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LUBRICATING OIL

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22 Claims. (Cl. 252—48)

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

It is generally conceded that in the recent development of internal combustion engines, and particularly engines designed for heavy duty service, the increase in operating temperatures, together with the reduction of clearances and the use of hard bearing alloys, such as copper-lead, cadmium silver, etc., have set up such severe operating conditions as to necessitate an improvement in the highly solvent-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 ring temperatures range from approximately 425 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 as corrosion, oxidation and resin formation in the solvent-refined mineral lubricating oils with the resultant deleterious effect on the efficiency of the engines. The nature and extent of these problems depends upon the conditions of operation of the particular engine type, the type and extent of refining of the base oil used, and numerous other factors.

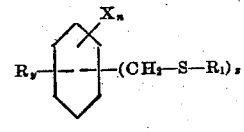
The tendency of mineral lubricating oils to deposit gums, resins, soot, and varnish-like materials about the valves, rings, pistons, cylinders and other engine parts can be largely overcome by the addition of certain types of additive ingredients which possess detergent qualities when dissolved or dispersed in lubricating oils. By detergent property 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 those accumulations or deposits.

In addition thereto, the added tendency of these oils 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 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 or elimination of weight loss of the lubricating surfaces, particularly bearing surfaces, which result from the corrosive action of the mineral lubricating oil.

It is the object of the present invention to provide a mineral oil composition which possesses the above-mentioned detergent and anti-oxidant or anti-corrosive properties by incorporating in a mineral lubricating oil a novel additive ingredient of multi-functional activity.

A further object of this invention is to provide a mineral oil composition possessing detergent properties and enhanced anti-oxidant or anti-corrosive properties by combining with the above-mentioned multi-functional additive an auxiliary additive ingredient and incorporating the combination in a lubricating mineral oil.

The invention is based upon the discovery of a novel class of multi-functional additives which may be broadly described as oil-soluble or oil-miscible hydroxy aromatic or mercapto aromatic methylene thioethers and/or the metal derivatives thereof. It has been found that when small proportions of a compound within the scope of the above general class are blended with a mineral lubricating oil, a mineral oil composition is formed possessing excellent detergent and anti-oxidant or anti-corrosive properties. The compounds of the present invention may be described as that class of aromatic compounds which contain at least one radical of the type —CH_2—S—R_1 attached to a nuclear carbon atom and at least one hydroxy (OH) or sulfhydryl (SH) radical or their metal salts. Specifically these compounds may be represented by the following structural formula



in which R may be a hydrogen, alkyl, aryl, cycloalkyl, aralkyl or naphthenyl radical, and R_1 may be an alkyl, aryl, cycloalkyl, aralkyl or naphthenyl radical. These radicals may contain further substituents which do not affect the oil-solubility of the compound, as, for example, halogen, sulfur, oxygen, or nitrogen derivatives. X may be either an hydroxyl (OH) or sulfhydryl (SH) radical or metal salts thereof, and n, y and z are integers of 1 or more. y and z are usually either 1, 2, 3 or 4, whereas n may be either 1, 2 or 3, depending upon the valences of the aromatic nucleus not satisfied by other substituents or residual hydrogen. The aromatic nucleus diagrammatically shown may be substituted by a naphthenyl, anthracyl or any other condensed aromatic nucleus. The positions of the substituents are purely diagrammatic and may be connected to any position in the aromatic nucleus. The metal derivatives of this class of compounds which are formed by the substitution of the replaceable hydrogen in the hydroxyl radical (OH) or the sulfhydryl radical (SH) include any of the following metals: sodium, potassium, lithium, calcium, barium, strontium, magnesium, zinc, iron, cobalt, nickel, aluminum, manganese, and chromium.

As illustrating the type of compounds within the scope of the above classification, the following compounds are presented, together with their relationship to the general classification. It is to be understood that the above-mentioned metals may be substituted for the replaceable hydrogen in the following compounds and that the scope of the present invention is not limited to the following specific compounds or their metal salts:

