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LUBRICATING OIL COMPOSITIONS

Andrew D. Abbott, Ross, Oliver L. Harle, Berkeley, and John R. Thomas, Albany, Calif., assignors to California Research Corporation, San Francisco, Calif., a corporation of Delaware

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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 this 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 engine.

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 a metal compound selected from the group consisting of acids, oxides and salts of selenium, silicon, tungsten, vanadium and zirconium with a metal chelating agent having two functional groups in vicinal or beta position to one another on the carbon skeleton of a hydrocarbon linkage 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 chelates are substantially noncorrosive.

The "metal chelating agent" referred to above is the accepted terminology for a definite and well-known class of chemical compounds. Such compounds have been heretofore described in many published texts including the recent book entitled "Chemistry of the Metal Chelate Compounds," by Martell and Calvin which was published by Prentice-Hall, Inc., of New York in 1952. For present purposes the more suitable compounds of this class are members of the group consisting of glycols, dithiols, mercapto alcohols, amino alcohols, amino thiols, dicarboxylic acids, hydroxycarboxylic acids, mercaptocarboxylic acids, aminocarboxylic acids, beta-diketones, beta-keto carboxylic acid esters, dihydroxy benzenes, dimercaptobenzenes, mercaptohydroxy benzenes, diamino benzenes, aminohydroxy benzenes, aminomercapto benzenes, hydroxycarboxy benzenes, aminocarboxy benzenes, and mercaptocarboxy benzenes having the two functional groups in vicinal or beta position to one another on the carbon skeleton.

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 remarkably 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 the lubricating oil compositions according to this invention are prepared by the reaction of a mixture of the acid, salt or oxide of the metal and

chelating agent. 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 functional groups of a single glycol, dithiol, polyhydroxy benzene, etc. react with the 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 chelating agents are formed including the metal of the group consisting of selenium, silicon, tungsten, vanadium, or zirconium.

The preferred chelates of the above type are oil-soluble and the chelating agents are usually selected so as to impart oil solubility to the complex or chelate. Chelating agents containing from 2 to 18 carbon atoms are usually suitable since the less oil-soluble chelates may be used in combination with dispersants such as alkaline earth metal petroleum sulfonates or oil-solubilizing agents such as glycols and other polyhydric alcohols. Those containing from 6 to 10 carbon atoms in the carbon skeleton are preferred since they impart an optimum degree of oil solubility to the chelate or complex.

Examples of suitable chelating agents within the above-described class include vicinal- and beta-diols such as ethylene glycol and 2-ethylhexanediol-1,3; vicinal- and beta-dithiols such as ethylene mercaptan and 1,3-propanedithiol; vicinal- and beta-mercapto alcohols such as beta-mercaptoethanol, 3-mercapto-propane-1-ol; vicinal- and beta-diamines such as ethylenediamine and propylenediamine; vicinal- and beta-amino alcohols such as ethanolamine and 3-aminopropane-1-ol; vicinal- and beta-aminothiols such as thioethanolamine and 3-amine-1-mercaptopropane; vicinal- and beta-dicarboxylic acids such as oxalic acid and malonic acid; vicinal- and beta-hydroxy carboxylic acids such as glycolic acid and beta-hydroxybutyric acid; vicinal- and beta-mercapto carboxylic acids such as thioglycolic acid and beta-mercaptobutyric acid; vicinal- and beta-amino carboxylic acids such as glycine and beta-aminobutyric acid; beta-diketones such as acetylacetone and benzoylacetone; beta-ketocarboxylic acid esters such as ethylacetoacetate; etc. The foregoing compounds are characterized by normal or branched carbon skeletons. They may have substituted in various positions along the carbon skeleton, aromatic and substituted aromatic rings; hydroxy, alkoxy, and aryloxy radicals; sulfhydryl, alkylthioether, arylthioether, alkylthioester, and arylthioester groups; acyl, aroyl, thioacyl and thioaroyl radicals; amino, alkylamino, arylamino, acylamido and aroylamido radicals; and nitro, halogen and sulfato groups. However, preferred chelating agents of the aforementioned type for present purposes are those having an aliphatic hydrocarbon group between the two functional groups.

