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LUBRICANT COMPOSITIONS

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This invention relates to novel lubricant compositions. More particularly, the invention is concerned with novel lubricating oil compositions having improved oxidation and corrosion inhibiting properties.

Lubricating oils generally have a tendency to deteriorate due to oxidation and form decomposition products which are corrosive to metals. Since lubricating oils in use today almost invariably come into contact with metal surfaces, the problem of overcoming oxidation and corrosion is considered to be one of major importance. Operating conditions encountered in modern internal combustion engines in which these oils are commonly employed involve increased temperatures, higher speeds and reduced clearances which tend to promote decomposition and the formation of corrosive products. Furthermore, these engines generally employ alloy metal bearings which, besides their possible catalytic effect on the decomposition of the hydrocarbon type mineral lubricating oils, are easily corroded and this, in turn, has seriously accentuated the oxidation and corrosion problems in mineral lubricating oils.

Inhibitors have been added to lubricating oils to improve their resistance to decomposition and avoid corrosivity. Mineral lubricating oils for internal combustion engines, due to the severity of their service, have also been compounded with additional agents such as wear inhibitors, sludge inhibitors and detergents to loosen and suspend products of decomposition and counteract their effect. Unfortunately, many of these agents may adversely affect the efficiency of the oxidation and corrosion inhibitors and it is a problem to find inhibitors which will function in combination with them. Furthermore, some of the most effective oxidation and corrosion inhibitors contain active sulfur and are, therefore, extremely corrosive to silver and similar metals which are subject to attack by active sulfur. These types of metals, although once not so widely used in contact with lubricating oils and therefore considered to constitute only a minor problem, are being increasingly employed today. Particularly in certain important classes of internal combustion engines as, for example, marine and railroad diesel engines, silver metal-containing bearings are more and more common and the problem of providing proper lubrication for them is one of major importance.

It is, therefore, a general object of this invention to provide lubricating oil compositions having improved antioxidant and anticorrosion properties.

A more particular object of the invention is to provide lubricating oil compositions which are noncorrosive to silver and similar metals.

Another more particular object is the provision of mineral lubricating oil compositions in which the tendency to corrode alloy bearings of internal combustion engines has been inhibited.

A further and somewhat related object is to provide compounded mineral lubricating oil compositions having improved anticorrosion properties without adversely affecting the stabilizing, deterging and lubricating qualities of the hydrocarbon oil composition.

Another and still more particular object of the invention is the provision of mineral lubricating oil compositions which are noncorrosive to silver metal containing bearings of the type employed in railroad diesel engines.

Additional objects of the invention will become apparent from the description and claims which follow.

In the accomplishment of the above objects, it has been found that compositions comprising an oil of lubricating viscosity and a complex of molybdic acid with a member of the group consisting of glycols and polyhydroxy benzenes have greatly enhanced anticorrosion properties. It has also been found that, in particular, compositions comprising a compounded mineral lubricating oil for internal combustion engines which is normally corrosive to alloy bearings and such a complex are substantially noncorrosive.

The normal tendency of oils to become oxidized and corrosive is definitely inhibited in the improved compositions of the invention. Metal surfaces in general are not corroded by contact with these compositions and internal combustion engine alloy bearings, in particular, are remakably benefited. Bearings of silver and similar metals which, as stated above are increasingly important due to their presently expanded use in marine and railroad diesel engines, are not corroded by these compositions whereas conventional oxidation inhibited oils have severely pitted and corroded such bearings. The advantages of these improvements are obtained in the compositions of this invention without loss of stability or detergency in the composition.

The complexes of molybdic acid are not only very effective alone in the oils as primary inhibitors of oxidation but also function in combination with other antioxidants as auxiliary inhibitors. They are, in addition, remarkably effective as metal deactivators for the common bearing metals, such as copper and lead, which normally tend to accelerate the decomposition of lubricating oil compositions.

The molybdic acid complexes of the compositions according to this invention are prepared by the reaction of a mixture of molybdic acid and glycol or polyhydroxy benzene. The mixtures are ordinarily heated to accelerate the reaction. Although the nature of the reaction is not definitely known, it is believed that two of the hydroxyl groups of a single glycol or polyhydroxy benzene react with the molybdic acid to form what is commonly termed a "metal chelate compound." These compounds are characterized by a "claw" type of structure in which one or more rings of similar or unlike structure due to the use of mixed glycols or polyhydroxy benzenes are formed including the molybdenum.