R=alkyl, R_1=alkyl

n, y, z=1, X=OH
Amylthiomethyl tridecyl phenol

X=SH
Amylthiomethyl tridecyl thiophenol

n, y=1, *z*=2, X=OH
Di (butylthiomethyl) octyl phenol

X=SH
Di (butylthiomethyl) octyl thiophenol

n=1, *y*=2, *z*=1, X=OH
Amylthiomethyl dioctadecyl naphthol

X=SH
Amylthiomethyl dioctadecyl thionaphthol

n=1, *y, z*=2, X=OH
Di (octylthiomethyl diamyl phenol

X=SH
Di (octylthiomethyl) diamyl thiophenol

n=3, *y, z*=1, X=OH
Amylthiomethyl undecyl pyrogallol

n=2, *y*=1, *z*=2, X=OH
Di (amylthiomethyl) undecyl resorcinol

n=3, *y*=2, *z*=1 X=OH
Amylthiomethyl dioctyl pyrogallol

In the following compounds X is an hydroxyl radical, although the corresponding thio compounds, e. g., where X is a sulfhydryl radical, may also be used:

R=hydrogen, R_1=alkyl

n=1, *y*=3, *z*= 2
Di (butylthiomethyl) phenol

n=1, *y*=2, *z*= 3
Tri (octylthiomethyl) phenol

n, y, z= 2
Di (amylthiomethyl) resorcinol

n=2, *y*=1, *z*=3
Tri (amylthiomethyl) resorcinol

R=cycloalkyl, R_1=alkyl

n, y, z=1
Butylthiomethyl cyclohexyl phenol

n, y=1, *z*=2
Di (butylthiomethyl) cyclohexyl phenol

n=1, *y*=2, *z*=1
Butylthiomethyl di-cyclohexyl phenol

n=2, *y, z*=1
Octylthiomethyl cyclohexyl resorcinol

n=2, *y*=1, *z*=2
Di (octylthiomethyl) cyclohexyl resorcinol

n, y=2, *z*=1
Octylthiomethyl di-cyclohexyl resorcinol

R=aralkyl, R_1=alkyl

n, y, z=1
Hexylthiomethyl benzyl naphthol

n, y=1, *z*=2
Di (hexylthiomethyl) benzyl naphthol

n=1, *y*=2, *z*=1
Hexylthiomethyl dibenzyl naphthol

n=2, *y, z*=1
Hexylthiomethyl benzyl resorcinol

n=2, *y*=1, *z*=2
Di (hexylthiomethyl) benzyl resorcinol

n, y=2, *z*=1
Hexylthiomethyl dibenzyl resorcinol

R=aryl, R_1=alkyl

n, y, z=1
Amylthiomethyl phenyl phenol

n, y=1, *z*=2
Di (amylthiomethyl) phenyl phenol

n=1, *y*=2, *z*=1
Amylthiomethyl diphenyl phenol

n=2, *y, z*=1
Amylthiomethyl phenyl resorcinol

n=2, *y*=1, *z*=2
Di (amylthiomethyl) phenyl resorcinol

n, y=2, *z*=1
Amylthiomethyl diphenyl resorcinol

R=naphthenyl, R_1=alkyl

n, y, z=1
Octylthiomethyl naphthenyl naphthol

n, y=1, *z*=2
Di (octylthiomethyl) naphthenyl naphthol

n=3, *y, z*=1
Octylthiomethyl naphthenyl pyrogallol

n=2, *y*=1, *z*=2
Di (octylthiomethyl) naphthenyl resorcinol

R=alkyl, R_1=aryl

n, y, z=1
Phenylthiomethyl octyl phenol

n, y=1, *z*= 2
Di (phenylthiomethyl) octyl phenol

n=1, *y, z*=2
Di (phenylthiomethyl) dioctyl phenol

n=2, *y, z*=1
Phenylthiomethyl undecyl resorcinol

n=2, *y*=1, *z*=2
Di (phenylthiomethyl) undecyl resorcinol

n, y=2, *z*=1
Phenylthiomethyl dioctyl resorcinol

R=hydrogen, R_1=aryl

n=1, *y*=3, *z*=2
Di (phenylthiomethyl) phenol

n=1, *y*=2, *z*=3
Tri (phenylthiomethyl) phenol

n, y, z=2
Di (phenylthiomethyl) resorcinol

R=alkyl, R_1=cycloalkyl

n, y, z=1
Cyclohexylthiomethyl octadecyl naphthol

n, y=1, *z*=2
Di (cyclohexylthiomethyl) octadecyl naphthol

n=1, *y, z*=2
