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P-XYLYLENEDIAMINE SALTS OF GLYCOL BORIC ACIDS

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4 Claims. (Cl. 260—462)

This invention relates to a new class of amine salts. More particularly, the invention is concerned with a novel class of amine salts of glycol borates having superior corrosion inhibiting properties.

The present application is a division of Warren Lowe application Serial No. 477,955, filed December 27, 1954, and is specifically concerned with a superior new class of glycol and polyhydroxybenzene borate amine salts.

During their normal service, lubricating oil compositions tend to become corrosive to metals. This is particularly so when they are employed in modern internal combustion engines which are operated under conditions involving increased temperature changes, higher speeds and reduced clearances, all of which conditions aggravate the formation of corrosive decomposition products in the oil. Alloy metal bearings commonly employed in such engines make the problem all the more serious, since they are especially subject to corrosive attack and furthermore, may have a catalytic effect on the decomposition of lubricating oils with which they come into contact, thereby causing additional corrositivity in the oil.

The addition of inhibitors to lubricating oil compositions, generally, for the purpose of improving their resistance to the formation and effect of corrosive products has not been entirely satisfactory. A great many of these additives are only moderately effective and permit the bearings and other metal surfaces coming into contact with the lubricating oil composition to be slowly but eventually corroded to a degree where interruption of engine operation for overhaul and replacement of parts becomes necessary. Furthermore, many of the more effective additives are active only for a limited period and require replenishing or a complete change of the lubricating oil composition. Still other additives, although effective as corrosion inhibitors, are so insoluble in oils of lubricating viscosity that special solubilizing or dispersing agents are necessary to retain them in the composition.

Corrosion inhibitors for lubricating oil compositions are further handicapped by the fact that oils of this type are commonly compounded with other additives such as detergents, sludge inhibitors and the like which are designed to loosen, suspend and otherwise minimize the effect of decomposition products formed in the oils during their normal service. Many of these compounding agents, besides adding to the corrosivity of the oil themselves, have an adverse effect on the activity of the corrosion inhibitors employed heretofore, and it is necessary to find inhibitors which will function in combination with them.

Furthermore, additives for the inhibition of oxidation or corrosion in lubricating oil compositions prior to this invention have generally contained some form of active sulfur. This has made such compositions undesirable for the lubrication of silver and similar metal-containing bearings which are especially susceptible to attack by active sulfur. Since silver and similar metal-containing bearings are being increasingly employed today, particularly in certain important classes of internal combustion engines such as marine and railroad diesel engines, it has become necessary to find a lubricant composition which is inhibited against corrosion without the use of sulfur-containing additives.

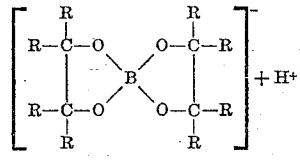
According to the present invention, a new and unusually effective compound having improved corrosion inhibiting properties has been found consisting of a p-xylylenediamine salt of an acid compound selected from the group consisting of glycol boric acids and vicinal dihydroxybenzene boric acids.

The new lubricating oil composition containing a new corrosion inhibiting amine salt in accordance with the present invention is characterized by remarkable corrosion inhibiting properties for metal surfaces and alloy bearings over extended periods of operation. The composition is unusually stable under normal operating conditions without the use of stabilizers and dispersing agents. There is no reduction of corrosion inhibition due to deposition of the additive. A further outstanding characteristic of the composition, however, lies in the fact that these beneficial properties are obtained without adverse effect from other conventional additives commonly employed in lubricant compositions. The lubricating oil compositions containing a new corrosion inhibiting amine salt of the invention possess still another advantage in that they are unusually effective lubricants for particular alloy metal bearings such as the silver metal-containing bearings of marine and railroad diesel engines.