The glycols which are reacted with the molybdic acid are preferably α- and β-alkane diols containing from 2 to 18 carbon atoms. Such glycols include, for example, ethylene glycol, 1,2- and 1,3-propanediol, 1,3-pentanediol, 2,3-butanediol, 1,2-hexanediol, 2-methyl-1,3-pentane-diol, 1,2- and 1,3-octylene glycols including 2-ethylhexane-1,3-diol, 1,2-dodecanediol, 2,4-diethyl-octane-1,3-diol, and 2,4,6-triethyl-decane-1,3-diol. The glycols containing from 6 to 10 carbon atoms are more preferred since they impart an optimum degree of oil solubility to the molybdate. α- and β-octylene glycols such as 2-ethylhexane-1,3-diol have been found to be the most satisfactory for present purposes since they give unusually effective oxidation and corrosion inhibitors.

The polyhydroxy benzenes are preferably vicinal dihydric phenols such as catechol, 3,4-dihydroxy toluene, tert.-butylcatechol, cetylcatechol, and the like. They may contain additional hydroxyl groups, as for example, 1,2,4-trihydroxy benzene. Alkyl catechols containing from 2

to 18 carbon atoms in the alkyl group are at present most preferred since the molybdates prepared from them possess the most satisfactory oil solubility characteristics.

Although it is convenient for the sake of illustration to refer to the reaction of molybdic acid with the glycol or polyhydroxy benzene or mixtures thereof to form the complexes for the lubricating oil compositions of this invention, other molybdic acid compounds may also be employed. Such compounds include molybdic anhydride, ammonium molybdate, ammonium para-molybdate and molybdanyl chloride.

The complex of molybdic acid with glycol or polyhydroxy benzene is present in the compositions of the invention in an amount at least sufficient to inhibit corrosion or oxidation. Small amounts, usually from about 0.01 to about 5.0 percent by weight based on the oil, are effective. Proportions ranging from about 0.05 to about 1.0 percent are preferred in most lubricating oil compositions. Concentrates containing larger proportions, up to 50 percent, either in solution or suspension, are particularly suitable in compounding operations.

Any of the well known types of oils of lubricating viscosity are suitable base oils for the compositions of the invention. They include hydrocarbon or mineral lubricating oils of naphthenic, paraffinic, and mixed naphthenic and paraffinic types. They may be refined by any of the conventional methods such as solvent refining and acid refining. Synthetic hydrocarbon oils of the alkylene polymer type or those derived from coal and shale may also be employed. Alkylene oxide polymers and their derivatives such as the propylene oxide polymers and their ethyl esters and acetyl derivatives in which the terminal hydroxyl groups have been modified are also suitable. Synthetic oils of the dicarboxylic acid ester type including dibutyl adipate, di-2-ethylhexyl sebacate, di-n-hexyl fumaric polymer, di-lauryl acylate, and the like may be used. Alkyl benzene types of synthetic oils such as tetradecyl benzene, etc. are also included. Liquid esters of acids of phosphorus including tricresyl phosphate, diethyl esters of decane phosphonic acid, and the like may also be employed. Also suitable are the polysiloxane oils of the type of polyalkyl-, polyaryl-, polyalkoxy- and polyaryloxy siloxanes such as polymethyl siloxane, polymethylphenyl siloxane and polymethoxyphenoxy siloxane and silicate ester oils such as tetraalkyl- and tetraaryl silicates of the tetra-2-ethylhexyl silicate and tetra-p-tert.-butylphenyl silicate types.

In a preferred embodiment of the invention, as mentioned above, the complexes of molybdic acid with glycol or polyhydroxy benzene are employed in combination with compounded mineral lubricating oils of the internal combustion engine type which are normally corrosive to alloy bearings. In such an embodiment, as in the case of the other, straight oils of lubricating viscosity, a major proportion of the lubricating oil normally corrosive to metals and/or subject to oxidation and a small amount, sufficient to inhibit said corrosion and/or oxidation, of a molybic acid complex provides a remarkably improved composition. These compounded oils customarily contain detergents such as the oil-soluble petroleum sulfonates and stabilizers such as the metal alkyl phenates. Other agents such as oiliness agents, viscosity index improvers, pour point depressants, blooming agents, peptizing agents, etc. may also be present.

In further illustration of the invention, the following examples are submitted showing the preparation of the molybdic acid complexes and evaluation of their effectiveness as corrosion inhibitors and antioxidants in oil composition. Unless otherwise specified the proportions given in these examples are on a weight basis.