Di (cyclohexylthiomethyl) dioctadecyl naphthol

n=1, *y*=2, *z*=1
Cyclohexylthiomethyl diamyl phenol

n=2, *y, z*=1
Cyclohexylthiomethyl octyl resorcinol

n=2, *y*=1, *z*=2
Di (cyclohexylthiomethyl) octyl resorcinol

n, y=2, *z*=1
Cyclohexylthiomethyl dioctyl resorcinol

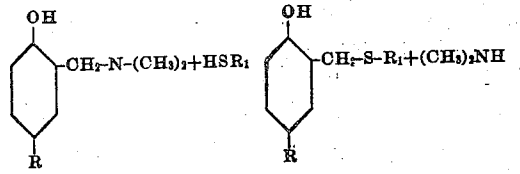
R=hydrogen, R_1=cycloalkyl

n=1, *y*=3, *z*=2
Di (cyclohexylthiomethyl) phenol

n=1, *y*=2, *z*=3
Tri (cyclohexylthiomethyl) phenol
n=3, *y*=1, *z*=2
Di (cyclohexylthiomethyl) pyrogallol
n, *y*, *z*=2
Di (cyclohexylthiomethyl) hydroquinone
R=*alkyl*, R_1=*aralkyl*
n, *y*, *z*=1
Benzylthiomethyl octyl phenol
n, *y*=1, *z*= 2
Di (benzylthiomethyl) octyl phenol
n=1, *y*=2, *z*=1
Benzylthiomethyl dioctyl phenol
n=1, *y*, *z*=2
Di (benzylthiomethyl) dioctyl phenol
n=2, *y*, *z*=1
Benzylthiomethyl undecyl hydroquinone
n=2, *y*=1, *z*=2
Di (benzylthiomethyl) undecyl hydroquinone
n, *y*=2, *z*=1
Benzylthiomethyl diundecyl hydroquinone
R=*hydrogen*, R_1=*aralkyl*
n=1, *y*=3, *z*=2
Di (benzylthiomethyl) phenol
n=1, *y*=2, *z*=3
Tri (benzylthiomethyl) phenol
n, *y*, *z*=2
Di (benzylthiomethyl) resorcinol
R=*alkyl*, R_1 *naphthenyl*
n, *y*, *z*=1
Naphthenylthiomethyl octyl naphthol
n, *y*=1, *z*=2
Di (naphthenylthiomethyl) octyl naphthol
n=1, *y*=2, *z*=1
Naphthenylthiomethyl dioctyl naphthol
n=2, *y*, *z*=1
Naphthenylthiomethyl undecyl resorcinol
n=2, *y*=1, *z*=2
Di (naphthenylthiomethyl) undecyl resorcinol
R=*hydrogen*, R_1=*naphthenyl*
n=1, *y*=3, *z*=2
Di (naphthenylthiomethyl) phenol
n=1, *y*=2, *z*=3
Tri (naphthenylthiomethyl) phenol
n, *y*, *z*=2
Di (naphthenylthiomethyl) resorcinol
R=*tertiary aminomethyl*, R_1=*alkyl*
n=1, *y*=2, *z*=1
Amylthiomethyl di(dimethylaminoethyl) phenol
n=1, *y*=1, *z*=2
Di (amylthiomethyl) dimethylaminomethyl phenol
n=2, *y*=1, *z*=1
Amylthiomethyl morpholinomethyl resorcinol

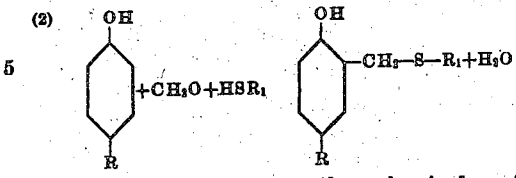
The general class of compounds represented by the foregoing may be prepared by the following reaction:

(1)



They may also be prepared by the interaction of alkylated phenol, formaldehyde and mercaptan as shown:

(2)



However, any of the other classical method of synthesis may be used, and the following examples are mentioned as illustrating one method of preparation:

EXAMPLE I

In preparing amylthiomethyl octyl phenol according to reaction No. 1, 106 grams of dimethylaminomethyl octyl phenol and 210 grams of amyl mercaptan were intimately mixed with agitation and refluxed for 35 hours. Dimethylamine was given off and after the evolution was complete the reaction mixture was transferred to a distilling flask and distilled under vacuum. The product was collected at 150 to 190° C. at three millimeters pressure. The resulting amylthiomethyl octyl phenol was obtained as a clear, light yellow liquid (B. P. 160–170° C. at three millimeters mercury) and analyzed 9.3% sulfur.

