

UNITED STATES PATENT OFFICE

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MINERAL OIL COMPOSITION

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17 Claims. (Cl. 252—53)

This invention relates to an improved lubricating oil adapted for use in internal combustion engines and particularly to lubricating oil having one or more additive ingredient 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.

It is the object of the present invention to provide a mineral oil composition which pos-

sesses the above mentioned detergent properties.

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

These compounds may be broadly described as oil-soluble cycloaliphatic - aliphatic ether - alcohols and their corresponding metal alcoholates. These compounds possess a 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. together with their substituted derivatives. The polycyclic nuclei may be derived from such compounds as bicyclo-hexane, bicyclooctane, decahydronaphthalene and the compounds obtained from petroleum oil, usually re-

range of 0.1 and 5.0 per cent by weight depending upon the particular base oil used and the type of engine and service involved. However, the range of proportions between 0.25 and 2.0 per cent by weight has been found to be particularly effective in imparting excellent detergent properties to the mineral lubricating oil.

In illustrating the methods of preparing the aforementioned 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

400 grams of diamyl cyclohexoxy ethanol prepared in accordance with Example I was added to a solution of 40.0 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.

As a test to indicate the effectiveness of the compounded oils proposed by the present invention under actual operating conditions, a special test was devised which is a modification of the test described in Diesel Lubricant Test Manual, Laboratory Test No. 1, issued by the Caterpillar Tractor Company. This test was carried out in a single cylinder Diesel engine operating at 900 R. P. M. with a water jacket temperature of 175° F. and run continuously for periods of 120 and 240 hours or until rings are stuck as indicated by the increase in blow-by. The crankcase oil was drained every sixty hours and fresh oil added thereto. At the end of each test period, the engine was thoroughly examined and any carbonaceous deposits, lacquer and sludge formation, etc. were noted and the principal engine parts classified according to their condition. In the present instance the reference oil was a mixed base sol-

vent-refined, dewaxed Mid-Continent lubricating oil of an SAE 30 grade. The results of the test runs on the reference oil and the reference oil containing 0.5% calcium diamyl cyclohexoxy ethylate are as follows:

Reference oil

Engine part	120 hours	240 hours
Piston crown.....	Normal.....	Normal.....
Scuffing above heat groove.....	B.....	B.....
Heat groove.....	B.....	B.....
Ring grooves.....	A.....	B.....
Piston skirt.....	C.....	C.....
Under piston deposit.....	B.....	B.....
Filter.....	A.....	B.....
Ring lands.....	A.....	B.....
Rings stuck.....	None.....	One.....
Ring cleanliness.....	#1, 2 clean; 3, 4 lacquer; #5, 6 slight sludge.	#1, 2, 3, clean; #4, 5, 6 black lacquer.
Bearing weight loss (grams).....		0.027.

Reference oil plus 0.5% calcium diamyl cyclohexoxyethylate

Engine part	120 hours	240 hours
Piston crown.....	Normal.....	Normal.....
Scuffing above heat groove.....	B.....	C.....
Heat grooves.....	B.....	B.....
Ring grooves.....	A.....	A.....
Piston skirt.....	A.....	A.....
Under piston deposit.....	A.....	A.....
Filter.....	A.....	A.....
Ring lands.....	A.....	A.....
Rings stuck.....	None.....	None.....
Ring cleanliness.....	All clean.....	All clean.....
Copper-lead bearing weight loss, grams.....		0.017.

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Engine part	Rating	Condition noted
Scuffing above heat groove.....	A B C D	No scuffing to very fine scuffing. Up to 50% scuffed. Up to 75% scuffed. Over 75% scuffed.
Heat groove.....	A B C D	Open to 10% plugged. Up to 50% plugged. Up to 75% plugged. Over 75% plugged.
Ring groove.....	A B C	Clean to heavy lacquer. Slight carbon in No. 1 and 2 grooves. Heavier deposits.
Piston skirt.....	A B C D	Clean to very slight trace of varnish. Trace varnish to light varnish. Heavy varnish to lacquer. Very heavy varnish.
Under piston deposit.....	A B C	Clean to discoloration. Trace deposit. Heavy deposit.
Filter.....	A B C	Clean to mesh pattern visible. Mesh pattern visible to slight amount mud sludge. Heavy mud or carbonaceous deposit.
Ring land.....	A B	Clean to heavy varnish. Heavy varnish to carbon deposit.

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

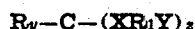
I claim:

1. A lubricant consisting essentially of a mineral lubricating oil and having incorporated therein a small proportion, sufficient to impart antioxidant properties to said lubricating oil, of an oil-soluble compound selected from the group consisting of cycloaliphatic-aliphatic ether-alcohols and their corresponding metal alcoholates.