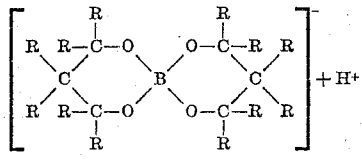
The p-xylylenediamine salts of glycol boric acids or vicinal dihydroxybenzene boric acids which provide the new and unusually effective corrosion inhibited lubricating oil compositions according to the invention are novel compounds. They are prepared by the addition of p-xylylenediamine to the glycol boric acid or vicinal dihydroxybenzene boric acid. The reaction is straightforward, and the salt is obtained merely by heating a mixture of p-xylylenediamine and the glycol boric acid or vicinal dihydroxybenzene boric acid at a temperature at which reaction occurs until the reaction is complete. Stoichiometric amounts of p-xylylenediamine are reacted with the glycol boric acid or vicinal dihydroxybenzene boric acid. Preferably molar excesses of p-xylylenediamine up to 30% or more are used to insure complete reaction. Temperatures of from about 50° C. to about 80° C. are preferred, although some reaction will occur at temperatures below and above this range, as, for example, from 25° C. up to 100° C. and higher. Inert solvents may be used, if desired, in the reaction to facilitate the handling of materials.

The glycol boric acids and vicinal dihydroxy benzene boric acids referred to above are complexes prepared by the reaction of a mixture of boric acid and glycol or polyhydroxybenzene. 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-

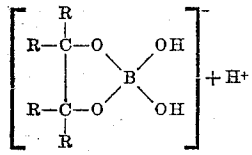
benzene react with the boric acid to form what is commonly termed a "metal chelate compound." These compounds are characterized by a "claw" type of structure in which one or more rings of a similar or unlike structure due to the use of mixed glycols or polyhydroxybenzenes are formed to include the boron. For convenience, the structure of the compounds may be illustrated by the following formulae:



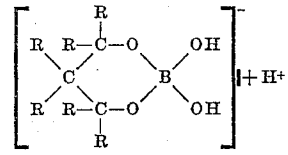
Di-alpha-glycol borates



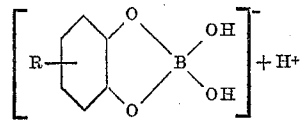
Di-beta-glycol borates



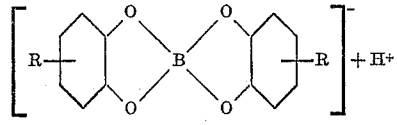
Mono-alpha-glycol borates



Mono-beta-glycol borates



Mono-pyrocatechol borates



Di-(pyrocatechol) borates

wherein R is hydrogen or a group of hydrocarbon structure as hereinafter defined.

The glycols which are reacted with the boric acid are preferably α- and β-alkanediols 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-pentanediol, 1,2- and 1,3-octylene glycols including 2-ethyl-1,3-hexanediol, 1,2-dodecanediol, 2,4-diethyl-1,3-octanediol, and 2,4,6-triethyl-1,3-decanediol. Glycols containing from 6 to 10 carbon atoms are more preferred, since they impart an optimum degree of oil solubility to the final product. α- and β-octylene glycols such as 2-ethyl-1,2-hexanediol and 2-ethyl-1,3-hexanediol are most satisfactory for present purposes.

The polyhydroxybenzenes 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 compounds prepared from them possess the most satisfactory oil solubility characteristics.

The acid compounds of boric acid and glycols or polyhydroxybenzenes referred to above are more fully described in the co-pending patent application of John R. Thomas and Oliver L. Harle, Serial No. 440,264, filed June 29, 1954, now Patent No. 2,795,548. The p-xylylenediamine is a known compound and may be conveniently obtained by the conversion of terephthalic acid to terephthalodinitrile, which may then be hydrogenated to give the p-xylylenediamine.

The p-xylylenediamine salt of the acid compound of boric acid and a member selected from the group consisting of glycols and vicinal polyhydroxybenzenes, as already mentioned, is present in the lubricating oil composition in a minor portion, sufficient to inhibit corrosion. Generally, amounts from 0.01 to about 10.0% by weight of the lubricating oil composition are very satisfactory. Lubricating oil concentrates containing larger amounts of the corrosion inhibitor, up to 30% by weight or more, constitute a specific embodiment of the invention. The unusual stability of these lubricating oil compositions is particularly adapted to the preparation of such concentrates which would not be possible with conventional additives. For present purposes, the preferred lubricating oil compositions contain from about 0.1 to 5.0% by weight. Such compositions are unusually stable and provide remarkably effective corrosion inhibition for extended periods in the operation of internal combustion engines.

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.

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, 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.

