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CORROSION INHIBITED LUBRICANT COMPOSITION

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This invention relates to a novel corrosion inhibited lubricant composition. More particularly, the invention is concerned with a new and unusually effective lubricating oil composition having improved corrosion inhibiting properties.

Lubricating oils generally have a tendency to become corrosive to metals during their normal service due to oxidation and the formation of decomposition products. Modern internal combustion engines in particular are operated under conditions which involve increased temperature changes, higher speeds and reduced clearances, all of which conditions aggravate the formation of corrosive decomposition products. Furthermore, these engines commonly employ alloy metal bearings which, besides their possible catalytic effect on the decomposition of lubricating oils, are especially subject to corrosive attack.

Corrosion inhibitors which have been added heretofore to lubricating oils in general to improve their resistance to the formation and effect of corrosive products have not been entirely satisfactory. Many of the additives are only partly effective and permit the bearings and other metal surfaces to be slowly but eventually corroded away. Other additives which are substantially effective at the outset are used up during service and are therefore active only for a limited period.

Another, more specific disadvantage of the corrosion inhibitors employed prior to this has been due to the fact that lubricating oils for internal combustion engines are commonly compounded with additives such as wear inhibitors, pour point depressants, sludge inhibitors, detergents and the like to loosen, suspend and otherwise counteract the effect of decomposition products and provide efficient lubrication. Unfortunately, many of these agents adversely affect the activity of the corrosion inhibitors, and it is necessary to find inhibitors which will function in combination with them.

Furthermore, many of the most effective corrosion inhibitors known prior to this invention contain active sulfur in some form and are therefore undesirable for use with silver and similar metal-containing bearings which are subject to attack by active sulfur. These types of bearings, although once not so widely used 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 from the standpoint of low corrosivity and improved lubricity is one of major importance.

A superior new corrosion inhibited lubricant composition has now been found comprising a major portion of an oil of lubricating viscosity corrosive to metal surfaces in normal use and a minor portion, sufficient to inhibit corrosion, of p-xylylenediamine.

The novel lubricant composition according to the invention is characterized by remarkable corrosion inhibiting properties for metal surfaces and alloy bearings over extended periods of operation. A further outstanding characteristic of the composition lies in the fact that these beneficial properties are obtained without adverse effect from other conventional additives commonly employed in lubricant compositions. Still another advantage of the lubricant composition according to the invention is its ability to provide unusually effective lubrication for particular alloy bearings such as the silver metal-containing bearings more and more commonly found in marine and railroad diesel engines.

In a more specific and preferred embodiment the present invention is concerned with a lubricant composition comprising an oil of lubricating viscosity in combination with a lubricating oil detergent additive, said combination being corrosive to metal surfaces in normal use, and a minor portion, sufficient to inhibit corrosion, of p-xylylenediamine, said minor portion of lubricating oil detergent additive being sufficient to suspend said p-xylylenediamine in the oil of lubricating viscosity.

The lubricating oil detergent additive of the composition is a well known type of additive generally used in lubricant compositions. The term, as employed here in its commonly accepted sense, denotes a recognized class of chemical compounds which are known for their function of enabling a lubricating oil medium to maintain oxidation products, resins, and other types of insoluble materials in suspension or dispersion in the oil. Such detergent compounds in lubricant compositions in actual use may remove naturally formed protective films from metal surfaces thus rendering the compositions more corrosive. Illustrative lubricating oil detergent additives fall within general classes of types. Examples of the better known classes are the metal salts of naphthenic acids such as aluminum naphthenate; metal salts of fatty acids and substituted fatty acids such as calcium stearate, calcium phenyl stearate, basic calcium phenyl stearate and calcium dichlorostearate; metal salts of aromatic acids and substituted aromatic acids such as calcium octyl salicylate and basic calcium actyl salicylate; metal salts of petroleum sulfonic acids such as calcium sulfonate and basic calcium sulfonate; metal salts of alkyl phenol sulfides such as barium amyl phenol sulfide; metal salts of alkyl phenols such as aluminum dicetyl phenate and calcium dicetyl phenate; metal salts of thiophosphoric acid esters such as the zinc salt of the p-tert.amylphenyl ester of dithiophosphoric acid; and metal salts of wax substituted phenol derivatives such as the wax substituted metal phenates. Presently preferred are the alkaline earth metal petroleum sulfonates and alkaline earth metal phenates such as basic calcium petroleum sulfonate, calcium cetyl phenate and sulfurized calcium cetyl phenate. These particular lubricating oil detergent additives alone and together, are found to be unusually effective when combined with the p-xylylene diamine in lubricant compositions for internal combustion engine use according to this invention.