2. A lubricant as claimed in claim 1 in which the cycloaliphatic constituent contains a cyclohexyl radical.

3. A lubricant comprising a major proportion of a mineral lubricating oil and 0.1 to 5% by

weight of an oil-soluble compound of the following general formula

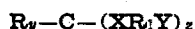


in which C is a cycloaliphatic radical, R is a radical from the group consisting of a hydrogen, alkyl, aryl, aralkyl, cycloalkyl and naphthenyl radicals, R_1 is an aliphatic radical, X is an element from the group consisting of oxygen and sulfur, Y is a radical selected from the group consisting of hydroxyl and sulfhydryl radicals and metal salts thereof, and y and z are integers of at least one.

4. An improved lubricant as claimed in claim 3 in which Y is a metal oxide.

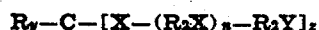
5. A lubricant consisting essentially of a mineral lubricating oil and having incorporated therein 0.1 to 5.0% by weight of an oil-soluble alkylated cyclohexyl-aliphatic ether-alcoholate.

6. An improved lubricant comprising a mineral lubricating oil containing 0.1 to 5.0 per cent 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, R_1 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.

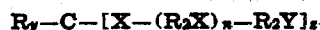
7. An improved lubricating oil adapted for use in internal combustion engines comprising a mineral lubricating oil having incorporated therein 0.1 to 5.0% by weight of a compound of the following general formula



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, 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 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.

8. An improved lubricating oil as claimed in claim 7 in which Y is a metal oxide.

9. An improved lubricant comprising a mineral lubricating oil containing 0.25 to 2.0 per cent by weight of a compound of the following general formula

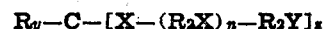


in which C is a cycloaliphatic radical, R is a radical selected from the group consisting of hydrogen, alkyl, aryl, aralkyl, cycloalkyl, and naphthenyl radicals, R_2 is an aliphatic radical containing from 1 to 5 carbon atoms, X is an element selected from the group consisting of oxygen and sulfur, Y is 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.

10. A mineral oil composition comprising a mineral lubricating oil containing 0.1 to 5.0% by weight of an oil-soluble alkaline earth metal salt of a cycloaliphatic-aliphatic ether-alcohol.

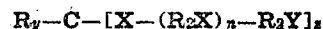
11. An improved lubricant comprising a min-

eral lubricating oil containing 0.1 to 5.0% by weight of an oil-soluble compound of the following general formula:



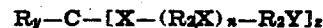
in which C is a cycloaliphatic radical, R is an alkyl radical, R_2 is a hydrocarbon radical containing up to 5 carbon atoms, X is an element selected from the group consisting of oxygen and sulfur, Y is a radical selected from the group consisting of hydroxyl and sulfhydryl radicals and metal salts thereof, 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.

12. An improved lubricant comprising a mineral lubricating oil containing 0.1 to 5.0% by weight of an oil-soluble compound of the following general formula:



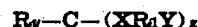
in which C is a cyclohexyl radical, R is an alkyl radical, R_2 is an aliphatic radical containing two carbon atoms, X is oxygen, Y is an alkaline earth metal oxide, y is an integer of at least one, z is one, and n is 0.

13. An improved lubricating oil comprising a mineral lubricating oil containing 0.1 to 5.0% by weight of a 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, R_2 is an aliphatic radical containing two 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 0.

14. A lubricant comprising a major proportion of a mineral lubricating oil and 0.1 to 5.0% 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, R_1 is an aliphatic radical, X is an element from the group consisting of oxygen and sulfur, Y is a metal sulfide radical, and y and z are integers of at least one.

15. An improved lubricating oil adapted for use in internal combustion engines comprising a mineral lubricating oil having incorporated therein 0.1 to 5.0% by weight of a compound of the following general formula

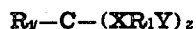


in which C is a cycloaliphatic radical, R is a radical selected from the group consisting of hydrogen, alkyl, aryl, aralkyl, cycloalkyl, and naphthenyl radicals, R_2 is an aliphatic radical containing from 1 to 5 carbon atoms, X is an element selected from the group consisting of oxygen and sulfur, Y is a metal sulfide radical, 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.

16. A lubricant comprising a mineral lubricating oil having incorporated therein an amount, less than 5% by weight, but sufficient to impart anti-oxidant properties to said oil, of an oil-sol-

able compound selected from the group consisting of cycloaliphatic-aliphatic ether-alcohols and their corresponding metal alcoholates.

17. A lubricant comprising a mineral lubricating oil having incorporated therein a small amount, less than 5% by weight, but sufficient to impart anti-oxidant properties to said oil, 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 the metal salts thereof, and y and z are integers of at least one.

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