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METAL-CONTAINING ORGANIC PHOSPHATE COMPOSITIONS

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ABSTRACT OF THE DISCLOSURE

Corrosion of metal surfaces is inhibited by application to such surfaces of a composition comprising in combination (A) the reaction product of a polyvalent metal salt of an acid phosphate ester and an organic epoxide, and (B) a basic metal salt of an oil soluble sulfonic or carboxylic acid.

This invention relates to novel, metal-containing organic phosphate compositions and, more particularly, to a method of inhibiting the corrosion of metal surfaces by the application of such compositions to metal surfaces.

The corrosion of metal articles is of obvious economic significance in many industrial applications and, as a consequence, the inhibition of such corrosion is a matter of prime consideration. It is particularly significant to users of steel and other ferrous alloys. The corrosion of such ferrous metal alloys is largely a matter of rust formation, which in turn involves the overall conversion of the free metal to its oxides.

The theory which best explains such oxidation of ferrous metal articles postulates the essential presence of both water and oxygen. Even minute traces of moisture are sufficient, according to this theory, to induce dissolution of iron therein and the formation of ferrous hydroxide until the water becomes saturated with ferrous ions. The presence of oxygen causes oxidation of the resulting ferrous hydroxide to ferric hydroxide, which settles out of solution and is ultimately converted to ferric oxide or rust.

The above sequence of reactions can be prevented, or at least in large measure inhibited, by relatively impermeable coatings which have the effect of excluding moisture and/or oxygen from contact with the metal surface. It is important, therefore, that these coatings adhere tightly to the metal surface and resist flaking, crazing, blistering, powdering, and other forms of loss of adhesion. A satisfactory corrosion-proofing coating, therefore, must have the ability to resist weathering, high humidity, and corrosive atmospheres such as salt-laden mist or fog, air contaminated with industrial waste, etc., so that a uniform protective film is maintained on all or most of the metal surface.

The rust-profing of small metal parts such as nuts, bolts and screws has been particularly troublesome because of the difficulty of coating the more inaccessible areas of these parts such as the grooves between the threads.

Furthermore, a coating for such small parts must also be inexpensive and easily applied.

It is, therefore, an object of this invention to provide novel metal-containing organic compositions.

It is also an object of this invention to provide a method for inhibiting the corrosion of metal articles.

It is a further object of this invention to provide a means for substantially increasing the corrosion resistance of phosphated metal surfaces.

These and other objects are obtained by providing a composition comprising

(A) a metal-containing organic phosphate complex prepared by the process which comprises the reaction of

(I) a polyvalent metal salt of an acid phosphate ester derived from the reaction of phosphorus pentoxide or phosphoric acid with a mixture of a monohydric alcohol and from about 0.25 to about 4.0 equivalents of a polyhydric alcohol with (II) at least about 0.1 equivalent of an organic epoxide, and

(B) a basic alkali or alkaline earth metal salt of a sulfonic or carboxylic acid having at least about 12 aliphatic carbon atoms, said salt having a metal ratio of at least about 1.1.

Thin films of the composition of this invention are effective in inhibiting the corrosion of metal surfaces, especially phosphated ferrous metal surfaces. Such thin films provide a degree of protection from corrosion hitherto not achieved. The corrosion-inhibiting films may be applied to metal surfaces by any of the ordinary methods such as brushing, spraying, dip-coating, flow-coating, roller-coating, and the like. The viscosity of the corrosion-inhibiting composition may be adjusted for the particular method of application by adding a suitable amount of a solvent such as mineral oil or a volatile diluent such as benzene, xylene, aromatic petroleum spirits and turpentine. The metal surface which has been thus coated is dried either by exposure to air or by means of a baking procedure.

COMPONENT A

As mentioned above, component (A) is a metal-containing organic phosphate complex prepared by the process which comprises the reaction of (I) a polyvalent metal salt of an acid phosphate ester derived from the reaction of phosphorus pentoxide or phosphoric acid with a mixture of a monohydric alcohol and from about 0.25 to about 4.0 equivalents of a polyhydric alcohol with (II) at least about 0.1 equivalent of an organic epoxide. The preparation of these phosphate complexes is described in U.S. Patent No. 3,215,716.

The acid phosphate esters required for the preparation of starting material (I) are made, as indicated, by the reaction of phosphorus pentoxide or phosphoric acid with a mixture of a monohydric alcohol and a polyhydric alcohol. The precise nature of this reaction is not entirely clear, but it is known that a mixture of phosphate esters is formed. This mixture consists principally of acid phosphate esters, i.e., compounds of the general formula:

$$(RO)_xPO(OH)_{3-x}$$

where x equals 1 or 2 and R is an organic radical, although some neutral triesters of the formula $(RO)_3PO$ may also be formed.

The nature and the stoichiometry of the reaction are complicated further in the present invention by the fact that one of the reactants is a polyhydric alcohol. It is possible, therefore, that the polyhydric alcohol forms cyclic and/or polymeric phosphate esters when it reacts with phosphorus pentoxide.