Nonmetallic lubricating oil detergent additives are also suitable for the lubricant compositions of the invention.

This type of lubricating oil detergent additive, for present purposes, may be conveniently described as a macromolecular copolymer characterized by oil solubilizing monomer groups and polar-type monomer groups which apparently provide the detergent effect. The oil solubilizing monomer which is well known in the field of polymeric lubricating oil viscosity index improvers may be an olefin such as hexadecene-1 or p-octyl styrene; an ester such as allyl stearate or lauryl methacrylate; an ether such as vinyl n-butyl ether; or a ketone such as methallyl isobutyl ketone. The polar type monomer group may be an unsaturated monocarboxylic acid such as methacrylic acid, amides and esters thereof such as n-lauryl acrylamide and pentaerythritol monomethacrylate, unsaturated dicarboxylic acids such as maleic acid and amides and esters thereof such as the half-amides, half-esters, diamides and diesters as illustrated by the N,N-di-tert.butyl monoamide of maleic acid, monopentaerythritol ester of maleic acid and similar diamides and diesters.

Other oil-soluble dispersants may be included in the lubricant compositions either in addition to or in lieu of the metallic and nonmetallic lubricating oil detergent additives described above. Such dispersants are illustrated by the phosphatides such as animal lecithin and the partial or complete esters of long-chain carboxylic acids with polyhydric alcohols such as pentaerythritol mono-oleate and glycerol sorbitan laurate. These materials, like the other dispersants or lubricating oil detergent additives mentioned previously, also serve to maintain the p-xylylenediamine of the present compositions in stable suspension. Thus, the p-xylylenediamine is circulated freely in the lubricating oil system wherever corrodible metal surfaces are encountered to effectively inhibit corrosion and promote improved lubrication of rubbing surfaces.

The p-xylylenediamine is a known material. It may be conveniently derived by converting terephthalic acid to the terephthaladinitrile which is then hydrogenated to give the p-xylylenediamine. In view of the remarkably improved corrosion-inhibited lubricant compositions obtained when it is combined with oils of lubricating viscosity, however, a brief review of its more important characteristics may be appropriate here. Structurally, the p-xylylenediamine is unique in that the two amine groups are attached to methylene groups which are separated by the benzene ring as illustrated by the following formula:



This particular amine, it will be noted, is unlike other amines in that the two amine groups are located where they will be able to function most effectively without affecting each other. Other diamines of both aliphatic and aromatic types generally lack the structural characteristics of the p-xylylenediamine and this can lead to undesirable variations in their effectiveness under the many different conditions of operation encountered with lubricant compositions.

The compositions of this invention containing the p-xylylenediamine, as described above, are surprisingly more effective in the inhibition of corrosion of metal surfaces such as alloy metal bearings and the like than similar compositions containing their homologue, p-phenylenediamine. Still more unexpected is the fact that the p-xylylene-diamine is a much better corrosion inhibitor than its isomer, m-xylylenediamine. So far as is known, it has never been suggested heretofore that either of these xylylenediamines might be effective in lubricant compositions as corrosion inhibitors, let alone that p-xylylenediamine would be far superior to its isomer, m-xylylenediamine in such a capacity.