EXAMPLE II

65 grams of amylthiomethyl octyl phenol, 22 grams of barium hydroxide, and 250 cc. of toluene were intimately mixed under agitation and refluxed under an automatic water separator until no more water was eliminated from the reaction. Filter-cel was added to the reaction mixture and the excess barium hydroxide filtered out. The filtrate was freed of toluene by heating under vacuum and the resulting barium amylthiomethyl octyl phenolate was obtained as a clear, brittle, light-brown solid, which was dissolved in an equal weight of lubricating oil. The 50% concentrate analyzed 8.3% barium and 4.35% sulfur.

EXAMPLE III

A partially substituted product was obtained by reacting tri (dimethylaminomethyl) phenol under mild conditions in accordance with reaction No. 1. In this reaction 265 grams of tri (dimethylaminomethyl) phenol, 500 grams of amyl mercaptan, and 400 cc. of toluene were stirred together and refluxed for 60 hours. Dimethylamine was given off and after the evolution was complete the toluene and excess amyl mercaptan were distilled off at atmospheric pressure and a small intermediate fraction was collected which boiled up to 150° C. at 10 millimeters mercury. The residual amylthiomethyl di (dimethylaminomethyl) phenol appeared as a light brown oil and analyzed 7.42% sulfur and 9.02% nitrogen.

The proportions of these multi-functional additives added to a mineral lubricating oil may vary between 0.1 and 5.0% by weight, depending upon the particular base oil used and the type of engine and service involved. However, the range and proportions between 0.25 and 2.0% by weight have been found to be particularly effective in imparting excellent detergent and anti-corrosive properties to the mineral lubricating oil.

An additional feature of the present invention is a combination of the foregoing multi-functional additives with an auxiliary additive to further enhance the anti-oxidant or anti-cor-

rosive properties of the mineral oil composition with which the additives are used in certain Diesel and gasoline engines designed for heavy duty service. A higher degree of anti-oxidant or anti-corrosive properties is desired and it is for this purpose that an auxiliary additive ingredient is added to the compounds aforementioned.

The class of compounds which may be used to impart the additional anti-corrosive properties may be any one of the generally accepted sulfurized anti-corrosives. Among the particularly effective sulfurized anti-corrosive compounds found suitable for purposes of the invention are the sulfurized esters of oleic acid, such as sulfurized ethyl oleate; sulfurized high-boiling gasoline polymers, such as the sulfurized clay tower polymers; sulfurized fatty oils, such as sulfurized sperm oil; sulfurized wax compounds, such as sulfurized paraffin wax; sulfurized resins, such as sulfurized abietene; sulfurized tall oil; and sulfurized terpene hydrocarbons, such as the sulfurized terpinolenes and isomers thereof which are disclosed and claimed in the copending application of Knowles, McCoy and Patterson, Serial No. 391,468, filed May 2, 1941. The amount of sulfurized compound added to the mineral lubricating oil in combination with the multi-functional additive is usually within the proportion range of 0.5 and 5.0% by weight and preferably between 1.0% and 3.0%, depending upon the type of lubricating oil used.

These sulfurized auxiliary additives may be prepared in accordance with the copending applications of Knowles and McCoy, Serial Nos. 358,876; 358,877 and 358,878, respectively, all filed September 28, 1940, wherein a light-colored sulfurized material is prepared by the direct action of sulfur on the material to be sulfurized at approximately 300° F. in the presence of water and under pressure of hydrogen sulfide. This pressure, which is at least 50 pounds per square inch, is maintained until all the free sulfur has entered into combination which usually requires from one-half to three hours. The sulfurized products formed by this process are directly soluble in a mineral oil and possess the added advantage in that the reaction product is a light-colored compound as against the usually dark-colored sulfurized compounds.

As illustrative of the anti-corrosive properties of a lubricating oil containing either or both of the aforementioned class of compounds, the results of the following empirical tests are presented. A copper-lead bearing specimen, encased in a special non-wear bushing and rotatably mounted on a stainless steel shaft, was 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. The bearing specimen was weighed before the test and after the 10 hour period and the loss in weight recorded in milligrams. Two reference oils were used in this test and will be referred to as "Reference oil A" and "Reference oil B." Both of these reference oils were solvent-refined, dewaxed Mid-Continent lubricating oil distillates of SAE 30 grade, reference oil A being a paraffin-naphthene (1:1) base oil and reference oil B being a paraffin base oil. To these reference oils were added varying proportions of the additives of the present invention taken individually and in combination and the results compared. The results of two runs at both 250° F. and 350° F. are presented:

BEARING CORROSION—COPPER LEAD (10 HOURS)

Loss of weight in mgs.