In any event, the acid phosphate esters resulting from the reaction of one mole of phosphorus pentoxide with from about 2 to about 6 equivalents of a mixture of monohydric and polyhydric alcohols are useful in the preparation of starting material (I). The term "equivalent" as used herein reflects the hydroxyl equivalency of the alcohol. Thus, for example, 1 mole of octyl alcohol is 1 equivalent thereof, 1 mole of ethylene glycol is 2 equivalents thereof, annd 1 mole of glycerol is 3 equivalents thereof.

Less than 2 or more than 6 equivalents of alcohol can be used, if desired, in the reaction with one mole of phosphorus pentoxide, although such amounts are not preferred for reasons of economy. When fewer than 2 equivalents of alcohol are used, some unreacted phosphorus pentoxide may remain in the product or precipi-

tate therefrom. On the other hand, when substantially more than 6 equivalents of alcohol are used, unreacted alcohol would be present in the product. For the purpose of the present invention it is generally preferred to employ from about 3 to about 5 equivalents of the alcohol mixture per mole of phosphorus pentoxide (or phosphoric acid).

The monohydric alcohols useful in the preparation of starting material (I) are principally the non-benzenoid alcohols, i.e., the aliphatic and cycloaliphatic alcohols, although in some instances aromatic and/or heterocyclic substituents may be present. Thus, suitable monohydric alcohols are, e.g., propyl, isopropyl, butyl, isobutyl, amyl, hexyl, cyclohexyl, heptyl, methylcyclohexyl, octyl, isooctyl, decyl, lauryl, tridecyl, oleyl, benzyl, beta-phenethyl, alpha-pyridylethyl, etc., alcohols. Mixtures of such alcohols can also be used if desired. Substituents such as, e.g., chloro, bromo, fluoro, nitro, nitroso, ester, ether, sulfide, keto, etc., which do not prevent the desired reaction may also be present in the alcohol. In most instances, however, the monohydric alcohol will be an unsubstituted alkanol.

The polyhydric alcohols useful in the preparation of starting material (I) are principally glycols, i.e., dihydric alcohols, although trihydric, tetrahydric, and higher polyhydric alcohols may also be used. In certain instances, they may contain aromatic and/or heterocyclic substituents as well as chloro, bromo, fluoro, nitro, nitroso, ether, ester, sulfide, keto, etc., substituents. Thus, suitable polyhydric alcohols are, e.g., ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, dipropylene glycol, 1,3-butanediol, glycerol, glycerol monooleate, mono-phenyl ether of glycerol, mono-benzyl ether of glycerol, 1,3,5-hexanetriol, pentaerythritol, sorbitol dioctanoate, pentaerythritol dioleate, and the like. In lieu of a single polyhydric alcohol, mixtures of two or more of such alcohols may be employed.

As indicated, starting material (I) is prepared from a mixture of monohydric and polyhydric alcohols. The mixture may contain a single monohydric and a single polyhydric alcohol, or a plurality of one or both of such alcohols. For the purpose of this invention, best results are achieved when there is present from 0.25 to about 4.0 equivalents of polyhydric alcohol per equivalent of monohydric alcohol. Mixtures of isooctyl alcohol and dipropylene glycol are very satisfactory and a particular preference is expressed for a mixture in which these alcohols are present in about equivalent amounts.

The reaction between the alcohol mixture and phosphorus pentoxide or phosphoric acid is exothermic and can be carried out conveniently at a temperature ranging from room temperature or below to a temperature just beneath the decomposition point of the mixture. Generally, reaction temperatures within the range of from about 40° C. to about 200° C. are most satisfactory. The reaction time required varies according to the temperature and to the hydroxyl activity of the alcohols. At the higher temperatures, as little as 5 or 10 minutes may be sufficient for complete reaction. On the other hand, at room temperature 12 or more hours may be required. Generally it is most convenient to heat the alcohol mixture with phosphorus pentoxide or phosphoric acid for 0.5 to 8 hours at 60–120° C. In any event, the reaction is carried out until periodic acid number determinations on the reaction mass indicate that no more acid phosphate esters are being formed.

The acid phosphate esters useful in the process of this invention can also be prepared by separately reacting phosphorus oxide or phosphoric acid with the monohydric and polyhydric alcohols and then mixing the esters so formed. As mentioned below, solvents may be used when the phosphate esters are viscous or otherwise difficult to handle.

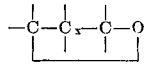
To facilitate mixing and handling, the reaction may be conducted in the presence of an inert solvent. Generally such solvent is a petroleum distillate hydrocarbon, an aromatic hydrocarbon, an ether, or a lower chlorinated alkane, although mixtures of any such solvents can be used. Typical solvents include, e.g., petroleum aromatic spirits boiling in the range of 250°–400° F., benzene, xylene, toluene, mesitylene, ethylene dichloride, diisopropyl ether, etc. In most instances, the solvent is allowed to remain in the acid phosphate esters and ultimately the metal-containing organic phosphate complex, where it serves as a vehicle for the convenient application of films to metal surfaces.

The conversion of the acid phosphate esters to the polyvalent metal salt may be carried out by any of the various known methods for the preparation of salts of organic acids such as, e.g., reaction of the acid-esters with a polyvalent metal base such as a metal oxide, hydroxide, or carbonate. Other suitable methods include, e.g., reaction of the acid-esters with a finely divided polyvalent metal, or the metathesis of a monovalent metal salt of the acid-esters with a soluble salt of the polyvalent metal such as, e.g., a nitrate, chloride, or acetate thereof.