EXAMPLE 1

Molybdic acid (commercial grade) is added to a solution of 50 parts of 4-t-butylcatechol in an alcohol-water mixture with stirring and gentle heating until some molybdic acid remains undissolved. On further heating, a mixture containing the 4-t-butylcatechol molybdate formed solidifies and is collected by filtration. The red-brown solid thus obtained is dissolved in hot methanol and filtered to remove excess molybdic acid. On concentrating the filtrate by evaporation, the 4-t-butylcatechol molybdate crystallizes as garnet-red needles.

Other complexes similar to the above are also prepared by the reaction of molybdic acid with glycols and polyhydroxy benzenes. The physical properties of these complexes are briefly described in the following table.

Table I

Product	Appearance	Solubility			
		Ether	Hexane	Alcohol	Mineral Oil
Ethylene glycol molybdate.	colorless prisms.	sl. s.	i.	s.	i.
2-ethyl-1, 3-hexanediol molybdate.	brown glass.	s.	s.	s.	s.
4-t-butylcatechol molybdate.	red needles.	sl. s.	i.	s.	v. sl. s.
2, 3-butanediol molybdate.	colorless prisms.	sl. s.	v. sl. s.	s.	v. sl. s.

The molybdic acid complexes are also conveniently prepared in the form of concentrates suitable for addition to base oils of lubricating viscosity in the preparation of the compositions according to this invention. The following examples are illustrative.

EXAMPLE 2

100 parts of ammonium molybdate, 600 parts of ethylene glycol and 200 parts of toluene are mixed and refluxed with continuous water separation of 17 hours. The refluxed mixture is then transferred to a separatory funnel and the toluene layer is removed. The product layer along with the excess ethylene glycol is blended into 1000 parts of a lubricating oil mixture consisting of basic calcium petroleum sulfonate and a mineral oil analyzing 4.35 percent by weight total calcium. The excess glycol is then removed by a vacuum distillation.

EXAMPLE 3

122.5 parts of molybdenum trioxide are dissolved in a solution of 190 parts of concentrated ammonium hydroxide (about 28 percent by weight ammonia) in 250 parts of water. This solution is added to 870 parts of 2-ethyl-1,3-hexane-diol and 260 parts of toluene with constant agitation. The mixture is heated to reflux temperature and the water removed as toluene-water azeotrope. Toluene itself is then refluxed for about 6 hours during which period an additional small quantity of water is collected. The reaction mixture is filtered to remove unreacted solid material. 325 parts of mineral neutral oil is then added to the filtrate and the solution stripped to about 155° C. pot temperature under about 1 mm. Hg pressure. 579 parts of 2-ethyl-1,3-hexane-diol molybdate concentrate analyzing 12.5 percent by weight molybdenum is obtained.

EXAMPLE 4

60 parts of solid ammonium molybdate having the formula $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ are added to 348 parts of 2-ethyl-1,3-hexanediol and 130 parts of xylene. The mixture is agitated mechanically and the xylene refluxed for 6 hours during which time the water evolved is separated from the refluxing xylene. The mixture is then filtered to remove unreacted solid material. The filtrate is blended with about 130 parts of mineral neutral oil and stripped to a pot temperature of about 160° C. at about 1 mm. Hg pressure to give the 2-ethyl-1,3-hexane-diol molybdate concentrate.

EXAMPLE 5

To a mixture of 184 parts of 2-methyl-2,4-pentane-diol and 120 parts of toluene are added 50 parts of crystalline ammonium molybdate of the formula

$$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$$

The mixture is agitated mechanically and the toluene refluxed for about 12 hours during which time the water evolved is separated from the refluxing toluene. The reaction mixture is filtered to remove solid unreacted material and the filtrate is stripped of toluene and unreacted 2-methyl-2,4-pentane-diol by heating to about 95° C. under a pressure of about 1 mm. Hg. The 2-methyl-2,4-pentane-diol molybdate thus obtained is then blended with a base oil containing basic calcium petroleum sulfonate and a heavy metal alkyl phenate.

EXAMPLE 6

144 parts of molybdenum trioxide are dissolved in a solution of 285 parts of water and 225 parts of concentrated ammonium hydroxide containing about 28 per cent by weight ammonium. This solution is added gradually to 450 parts of 2,3-butane-diol and 100 parts of toluene. The mixture is constantly agitated and the toluene refluxed as in the above examples to remove the water over a period of about 6 hours. Solid unreacted materials are removed by filtration. The filtrate is then added to a concentrated solution of a basic calcium petroleum sulfonate in mineral neutral oil to give two moles of molybdenum for every three moles of calcium present. The mixture is then stripped free of solvent and unused glycol to obtain a 2,3-butane-diol molybdate concentrate.

