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LUBRICANT COMPOSITION

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This invention relates to a novel 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 and accentuate the need for improved lubricating ability in the lubricant composition. 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 and alteration of their friction characteristics which places a greater burden on the lubricity of the lubricant composition.

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.

In accordance with the present invention, a superior new lubricant composition having improved corrosion inhibiting properties has 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 a member of the group consisting of m-hexahydrophthalic acid, p-hexahydrophthalic acid and ammonium and N-alkyl ammonium salts thereof having alkyl groups of up to 24 carbon atoms each.

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. It also provides a greatly improved quality of lubrication for bearings and other rubbing surfaces. 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 a mineral lubricating oil 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 a member of the group consisting of m-hexahydrophthalic acid, p-hexahydrophthalic acid and ammonium and N-alkyl ammonium salts thereof having alkyl groups of up to 24 carbon atoms each. 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 octyl 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 are found to be unusually effective when combined with the m- and p-hexahydrophthalic acids and derivatives or mixtures thereof in corrosion-inhibited lubricant compositions according to this invention.

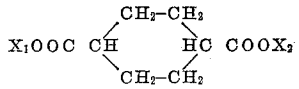
Nonmetallic lubricating oil detergent additives are also suitable for the lubricant compositions of the invention. This type of lubricating oil detergent additive, for present purposes, may be conveniently described as a macromolecular copolymer characterized by oil solubilizing monomer groups and polar-type monomer groups which apparently provide the detergent effect. The oil solu-

bilizing monomer which is well known in the field of polymeric lubricating oil viscosity index improvers may be an olefin such as hexadecene-1 or 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.

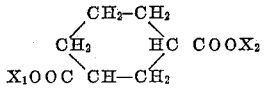
Other oil-soluble dispersants may be included in the lubricant compositions either in addition to or in lieu of the metallic and nonmetallic lubricating oil detergent additives described above. Such dispersants are illustrated by the phosphatides such as animal lecithin and the partial or complete esters 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, serve to maintain the m- and p-hexahydrophthalic acids or their derivatives of the present compositions in stable dispersion. Thus, the acids or their derivatives are 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 m- and p-hexahydrophthalic acids and their ammonium salts are commercially available materials or are conveniently derived from such materials by conventional reactions such as the hydrogenation of phthalic acids, neutralization with ammonium and amine bases, etc.

Although the m- and p-hexahydrophthalic acids and their ammonium and N-alkyl ammonium salts are generally known materials, a brief review of certain of their more predominant and unusual characteristics may be appropriate here in view of the remarkably improved lubricant compositions obtained when they are combined with oils of lubricating viscosity. Structurally, the m- and p-hexahydrophthalic acids and their derivatives are unique in that the carboxyl-containing groups are separated by a cyclohexane ring as illustrated by the following formulae:



p-Hexahydrophthalic acid and derivatives



m-Hexahydrophthalic acid and derivatives

wherein X_1 and X_2, which may be the same or different, are members of the group consisting of hydrogen and ammonium and N-alkyl ammonium groups having alkyl groups of up to 24 carbon atoms each. The ammonium and N-alkyl ammonium groups have the formula:

$$-NH_{4-n}R_n$$

in which R is an alkyl group having up to 24 carbon atoms and n is an integer of from 0 to 3, inclusive. Either the cis or trans isomers of the m- and p-hexahydrophthalic acids and their derivatives or mixtures thereof are suitable. Presently preferred are the p-hexahydrophthalic acids and their ammonium salts. In the N-alkyl ammonium salts the trans isomers of p-hexahydrophthalic acid are most preferred for their unusual effectiveness.

It will be noted that the above hexahydrophthalic acids and their derivatives are unlike other dicarboxylic acids and derivatives in that the functional carboxyl-containing groups are located where they will be able to act most effectively. Other dicarboxylic acids and derivatives of both aliphatic and aromatic types may cyclize and form anhydrides, etc., which may not be as effective as the acids or their derivatives.