The polyvalent metal of starting material (A) may be any light or heavy polyvalent metal such as, e.g., zinc, cadmium, lead, iron, cobalt, nickel, barium, calcium, strontium, magnesium, copper, bismuth, tin, chromium, or manganese. A preference is expressed for the polyvalent metals of Group II of the Periodic Table and of these, zinc is particularly preferred. A highly effective starting material (I) for the purpose of the present invention is the zinc salt of the acid phosphate esters formed by the reaction of a mixture of equivalent amounts of isooctyl alcohol and dipropylene glycol with phosphorus pentoxide.

The formation of the metal-containing organic phosphate complex of component (A) involves, as indicated, a reaction between starting material (I), the polyvalent metal salt of certain acid phosphate esters, and starting material (II), the organic epoxide.

The organic epoxides, i.e., compounds containing at least one



linkage where x is zero or a small integer, suitable for the purpose of this invention include the various substituted and unsubstituted alkylene oxides containing at least two aliphatic carbon atoms, such as, e.g., ethylene oxide, 1,2-propylene oxide 1,3-propylene oxide, 1,2-butylene oxide, pentamethylene oxide, hexamethylene oxide, 1,2-octylene oxide, cyclohexene oxide, methyl cyclohexene oxide, 1,2,11,12-diepoxydodecane, styrene oxide, alpha-methyl styrene oxide, beta-propiolactone, methyl epoxycaprylate, ethyl epoxypalmitate, propyl epoxymyristate, butyl epoxystearate, epoxidized soyabean oil, and the like. Of the various available organic epoxides, it is preferred to use those which contain at least 12 carbon atoms. Especially preferred are those epoxides which contain at least 12 carbon atoms and also a carboxylic ester group in the molecule. Thus, the commercially available epoxidized carboxylic ester, butyl epoxystearate, is very satisfactory as starting material (II) for the purpose of this invention. If desired, the organic epoxide may also contain substituents such as, e.g., chloro, bromo, fluoro, nitro, nitroso, ether, sulfide, keto, etc., in the molecule.

The stoichiometry of the reaction of the polyvalent metal salt of the acid phosphate ester with the organic epoxide, to form the metal-containing organic phosphate complex of component (A) is not precisely known. There are indications, however, that the reaction involves about one equivalent each of the polyvalent metal salt and the organic epoxide (for this reaction, one equivalent of an epoxide is the same as one mole thereof). This is not to say that complexes made from one equivalent of the polyvalent metal salt and less than or more than one equiva-

lent of the organic epoxide are unsuited for the purpose of this invention. Complexes prepared using as little as 0.1 or 0.25 equivalent or as much as 1.5 to 2 or more equivalents of the organic epoxide per equivalent of polyvalent metal salt are satisfactory for the purpose of this invention.

The reaction between the organic epoxide and the polyvalent metal salt of the acid phosphate esters is only slightly exothermic, so in order to insure complete reaction some heat is generally supplied to the reaction mass. The time and temperature for this reaction are not particularly critical; satisfactory results may be obtained by maintaining the mass for 0.5–6 hours at a temperature within the range of from about 40° C. to about 150° C. Ordinarily, the product is clear and does not require a filtration. In some instances, however, it may be desirable to filter the product, particularly when the polyvalent metal salt starting material has not been purified.

The following examples are offered to illustrate specific modes of preparing component (A). All parts are by weight uness otherwise indicated.

Example 1

Dipropylene glycol (49 parts 0.73 equivalent), 95 parts (0.73 equivalent) of isooctyl alcohol, and 133 parts of aromatic petroleum spirits boiling in the range of 316°–349° F. are introduced into a reaction vessel. The whole is stirred at room temperature and 60 parts (0.42 mole) of phosphorus pentoxide is introduced portionwise over a period of about 0.5 hour. The heat of reaction causes the temperature to rise to about 80° C. After all of the phosphorus pentoxide has been added, the whole is stirred for an additional 0.5 hour at 95° C. The resulting acid phosphate esters show an acid number of 91 with bromphenol blue as an indicator.

The mixture of acid phosphate esters is converted to the corresponding zinc salt by reacting it with 34.5 parts of zinc oxide for 2.5 hours at 95° C. Thereafter 356 parts (one equivalent per equivalent of zinc salt) of butyl epoxystearate is added to the zinc salt at 88° C. over a period of about one hour and the whole is stirred for 4 hours at 90° C. Filtration of the mass yields 684 parts of a zinc-containing organic phosphate complex having the following analysis: Percent phosphorus, 3.55; percent zinc, 3.78; and specific gravity, 1.009.

Example 2

A cadmium-containing organic phosphate complex is made in the manner set forth in Example 1, except that 54.5 parts of cadmium oxide is used in leu of the specified amount of zinc oxide.

Example 3

A lead-containing organic phosphate complex is made in the manner set forth in Example 1, except that 95 parts of lead monoxide is used in lieu of the specified amount of zinc oxide.