The effectiveness of the lubricating oil compositions of the invention is demonstrated by the copper-lead strip corrosion test. In this test a polished copper-lead strip is weighed and immersed in 300 cc. of test oil in a 400-milliliter lipless Erlenmeyer beaker. The test oil is maintained at 340° F. and stirred with a mechanical stirrer at 1000 R. P. M. After two hours a synthetic naphthenate catalyst is added to provide the following catalytic metals:

	Percent by weight
Iron	0.008
Lead	0.004
Copper	0.002
Manganese	0.0005
Chromium	0.004

The test is continued 20 hours. The copper-lead strip is then removed, rubbed vigorously with a soft cloth and weighed to determine the net weight loss.

The test oils in this instance include both a mineral lubricating oil which is an acid refined medicinal type white mineral oil and a compounded mineral lubricating oil of the internal combustion engine type which is normally corrosive to alloy bearings. In this case the compounded oil (A) consists of a solvent refined SAE 40 mineral lubricating oil base having a viscosity index of 60 and containing 10 millimoles per kilogram of neutral calcium petroleum sulfonate and 20 millimoles per kilogram of calcium alkyl phenate. Compounded oil (B) consists of the same base oil but contains 28 millimoles per kilogram of a basic calcium petroleum sulfonate. Compounded oil (C) is the same except that 40 millimoles per kilogram of the basic calcium petroleum sulfonate were employed. The results of the tests are shown in the following table. The concentrations of molybdic acid complex employed are given in millimoles of molybdenum per kilogram of oil.

Table II

COPPER-LEAD STRIP CORROSION TEST

Additive	Base Oil	Copper-Lead Strip Weight Loss (mg.)
None	Mineral lub. oil	58.5
20 mM./kg. 2-ethyl-1,3-hexane-diol molybdate.	Same	14.0
20 mM./kg. 4-t-butylcatechol molybdate.	Same	2.5
None	Compounded Oil A	253.1
2 mM./kg. ethylene glycol molybdate	Same	7.3
2 mM./kg. 2-ethyl-1, 3-hexane-diol molybdate.	Same	7.0
20 mM./kg. 2-ethyl-1, 3-hexane-diol molybdate.	Same	0.9
20 mM./kg. 2-methyl-1, 3-pentane-diol molybdate.	Same	2.3
20 mM./kg. 4-t-butylcatechol molybdate.	Same	2.2
None	Compounded Oil B	219.0
20 mM./kg. ethylene glycol molybdate	Same	1.9
20 mM./kg. 2-ethyl-1,3-hexane-diol molybdate.	Same	3.0
20 mM./kg. 2-3 butanediol molybdate	Compounded Oil C	2.6

As shown by the above test data, straight mineral lubricating oil alone gave a copper-lead strip weight loss due to corrosion of over 58 milligrams in the 20-hour period. By way of distinction, compositions in accordance with this invention containing the same straight mineral lubricating oil base and molybdate corrosion inhibitors gave as little as 2.5 milligrams weight loss. In the case of the conventional compounded mineral lubricating oils of the internal combustion engine type, the improvement was even more remarkable. The different compounded oils alone gave copper-lead strip weight losses ranging as high as 253 milligrams whereas the lubricating oil compositions of this invention containing the same compounded base oil plus a glycol or polyhydroxy benzene complex of molybdic acid resulted in very little corrosion loss, one being as low as 0.9 milligram.

The performance characteristics of the lubricating oil compositions of this invention are also illustrated by their evaluation in a number of engine tests. The engine test procedures and techniques, though conventional and well known in the lubricating oil art, are briefly described for the sake of convenience in the following paragraphs along with the test data.

In the L–4 engine test the corrosion characteristics of the oils are determined in a Chevrolet standard 6-cylinder engine in a typical laboratory installation. Weighed copper-lead test bearings and new piston rings are installed. The test is run at a constant engine speed at about 300 R. P. M. under a load of 30 brake horse-power for a total of 36 hours subsequent to a run-in period of 8 hours. The outlet temperature of the jacket coolant is 200° F. and the oil sump temperature is 280° F. At the conclusion of the test the engine is disassembled and inspected for varnish and sludge deposits and the various parts are rated on a cleanliness scale of 0 to 10. The bearings are weighed to determine the weight loss per whole bearing due to corrosion. Illustrative test results on the compositions of the invention using compounded oil (A) as described above are given in the following table:

Table III

Oil	Weight Loss, mg./Whole Bearing
Compounded oil (A) (reference oil)	More than 500.
20 mM./kg. 2-ethyl-1,3-hexane-diol molybdate in reference oil	94.

