

1

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CORROSION INHIBITED LUBRICANT COMPOSITION

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This invention relates to a superior new corrosion inhibited lubricant composition. More particularly, the invention is concerned with a novel lubricating oil composition having improved corrosion inhibiting properties compared to similar compositions of the prior art.

Lubricating oils in general have a tendency to form decomposition products due to oxidation. Many of these decomposition products are highly corrosive to metals. Since lubricating oils during normal use come into contact with metal surfaces, the problem of controlling this corrosivity is one of major importance.

The decomposition and formation of corrosive products in lubricating oils are promoted in particular by the increased temperatures, higher speeds and reduced clearances which are commonly encountered in modern internal combustion engines today. Such engines also generally employ alloy metal bearings which are not only subject to corrosive attack, but also exert a possible catalytic effect on the decomposition of the oil.

Present day lubricating oils for internal combustion engines are also commonly compounded with agents such as detergents, sludge inhibitors, wear inhibitors and the like which are designed to loosen and suspend products of decomposition and counteract their effect. Many of these agents add to the corrosivity of the decomposition products and also have an adverse effect on the efficiency of the oxidation and corrosion inhibitors. It therefore becomes necessary to find inhibitors which will function in combination with conventional detergents and sludge inhibitors in lubricating oil compositions.

Oxidation and corrosion inhibitors which have been added to lubricating oils heretofore to improve their resistance to decomposition and corrosivity usually contain active sulfur in some form. Compositions containing such inhibitors are generally unsuitable for use with silver bearings and the like which are subject to attack by active sulfur. Although at one time this would have been only a minor problem, today the increasing use of silver alloy metal bearings in important classes of internal combustion engines such as marine and railroad diesel engines emphasizes the need for corrosion inhibitors which do not depend on active sulfur-containing compounds for their effectiveness.

Improved corrosion inhibited lubricating oil compositions comprising lubricating oil and a phthalic acid have been prepared which have many advantages over previously known lubricant compositions containing conventional corrosion inhibitors. These compositions are described in Lowe and Stewart application Serial No. 478,517 and Stewart and Lowe application Serial No. 478,538, both of which were filed December 29, 1954, both now abandoned. Other unusually effective corrosion inhibited lubricant compositions containing titanic acid complexes of glycols and polyhydroxy benzenes have also been described in Lowe application Serial No. 440,280, filed June 29, 1954.

A superior new lubricant composition has now been

2

found comprising a major portion of an oil of lubricating viscosity and a minor portion, sufficient to inhibit corrosion, of the reaction product of a phthalic acid selected from the group consisting of isophthalic acid and terephthalic acid reacted with a titanic acid complex of a member of the group consisting of glycols and polyhydroxy benzenes. This new lubricant composition has enhanced anticorrosion properties which are substantially superior to such properties of similar compositions employed heretofore as discussed above.

The lubricant compositions according to this invention containing the combination of phthalic acid and titanic acid complex of glycol or polyhydroxy benzene are surprisingly more effective in the inhibition of corrosion than lubricant compositions containing either of these additives alone. This is all the more remarkable in view of the fact that lubricant compositions containing the phthalic acid and titanic acid complexes of glycols and polyhydroxy benzenes individually have heretofore been considered outstanding corrosion inhibitors over which improvement would be exceedingly difficult.

The compositions of the invention are further distinguished in that they may contain much larger amounts of the very effective phthalic acid corrosion inhibitor in stable form than are possible with lubricant compositions containing it alone. Isophthalic acid and terephthalic acid, although excellent corrosion inhibitors, are in general very sparingly soluble in oils of lubricating viscosity, and the incorporation of effective amounts of such inhibitors in lubricant compositions presents a problem. Suspending agents such as lubricating oil detergent additives may be necessary to maintain the phthalic acids in stable form in the lubricant compositions. The reaction products of isophthalic acid and/or terephthalic acid with titanic acid complexes which are employed in the lubricant compositions according to this invention have greatly improved solubility characteristics compared to the phthalic acids themselves. Much larger and more effective proportions of the phthalic acid and titanic acid complex reaction product corrosion inhibitor may thus be readily incorporated without the need of suspending agents to give lubricant compositions capable of providing corrosion inhibition over extended periods of operation.