Example 4

A barium-containing organic phosphate complex is made in the manner set forth in Example 1, except that 73 parts of barium hydroxide is used in lieu of the specified amount of zinc oxide.

Example 5

A tin-containing organic phosphate complex is made in the manner set forth in Example 1, except that 57 parts of stannic oxide is used in lieu of the specified amount of zinc oxide.

Example 6

Isooctyl alcohol (520 parts, 4 equivalents), 268 parts of isopropylene glycol (4 equivalents), and 1031 parts of toluene solvent are introduced into a reaction vessel. The whole is stirred and 243 parts (1.71 moles) of phosphorus pentoxide is added portionwise over a period of 2 hours. The exothermic character of the reaction causes the temperature to rise from room temperature to 60° C. To insure complete reaction, the whole is stirred for an additional 4 hours at 60° C. The resulting 50% solution of the acid phosphate esters in toluene shows an acid number of 88 with bromphenol blue as an indicator.

The toluene solution of acid esters (1000 parts) is converted to the corresponding zinc salt by reaction with 83 parts of zinc oxide for 5.5 hours at 40–45° C. Filtration yields a clear, light-yellow toluene solution of the zinc salt. This toluene solution (360 parts, containing 0.34 equivalent of zinc salt) is heated with 25 parts (0.34 equivalent) of beta-propiolactone for 5.5 hours at 50–60° C. to yield the desired zinc-containing organic phosphate complex as a 55% solution in toluene. It has the following analysis: Percent phosphorus, 4.26 and percent zinc, 5.05.

Example 7

A toluene solution of acid phosphate esters is made in the manner set forth in Example 6.

Nine hundred and ninety four parts of the indicated toluene solution of acid phosphate esters is heated with 76 parts of calcium hydroxide for 5 hours at 45–60° C. Filtration yields the calcium salt of the acid phosphate esters as a 51% solution in toluene.

Three hundred and twenty five parts (0.52 equivalent) of the toluene solution of the calcium salt is heated with 220 parts (0.52 equivalent) of 85% butyl epoxystearate for 5 hours at 50–60° C. to prepare the desired calcium-containing organic phosphate complex as a 71% solution in toluene. It has the following analysis: Percent phosphorus, 2.34 and percent calcium, 1.65.

Example 8

A batch of acid phosphate esters is made in the manner set forth in Example 6, except that the amount of toluene solvent employed is reduced to 443 parts so as to yield a more concentrated (70%) solution of the esters in toluene.

This toluene solution (290 parts) is neutralized with a mixture of 28.2 parts of zinc oxide and 11.2 parts of calcium hydroxide for 3 hours at 50–70° C. Filtration of the mass yields a mixed zinc-calcium salt of the acid phosphate esters as a 73% solution in toluene.

The mixed zinc-calcium salt (116.2 parts, 0.19 equivalent) and 80.4 parts (0.19 equivalent) of 85% butyl epoxystearate are heated for 6 hours at 50–60° C. to prepare an 84% solution in toluene of a calcium and zinc-containing organic phosphate complex. It shows the following analysis: Percent phosphorus, 2.69; percent calcium, 0.22; and percent zinc, 3.13.

Example 9

A zinc-containing organic phosphate complex is made in the manner set forth in Example 1, except for the following differences: 58 parts of 1,2-propylene oxide is used in lieu of the butyl epoxystearate and the reaction between the zinc salt of the acid phosphate esters and the 1,2-propylene oxide is carried out at 30°–35° C. rather than 88°–90° C.

Example 10

A zinc-containing organic phosphate complex is made in the manner set forth in Example 1, except that 136 parts (0.73 equivalent) of lauryl alcohol and 39 parts (0.73 equivalent) of diethylene glycol are used in lieu of the specified amounts of isooctyl alcohol and dipropylene glycol.

Example 11

A zinc-containing organic phosphate complex is made in the manner set forth in Example 1, except that 185 parts (1.17 equivalents) of n-decanol-1 and 7.9 parts (0.29 equivalent) of pentaerythritol are used in lieu of the specified amounts of isooctyl alcohol and dipropylene glycol.

Example 12

A solution of 49 parts (0.73 equivalent) of dipropyl-

ene glycol, 95 parts (0.73 equivalent) of isooctyl alcohol and 133 parts of toluene is prepared, and 60 parts (0.423 mole) of phosphorus pentoxide is added over a period of about 0.5 hour at a temperature of from about 50° C. to about 90° C. After all of the phosphorus pentoxide is added, the mixture is stirred for an additional 5 hours at about 90° C. The resulting acid phosphate ester mixture has an acid number of 75 with bromphenol blue as an indicator.

This mixture of acid phosphate esters is converted to the corresponding zinc salt by reaction with 34.5 parts of zinc oxide for one hour at 93° C. The water and toluene is removed by heating the mixture to 160° C./100 mm. in 9 hours. Thereafter, 356 parts (1 equivalent per equivalent of zinc salt) of butyl epoxystearate is added to the zinc salt over a period of one hour at about 125° C. and the mixture is then maintained for 4 hours at about 95° C. The mixture is filtered and the filtrate has the following analysis: Percent phosphorus, 4.71; percent zinc, 4.85; and specific gravity, 1.0515.