Also suitable as chelating agents are various carbocyclic or aromatic chelating agents including vicinal-dihydroxy aromatic or carbocyclic compounds such as pyrocatechol, 4-t-butylpyrocatechol and dihydroxycyclohexane; vicinal-dimercaptoaromatic compounds such as thiocatechol; vicinal - mercaptohydroxy aromatic compounds such as monothiocatechol or mercaptohydroxy benzene; vicinal - diaminoaromatic compounds such as orthophenylenediamine; vicinal - aminohydroxyaromatic compounds such as orthoaminophenol; vicinal-aminomercaptoaromatic compounds such as orthoaminothiophenol; vicinal-hydroxycarboxyaromatic compounds such as salicyclic acid; vicinal - aminocarboxyaromatic compounds such as orthoaminobenzoic acid; vicinal-mercaptocarboxyaromatic compounds such as orthomercaptobenzoic acid, etc. The aforementioned carbocyclic or aromatic chelating agents may have various ring substituents including aromatic and substituted aromatic rings; hydroxy, alkoxy, and aryloxy radicals, sulfhydryl, alkylthioether, arylthioether, alkylthioester, and arylthioester groups; acyl, aroyl, thioacyl and thioaroyl radicals; amino, alkylamino, arylamino, acylamido, and aroylamido radicals; and nitro, halogen and sulfato groups. For present purposes those aromatic chelating agents having the two functional groups on a benzene ring or an alkyl benzene containing from 2 to 18 carbon atoms in the alkyl group are preferred since the chelates of the above-described metals are prepared with them possess the most satisfactory oil-solubility characteristics.

The most suitable chelating agents of the above-mentioned classes for present purposes are members of the group consisting of alpha- and beta-alkanediols of 2 to 18 and preferably from 6 to 10 carbon atoms, alkyl vicinal-dihydroxy benzenes having from 2 to 18 and preferably from 4 to 16 carbon atoms in the alkyl group, beta-diketones of from 4 to 18 and preferably from 6 to 10 carbon atoms, beta-ketocarboxylic acid esters of from 4 to 18 and preferably from 6 to 10 carbon atoms, and vicinal- and beta-dicarboxylic and hydroxycarboxylic acids of from 2 to 18 and preferably from 6 to 10 carbon atoms. Illustrative chelating agents of this particular group are ethylene glycol, 2-ethylhexanediol - 1,3, 4 - t - butylpyrocatechol, cetylpyrocatechol, acetylacetone, benzoylacetone, ethyl acetoacetate, oxalic acid, glycolic acid and alpha-hydroxydecanoic acid. These chelating agents give complexes of the previously described types which are superior corrosion and/or oxidation inhibitors in the lubricating oil compositions of the invention.

Out of the above-mentioned class of chelate-forming metals, vanadium is presently preferred. The complexes of acids, oxides and salts of vanadium with the more suitable chelating agents just described, particularly the alpha- and beta-alkanediols, the alkyl vicinal-dihydroxy benzenes and the beta-diketones are unusually easy to prepare in excellent yields. Furthermore, when these complexes are added to oils of lubricating viscosity they provide unique compositions of greatly improved resistance to oxidation and the development of corrosion characteristics due to oxidative deterioration of the oil.

Although it is convenient for the sake of illustration in the above description of the invention to refer to the reaction of an acid of the metal with the various chelating agents or mixtures thereof to form the complexes for the lubricating oil compositions, other compounds of the metals such as the oxides and salts mentioned above may also be employed to provide similar chelates. Suitable acids include tungstic acid, vanadic acid and silicic acid as illustrative examples. Oxides of the metals which form complexes with the chelating agents adapted for use in the lubricating oil compositions of the invention are illustrated by compounds such as selenium dioxide, vanadium pentoxide, etc. Suitable salts of the metals may be either inorganic salts such as zirconium nitrate, ammonium meta-vanadate, vanadyl chloride, vanadyl sulfate, silicon tetrachloride, etc., or organic salts such as salts of carboxylic acids, for example, silicon tetraacetate, and amine base salts such as ethanolaminetungstate, and the like. The inorganic salts are presently preferred since they are more commonly available and give excellent results.

Various amine salts of the acid complexes of the metals and chelating agents referred to above may also be employed advantageously in the lubricating oil compositions of the invention. These amine salts are conveniently prepared by heating a mixture of the acid complex with an organic amine such as trimethylamine, triethanolamine, laurylamine, phenyl-alpha-naphthylamine, xylylene diamines, aminophenol, pyridine, and morpholine. Esters of the acid complexes such as the monobutyl esters and monopentaerythritol esters are also suitable. Such substituted complexes are generally charactreized by enhanced oil solubility which may be desirable in the compounding of certain mineral lubricating oil compositions.