Oil tested	250° F.	350° F.
Reference oil A	4, 6	142, 177
Reference oil B	4, 5	167, 199
Reference oil B+0.5% amylthiomethyl octyl phenol	1, 2	26, 51
Reference oil B+0.5% amylthiomethyl di (dimethylaminomethyl) phenol	0, 0	15, 35
Reference oil A+0.5% barium amylthiomethyl octyl phenolate	0, 1	138, 161
Reference oil A+0.5% barium amylthiomethyl octyl phenolate+3.0% sulfurized sperm oil	1, 1	46, 46
Reference oil A+0.5% barium amylthiomethyl octyl phenolate+1.0% sulfurized terpinolene	0, 1	0, 0
Reference oil A+0.5% barium amylthiomethyl octyl phenolate+3.0% sulfurized clay tower polymers	2, 0	1, 0
Reference oil A+0.5% barium amylthiomethyl octyl phenolate+2.0% sulfurized ethyl oleate	1, 2	3, 2

An illustration of the detergent properties of the additives of the present invention may be shown by the results of an empirical test which was designed to indicate the performance of the additives in preventing the accumulation or deposition of varnish or lacquer deposits on the engine parts. This test is carried out in a single cylinder standard Lauson engine by operating with the compounded oil of the present invention under extremely severe conditions for the purpose of developing varnish and lacquer. The conditions of operation attempt to simulate the severe operating conditions encountered in the field by running the engine continuously at 1800 R. P. M. for 24 hours, with the jacket temperature at 212° F., the crankcase temperature at 300° F., fuel fed at 10 cc. per 30 seconds, and a crankcase ventilation of 0.4 cubic feet of air per minute. At the end of this period the engine was dismantled, the piston removed and examined, the amount of varnish depoisted upon the piston determined, and the oil classified according to a visual classification of A, B, C, D and E (A=clean; B=light varnish; C=medium varnish; D=heavy varnish; and E=very heavy varnish). The following results were obtained with a solvent-refined, dewaxed Mid-Continent lubricating oil of an SAE 20 grade as the reference oil, and compared with the reference oil containing the proposed additive:

LAUSON ENGINE VARNISH TEST

Oil tested	Wt. of varnish in grams	Rating
Reference oil	0.074	E
Reference oil+0.5% barium amylthiomethyl octylphenolate	0.011	B

As a final 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 a Diesel Lubricant Test Manual, Laboratory Test No. 1, put out by the Caterpillar Tractor Company. This test was carried 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 blowby.

The crankcase oil was drained every 60 hours and fresh oil added thereto. At the end of the 120 and 240 hour runs the engine was thoroughly examined and any carbonaceous deposits, lacquer formation, or corrosion characteristics noted. In the present instance the reference oil used was a solvent-refined, dewaxed Mid-Continent lubricating oil of SAE 30 grade:

Engine part	Reference oil	Reference oil+0.5% barium amylthiomethyl octylphenolate
Piston crown:		
120 hours	Normal	Normal.
240 hours	do	Do.
Piston rings:		
120 hours	Nos. 3 and 4 slight lacquer; Nos. 5 and 6 sludge deposit with No. 5 sticking and No. 6 slight sticking.	Nos. 1, 2 and 3 clean; No. 4 heavy lacquer; No. 5 lacquer; No. 6 light lacquer; no ring sticking.
240 hours	Nos. 1, 2 and 3 clean, but No. 1 ring 90% stuck in ring groove; Nos. 4, 5 and 6 show lacquer on top of ring and signs of sticking.	Nos. 1, 2 and 3 clean; Nos. 4 and 5 heavy lacquer; No. 6 lacquer; no ring sticking
Ring grooves:		
120 hours	All clean	No. 1 trace deposit; Nos. 2 and 3 heavy lacquer; No. 4 lacquer; No. 5 light lacquer; No. 6 heavy varnish.
240 hours	No. 1 hard carbon buildup; Nos. 2, 4, 5 and 6 black lacquer; No. 3 trace of lacquer.	Nos. 1 and 2 trace deposit; Nos. 3, 4 and 5 heavy lacquer; No. 6 lacquer.
Piston skirt:		
120 hours	1" ring of heavy brown varnish and other spotted areas; 4" dark brown varnish formation extending along axis of piston.	Trace of varnish on thrust side and 3" brown varnish formation along axis of anti-thrust side.
240 hours	2" ring of brown varnish around piston and 3" black-brown varnish formation along axis of piston.	Trace varnish both thrust and anti-thrust sides.
Under piston deposit:		
120 hours		Trace.
240 hours	Black, granular deposit	Same as 120 hours.
Oil filter:		
120 hours	Light coating of lint sludge	Covered with lint—mesh outline visible.
240 hours	Surface covered with lint sludge, no mesh visible.	Covered with lint—mesh pattern visible.