The improved lubricant compositions of the invention definitely inhibit the tendency of oils to be corrosive to metal surfaces. When employed in the form of internal combustion engine lubricants which are normally corrosive to alloy metal bearings, it is found that the lubricant compositions of the invention are substantially non-corrosive to the bearings, even under the more stringent operating conditions encountered in these internal combustion engines.

The lubricant compositions have a further more particular advantage in that they are free of active sulfur and are, therefore, ideally suited for use with important classes of internal combustion engines such as railroad and marine diesel engines which employ alloy bearings of silver and similar metals that are subject to attack by active sulfur.

The novel corrosion inhibited lubricating oil compositions of the invention are also outstanding in that they may be compounded with additional agents such as detergents, sludge inhibitors and wear inhibitors without adversely affecting their corrosion inhibiting properties. The compositions also apparently act as metal deactivators for the common bearing metals such as copper and lead which usually accelerate the decomposition of lubricating oils.

The reaction product of isophthalic acid and/or terephthalic acid with the titanic acid complex is obtained by mixing the phthalic acid and titanic acid complex to-

gether. The reaction proceeds readily at room temperature (about 75° F.). However, heating the mixture to temperatures of from about 100° F. to about 300° F. is preferred to accelerate the reaction and insure completion.

The titanac acid complexes of glycols and polyhydroxy benzenes may be any of those described in Lowe application Serial No. 440,280. These compounds are characterized by a "claw" type of structure in which one or more rings of similar or unlike structure, due to the use of mixed glycols or polyhydroxy benzenes, are formed to include the titanium. Such compounds are commonly termed "metal chelates" in published literature. Although these compounds are referred to as "titanic acid complexes" for convenience, it is not necessary that they be formed by the reaction of titanac acid and glycol or polyhydroxy benzene. As a matter of actual practice, for present purposes, it is preferred to prepare the titanac acid complexes by mixing the more reactive titanac acid derivatives such as the titanium tetrahalides or titanium tetraalkyl esters with glycol or polyhydroxy benzene. The mixtures are ordinarily heated to accelerate the reaction.

As mentioned in the patent application of Lowe referred to above, the glycols which are reacted with the titanac acid derivative are preferably α and β -alkane diols containing from 2 to 18 carbon atoms. Examples of these glycols include ethylene glycol, pentanediol-1,3,2-ethylhexanediol-1,3, 2,4,6-triethyldecandiol-1,3 and the like. The glycols of from 6 to 10 carbon atoms are preferred, since they import an optimum degree of oil solubility to the glycol titanate reaction product with isophthalic acid and/or terephthalic acid and provide lubricant compositions which are unusually effective in the inhibition of corrosion.

The polyhydroxy benzenes are most suitably the vicinal dihydric phenols such as catechol, tertiary butylcatechol and the like. Alkyl catechols containing from 2 to 18 carbon atoms in the alkyl groups are presently preferred, since they produce the most effective titanates in combination with phthalic acids.

The phthalic acid may be any of the phthalic acids referred to in the Lowe and Stewart application Serial No. 478,517 and Stewart and Lowe application Serial No. 478,538 already mentioned. For present purposes, terephthalic acid and isophthalic acid, particularly the latter, are preferred for the highly effective corrosion inhibiting lubricant compositions which are obtained when they are combined with titanac acid complexes in accordance with this invention.

The combination of phthalic acid and titanac acid complex of glycols and polyhydroxy benzenes is present in the lubricant compositions of the invention in amounts at least sufficient to inhibit corrosion. Small amounts, usually from about 0.01 to 10.0% by weight, based on the oil, are particularly suitable. Proportions ranging from about 0.5 to about 5.0% are preferred in most lubricating oil compositions to take advantage of enhanced solubility and provide the highest degree of effectiveness. Concentrates containing larger proportions, up to 50%, either in solution or suspension are useful in compounding operations. In this latter respect, the present invention finds particular utility, since increased amounts of phthalic acid may be incorporated due to their enhanced solubility in the form of the phthalic acid and titanac acid complex combinations.

The combination of phthalic acid with the titanac acid complex of glycols or polyhydroxy benzenes in the compositions of this invention includes a wide range of relative proportions of the phthalic acid and titanac acid complexes, since in any such combination the performance of either inhibitor will be enhanced by the addition of any amount of the other inhibitor. The more suitable ratios of titanac acid complex to phthalic acid, however, lie in the range of from about 0.5 to about 5 moles of titanac acid complex to 1 mole of phthalic acid. Preferably, with the superior terephthalic acid and isophthalic acid com-

binations referred to above, the ratios lie in the range of from about 2 to about 5 moles of titanac acid complex for each mole of phthalic acid.