The piston rating was 9.9 on a cleanliness scale of 0 to 10 and the total engine varnish and sludge deposit rating was 98.0 on a scale of 0 to 100. Not only is the test oil

of the composition of the invention effective in reducing the bearing corrosion loss from more than 500 milligrams to less than 100 milligrams per bearing, but it also gives a very high performance rating so far as engine cleanliness and varnish and sludge deposits are concerned.

In the L–1 engine test the detergency characteristics of the lubricating oil compositions of the invention are evaluated in a single cylinder Caterpillar diesel test engine. The piston rings, cylinder liner, valves, etc. are standard production units of the diesel type. The engine is operated at a speed of 1000 R. P. M. under a load of approximately 20 brake horse-power. The outlet jacket temperature of the coolant is 175–180° F. and the oil temperature to the bearings is 145–150° F. After 120 hours' operation with 0.4 percent sulfur-containing fuel, the engine is inspected for cleanliness. Compounded oil (A), the reference oil, is the same as described above. Illustrative test data are set out in the following table:

Table IV

Oil	Engine Condition
Compounded oil (A) (reference oil)	Clean.
20 mM./kg. 2-ethyl-1,3-hexane-diol molybdate in reference oil	Clean.
20 mM./kg. ethylene glycol molybdate in reference oil	Clean.

The above test data show that the lubricating oil compositions of the invention are excellent diesel engine lubricating oils of the heavy duty type.

The L–1 and L–4 engine tests referred to above are more fully described in the C. R. C. Handbook, 1946 edition, Coordinating Research Council, New York, New York.

In the Navy propulsion load test described in Mil. P–17269 (Ships) 17 July 1952, the compositions of the invention are evaluated as diesel engine lubricating oils under severe operating conditions. The tests are run in a General Motors' 4-cylinder diesel engine using one percent sulfur fuel. Copper-lead bearings are employed. The tests are run at a constant speed of 1800 R. P. M. under a load of 30 brake horse-power per cylinder. The crankcase temperature is 250° F. The present test is run continuously to simulate railroad diesel engine performance unlike the standard Navy test procedure which permits regular 4-hour shutdown periods. Sea water was also excluded for the same reason. Compounded oil (A), the reference oil, is the same as described above. Test results are as follows:

Table V

Oil	Weight Loss, mgs./Whole Bearing (Hours)				
	50	100	150	200	300
Compounded oil (A) (reference oil)	70	830	2,000	------	------
20 mM./kg. ethylene glycol molybdate in reference oil	------	31	------	------	------
20 mM./kg. 2-ethyl-1,3-hexanediol molybdate in reference oil	------	9	------	------	256

The performance of the lubricating oil compositions of the invention is also evaluated by the Navy Series B. Test. This test is more fully described in Mil. P–17273 (Ships) 15 July 1952. The test conditions are similar to those of the Navy propulsion load test given above except that normal operating conditions are maintained. Copper-lead bearings are employed. Compounded oil (A), the reference oil, is the same as described above. Illustrative test results are as follows:

Table VI

Oil	Weight Loss, mgs. after 300 hours per Whole Bearing
Compounded oil (A) (reference oil)	Greater than 2,500.
20 mM./kg. 2-ethyl-1,3-hexane-diol molybdate in reference oil	36.

In both of the Navy engine tests shown above, the bearing weight loss due to corrosion by the reference oil, a conventional heavy duty compounded oil, was extremely high. Such an oil would be impossible to use for any prolonged period of time without shutdown. By way of distinction, the lubricating oil composition of the invention containing molybdate complexes gives remarkably low corrosion losses after as much as 300 hours of continuous operation. Greatly extended periods of trouble-free operation of diesel engines are thus possible with these improved oils.

Since, as noted above, silver metal-containing bearings are more and more common in diesel engines, the corrosive effect of the lubricating oil compositions of the invention on silver bearings is determined in comparison with a conventional oxidation and corrosion inhibited compounded lubricating oil. This test is run in a 4-cylinder diesel engine using one percent sulfur fuel. The procedure is the same as outlined in the Navy Series B tests given above. The conventional oxidation and corrosion inhibited compounded oil is a solvent refined SAE 40 viscosity mineral lubricating oil having a viscosity index of 60. It contains 10 mM./kg. of zinc dialkyl dithiophosphate and 0.25 percent by weight of a sulfurized diparaffin sulfide. Compounded oil (A), the uninhibited reference oil previously described and shown to be highly corrosive to copper-lead bearings, is also evaluated. Illustrative test results are given in the following table:

Table VII

Oil	Silver Bearing Weight Loss, mgs./Whole Bearing after 300 Hours
Conventional inhibited oil	252
Compounded oil (A) (reference oil)	50
20 mM./kg. 2-ethyl-1,3-hexane-diol molybdate in reference oil	50

From the above test data it will be seen that the conventional oxidation and corrosion inhibited compounded lubricating oil causes a much greater silver bearing weight loss than the lubricating oil compositions of the invention. Although the weight losses of both compounded oil (A), the reference oil, and the compositions of the invention are low, it must be borne in mind that the reference oil has been shown to be unsatisfactory in the copper-lead bearing tests set out above. It is a further fact that, aside from corrosion losses, silver metal-containing bearings are extremely sensitive to lubricant compositions containing active sulfur type corrosion inhibitors and such compositions generally provide an unsatisfactorily low degree of lubricity for silver bearing surfaces.

The effectiveness of the lubricating oil compositions of the invention as antioxidants in conventional engine oil compositions is also determined in a series of oxidation tests. In these tests the oil is maintained at a temperature of 340° F. under a pressure of one atmosphere of oxygen. During the test the oil is agitated by a high speed glass stirrer and the amount of oxygen added is recorded. An oxidation catalyst in the amount of 0.1 percent by weight iron naphthenate and 0.1 percent by weight copper naphthenate is added. The oxidation rate in cubic centimeters of oxygen per 100 grams of oil per hour is meas-

ured. Compounded oil (A) is the same oil as described above.

Table VIII

Oil	Oxidation Rate, cc. O_2/100 g. oil/hr.
Compounded oil (A) (reference oil)	4,000
20 mM./kg. 2-ethyl-1,3-hexane-diol molybdate in reference oil	290
Compounded oil (A) taken from Navy propulsion load test after 50 hours—no catalyst	4,600
20 mM./kg. 2-ethyl-1,3-hexane-diol molybdate in compounded oil (A) taken from Navy propulsion load test after 50 hours—no catalyst	290

The antioxidant properties of the lubricating oil compositions of the invention are also evaluated in tests for determining the oxidation inhibition period. In these tests the oil is contained in a large glass tube equipped with a high speed glass stirrer. The oil temperature is 340° F. and a pressure of about one atmosphere of pure oxygen is maintained. The volume of oxygen added is automatically recorded and the time in hours required for 100 grams of oil to absorb 1200 cc. of oxygen is called the inhibition period. Illustrative test results are as follows:

Table IX

Oil	Inhibition Period in Hours
Heavy medicinal white oil (reference oil)	0.0
0.2% by weight 2-ethyl-1,3-hexane-diol molybdate in reference oil	0.9
0.2% by weight 2-ethyl-1,3-hexane-diol molybdate and 0.2% by weight phenyl-α-naphthylamine in reference oil	64.0
0.2% by weight 2-ethyl-1,3-hexane-diol molybdate and 0.2% by weight 4-t-butylcatechol in reference oil	6.3
0.2% by weight phenyl-α-naphthylamine in reference oil	3.3
0.2% by weight 4-t-butylcatechol in reference oil	2.7

The test data of the above tables show that lubricating oil compositions containing the complexes of the invention are effectively inhibited against oxidation whereas similar lubricating oil compositions without the molybdic acid complexes are susceptible to a very high rate of oxidation. The test results of the above tables also show that when conventional oxidation inhibitors of the diaryl amine and polyhydroxy benzene type illustrated by phenyl-α-naphthylamine and 4-t-butylcatechol, respectively, are employed in the compositions according to this invention, a marked improvement in the effect of the primary oxidation inhibitor is obtained, indicating synergism of the conventional antioxidant and the molybdate.

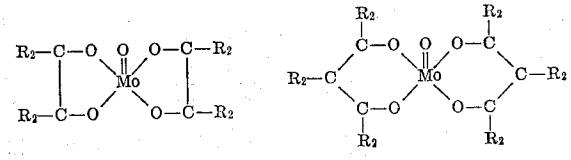
Other conventional oxidation inhibitors of the diaryl amine type which are suitable for employment in the improved compositions of the invention include p-hydroxy diphenyl amine, p,p'-dihydroxy diphenyl amine, diphenyl-p-phenylene diamine, diphenyl amine, phenothiazine, di-β-naphthylamine, etc. Other polyhydroxy aromatic compounds include 1,2-dihydroxy naphthalene, hydroquinone, di - t - butyl - resorcinol, 1,2 - dihydroxy-4-amino naphthalene, etc. Other oxidation inhibitors of these general types are also well known in the art.