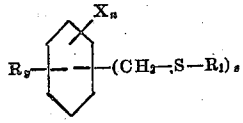
The multi-functional additives of the present invention may further be used in combination with other additive ingredients such as pour point depressors, oiliness agents, extreme pressure agents, blooming agents, viscosity index improving agents, color stabilizers, etc., without departing from the spirit of the invention.

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.

We claim:

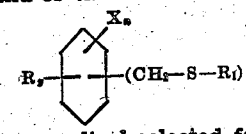
1. An improved lubricating oil comprising a mineral lubricating oil having incorporated therein a small proportion of an aromatic methylene thioether containing at least one substituent linked to an aromatic nucleus selected from the group consisting of hydroxyl and sulfhydryl radicals and metal salts thereof.

2. An improved lubricating oil adapted for use in internal combustion engines, comprising a mineral lubricating oil containing a small amount of a compound of the following general formula



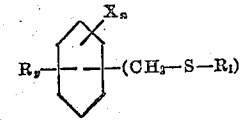
wherein R is a radical selected from the group consisting of hydrogen, alkyl, aryl, cycloalkyl, aralkyl and naphthenyl radicals, R_1 is a radical selected from the group consisting of alkyl, aryl, cycloalkyl, aralkyl and naphthenyl radicals, X is a substituent selected from the group consisting of hydroxyl and sulfhydryl radicals and metal salts thereof, and n, y and z are integers of at least 1.

3. An improved lubricating oil adapted for use in internal combustion engines, comprising a mineral lubricating oil containing a small amount of a compound of the following general formula



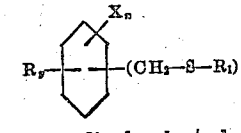
wherein R is a radical selected from the group consisting of hydrogen, alkyl, aryl, cycloalkyl, aralkyl and naphthenyl radicals, R_1 is a radical selected from the group consisting of alkyl, aryl, cycloalkyl, aralkyl and naphthenyl radicals, X is a hydroxyl radical, and n, y and z are integers of at least 1.

4. An improved lubricating oil adapted for use in internal combustion engines, comprising a mineral lubricating oil containing a small amount of a compound of the following general formula



wherein R is a radical selected from the group consisting of hydrogen, alkyl, aryl, cycloalkyl, aralkyl and naphthenyl radicals, R_1 is a radical selected from the group consisting of alkyl, aryl, cycloalkyl, aralkyl and naphthenyl radicals, X is a metal oxide, and n, y and z are integers of at least 1.

5. An improved lubricating oil adapted for use in internal combustion engines, comprising a mineral lubricating oil containing a small amount of a compound of the following general formula



wherein R is a radical selected from the group consisting of hydrogen, alkyl, aryl, cycloalkyl, aralkyl and naphthenyl radicals, R_1 is a radical selected from the group consisting of alkyl, aryl, cycloalkyl, aralkyl and naphthenyl radicals, X is a substituent selected from the group consisting of hydroxyl and sulfhydryl radicals and metal salts thereof, n is equal to 1, and y and z are integers of at least 1.

6. An improved lubricating oil comprising a mineral lubricating oil having incorporated therein 0.1 to 5.0% by weight of an aromatic methylene thioether containing at least one substituent linked to an aromatic nucleus selected from the group consisting of hydroxyl and sulfhydryl radicals and metal salts thereof.