The complex of the metal compound described above 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 azelate, 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 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 the 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 representative 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

A solution of 0.1 mole of tungstic acid in 50 milliliters of concentrated ammonium hydroxide and 100 milliliters of water is heated with stirring on a steam plate. During the heating and stirring, 0.2 mole of 4-t-butylcathechol dissolved in 100 milliliters of methanol is slowly added. After 15 minutes of contined heating and stirring the mixture is cooled to room temperature and a crystalline product consisting of crude ammonium 4-t-butylcathechol tungstate is formed.

The crude ammonium 4-t-butylcathechol tungstate obtained above is separated from the liquid phase by filtration. It is then washed with aqueous methanol to remove impurities and unreacted 4-tert.-butylcathechol and dried in a vacuum oven at about 70° C. The dried product consisting of purified ammonium 4-tert.-butylcatechol tungstate is used directly in the preparation of oxidation and corrosion inhibited lubricating oil compositions.

EXAMPLE 2

To a solution of 11.1 grams (0.10 mole) of selenium dioxide in 100 milliliters of methanol is added 33.2 grams (0.20 mole) of 4-tert.-butylcatechol and 50 milliliters of concentrated ammonium hydroxide (about 28% ammonia). The mixture is concentrated to a viscous residue by heating and evaporation. The viscous residue is then dissolved in 200 milliliters of toluene and heated on a steam plate to expell the last traces of water. The solution of selenium 4-tert.-butylcatechol is used as a concentrate in blending corrosion and oxidation inhibited lubricating oil compositions.

EXAMPLE 3

A solution of 42.9 grams (0.10 mole) of zirconium nitrate pentahydrate in 100 milliliters of warm methanol is added to a solution of 49.8 grams (0.30 mole) of 4-tert.-butylcatechol in 100 milliliters of methanol. To the resulting green solution is added 50 milliliters of concentrated ammonium hydroxide (about 28% ammonia) with vigorous stirring. The crude ammonium 4-tert.-butylcatechol zirconate is obtained as a light green precipitate.

The crude ammonium 4-tert.-butylcatechol zirconate is separated from the liquid phase by filtration. It is then purified by washing with aqueous methanol and dried in a vacuum oven at about 90° C. The purified ammonium 4-tert.-butylcatechol zirconate thus obtained in the form of a light green dry powder is used directly in the blending of lubricating oil compositions.

EXAMPLE 4

40.0 grams (0.34 mole) of ammonium meta-vanadate, 234 grams (1.6 moles) of 2-ethylhexanediol-1,3, and 125 milliliters of toluene are charged to a flask equipped with a mechanical stirrer, reflux condenser and water separator. Toluene is refluxed from the stirred reactants by heating for about 70 minutes and 16.5 milliliters of water is separated during this period. The reaction mixture becomes viscous at this point and it is desirable to terminate the reaction. The reaction mixture is dissolved in acetone filtered to remove solids which may be present and transferred to a distillation flask. The solvents and unreacted glycol are stripped from the reaction mixture by distillation at a reduced pressure of about 1 mm. Hg up to a temperature of about 127° C.

The stripped product obtained above consists of (2-ethylhexanediol-1,3) meta-vanadate and weighs about 157 grams. It is used directly in the preparation of compounded oils of lubricating viscosity.

EXAMPLE 5

30 grams of vanadyl sulfate is dissolved in 170 milliliters of water. The resulting solution is neutralized with saturated aqueous sodium carbonate solution and allowed to stand overnight. The vanadyl hydroxide which is formed as percipitate is removed by filtration and washed with water and alcohol. The precipitate is then stirred with 124 grams of acetylacetone dissolved in 100 milliliters of acetone. The mixture is warmed on a steam plate until the gray hydroxide color disappears. On cooling a bluish-green crystalline material is formed. This material, consisting of vanadyl bisacetylacetonate, is separated and employed directly in the preparation of lubricating oil compositions.

EXAMPLE 6

Vanadyl bisbenzoylacetonate is prepared according to a method similar to that of the above example using benzoylacetone in place of the acetylacetone. The crystalline product thus prepared is used directly in the compounding of mineral lubricating oil compositions.

EXAMPLE 7

23 grams of vanadium pentoxide, 40 grams of 2-ethylhexanediol-1,3 and 50 milliliters of xylene are added to a glass reaction vessel equipped with mechanical stirrer, reflux condenser and a water separation trap. The mixture is heated to reflux temperature and agitated mechanically while refluxing for about 5 hours. 3.2 milliliters of water is separated during this period. About 20 grams of solid material is separated by filtration from the reaction mixture.

The liquid phase from the above filtration is stripped to about 120° C. at a pressure of about 1 mm. Hg to give the 2-ethylhexanediol-1,3 vanadate which is used directly in the preparation of corrosion inhibited lubricating oil compositions.