In the compositions of the invention including both conventional oxidation inhibitors and the molybdates, any amount of the conventional inhibitor sufficient to inhibit oxidation and any amount of the molybdate sufficient to enhance the action of the conventional inhibitor may be employed. Ordinarily, amounts of from 0.1 to 5.0 percent by weight of the composition of the conventional inhibitor and the molybdate each are sufficient. Preferably from 0.05 to 2 percent by weight of each inhibitor is employed in operations where there is little danger of encountering extremely high temperatures.

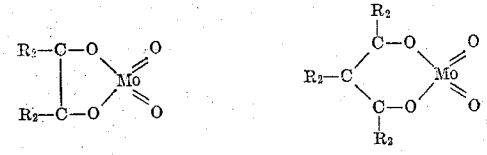
The amounts of conventional inhibitor and molybdate need not be the same in any given composition.

The nature of the improved lubricating oil compositions of the invention and their effectiveness should be readily apparent from the many illustrations given above. Oxidation and corrosivity in the compositions are definitely inhibited to a very substantial degree. Particularly corrodible metals such as engine alloy bearings of copper, lead, and the like, as well as bearings of silver, are not adversely affected. This is indeed remarkable since the problem of devising lubricant compositions uniformly noncorrosive to both types of bearing metals has long confronted workers in the art. As shown by the actual tests set out above, the advantages of these improvements are obtained without loss of other desirable properties of the lubricant compositions.

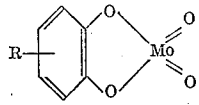
As mentioned above, the molybdenum compounds of the compositions according to this invention are preferably formed from molybdic acid or salts thereof and an alpha- or beta-diol or vicinal dihydroxy benzene. Although the present invention is in no way limited to any theory concerning the structure of the compounds, it is believed that they may be illustrated by the followinng formulae:



Di-glycol molybdates



Mono-glycol molybdates



Pyrocatechol molybdates

wherein R is hydrogen or a group of hydrocarbon structure as previously described. The formulae shown here represent the acid anhydride forms of these materials. By reaction with water these materials can readily be converted to the acid forms.

Although the above types of compounds are distinctly preferred in the compositions of the invention, other compounds of similar structure having substituents on the hydrocarbon groups which do not adversely affect the reaction may likewise be employed. Such substituents include: hydroxyl groups, as when a polyhydroxy-alcohol or benzene such as glycerol, pentaerythritol, sorbitol or trihydroxy benzene is used; ester groups, as when glycerol monooleate or sorbitan monooleate is used; and halogens, ethers, amides, etc., as will be apparent to those skilled in the art from the above description of the invention.

Although the compositions of the invention have been primarily described as crankcase lubricants for internal combustion engines, they are also useful as turbine oils, hydraulic fluids, instrument oils, constituent oils in grease manufacture, ice-machine oils, and the like.

Although the complexes of molybdic acid with glycol or polyhydroxy benzene, as described above, are distinctly superior and provide the preferred lubricating oil compositions of the invention, various amine salts of the molybdic acid complexes may also be employed advantageously. These amine salts are prepared by heating a mixture of the complex of molybdic acid with glycol

or polyhydroxy benzene and an organic amine such as trimethyl amine, triethanol amine, lauryl amine, phenyl-α-naphthylamine, meta-xylylene diamine, para-xylylene diamine, amino phenol, pyridine, morpholine, etc. Other substituted molybdates which also may be employed include the esters of the molybdic acid complexes such as the monobutyl ester of di(2-ethylhexanediol-1,3 molybdate, monopentaerythritol di(2 - ethylhexanediol - 1,3) molybdate, etc.

The effectiveness of the lubricating oil compositions containing an amine salt of a molybdic acid complex as illustrated above is determined in the copper-lead strip corrosion test previously described in this specification. The reference oil in this case is a compounded oil comprising a solvent refined SAE 40 mineral lubricating oil base having a viscosity index of 60 and containing 10 mM./kg. of neutral calcium petroleum sulfonate and 20 mM./kg. of calcium alkyl phenate, sulfurized. Results of the test are as follows:

Table X

Oil	Copper-Lead Strip Weight Loss (mgs.)
Compounded oil (reference oil)	253.1
20 mM./kg. octylene glycol molybdate 2-ethylhexylamine salt in ref. oil	3.6
20 mM./kg. ethylene glycol molybdate 2-ethylhexylamine salt in ref. oil	6.5
40 mM./kg. 2-ethylhexylamine in ref. oil	560.7

The effectiveness of the derivatives of the molybdic acid complexes as corrosion inhibitors is readily apparent from the above test results. Very little weight loss is obtained with compositions containing the glycol molybdate amine salts whereas the uninhibited reference oil alone gives an objectionably high corrosion weight loss. The fact that the excellent effects obtained by the use of the compositions of the invention are not due merely to a simple addition of the amine is also illustrated by the test data. Although 2-ethylhexylamine salts of the molybdates give corrosion losses as low as 3.6 milligrams, the 2-ethylhexylamine alone in the same reference oil results in a very high corrosion loss of over 560 milligrams.