In accordance with a preferred embodiment of the invention, as already described, a lubricating oil detergent additive is present in a minor amount, sufficient to suspend the p-xylylenediamine in the oil of lubricating viscosity. Amounts up to 20% by weight of the lubricant composition are generally suitable for this purpose, although concentrates for use in blending operations to prepare the lubricant compositions of the invention may contain up to 50% by weight or more of the detergent. For present purposes, very superior lubricant compositions are obtained with from 0.1 to 10% by weight of the detergent.

The p-xylylenediamine is present in the lubricant composition in a minor portion, sufficient to inhibit corrosion, as stated above. Generally, amounts up to about 1.0% by weight of the lubricant composition are very satisfactory. Larger amounts, up to 10% or more, may be used in the preparation of concentrates. For present purposes the preferred lubricant compositions contain from about 0.001 to 0.5% by weight. Such compositions are unusually stable and provide remarkably effective corrosion inhibition for extended periods.

Any of the well known types of oils of lubricating viscosity are suitable base oils for the compositions of the invention. In normal usage these oils are corrosive to metal surfaces. 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 fumarate 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.

As already mentioned, the corrosion inhibiting compositions of this invention are outstanding in that they are unusually effective in the form of compounded lubricating oils containing conventional additives such as oxidation inhibitors, detergents or dispersants, sludge inhibitors, pour depressants, VI improvers, antifoaming agents, rust inhibitors, oiliness or film strengthening agents, wear inhibitors, dyes and the like. A great many of these compounded oils are generally corrosive to metal surfaces and alloy metal bearings in particular, and it is an exceptional attribute of the present compositions whereby corrosion inhibited compounded lubricating oils are provided. A further very desirable feature of the compositions according to the invention is the fact that the corrosion inhibition is obtained without any noticeable adverse effect on the other additives, thus permitting more efficient all around lubrication of internal combustion engines and other types of machines where unusually severe conditions of service are more and more commonly encountered.

Mineral lubricating oils are preferred in the compounded lubricating oil compositions of the invention since such oils are generally compounded for internal combustion engine use are unusually corrosive to metal surfaces and are thus most greatly benefited by the addition of p-xylylenediamine.

The following examples are submitted as addition illustrations of the invention. These examples show the preparation of the various lubricant compositions and

the evaluation of their effectiveness as corrosion inhibitors. The proportions given in these examples, unless otherwise specified, are on a weight basis and include both percent (%) and millimoles per kilogram (mM/kg.) of the various additives.

EXAMPLE I

Approximately 350 parts of a mineral oil concentrate consisting of a solvent refined SAE 30 mineral lubricating oil base, 10 mM/kg. of basic calcium petroleum sulfonate analyzing 1.67% calcium and 36 mM/kg. of a sulfurized basic calcium alkyl phenate analyzing 3.10% calcium was charged to a reaction vessel equipped with stirring and heating means. The contents were heated up to 160° F. 0.175 part of p-xylylendiamine was added to the reaction vessel and the contents were stirred at 200° F. for about 10 minutes. The resulting composition was a solvent refined SAE 30 mineral lubricating oil containing 10 mM/kg. of basic calcium petroleum sulfonate analyzing 1.67% calcium, 36 mM/kg. sulfurized basic calcium alkyl phenate analyzing 4.4% calcium and 0.05% p-xylylenediamine.

By the same general procedure as outlines in the above example additional corrosion inhibited lubricant compositions were prepared in illustration of the invention. They contained both mineral oils and a variety of synthetic oils used either alone with the p-xylylenediamine or in combination with conventional lubricating oil additives to illustrate the overall effectiveness of the compositions in accordance with this invention. The compositions and their effectiveness in standard lubricating oil tests for determining corrosion inhibition are listed in the following table. This table shows specific results obtained by the Copper-Lead Strip Corrosion Test.