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 ethers and esters 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, dilauryl 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.

The corrosion inhibiting compositions of this invention are also 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. These compounded oils in normal use are generally corrosive to metal surfaces and alloy metal bearings in particular, and it is an exceptional attribute to 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.

A preferred embodiment of the present invention lies in the provision of a particularly effective lubricant composition comprising a major portion of a mineral lubricating oil in combination with 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 the reaction product of a phthalic acid selected from the group consisting of isophthalic acid and terephthalic acid with a titanac acid complex of glycols containing from 6 to 10 carbon atoms each. The sulfonates and phenates are present in any amounts sufficient to render the combination corrosive but most suitably in amounts of from about 0.1% to about 10% by weight of each, based on the compositions. Calcium and barium are illustrative of the alkaline earth metals. Such compositions are outstandingly effective as lubricants for internal combustion engines.

The following examples are submitted as additional illustrations of the invention. These examples show the preparation of the reaction products of the invention and 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.

5

EXAMPLE I

This example illustrates the preparation of the reaction product of isophthalic acid with dihydroxy di(octylene glycol)titanate in 1:2 molar ratio.

Into a one-liter, three-necked flask is charged 148.8 grams of 50% by weight dihydroxy di(octylene glycol)-titanate in cyclohexane solvent, 16.6 grams of isophthalic acid, 50 ml. ethanol and 100 ml. benzene. The flask is fitted with a thermometer, reflux condenser and stirrer. The mixture is heated to 120° F. at which point it becomes homogeneous. After stirring vigorously at reflux temperature for about two hours, the solvents are stripped off by distillation up to 350° F. at a pressure equal to about 2 mm. mercury. The reaction product obtained as residue is a yellow, tacky solid material.

4 grams of crude reaction product obtained above is dissolved in about 50 ml. of benzene at room temperature. 200 ml. of acetone is added to precipitate out a white, powdery material. 2.26 grams of the white, powdery material is thus recovered, amounting to a yield of 56.2% by weight based on the crude reaction product. This material has the following analysis:

Percent Ti=16.9, 16.2
Percent C=50.38, 51.33
Percent H=7.30, 7.01
Percent O=24.42, 25.46

The white powder melts at a temperature of about 200° F.

EXAMPLE II

The preparation of the reaction product of isophthalic acid with butyl tri(octylene glycol)titanate in 1:2 molar ratio is illustrated in this example.

55.68 grams butyl tri(octylene glycol)titanate (60% active in butyl alcohol), 4.98 grams of isophthalic acid, 20 ml. ethylether and 40 ml. benzene are charged into a 250 ml. glass reaction flask. The mixture is stirred on a steam plate at a temperature of about 200° F. until it becomes homogeneous. The ether, benzene and butyl alcohol are evaporated by continued heating on a steam plate during which nitrogen gas is bubbled through the reaction mixture. The product thus obtained as a residue is a yellow, resinous material having a softening point of about 212° F. The enhanced solubility of the product compared to the reactants is shown in the following table:

Material	Benzene
Isophthalic acid.....	Insol.
Butyl tri (octylene glycol) titanate.....	Sol.
Reaction product.....	Sol.

From the above table it can be seen that the reaction product is soluble in hydrocarbons, whereas the isophthalic acid is insoluble.

EXAMPLE III

This example illustrates the preparation of the reaction product of isophthalic acid with butyl tri(octylene glycol)-titanate in 1:2 molar ratio and its incorporation into a lubricant composition.

Into a one-liter, three-necked flask equipped with thermometer, reflux condenser, stirring means and addition funnel is charged 218 grams butyl tri(octylene glycol)-titanate as a 60% solution in butanol, 19.5 grams isophthalic acid, 100 ml. isopropanol and 400 ml. benzene. The mixture is homogeneous at about 120° F. It is stirred vigorously at reflux temperature for about 2 hours. Following this the solvents are stripped off by heating to 350° F. at a pressure of about 2 mm. mercury. The residue is a yellow, tacky material which is readily soluble in ethylether.