We claim:

1. A lubricant composition comprising an oil of lubricating viscosity and a molybdic acid complex of a member of the group consisting of α- and β-alkane diols of 2 to 18 carbon atoms and alkyl vincinal dihydroxy benzenes containing from 2 to 18 carbon atoms in the alkyl group, said molybdic acid complex being in an amount sufficient to inhibit corrosion.

2. A lubricant composition comprising an oil of lubricating viscosity and a molybdic acid complex of an alkyl vicinal dihydroxy benzene containing from 2 to 18 carbon atoms in the alkyl group in an amount sufficient to inhibit corrosion.

3. A lubricant composition comprising an oil of lubricating viscosity and a molybdic acid complex of an α-alkane diol of 2 to 18 carbon atoms in an amount sufficient to inhibit corrosion.

4. A lubricant composition comprising an oil of lubricating viscosity and a molybdic acid complex of a β-alkane diol of 2 to 18 carbon atoms in an amount sufficient to inhibit corrosion.

5. A lubricant composition comprising an oil of lubricating viscosity and 0.01 to 5.0 percent by weight based on the oil of a molybdic acid complex of 2-ethylhexane-1,3-diol.

6. A lubricant composition comprising an oil of lubricating viscosity and from about 0.01 to about 5.0 percent by weight based on the oil of a molybdic acid complex of 4-tert.-butyl pyrocatechol.

7. A lubricant composition comprising a mineral lubricating oil for internal combustion engines which is normally corrosive to alloy bearings and a molybdic acid complex of a member of the group consisting of α- and β-alkane diols of 2 to 18 carbon atoms and alkyl vicinal dihydroxy benzenes containing from 2 to 18 carbon atoms in the alkyl group, said molybdic acid complex being in an amount sufficient to inhibit corrosion.

8. A lubricant composition comprising a mineral lubricating oil for internal combustion engines which is normally corrosive to alloy bearings and a molybdic acid complex of an alkyl vicinal dihydroxy benzene containing from 2 to 18 carbon atoms in the alkyl group in an amount sufficient to inhibit corrosion.

9. A lubricant composition comprising a mineral lubricating oil for internal combustion engines which is normally corrosive to alloy bearings and a molybdic acid complex of an α-alkane diol containing from 2 to 18 carbon atoms in an amount sufficient to inhibit corrosion.

10. A lubricant composition comprising a mineral lubricating oil for internal combustion engines which is normally corrosive to alloy bearings and a molybdic acid complex of a β-alkane diol containing from 2 to 18 carbon atoms in an amount sufficient to inhibit corrosion.

11. A lubricant composition comprising a mineral lubricating oil for internal combustion engines which is normally corrosive to alloy bearings and from about 0.01 to about 5.0 percent by weight based on the oil of a molybdic acid complex of 2-ethylhexane-1,3-diol.

12. A lubricant composition comprising a mineral lubricating oil for internal combustion engines which is normally corrosive to alloy bearings and from about 0.01 to about 5.0 percent by weight based on the oil of a molybdic acid complex of 4-tert.-butyl pyrocatechol.

13. A lubricant composition comprising a mineral lubricating oil for internal combustion engines which is normally corrosive to alloy bearings and from about 0.01 to about 5.0 percent by weight based on the oil of a molybdic acid complex of ethylene glycol.

14. A lubricant composition comprising a mineral lubricating oil for internal combustion engines which is normally corrosive to alloy bearings, from about 0.01 to about 5.0 percent by weight based on the oil of a molybdic acid complex of a member of the group consisting of α- and β-alkane diols of 2 to 18 carbon atoms and alkyl vicinal dihydroxy benzenes containing from 2 to 18 carbon atoms in the alkyl group; and from about 0.01 to about 5.0 percent by weight based on the oil of a diaryl amine oxidation inhibitor.

References Cited in the file of this patent

UNITED STATES PATENTS

2,144,654	Guthmann	Jan. 24, 1939
2,161,184	McKone et al.	June 6, 1939
2,305,627	Lincoln et al.	Dec. 22, 1942
2,410,652	Griffin et al.	Nov. 5, 1946
2,465,296	Swiss	Mar. 22, 1949