluene were added and the ammonia evaporated off. The toluene solution of calcium diamyl cyclohexoxy ethylate was warmed and filtered. The toluene was removed by distillation in vacuo and the calcium salt dissolved in an equal weight of lubricating oil to give a 50% concentrate.

It is to be understood that in place of the diamyl cyclohexanol used in Example I, other substituted or unsubstituted cycloaliphatic compounds may be used and that in place of the alcohol, other aliphatic alcohols or mercaptans may be used. Further, the calcium of Example II may be substituted by any of the other metals, previously mentioned.

In accordance with the object of the present invention, a mineral oil composition possessing combined detergent, anti-oxidant, and anti-corrosive properties is obtained by combining the foregoing detergent additive component with an oil-soluble additive component possessing anti-oxidant and anti-corrosive properties.

It has been found in preparing a finished lubricant that it is usually necessary to provide a mineral oil composition possessing both detergent and anti-corrosive properties. The relative amounts of these component factors which are necessary in a lubricant depend upon the particular service and operating conditions involved. The anti-oxidant and/or anti-corrosive component of the finished lubricant must necessarily be compatible with the detergent component to produce an additive effect in the resulting mineral oil composition. Among the particular types of anti-corrosives and anti-oxidant components which may be combined with the foregoing detergent component in accordance with the invention are the organic esters of phosphorus acids, sulfurized esters of fatty acids, sulfurized fatty oils, sulfurized wax compounds, sulfurized terpenes, sulfurized resins, aromatic amino compounds, aromatic

sulfur compounds such as aromatic sulfides and aromatic thio ethers, etc. As specific examples of these anti-corrosive compounds may be mentioned tri (dimethylaminomethyl) phenol, amylthiomethyl octyl phenol, di (amylthiomethyl) phenol, polymerphenol disulfide, sulfurized wax, sulfurized ethyl oleate, sulfurized terpinolene, sulfurized sperm oil and cresyl thiophosphite.

As previously mentioned, the range of proportions of the individual additive components when used in combination vary with the particular service and operating conditions involved. It is therefore desirable to set forth the limits and preferred ranges of these components in four of the more common uses.

	Detergent		Anti-corrosive	
	Limits	Preferred range	Limits	Preferred range
Motor oils.....	0.1-1.5	0.1-0.5	0.1-3.5	0.1-2.0
Diesel oils and heavy duty motor oils.....	0.1-3.0	0.25-2.0	0.1-5.0	0.5-3.0
Airplane oils.....	0.1-2.0	0.25-1.0	0.1-5.0	0.5-2.0
Turbine oils.....	0.01-0.5	0.01-0.1	0.01-2.0	0.01-0.2

In order to illustrate the improving qualities of the aforementioned combinations in a mineral lubricating oil, the results of the following empirical test are presented. This test consists of a coarse structure copper-lead bearing specimen encased in a special non-wear bushing rotatably mounted on a stainless steel shaft and immersed in a glass pot of the oil to be tested. The tested oil was heated to a controlled temperature of either 250° F. or 350° F. and continuously circulated between the bearing specimen and the shaft for 10 hours. Throughout the test the oil was continuously agitated by means of copper baffles which acted as oxidation accelerators. The bearing specimen was weighed before the test and after the 10-hour period, and the loss of weight recorded in milligrams. The reference oil of this test was a mixed base solvent-refined dewaxed Mid-Continent lubricating oil of an S. A. E. 30 grade. To the reference oil was added varying proportions of the combination of additives of the present invention using calcium diamylcyclohexoxyethylate as the reference detergent component. The results of two runs at both 250° F. and 350° F. are presented:

BEARING CORROSION—COPPER-LEAD (TEN HOURS)

Loss of weight in mg.