The m-hexahydrophthalic acid and p-hexahydrophthalic acid and their ammonium derivatives may be employed in combinations in lubricating oil compositions in accordance with the invention. This may be advantageous where conditions of operation and the like are such that the solubility of the acid or derivatives thereof becomes critical. In a case of this type, the lubricating oil composition may be saturated with one of the acids or derivatives and still be capable of incorporating an additional amount of the other acid or derivatives thereof to augment the corrosion inhibiting properties of the composition.

The compositions of this invention containing the hexahydrophthalic acids, their derivatives and mixtures thereof, as described above, are surprisingly more effective in the inhibition of corrosion of metal surfaces such as alloy metal bearnigs and the like than similar compositions containing the isomeric anhydride-forming dicarboxylic acid, o-hexahydrophthalic acid. Still more unexpected is the fact that the p-hexahydrophthalic acid and its derivatives are generally much better corrosion inhibitors than the m-hexahydrophthalic acid or its derivatives.

The hexahydrophthalic acid, ammonium derivatives or mixtures thereof may be dispersed in the base oil of lubricating viscosity according to several different methods. Suitable suspensions may be prepared by dispersing the acids or derivatives in the oil by grinding the components together in a paint mill, colloid mill or the like. The oil may be heated to increase the solubility of the corrosion inhibitor. Mutual solvents such as alcohols of the isopropyl alcohol type may also be used to produce the compositions.

As already mentioned, the corrosion-inhibiting, m- and p-hexahydrophthalic acids, derivatives and mixtures thereof are present in the lubricant composition according to the invention in a minor portion, sufficient to inhibit corrosion. Generally, amounts up to about 1.0% by weight of the lubricant are very satisfactory, since they give the desired corrosion inhibition without undesirable physical changes such as thickening of the lubricant composition. For present purposes, 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.

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 phthalic acid 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.

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 fumaric polymer, dilauryl 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 and phosphorus including tricryesyl 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, V. I. improvers, antifoaming agents, rust inhibitors, corrosion 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 corrision 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 as generally compounded for internal combustion engine use are unusually corrosive to metal surfaces and are thus most greatly benefited by the addition of the particular hexahydrophthalic acids and their ammonium salts.

A number of corrosion-inhibited lubricating oil compositions containing m- and p-hexahydrophthalic acids or their derivatives as the corrosion inhibitor were prepared according to the procedures described above. Several different compositions exemplifying various types of corrosion inhibitors according to the invention and their effectiveness in standard lubricating oil tests for determining corrosion inhibition are listed in the following tables.

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:

0.008% by weight ---------- Iron
0.004% by weight ---------- Lead
0.002% by weight ---------- Copper
0.0005% by weight ---------- Manganese
0.004% by weight ---------- Chromium

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 test oils employ as the reference oil a conventional compounded oil, namely, 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. Illustrative test results are shown in the following table. The concentrations of hexahydrophthalic acid

or derivative or mixtures thereof employed are given in percent by weight of the composition.

TABLE I

Copper-lead strip corrosion test

Additive and Oil	Copper-Lead Strip Weight Loss (Mg.)
None—reference oil alone	250-300
0.2% Dimethyl-m-hexahydrophthalic acid	168.9
0.04% p-(Trans)hexahydrophthalic acid	10.0
0.04% p-(Cis)hexahydrophthalic acid	32.6
0.05% p-(Cis)hexahydrophthalic acid	23.6
0.10% p-(Cis)hexahydrophthalic acid	18.4
0.20% p-(Cis)hexahydrophthalic acid	48.7
0.05% m-Hexahydrophthalic acid	31.7
0.01% m-Hexahydrophthalic acid	52.0
0.02% p-Hexahydrophthalic acid	21.5
0.03% p-Hexahydrophthalic acid	16.6
0.05% Orthohexahydrophthalic acid	239.9
0.05% p-(Trans)hexahydrophthalic acid	15.9
0.1% p-(Trans)hexahydrophthalic acid	15.2
0.05% m-(mixed Cis and Trans)hexahydrophthalic acid	38.8
0.2% Di(n-octadecyl ammonium)p-hexahydrophthalate-(trans)	67.8
0.2% Mono(n-octadecyl ammonium)p-hexahydrophthalate(cis)	67.0
0.3% Di(dioctadecyl ammonium)p-hexahydrophthalate-(cis)	36.0
0.3% Di(isooctadecyl ammonium)p-hexahydrophthalate-(cis)	47.2
0.2% Di(n-octadecyl ammonium)p-hexahydrophthalate-(cis)	8.5
0.2% Mono(n-octadecyl ammonium)m-hexahydrophthalate(trans and cis mixed)	58.5
0.2% Di(n-octadecyl ammonium)m-hexahydrophthalate (trans and cis mixed)	85.8