COMPONENT B

This component is a basic alkali or alkaline earth metal salt of a sulfonic or carboxylic acid having at least about 12 aliphatic carbon atoms and a metal ratio of at least about 1.1. These salts may be used in the liquid or gel form. The formation of gels from such salts is demonstrated in copending application Ser. No. 185,521, filed Apr. 6, 1962, now U.S. 3,242,079.

Examples of useful basic alkali and alkaline earth metal salts are the salts of lithium, sodium, potassium, magnesium, calcium, strontium, and barium with a long chain sulfonic acid or carboxylic acid. Mixtures of such salts are also useful. The acid should contain at least about 12 aliphatic carbon atoms in the molecule. The sulfonic acids include the aliphatic and the aromatic sulfonic acids. They are illustrated by the petroleum sulfonic acids or the acids obtained by treating an alkylated aromatic hydrocarbon with a sulfonating agent, e.g., chlorosulfonic acid, sulfur trioxide, oleum, sulfuric acid, or sulfur dioxide and chlorine. The sulfonic acids obtained by sulfonating alkylated benzene, naphthylene, phenol, phenol sulfide, or diphenyl oxide are especially useful.

Specific examples of the sulfonic acids are mahogany sulfonic acid, mono-wax (eicosane)-substituted naphthylene sulfonic acid, dodecylbenzene sulfonic acid, didodecylbenzene sulfonic acid, dinonylbenzene sulfonic acid, octadecyl-diphenyl ether sulfonic acid, octadecyl-diphenyl amine sulfonic acid, cetylchlorobenzene sulfonic acid, bis-cetylphenyl disulfide sulfonic acid, cetoxy-caprylbenzene sulfonic acid, dilauryl beta-naphthalene sulfonic acid, the sulfonic acid derived by the treatment of polyisobutene having a molecular weight of 1500 with chloro sulfonic acid, nitronaphthylene sulfonic acid, paraffin wax sulfonic acid, detylcyclopentane sulfonic acid, lauryl-cyclohexane sulfonic acid, and polyethylene (molecular weight of 750) sulfonic acid, etc. The carboxylic acids likewise may be aliphatic or aromatic acids. They are exemplified by palmitic acid, stearic acid, myristic acid, oleic acid, linoleic acid, behenic acid, hexatriacontanoic acid, tetrapropylene-substituted glutaric acid, polyisobutene (molecular weight of 5000)-substituted succinic acid, polypropylene(molecular weight of 10,000)-substituted succinic acid, octadecyl-substituted adipic acid, chlorostearic acid, 9-methyl-stearic acid, dichlorostearic acid, stearylbenzoic acid, poly wax(eicosane)-substituted naphthoic acid, dilauryl-decahydronaphthylene carboxylic acid, didodecyl-tetralin carboxylic acid, dioctyl-cyclohexane carboxylic acid, and the anhydrides of such acids.

An important aspect of the basic metal salts of the above-illustrated oil-soluble acids is that they have a metal ratio of at least about 1.1. The term "metal ratio" is used herein to designate the ratio of the total chemical equivalents of the metal in the metal salt to the chemical equivalents of the metal which is in the form of a normal salt, i.e., a neutral salt of the organic acid. To illustrate, a metal salt containing 5 equivalents of the metal per equivalent of the organic acid radical has a metal ratio of 5; and a neutral metal salt has a metal ratio of 1. The use of carbonated salts having a metal ratio between about 4.5 and 20 has been found to be most advantageous, although salts having still higher metal ratios likewise are effective.

A convenient process for preparing the metal salts comprises carbonating a substantially anhydrous mixture of the acid with at least about 1.1 chemical equivalents of an alkali or alkaline earth metal base per equivalent of the acid in the presence of a promoting agent. Carbonation of the mixture, though desirable for the preparation of the more basic salts is not required for the preparation of all salts. The metal base may be an alkali or alkaline earth metal oxide, hydroxide, bicarbonate, sulfide, mercaptide, hydride, alcoholate, or phenate. It is preferably an oxide, alcoholate, or hydroxide of lithium, barium, or calcium. The carbonation is carried out in a solvent which is preferably mineral oil. The solvent may be n-hexane, naphtha, n-decane, dodecane, benzene, toluene, xylene, or any other fluid hydrocarbon.

The promoting agent is preferably an alcohol or a phenol; it may be a marcaptan, amine, aci-nitro compound, or an enolic compound. The alcohols and phenols useful as the promoting agent include, for example, methanol, isopropanol, cyclohexanol, dodecanol, behenyl alcohol, ethylene glycol, diethylene glycol, monomethyl ether of ethylene glycol, glycerol, pentaerythritol, benzyl alcohol, phenol, catechol, p-tert-butylphenol, etc.

It will be noted that upon mixing with large amounts of metal base, the sulfonic or carboxylic acid forms a metal salt so that the process mixture before carbonation contains a metal salt of the acid and a large excess of the metal base. Such a mixture is heterogeneous primarily because of the presence of the large excess of the insoluble metal base. As carbonation proceeds, the metal base becomes solubilized in the organic phase and the carbonated product eventually becomes a homogeneous composition containing an unusually large amount of the metal. In many instances a homogeneous product is obtained when as little as 75% of the excess metal base is carbonated. For the sake of convenient reference in the specification and the claims of this invention, the term "carbonated, basic alkaline earth metal salt" of the oil-soluble acid designates the homogeneous, carbonated product without specific reference to the degree of conversion of the excess metal base by carbonation.