In the Copper-Lead Strip Corrosion Test, a polished copper-lead strip is weighed and immersed in 300 ml. of test oil contained in a 400 ml., lipless Berzelius beaker. The test oil is maintained at 340° F. under a pressure of 1 atmosphere of air and stirred with the mechanical stirrer at 1000 R. P. M. After 2 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 for 20 hours. The copper-lead strip is then removed, rubbed vigorously with a soft cloth and weighed to determine the net weight loss.

The lubricating oil compositions in the tests include a variety of base oils. Mineral oil (A) is an acid refined white mineral oil. Synthetic oil (B) is a poly-1,2-propylene glycol phenyl methyl diether having a molecular weight of 1200. Synthetic oil (C) is a di-2-ethylhexyl sebacate. Compounded oil (D) is a solvent refined SAE 40 mineral lubricating oil having a viscosity index of 60 and containing 10 mM/kg. of basic calcium petroleum sulfonate and 20 mM/kg. of sulfurized basic calcium cetyl phenate. Compounded oil (E) is the same mineral lubricating oil but contains only 10 mM/kg. basic calcium petroleum sulfonate. Compounded oil (F) is the same mineral lubricating oil but contains 14 mM/kg. lead cetyl phenate. Compounded oil (G) is an acid refined white mineral oil containing 10% by weight of a copolymeric detergent which is the copolymer of lauryl methacrylate with the diethylaminoethyl ester of acrylic acd sold by DuPont as Lubricating Oil Additive No. 565. Compounded oil (H) is the same oil but contains 20 mM/kg. sulfurized basic calcium cetyl phenate.

Illustrative test results are shown in the following table. Concentrations of the p-xylylenediamine employed are given in percent by weight of the composition.

Table

COPPER-LEAD STRIP CORROSION TEST

Additive and Oil	Copper-Lead Strip Weight Loss (Mg.)
None—Mineral Oil (A)	66.2
0.15% p-xylylenediamine in mineral oil (A)	0.0
None—Synthetic oil (B)	4.4
0.15% p-xylylenediamine in synthetic oil (B)	0.0
None—Synthetic oil (C)	46.8
0.15% p-xylylenediamine in synthetic oil (C)	11.6
None—Compounded oil (D)	250–300
0.25% o-phenylenediamine in compounded oil (D)	260.9
0.5% o-phenylenediamine in compounded oil (D)	216.2
0.25% m-phenylenediamine in compounded oil (D)	82.6
0.5% m-phenylenediamine in compounded oil (D)	82.2
0.25% p-phenylenediamine in compounded oil (D)	69.9
0.5% p-phenylenediamine in compounded oil (D)	67.9
0.25% m-xylylenediamine in compounded oil (D)	108.9
0.25% p-xylylenediamine in compounded oil (D)	3.3
0.10% p-xylylenediamine in compounded oil (D)	13.2
None—Compounded oil (E)	272.4
0.15% p-xylylenediamine in compounded oil (E)	17.5
None—Compounded oil (F)	270.4
0.15% p-xylylenediamine in compounded oil (F)	74.2
None—Compounded oil (G)	158.6
0.15% p-xylylenediamine in compounded oil (G)	0.0
None—Compounded oil (H)	172.6
0.15% p-xylylenediamine in compounded oil (H)	18.9

The above test data show that all of the various mineral oils and synthetic oils alone or in combination with conventional lubricating oil additives which are normally corrosive to metal surfaces are all benefited with the addition of p-xylylenediamine corrosion inhibitor in accordance with the invention. The effectiveness of oils of lubricating viscosity in general which are normally corrosive to metal surfaces in the corrosion inhibited compositions of the invention is illustrated by a representative group consisting of mineral lubricating oils, alkylene oxide polymer synthetic lubricating oils and dicarboxylic acid diester synthetic lubricating oils. In one particular combination, that employing compounded oil (D), the above test data show that the reference oil containing heavy duty lubricating oil detergent additives and stabilizers, when used alone, gives a copper-lead strip loss of over 250 mg. By way of distinction, compositions in accordance with this invention employing the same base oil with as little as 0.10% p-xylylenediamine, for example, give a very low corrosion loss of only 13.2 mg. This outstanding effectiveness of the present compositions containing p-xylylenediamine is remarkable, because the isomers and adjacent homologues of p-xylylenediamine (for example, m-xylylenediamine and p-phenylenediamine, respectively) in similar compositions are largely ineffective and, therefore, unsatisfactory as corrosion inhibitors.