The material is combined with a compounded internal combustion engine oil consisting of a solvent refined SAE

6

40 mineral lubricating oil-base having a viscosity index of 60 and containing 10 mM./kg. of calcium petroleum sulfonate and 20 mM./kg. of calcium alkyl phenate. This lubricant composition when tested in the copper-lead strip corrosion test and L-4 strip corrosion test, as described more particularly below, is found to be very effective in the inhibition of corrosion.

EXAMPLE IV

In this example the preparation of a lubricant composition containing the combination of isophthalic acid with butyl tri(octylene glycol)titanate is illustrated.

Into a two-liter, three-necked reaction flask is charged 43.5 grams of isophthalic acid (85% by weight isophthalic acid and 15% by weight terephthalic acid). The flask is equipped with thermometer, reflux condenser, stirring means and addition funnel. 486.5 grams of butyl tri(octylene glycol)titanate in butanol analyzing 60% active ingredient and 40% butanol is then added. 1008 grams of a solvent refined mineral lubricating oil and 250 ml. of ethyl ether are added. The mixture is stirred at reflux temperature, which is about 95° F., for about two hours. The solvents (ethyl ether and butanol) are slowly distilled off under a reduced pressure equal to about 3 mm. mercury. The reaction flask is then heated to about 250° F. at the same pressure.

1340 grams of oil concentrate is produced by the above process. It contains butyl trioctylene glycol titanate and isophthalic acid combined in a mole ratio of about 2 to 1. It is perfectly clear in appearance at room temperature, indicating that the isophthalic acid is present in a completely stable form. 2.56% by weight of the product in lubricating oil yields a composition containing 10 mM./kg. of titanium in the form of combined butyl trioctylene glycol titanic acid complex and isophthalic acid.

Additional lubricating oil compositions containing different titanic acid complexes and phthalic acids in accordance with the invention are prepared according to the procedure of the above example. Several illustrative compositions of these types are further referred to in the examples which follow.

In comparison it is noted that the isophthalic acid and terephthalic acid are much less soluble in the lubricating oil compositions than the superior new reaction products of isophthalic acid or terephthalic acid with the titanic acid complexes. For practical purposes, the maximum isophthalic acid or terephthalic acid that can be incorporated into the lubricant compositions runs about 0.3% by weight, whereas the reaction products of the phthalic acids with the titanic acid complexes used in the lubricant compositions of this invention may be present in amounts of about 1.0% or more to provide greater, more effective corrosion inhibition over a longer life.

The effectiveness of the lubricating oil compositions of the invention is also shown by their performance in the Copper-Lead Strip Corrosion Test. In this test a polished copper-lead strip is weighed and immersed in 300 ml. of test oil in a 400 ml. lipless Berzelius beaker. The test oil is maintained at 340° F. and stirred with a mechanical stirrer at 1000 R. P. M. After two hours a synthetic naphthenate catalyst is added to provide the catalytic metals commonly occurring in internal combustion engines. 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 a representative compounded mineral lubricating oil of the internal combustion engine type which is normally corrosive to alloy metal bearings. In this case the compounded oil consists of a solvent refined SAE 40 mineral lubricating oil base having a viscosity index of 60 and containing 10 mM./kg. of calcium petroleum sulfonate and 20 mM./kg. of calcium alkyl phenate. The results of the test are shown in the following table. The concentrations of corrosion inhibitor are given in percent by weight of the lubricant composition.

7
Table I

COPPER-LEAD STRIP CORROSION TEST

Additive	Copper-Lead Strip Weight Loss (mg.)
None—compounded oil alone.....	253.1
0.6% Butyl tri(octylene glycol)titanate in compounded oil.....	14.0
0.6% Tetra(octylene glycol)titanate in compounded oil.....	27.1
0.5% Butyl tri(octylene glycol)titanate and isophthalic acid in compounded oil (Example III).....	6.1
0.75% Butyl tri(octylene glycol)titanate and isophthalic acid in compounded oil (Example III).....	7.5
1.0% Butyl tri(octylene glycol)titanate and isophthalic acid in compounded oil (Example III).....	7.1
1.0% Butyl tri(octylene glycol)titanate and isophthalic acid (2 to 1 mole ratio) in compounded oil.....	7.1
1.0% Butyl tri(octylene glycol)titanate and terephthalic acid (2 to 1 mole ratio) in compounded oil.....	7.7
1.0% Tetra(octylene glycol)titanate and isophthalic acid (2 to 1 mole ratio) in compounded oil.....	4.4
1.0% Tetra(alkylene glycol)titanate and terephthalic acid (2 to 1 mole ratio) in compounded oil.....	8.4
0.5% Butyl tri(octylene glycol)titanate and isophthalic acid (2 to 1 mole ratio) in compounded oil.....	7.6
0.3% isophthalic acid (15% terephthalic acid) in compounded oil.....	13.8