Formation of the carbonated, basic metal salts having the high metal ratio of at least about 4.5 requires the presence in the carbonation step of a promoting agent such as is described previously. The amount of the promoting agent to be used is best defined in terms of its chemical equivalents per equivalent of the long chain sulfonic or carboxylic acid used. The amount may be as little as 0.1 equivalent or as much as 10 equivalents or even more per equivalent of the acid. The preferred amount is within the range from 0.25 to 5 equivalents per equivalent of the acid. It will be noted that the equivalent weight of the promoting agent is based upon the number of the functional radicals in the molecule. To illustrate, the equivalent weight of an alcohol is based upon the number of the alcoholic radicals in the molecules; that of a phenol is based upon the number of the hydroxyl radicals in the molecule; that of an amine is based upon the number of the amine radicals in the molecule; etc. Thus, methanol has one equivalent per mole; ethylene glycol has two equivalents per mole; a bis-phenol has two equivalents per mole; phenylenediamine has two equivalents per mole; nitro-propane has one equivalent per mole; acetylacetone has one equivalent per mole; etc.

The carbonation temperature depends to a large measure upon the promoting agent used. When a phenol is

used as the promoting agent the temperature usually ranges from about 80° C. to 300° C. and preferably from 100° C. to 200° C. When an alcohol or a mercaptan is used as the promoting agent the carbonation temperature usually will not exceed the reflux temperature of the reation mixture and preferably will not exceed 100° C.

After carbonation, the promoting agent, if it is a volatile substance, may be removed from the product by distillation. If the promoting agent is a non-volatile substance it is usually allowed to remain in the product. The methods for preparing the carbonated, basic metal salts include those described in, e.g., U.S. Patents 2,616,905, 2,616,924, 2,695,910, 2,971,014, and 3,027,235.

The following examples illustrate the preparation of carbonated, basic metal salts useful as component (B) in the compositions of this invention.

Example 13

To a mixture of 400 parts (by weight) of a 30% mineral oil solution of barium petroleum sulfonate (sulfate ash of 7.6%), 32.5 parts of octyl phenol, and 197 parts of water, there is added 73 parts of barium oxide within a period of 30 minutes at 57°–84° C. The mixture is heated at 100° C. for 1 hour to remove substantially all of the water and blown with 75 parts of carbon dioxide at 133°–170° C. within a period of 3 hours. A mixture of 1000 grams of the above carbonated intermediate product and 121.8 parts of octyl phenol and 234 parts of barium hydroxide is heated at 100° C. and then at 150° C. for one hour. The mixture is then blown with carbon dioxide at 150° C. for one hour at a rate of 3 cubic ft. per hour. The carbonated product is filtered and the filtrate is found to have a sulfate ash content of 39.8% and a metal ratio of 9.3.

Example 14

To a mixture of 3245 grams (12.5 equivalent) of barium petroleum sulfonate, 1460 grams (7.5 equivalents) of heptyl phenol, and 2100 grams of water in 8045 grams of mineral oil there is added at 82° C., 7400 grams (96.5 equivalents) of barium oxide. The addition of barium oxide caused the temperature to rise to 145° C. which temperature is maintained until all of the water has been distilled. The mixture then is blown with carbon dioxide until it is substantially neutral. The product is diluted with 5695 grams of mineral oil and filtered. The filtrate is found to have a barium sulfate ash content of 30.5% and a metal ratio of 8.1.

Example 15

A mixture of 1285 grams (1.0 equivalent) of 40 percent barium petroleum sulfonate and 590 ml. (12.5 equivalents of methanol is stirred at 55–60° C. while 301 grams (3.9 equivalents) of barium oxide is added portionwise over a period of one hour. The mixture is stirred an additional two hours at 45–55° C., then treated with carbon dioxide at 55–65° C. for two hours. The resulting mixture is freed of methanol by heating to 150° C. The residue is filtered through a siliceous filter aid, the clear brown filtrate showing the analyses: sulfate ash, 33.2%; neut. no., slightly acid; metal ratio, 4.7.

Example 16

A solution of 1928 grams (1.5 equivalent) of 40 percent barium petroleum sulfonate in 1004 grams of oil and 188 ml. (4.7 equivalents) of methanol is prepared and heated to 40° C. Carbon dioxide is bubbled into this solution and 796 grams (10.4 equivalents) of barium oxide is added portionwise over a period of two hours. The temperature is maintained between 40° C. and 70° C. throughout and when all the barium oxide has been added the carbon dioxide-treatment is continued for an additional four hours. The resulting mixture is then heated to 150° C. and held at this temperature for 30 minutes to remove any volatile material. The residue is filtered, yielding a clear, brown filtrate having the following analyses: Sulfate ash, 32.5%; neut. no., 1.2 (basic); metal ratio, 7.2.