EXAMPLE 8

40 grams of ammonium meta-vanadate, 600 grams of ethylene glycol and 200 milliliters of benzene are charged to a glass reaction vessel equipped with a mechanical stirrer, reflux condenser and water separation trap. The mixture is refluxed for about 10 hours with agitation, during which period 18.5 milliliters of water-ethylene glycol azeotrope analyzing about 66 percent water is separated.

The reflux product obtained above, amounting to about 435 grams, is combined with 200 grams of neutral mineral lubricating oil and about 200 grams of neutral mineral lubricating oil concentrate containing calcium alkyl phenate, sulfurized, analyzing 4.7 percent calcium and 3.08 percent sulfur. This mixture is stripped of solvents and unreacted glycol up to a temperature of about 135° C. at 1 mm. Hg pressure. A precipitate is formed which is removed by diluting the stripped mixture with an equal part of benzene and filtering out the insoluble precipitate.

The filtrate obtained above is stripped to remove the benzene. The stripped product, consisting of ethylene glycol meta-vanadate, is stable over a 48-hour period. It is employed as a concentrate in the blending of mineral lubricating oil compositions.

The vanadium complexes prepared above are obtained in excellent yields, some ranging as high as 98 percent based on the vanadium reagent consumed.

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 cubic centimeters of test oil in a 400-milliliter lipless Berzelius beaker. The test oil is maintained at 340° F. under a pressure of one atmosphere of air and stirred with a mechanical stirrer at 1000 R. P. M. After two hours a synthetic naphthenate catalyst is added, unless otherwise specified, 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 include various types of mineral lubricating oil compositions as reference oils. 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, sulfurized. Compounded oil (B) consists of the same base oil but contains 40 millimoles per kilogram of basic calcium petroleum sulfonate. Compounded oil (C) is a solvent refined SAE 30 mineral lubricating oil base containing 10 millimoles per kilogram of neutral calcium petroleum sulfonate and 4 millimoles per kilogram of calcium alkyl phenate, sulfurized. The results of the test are shown in the following table. The concentrations of complex employed are given in millimoles of metal per kilogram of oil or percent by weight of the composition.

Table I

COPPER-LEAD STRIP CORROSION TEST

Additive	Base Oil	Copper-Lead Strip Weight Loss (mgs.)
None	Compounded oil (A)	253.1
20 mM./kg. ammonium 4-t-butylcatechol tungstate.	Same	22.0
20 mM./kg. (2-ethylhexanediol-1,3) vanadate.	Same	4.0
20 mM./kg. zirconium bisacetylacetonate.	Same	30.0
20 mM./kg. ammonium 4-t-butylcatechol zirconate.	Same	59.9
20 mM./kg. selenium 4-tert.-butylcatecholate.	Same	67.4
0.3% by weight vanadyl bisacetylacetonate.	Same	32.4
0.3% by weight vanadyl bisbenzoylacetonate.	Same	31.8
0.77% by weight 2-ethylhexanediol-1,3 vanadate.	Same	3.2
None	Compounded oil (B)	225.0
20 mM./kg. 2-ethylhexanediol-1,3 vanadate.	Same	14.2
None	Compounded oil (C)	160.0
5 mM./kg. ethylene glycol vanadate.	Same	60.9

As shown by the above test data, the reference mineral lubricating oil compositions alone give copper-lead strip weight losses due to corrosion of over 250 milligrams in the 20-hour period. By way of distinction, compositions in accordance with this invention containing the same mineral lubricating oil base and a complex of the previously described type give as little as 3.2 milligrams for the same period. This shows that the compositions of the present invention are effectively inhibited against oxidation and/or corrosion characteristics due to the oxidative deterioration of the oil.

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. The advantages of these improvements are obtained without loss of other desirable properties of the lubricant compositions.

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, contituent oils in grease manufacture, ice-machine oils, and the like.

We claim:

1. A lubricant composition consisting essentially of a mineral lubricating oil for internal combustion engines containing minor amounts of alkaline earth metal petroleum sulfonate and alkaline earth metal alkyl phenate which is normally corrosive to alloy hearings and from about 0.01 to about 5.0 percent by weight based on the oil of a vanadate of alpha- and beta-glycols of 6 to 10 carbon atoms.

2. A lubricant composition consisting essentially of

mineral lubricating oil for internal combustion engines containing minor amounts of alkaline earth metal petroleum sulfonate and alkaline earth metal alkyl phenate which is normally corrosive to alloy bearings and from about 0.01 to about 5.0 percent by weight based on the oil of 2-ethylhexanediol-1,3 vanadate.

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