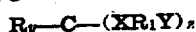
	250° F.	350° F.
Reference oil.....	5-8	240-261
Oil A (reference oil plus 0.5% calcium diamylcyclohexoxyethylate).....	2-8	273-267
Oil A plus 2.0% amylthiomethyl octylphenol.....	1-1	93-95
Oil A plus 1.0% tri(dimethylaminomethyl)phenol.....	0-0	19-6
Oil A plus 1.5% di(amylthiomethyl) phenol.....	0-0	70-35
Oil A plus 1.5% sulfurized wax.....	0-1	125-167
Oil A plus 2.0% sulfurized ethyl oleate.....	0-1	71-82
Oil A plus 1.5% sulfurized terpinolene.....	0-0	0-0
Oil A plus 3.0% sulfurized sperm oil.....	0-1	42-35
Oil A plus 1.5% cresyl thiophosphite.....	6-7	131-70
Oil A plus 1.5% benzyl diethyl dithiocarbamate.....	0-1	85-99
Oil A plus 1.5% polymerphenol disulfide.....	0-0	240-165

Obviously many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof and, therefore, only such limita-

tions should be imposed as are indicated in the appended claims.

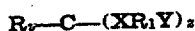
I claim:

1. A lubricant comprising a major proportion of a mineral lubricating oil and a minor proportion of a combination of an oil-soluble compound of the following general formula



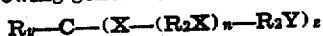
in which C is a cycloaliphatic radical, R is a radical from the group consisting of a hydrogen, alkyl, aryl, aralkyl, cycloalkyl and naphthenyl radicals, R₁ is an aliphatic radical, X is an element from the group consisting of oxygen and sulfur, Y is a radical selected from the group consisting of hydroxyl and sulfhydryl radicals and metal salts thereof, and y and z are integers of at least one; and an oil-soluble additive component possessing anti-oxidant and anti-corrosive properties.

2. A lubricant comprising a mineral lubricating oil having incorporated therein 0.1-3.0% by weight of an oil-soluble compound of the following general formula



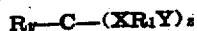
in which C is a cycloaliphatic radical, R is a radical from the group consisting of a hydrogen, alkyl, aryl, aralkyl, cycloalkyl and naphthenyl radicals, R₁ is an aliphatic radical, X is an element from the group consisting of oxygen and sulfur, Y is a radical selected from the group consisting of hydroxyl sulfhydryl radicals and metal salts thereof, and y and z are integers of at least one; and 0.1-5.0% by weight of an oil-soluble additive ingredient possessing anti-corrosive properties.

3. A lubricant comprising a major proportion of a mineral lubricating oil and a minor proportion of a combination of an oil-soluble compound of the following general formula



in which C is a cycloaliphatic radical, R is a radical selected from the group consisting of hydrogen, alkyl, aryl, aralkyl, cycloalkyl and naphthenyl radicals, R₂ is an aliphatic radical containing from 1 to 5 carbon atoms, X is an element selected from the group consisting of oxygen and sulfur, Y is a radical selected from the group consisting of hydroxyl and sulfhydryl radicals and metal salts thereof, y and z are integers of at least one, and n is a numeral selected from the group consisting of 0, 1, 2, 3, 4 and 5; and an oil-soluble additive component possessing anti-corrosive properties.

4. A lubricant comprising a major proportion of a mineral lubricating oil and a minor proportion of a combination of an oil-soluble compound of the following general formula:



in which C is a cycloaliphatic radical, R is a radical from the group consisting of hydrogen, alkyl, aryl, aralkyl, cycloalkyl and naphthenyl radicals, R₁ is an aliphatic radical, X is an element from the group consisting of oxygen and sulfur, Y is a radical selected from the group consisting of hydroxyl and sulfhydryl radicals and metal salts thereof, and y and z are integers of at least one; and an oil-soluble additive component, possessing anti-corrosive properties, selected from the group consisting of organic esters of sulfur-containing phosphorus acids, sulfurized fatty oils, sulfurized esters of fatty acids, sulfurized wax compounds, sulfurized terpenes, aromatic thio-

ethers, aromatic sulfides, and sulfur-containing carbamic acid derivatives.

5. A lubricant comprising a mineral lubricating oil and a minor proportion of the combination of an oil-soluble compound selected from the group consisting of alicycloxy aliphatic alcohols and their corresponding metal alcoholates, and an oil-soluble additive ingredient possessing anti-oxidant and anti-corrosive properties.