Example 17

A mixture of 574 grams (0.5 equivalent) of 40 percent barium petroleum sulfonate, 98 grams (1.0 equivalent) of furfuryl alcohol, and 762 grams of mineral oil is heated with stirring at 100° C. for an hour, then treated portionwise over a 15-minute period with 230 grams (3.0 equivalents) of barium oxide. During this latter period the temperature rises to 120° C. (because of the exothermic nature of the reaction of barium oxide and the alcohol); the mixture then is heated at 150–160° C. for an hour, and treated subsequently at this temperature for 1.5 hours with carbon dioxide. The material is concentrated by heating to a final temperature of 150° C./10 mm. then filtered to yield a clear, oil-soluble filtrate having the following analyses: sulfate ash, 21.4%; neut. no., 2.6 (basic); metal ratio, 6.1.

Example 18

To a mixture of 1145 grams of a mineral oil solution of a 40% solution of barium mahogany sulfonate (one equivalent) and 100 grams of methyl alcohol at 55° C. there is added 230 grams of barium oxide while the mixture is being blown with carbon dioxide at a rate of 2–3 cubic feet per hour. To this mixture there is added an additional 78 grams of methyl alcohol and then 925 grams of barium oxide while the mixture is being blown with carbon dioxide. The carbonated product is heated to 150° C. for one hour and filtered. The filtrate is found to have a metal ratio of 13.4.

Example 19

A mixture of 520 parts (by weight) of a mineral oil, 480 parts of a sodium petroleum sulfonate (molecular weight of 480), and 84 parts of water is heated at 100° C. for 4 hours. The mixture is then heated with 86 parts of a 76% aqueous solution of calcium chloride and 72 parts of lime (90% purity) at 100° C. for 2 hours, dehydrated by heating to a water content of less than 0.5%, cooled to 50° C., mixed with 130 parts of methyl alcohol, and then blown with carbon dioxide at 50° C. until substantially neutral. The mixture is then heated to 150° C. to distill off methyl alcohol and water and the resulting oil solution of the basic calcium sulfonate is filtered. The filtrate is found to have a calcium sulfate ash content of 16% and a metal ratio of 2.5.

Example 20

A mixture of 1050 parts of a slightly basic calcium sulfonate (metal ratio of 1.6), prepared according to the procedure of Example 19, 930 parts of mineral oil, 220 parts of methanol, 72 parts of isobutyl alcohol, and 38 parts of amyl alcohol is prepared, heated to 35° C., and subjected to the following operation cycle four times: mixing with 158 parts of 90% of calcium hydroxide and treating the mixture with carbon dioxide until it has a base number of 32–39. The resulting product is then heated to 155° C. during a period of 9 hours to remove the alcohols and then filtered through a siliceous filter and at this temperature the filtrate has a calcium sulfate ash content of 40%, a metal ratio of 16 and an oil content of 35%.

Example 21

A mixture of 1305 grams of the slightly basic carbonated calcium sulfonate of Example 19, 930 grams of mineral oil, 220 grams of methyl alcohol, 72 grams of isobutyl alcohol, and 38 grams of amyl alcohol is prepared, heated to 35° C., and subjected to the following operating cycle 4 times: mixing with 143 grams of 90% calcium hydroxide and treating the mixture with carbon dioxide until it has a base number of 32–39. The resulting product is then heated to 155° C. during a period

of 9 hours to remove the alcohols and then filtered through a siliceous filter-aid at this temperature. The filtrate has a calcium sulfate ash content of 39.5%, and a metal ratio of 12.2.

Example 22

A mixture of 520 parts of a mineral oil and 480 parts of a sodium petroleum sulfonate (molecular weight of 480) is heated to 90°–98° C., and 67 parts of calcium chloride (96%) and 76 parts of water are added over a period of 2 hours. The mixture is maintained at this temperature for an additional 2 hours whereupon 25.5 parts of calcium oxide (84–87%) is added and the mixture is stirred for 2 hours. The mixture is maintained at about 150° C. for 7.5 hours to remove water and is then filtered at this temperature. The filtrate is the desired product having a metal ratio of 1.4.

Example 23

The procedure of Example 21 is repeated except that the sodium petroleum sulfonate is replaced by an equivalent amount of sodium polydodecyl benzene sulfonate. The resulting highly basic metal salt has a calcium sulfate ash content of 41.5% and a metal ratio of 13.1.

Example 24

A highly basic metal salt is prepared by the procedure of Example 21 except that the slightly basic calcium sulfonate starting material having a metal ratio of 2.5 is replaced with tall oil acids (1250 parts by weight, having an equivalent weight of 340) and the total amount of calcium hydroxide used is 772 parts by weight. The resulting highly basic metal salt has a metal ratio of 5.2, a calcium sulfate ash content of 41%, and an oil content of 33%.

Example 25

A basic metal salt is prepared by the procedure described in Example 21 except that the slightly basic calcium sulfonate having a metal ratio of 2.5 is replaced with a mixture of that calcium sulfonate (280 parts by weight) and tall oil acids (970 parts by weight, having an equivalent weight of 340) and that the total amount of calcium hydroxide used is 930 parts by weight. The resulting highly basic metal salt of the process has a calcium sulfate ash content of 48%, a metal ratio of 7.7, and an oil content of 31%.