The following examples are submitted as additional 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

In this example the p-xylylenediamine salt of di(2-ethyl-1,2-hexanediol) boric acid was prepared. 1.36 parts of p-xylylenediamine and 3.06 parts of di(2-ethyl-1,2-hexanediol) boric acid were charged to a reaction vessel equipped with stirring and heating means. The mixture was stirred at 200° F. for about 10 minutes. The product was a viscous brown liquid which was soluble in mineral oil.

EXAMPLE II

In this example a lubricating oil composition containing 1% by weight of the p-xylylenediamine salt of di(2-ethyl-1,2-hexanediol) boric acid was prepared. 346.5 parts of a solvent refined SAE 30 mineral lubricating oil containing 10 mM./kg. basic calcium petroleum sulfonate analyzing 1.67% calcium and 36 mM./kg. sulfurized basic calcium alkyl phenate analyzing 3.10% calcium was charged to a reaction vessel equipped with stirring and heating means. 3.5 parts of the p-xylylenediamine salt of di(2-ethyl-1,2-hexanediol) boric acid prepared in Example I was then added. The mixture was stirred at about 160° F. for 20 minutes. The product was a stable lubricating oil composition completely clear in appearance indicating uniform miscibility of lubricating oil base and corrosion inhibitor.

Other p-xylylenediamine salts of glycol boric acid compounds and lubricating oil compositions containing them were prepared in accordance with the above-described procedures. The properties of these compositions and their effectiveness are illustrated by the following typical results of standard lubricating oil tests for determining corrosion inhibition. 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 reference oil of the compositions tested is a conventional compounded oil, namely, solvent refined SAE 30 mineral lubricating oil containing 10 mM./kg. of basic calcium petroleum sulfonate analyzing 1.67% calcium and 36 mM./kg. of sulfurized basic calcium alkyl phenate analyzing 3.10% calcium. The concentrations of p-xylylenediamine salt of the glycol borate complex are given in percent by weight of the composition.

Table

COPPER-LEAD STRIP CORROSION TEST

Additive	Copper-Lead Strip Weight Loss (mg.)
None—refernece oil alone	250-300
2.0% di(2-ethyl-1,3-hexanediol) boric acid	354
2.0% m-xylylenediamine salt of di(2-ethyl-1,3-hexanediol) boric acid	102.6
2.0% phenyl α-naphthylamine salt of di-(2-ethyl-1,3-hexanediol) boric acid	127.1
2.0% di(diethylaminoethyl) phenol salt of di(2-ethyl-1,3-hexanediol) boric acid	139.3
1.0% p-xylylenediamine salt of di(2-ethyl-1,3-hexanediol) boric acid	7.4
2.0% di(1,2-hexanediol) boric acid	350
1.0% p-xylylenediamine salt of di(1,2-hexanediol) boric acid	12.7

The above tests show that the reference oil, a conventional compounded lubricating oil containing a representative heavy duty oil detergent additive of the alkaline earth metal petroleum sulfonate type and stabilizer of the alkaline earth metal phenate type, when used alone, gives a copper-lead strip loss of over 250 mg. The addition of 2% by weight of di(2-ethyl-1,3-hexanediol) boric acid to the reference oil in the test causes an even greater copper-lead strip loss of about 354 mg. By way of distinction, lubricating oil compositions in accordance with the invention employing only 1% of the p-xylylenediamine salt of the glycol boric acid give a very low corrosion loss of only 7.4 mg. Such outstanding effectiveness of the present compositions is all the more remarkable, since it is not shared by similar compositions containing other amine salts of glycol and catechol boric acids, including the isomeric m-xylylenediamine salt.

Although the lubricating oil compositions of the invention have been described primarily for their effectiveness as internal combustion engine lubricants, a great many other applications are also possible. Such applications include their use as turbine oils, hydraulic fluids, instrument oils, constituent oils in grease manufacture, ice machine oils and the like.

I claim:

1. A p-xylylenediamine salt of a diglycol boric acid in which the glycol groups are identical α- and β-glycol groups and contain from 6 to 10 carbon atoms in each glycol group.

2. A p-xylylenediamine salt of a di-(α-alkanediol) boric acid in which the alkanediol groups are identical and contain from 6 to 10 carbon atoms each.

3. A p-xylylenediamine salt of di(2-ethyl-1,3-hexanediol) boric acid.

4. A p-xylylenediamine salt of di-(1,2-hexanediol) boric acid.

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