The above test data show that typically compounded mineral lubricating oils for internal combustion engines will give copper-lead strip weight losses in excess of 250 mg. On the other hand, compositions containing the same compounded mineral lubricating oil in combination with phthalic acid and titanic acid complexes in accordance with the present invention give remarkably low weight losses of as little as 4.4 mg. Such results are surprising, since they are substantially lower than the weight losses occurring when either phthalic acid or titanic complex is employed alone, even though these particular corrosion inhibitors have been considered particularly outstanding heretofore. In comparison with the remarkably effective new lubricant compositions of the invention, the test results show that about 200% more corrosion is obtained in lubricant compositions which employ the maximum practical amounts of isophthalic acid and terephthalic acid of about 0.3%.

In another test which is a modified version of the copper-lead strip corrosion test described above, the effectiveness of the corrosion inhibited lubricant compositions according to this invention in respect to rubbing surfaces is demonstrated. In this test, which is commonly termed the interrupted copper-lead strip corrosion test, the same procedure is followed as in the copper-lead strip corrosion test, except that the test is interrupted at four-hour intervals to insert a new copper-lead strip. The test results are then given in the cumulative weight loss of all the strips. By changing the strips during the test, a fresh, clean metal surface is periodically exposed to the corrosion inhibited composition. Thus, the wiping effect obtained in rubbing metal surfaces such as bearings is simulated, and it is shown what happens when any protective film laid down on the metal surface during operation is removed.

Table II

INTERRUPTED COPPER-LEAD STRIP CORROSION TEST

Additive	Total Copper-Lead Strip Weight Loss (mg.)
None—compounded oil alone.....	Approx. 700
2.0% Dibutyl di(octylene glycol)titanate in compounded oil.....	269
1.0% Butyl tri(octylene glycol)titanate and isophthalic acid (2 to 1 mole ratio) in compounded oil.....	14.2
1.0% Tetra(octylene glycol)titanate and terephthalic acid (2 to 1 mole ratio) in compounded oil.....	8.9

The test results reproduced in the above table demonstrate the effectiveness of lubricant compositions according to the invention under conditions where any protective coatings formed by the corrosion inhibitors on the

metal surfaces are removed, as they would be by rubbing action in the case of bearings during actual operation of internal combustion engines. The results show that the compositions containing combined phthalic acid and titanic acid complexes are surprisingly superior to compositions containing titanic acid complex alone.

The lubricating oil compositions illustrative of the invention are also evaluated for their effectiveness as inhibitors in gasoline-type internal combustion engines. This test is termed the "L-4 strip corrosion test" because of its correlation with the L-4 Chevrolet engine test referred to in the CRC Handbook, 1946 edition, Co-ordinating Research Council, New York, New York. In the test the same apparatus and conditions as described in the above Copper-Lead Strip Corrosion Test are employed with two essential modifications. The temperature is maintained at 295° F. to simulate lower temperatures encountered in gasoline engines, and a synthetic naphthenate catalyst is used containing lead in further duplication of gasoline engine operation. The reference oils are conventional compounded mineral lubricating oils of the types described in the above tests. The results of the test are as follows:

Table III

L-4 STRIP CORROSION TEST

Additive	Copper-Lead Strip Weight Loss (mg.)
None—compounded oil alone.....	250.0
0.1% Terephthalic acid in compounded oil.....	45.8
0.6% Butyl tri(octylene glycol)titanate in compounded oil.....	13.0
0.5% Butyl tri(octylene glycol)titanate and isophthalic acid in compounded oil (Example III).....	18.8
0.75% Butyl tri(octylene glycol)titanate and isophthalic acid in compounded oil (Example III).....	9.2
1.0% Butyl tri(octylene glycol)titanate and isophthalic acid in compounded oil (Example III).....	4.1
1.0% Butyl tri(octylene glycol)titanate and isophthalic acid (2 to 1 mole ratio) in compounded oil.....	4.1
1.0% Butyl tri(octylene glycol)titanate and terephthalic acid (3 to 1 mole ratio) in compounded oil.....	3.7

The illustrative test results tabulated above show that the lubricant compositions according to this invention are unusually effective under low temperature operating conditions such as those encountered in gasoline internal combustion engines. Although the corrosivity of compounded lubricating oils generally employed in this type of engine ordinarily runs as high as 250 mg. copper-lead strip weight loss, the compositions of the invention containing the combination of phthalic acid and titanic acid complex give strip corrosion losses of as little as 3.7 mg.