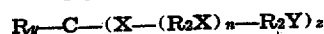
6. A lubricant comprising a major proportion of a mineral lubricating oil and a minor proportion of the combination of an oil-soluble compound selected from the group consisting of alicycloxy aliphatic alcohols and their corresponding metal alcoholates, and an oil-soluble sulfur-containing compound possessing anti-corrosive properties.

7. A lubricant comprising a mineral lubricating oil having incorporated therein 0.1-3.0% by weight of an oil-soluble compound selected from the group consisting of alicycloxy aliphatic alcohols and their corresponding metal alcoholates, and 0.01-5.0% by weight of an oil-soluble additive component possessing anti-oxidant and anti-corrosive properties.

8. A lubricant comprising a major proportion of a mineral lubricating oil, a minor proportion of the combination of an oil-soluble compound selected from the group consisting of alicycloxy aliphatic alcohols and their corresponding metal alcoholates, and an oil-soluble compound possessing anti-corrosive properties selected from the group consisting of organic esters of sulfur-containing phosphorus acids, sulfurized fatty oils, sulfurized esters of fatty acids, sulfurized wax compounds, sulfurized terpenes, aromatic thioethers, aromatic sulfides, and sulfur-containing carbamic acid derivatives.

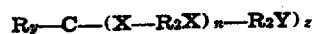
9. A lubricant comprising a mineral lubricating oil having incorporated therein a small amount of the combination of an oil-soluble metal alicycloxy aliphatic alcoholate, and an oil-soluble ingredient possessing anti-corrosive properties.

10. A lubricant comprising a major proportion of a mineral lubricating oil and a minor proportion of a combination of an oil-soluble compound of the following general formula:



in which C is a cycloaliphatic radical, R is a radical selected from the group consisting of hydrogen, alkyl, aryl, aralkyl, cycloalkyl and naphthenyl radicals, R₂ is an aliphatic radical containing from 1 to 5 carbon atoms, X is an element selected from the group consisting of oxygen and sulfur, Y is an alkaline earth metal oxide, y and z are integers of at least one, and n is a numeral selected from the group consisting of 0, 1, 2, 3, 4 and 5; and an oil-soluble sulfurized composition possessing anti-corrosive properties.

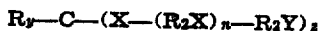
11. A lubricant comprising a major proportion of a mineral lubricating oil and a minor proportion of a combination of an oil-soluble compound of the following general formula:



in which C is a cycloaliphatic radical, R is a radical selected from the group consisting of hydrogen, alkyl, aryl, aralkyl, cycloalkyl and naphthenyl radicals, R₂ is an aliphatic radical containing from 1 to 5 carbon atoms, X is an element selected from the group consisting of oxygen and sulfur, Y is an alkaline earth metal ox-

ide, y and z are integers of at least one, and n is a numeral selected from the group consisting of 0, 1, 2, 3, 4 and 5; and an oil-soluble sulfur-containing carbamic acid derivative possessing anti-corrosive properties.

12. A lubricant comprising a major proportion of a mineral lubricating oil and a minor proportion of a combination of an oil-soluble compound of the following general formula:



in which C is a cycloaliphatic radical, R is a rad-

ical selected from the group consisting of hydrogen, alkyl, aryl, aralkyl, cycloalkyl and naphthyl radicals, R_2 is an aliphatic radical containing from 1 to 5 carbon atoms, X is an element selected from the group consisting of oxygen and sulfur, Y is an alkaline earth metal oxide, y and z are integers of at least one, and n is a numeral selected from the group consisting of 0, 1, 2, 3, 4 and 5; and an oil-soluble organic ester of sulfur-containing phosphorus acids possessing anti-corrosive properties.

RUSH F. McCLEARY.

CERTIFICATE OF CORRECTION.

Patent No. 2,369,908.

RUSH F. McCLEARY.

February 20, 1945.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, second column, line 17-18, strike out the comma and words ", ether alcohols"; page 3, second column, line 28, for "qalities" read --qualities--; page 4, first column, line 32, claim 2, after "hydroxyl" insert --and--; 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 5th day of June, A. D. 1945.

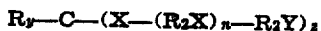
Leslie Frazer

(Seal)

Acting Commissioner of Patents.

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