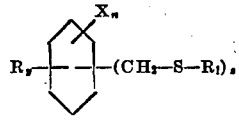
7. An improved lubricating oil comprising a mineral lubricating oil having incorporated therein 0.25 to 2.0% by weight of an aromatic methylene thioether containing at least one substituent linked to an aromatic nucleus selected from the group consisting of hydroxyl and sulfhydryl radicals and metal salts thereof.

8. An improved lubricating oil adapted for use in internal combustion engines, comprising a major proportion of a mineral lubricating oil and a minor proportion of an aromatic methylene thioether containing at least one substituent linked to an aromatic nucleus selected from the group consisting of hydroxyl and sulfhydryl radicals and metal salts thereof, and a sulfurized additive ingredient possessing anti-corrosive properties.

9. An improved lubricating oil adapted for use in internal combustion engines, comprising a major proportion of a mineral lubricating oil and a minor proportion of an aromatic methylene thioether containing at least one substituent linked to an aromatic nucleus selected from the group consisting of hydroxyl and sulfhydryl radicals and metal salts thereof, and a sulfurized additive ingredient selected from the group consisting of sulfurized esters of oleic acid, sulfurized high boiling gasoline polymers, sulfurized fatty oils, sulfurized wax compounds, sulfurized resins, sulfurized tall oil, and sulfurized terpene hydrocarbons.

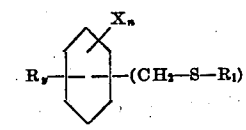
10. An improved lubricating oil adapted for use in internal combustion engines comprising a mineral lubricating oil containing 0.1 to 5.0% by weight of an aromatic methylene thioether containing at least one substituent linked to an aromatic nucleus selected from the group consisting of hydroxyl and sulfhydryl radicals and metal salts thereof, and 0.5 to 5.0% by weight of a sulfurized additive ingredient possessing anti-corrosive properties.

11. An improved lubricating oil adapted for use in internal combustion engines, comprising a mineral lubricating oil containing 0.25 to 2.0% by weight of a compound of the following general formula



wherein R is a radical selected from the group consisting of hydrogen, alkyl, aryl, cycloalkyl, aralkyl and naphthenyl radicals, R_1 is a radical selected from the group consisting of alkyl, aryl, cycloalkyl, aralkyl and naphthenyl radicals, X is a substituent selected from the group consisting of hydroxyl and sulfhydryl radicals and metal salts thereof, and n, y and z are integers of at least 1, and 1.0 to 3.0% by weight of a sulfurized additive ingredient selected from the group consisting of sulfurized esters of oleic acid, sulfurized high boiling gasoline polymers, sulfurized fatty oils, sulfurized wax compounds, sulfurized resins, sulfurized tall oil, and sulfurized terpene hydrocarbons.

12. An improved lubricant comprising a mineral lubricating oil and a small proportion of a compound of the following general formula:

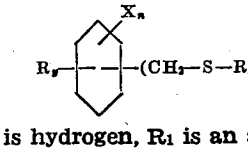


wherein R and R_1 are alkyl radicals, X is a substituent selected from the group consisting of hydroxyl and sulfhydryl radicals and metal salts thereof, and n, y and z are integers of at least 1.

13. An improved lubricant as claimed in claim 12, wherein X is an hydroxyl radical.

14. An improved lubricant according to claim 12, wherein X is a metal oxide.

15. An improved lubricant comprising a mineral lubricating oil and a small proportion of a compound of the following general formula:



wherein R is hydrogen, R_1 is an alkyl radical, X is a hydroxyl radical, and n, y and z are integers of at least 1.

16. An improved lubricant as claimed in claim 15, wherein n is 1, y is 3, and z is 2.

17. An improved lubricant as claimed in claim 15, wherein n is 1, y is 2 and z is 3.

18. An improved lubricant comprising a mineral lubricating oil having incorporated therein a small proportion of an alkyl phenol methylene thio ether.

19. An improved lubricant comprising a mineral lubricating oil having incorporated therein a small proportion of a metal salt of an alkyl phenol methylene thio ether.

20. An improved lubricant comprising a mineral oil having incorporated therein a small proportion of barium amylthiomethyl octyl phenolate.

21. An improved lubricant comprising a mineral lubricating oil having incorporated therein a small proportion of di (amylthiomethyl) phenol.

22. An improved lubricant comprising a mineral lubricating oil having incorporated therein a small proportion of amylthiomethyl di (dimethylaminomethyl) phenol.

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