Although the compositions of the invention have been described above primarily as internal combustion engine lubricants they are also suitable for other applications. Such applications include their use as gear lubricants, ice machine oils, instrument oils, constituent oils for grease manufacture, turbine oils and the like.

This application is a continuation-in-part of Warren Lowe patent application Serial No. 476,088, filed December 17, 1954, entitled Corrosion Inhibited Lubricant Composition, now abandoned.

I claim:

1. A lubricating composition comprising a major portion of an oil of lubricating viscosity corrosive to metal surfaces in normal use and a minor portion, sufficient to inhibit corrosion of p-xylylenediamine.

2. A lubricating composition comprising a major portion of a mineral lubricating oil corrosive to metal surfaces in normal use and a minor portion, sufficient to inhibit corrosion, of p-xylylenediamine.

3. A lubricating composition comprising a major portion of an oil of lubricating viscosity in combination with a minor portion of a lubricating oil detergent additive, said combination being corrosive to metal surfaces in normal use and a minor portion, sufficient to inhibit corrosion, of p-xylylenediamine, said minor portion of lubri-

cating oil detergent additive being sufficient to suspend said p-xylylenediamine in the oil of lubricating viscosity.

4. A lubricating composition comprising a major portion of a mineral lubricating oil in combination with a minor portion of a lubricating oil detergent additive, said combination being corrosive to metal surfaces in normal use and a minor portion, sufficient to inhibit corrosion, of p-xylylenediamine, said minor portion of lubricating oil detergent additive being sufficient to suspend said p-xylylenediamine in the mineral lubricating oil.

5. A lubricating composition comprising a major portion of a mineral lubricating oil in combination with a minor portion of an alkaline earth metal petroleum sulfonate, said combination being corrosive to metal surfaces in normal use and a minor portion, sufficient to inhibit corrosion, of p-xylylenediamine, said minor portion of alkaline earth metal petroleum sulfonate being sufficient to suspend said p-xylylenediamine in the mineral lubricating oil.

6. A lubricating composition comprising a major portion of a mineral lubricating oil in combination with a minor portion of an alkaline earth metal petroleum sulfonate and an alkaline earth metal alkyl phenate, said combination being corrosive to metal surfaces in normal use and a minor portion, sufficient to inhibit corrosion of p-xylylenediamine, said minor portion of alkaline earth metal petroleum sulfonate and alkaline earth metal

alkyl phenate being sufficient to suspend said p-xylylenediamine in the mineral lubricating oil.

7. A lubricating composition comprising a major portion of a mineral lubricating oil in combination with a minor portion of a calcium petroleum sulfonate, said combination being corrosive to metal surfaces in normal use and a minor portion, sufficient to inhibit corrosion, of p-xylylenediamine, said minor portion of calcium petroleum sulfonate being sufficient to suspend said p-xylylenediamine in the mineral lubricating oil.

8. A lubricating composition comprising a major portion of a mineral lubricating oil in combination with a minor portion of a calcium petroleum sulfonate and a calcium alkyl phenate, said combination being corrosive to metal surfaces in normal use and a minor portion, sufficient to inhibit corrosion of p-xylylenediamine, said minor portion of calcium petroleum sulfonate and calcium alkyl phenate being sufficient to suspend said p-xylylenediamine in the mineral lubricating oil.

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