The above test data show that the reference oil, a conventional compounded lubricating oil containing representative heavy duty lubricating oil additives and stabilizers, when used alone gives a high copper-lead strip loss of from 250 to 300 mg. By way of distinction, compositions in accordance with this invention employing as little as 0.1% or less of m- or p-hexahydrophthalic acid, its derivatives or mixtures thereof give surprisingly low corrosion losses of as little as 8.5 mg. As already mentioned, the p-hexahydrophthalic acid and its derivatives are generally superior to the corresponding m-isomers and are more preferred for that reason. In every case, however, the m- and p-hexahydrophthalic acids or derivatives are greatly superior to the corresponding ortho-hexahydrophthalic acid or its derivatives.

Particularly suitable derivatives of m- and p-hexahydrophthalic acid as shown by their effectiveness in the above table of test results are the N-alkyl ammonium salts containing a total of from 18 to 72 carbon atoms in the alkyl groups. From 8 to 24 carbon atoms in each of the alkyl groups are generally preferred for optimum solubility.

Although the improved lubricant compositions in accordance with this invention have been described above primarily as internal combustion engine lubricants, they are also suitable for other applications. Such applications include, by way of illustration, their use as gear lubricants, turbine oils, ice machine oils, instrument lubricants and constituent oils in grease manufacture.

This application is a continuation-in-part of Lowe and Stewart patent application Serial No. 478,517, filed December 29, 1954, now abandoned.

We claim:

1. A lubricant 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 a member of the group consisting of m-hexahydrophthalic acid and p-hexahydrophthalic acid and ammonium and N-alkyl ammonium salts thereof having alkyl groups of up to 24 carbon atoms each, said minor portion of lubricating oil detergent additive being sufficient to suspend said member in the mineral lubricating oil.

2. A lubricant 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 m-hexahydrophthalic acid, said minor portion of alkaline earth metal petroleum sulfonate and alkaline earth metal alkyl phenate being sufficient to suspend said m-hexahydrophthalic acid in the mineral lubricating oil.

3. A lubricant 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-hexahydrophthalic acid, said minor portion of alkaline earth metal petroleum sulfonate and alkaline earth metal alkyl phenate being sufficient to suspend said p-hexahydrophthalic acid in the mineral lubricating oil.

4. A lubricant 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 m-hexahydrophthalic acid, said minor portion of calcium petroleum sulfonate being sufficient to suspend said m-hexahydrophthalic acid in the mineral lubricating oil.

5. A lubricant 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 m-hexahydrophthalic acid, said minor portion of calcium petroleum sulfonate and calcium alkyl phenate being sufficient to suspend said m-hexahydrophthalic acid in the mineral lubricating oil.

6. A lubricant 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-hexahydrophthalic acid, said minor portion of calcium petroleum sulfonate and calcium alkyl phenate being sufficient to suspend said p-hexahydrophthalic acid in the mineral lubricating oil.

7. A lubricant 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 di(n-octadecyl ammonium)p-hexahydrophthalate, said minor portion of calcium petroleum sulfonate and calcium alkyl phenate being sufficient to suspend said di(n-octadecyl ammonium)p-hexahydrophthalate in the mineral lubricating oil.

References Cited in the file of this patent

UNITED STATES PATENTS

2,134,736	Reuter	Nov. 1, 1938
2,158,096	Werntz	May 16, 1939
2,280,474	Byrkit	Apr. 21, 1941
2,595,169	Rudel	Apr. 29, 1952