In the above examples the octylene glycol was illustrative of the β -alkanediois, namely 2-ethylhexanediol-1,3. The alkyl phenate was cetyl phenate, representative of the well known alkyl phenate lubricating oil additives.

The nature of the improved lubricating oil compositions of the invention and their effectiveness should be readily apparent from the many illustrations given above. Corrosivity in the compositions is definitely inhibited to a very substantial degree. Particularly corrosible 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.

Due to the enhanced solubility of the reaction products of isophthalic acid and/or terephthalic acid with the titanic acid complexes, substantial amounts of the corrosion inhibitor, of 0.5% by weight and more, may be employed in the lubricant compositions according to the inventions. Improvements are thus obtained over similar lubricant compositions containing either the phthalic acid or the titanic acid complexes alone. As shown by the actual tests set out above, the advantages of these improvements are obtained in many different types of engine service

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

I claim:

1. A lubricant composition comprising a major portion of a mineral lubricating oil in combination with 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 the reaction product of 1 mole of a phthalic acid selected from the group consisting of isophthalic acid and terephthalic acid with from about 0.5 to 5 moles of a glycol titanate selected from the group consisting of triglycol and tetraglycol titanates, said glycols containing from 6 to 10 carbon atoms each.

2. A lubricant composition comprising a major portion of a mineral lubricating oil in combination with an alkaline earth metal petroleum sulfonate and an alkaline earth metal alkyl phenate said combination being corrosive to metal surfaces in normal use and from about 0.01 to 5.0% by weight of the reaction product of 1 mole of a phthalic acid selected from the group consisting of isophthalic acid and terephthalic acid with from about 0.5 to 5 moles of a glycol titanate selected from the group consisting of triglycol and tetraglycol titanates, said glycols containing from 6 to 10 carbon atoms each.

3. A lubricant composition comprising a major portion of a mineral lubricating oil in combination with a calcium petroleum sulfonate and a calcium alkyl phenate said combination being corrosive to metal surfaces in normal use and from about 0.01 to 5.0% by weight of the reaction product of 1 mole of a phthalic acid selected from the group consisting of isophthalic acid and terephthalic acid with from about 0.5 to 5 moles of a glycol titanate selected from the group consisting of triglycol

and tetraglycol titanates, said glycols containing from 6 to 10 carbon atoms each.

4. A lubricant composition a major portion of a mineral lubricating oil in combination with a calcium petroleum sulfonate and a calcium alkyl phenate said combination being corrosive to metal surfaces in normal use and from about 0.01 to 5.0% by weight of the reaction product of 1 mole of a phthalic acid selected from the group consisting of isophthalic acid and terephthalic acid with 2 moles of a glycol titanate selected from the group consisting of triglycol and tetraglycol titanates, said glycols containing from 6 to 10 carbon atoms each.

5. A lubricant composition comprising a major portion of a mineral lubricating oil in combination with from about 0.1 to 10% of an alkaline earth metal petroleum sulfonate and from about 0.1 to 10% of an alkaline earth metal alkyl phenate said combination being corrosive to metal surfaces in normal use and from about 0.01 to 5.0% by weight of the reaction product of 1 mole of a phthalic acid selected from the group consisting of isophthalic acid and terephthalic acid with 2 moles of a glycol titanate selected from the group consisting of triglycol and tetraglycol titanates, said glycols containing from 6 to 10 carbon atoms each.

6. A composition comprising a major portion of a mineral lubricating oil in combination with from about 0.1 to 10% by weight of a calcium petroleum sulfonate and from about 0.1 to 10% by weight of a calcium alkyl phenate, said combination being corrosive to metal surfaces in normal use and from about 0.01 to 5% by weight of the reaction product of 1 mole of isophthalic acid heated with 2 moles of butyl tri(octylene glycol)titanate at a temperature of from about 100° F. to about 300° F.

References Cited in the file of this patent

UNITED STATES PATENTS

2,606,872	Gasser	Aug. 12, 1952
2,643,262	Bostwick	June 23, 1953