Example 26

A polyisobutenyl succinic anhydride having an acid number of 101 is prepared by the reaction of a chlorinated polyisobutene (having an average chlorine content of 4.3 weight percent and an average of 72 carbon atoms) with maleic anhydride at about 200° C. To a mixture of 278 parts (0.5 equivalent) of this polyisobutenyl succinic anhydride, 1544 parts of mineral oil, 55 parts of water and 58 parts of heptylphenol, there is added at 70° C., 460 parts (6.01 equivalents) of barium oxide. The mixture is heated to 150° C. over a period of 1.5 hours and is maintained at this temperature and blown with carbon dioxide until it is substantially neutral. The residue is dried and filtered. The resulting filtrate has a barium content of 14.5% and a metal ratio of 6.1.

Example 27

A mixture of 3600 parts (5 equivalents) of polydodecyl benzene sulfonic acid, 2580 parts of mineral oil, and 580 parts of heptylphenol is heated to 70° C. whereupon 1037 parts (24.7 equivalents) of lithium hydroxide monohydrate is added and the mixture refluxed for one hour. The mixture is dried by heating to 150° C. and 75 parts of isooctanol is added. The mixture is blown with carbon dioxide at 150–155° C. until the mixture is substantially neutral, and then filtered through a siliceous filter-aid. The filtrate has a sulfate ash content of 17.68 and a metal ratio of 4.8.

Example 28

To a mixture of 1048 parts (2 equivalents) of a polyisobutenyl succinic anhydride (prepared as in Example 26, from maleic anhydride and chlorinated polyisobutylene having an average chlorine content of 4.3% and an average of 67 carbon atoms), 1404 parts of mineral oil, 230 parts (1.2 equivalents) of heptylphenol, and 150 parts water at 90° C., there is added 692 parts (16.4 equivalents) of lithium hydroxide monohydrate over a period of 0.5 hour. Isooctanol (75 parts) is added and the mixture heated at about 105° C. for 1 hour, dried at 150° C. while blowing with nitrogen and then blown with carbon dioxide at 160°–70° C. until the mixture is substantially neutral. During the carbon dioxide blowing, 300 parts of mineral oil and 75 parts of isooctanol are added. The mixture is filtered through a filter-aid after an additional 300 parts of mineral oil is added. The filtrate is the desired product having a sulfate ash content of 22.1 and a metal ratio of 7.7.

Example 29

To a mixture of 443 parts (1 equivalent) of a polyisobutenyl succinic anhydride (having an acid number of 126 and prepared from maleic anhydride and chlorinated polyisobutene having an average chlorine content of 4.3 weight percent and an average of 56 carbon atoms), 450 parts of mineral oil and 20 parts of water, there is added at 30° C., 225 grams (1.5 equivalents) of lithium oxide. The addition is made over a 30 minute period. The mixture is maintained at 90°–100° C. for 4 hours, dried and filtered. The filtrate has a lithium content of 1.32% and a metal ratio of 1.3.

The novel, metal-containing compositions of this invention are obtained by mixing components (A) and (B) described previously. Generally, component (A) is combined with from about 0.5 to about 10 parts by weight of component (B). When component (A) is combined with from about 1 to about 5 parts by weight of component (B), the composition is especially effective to reduce the corrosion of metal surfaces to unexpectedly low levels. This synergism is completely unexpected.

The examples in Table I are presented to illustrate the compositions of this invention. As mentioned previously, these compositions may be prepared in solutions of mineral oil or volatile solvent such as xylene, toluene, mineral spirits, etc., and applied to the metal surfaces as solutions. The amount of diluent may range from trace amounts to about 80 to 90% or from about 0.1 to about 80 parts by weight of diluent. Generally, from about 0.1 to about 40 parts of diluent are incorporated into the composition.

TABLE I

Composition	Component (A) (Product of Example)	Component (B) (Product of Example)	Weight ratio (A:B)
A	7	13	1:5
B	1	21	1:4
C	1	21	1:3
D	12	21	1:49
E	6	22	2:1
F	8	18	1:9
G	[1] 1	21	2:3
H	7	25	1:6

[1] Diluted to contain 40% mineral oil.

The compositions of this invention are particularly effective when applied to metal articles which have been phosphated by means of known aqueous phosphating solutions, and especially those phosphating solutions which provide a dense, adherent, micro crystalline or amorphous phosphate coating upon the metal surface

such as described in detail in U.S. Patent No. 3,090,709.

The effectiveness of such treatment is illustrated by the following Salt Fog Corrosion Test. A number of ¼-inch self-tapping hex-head screws were cleaned, placed in a basket and phosphated by dipping in a solution comprising 67.4 parts (all parts are by weight) of water, 6.4 parts of 85% commercial phosphoric acid, 3.4 parts of zinc chloride, 6.4 parts of ammonium monophosphate, 15.4 parts of a zinc nitrate solution, and 1 part of a solution obtained by mixing the following ingredients: 44 parts of water, 35.6 parts of 85% commercial phosphoric acid, 5.2 parts of 65% commercial nitric acid, 14.2 parts of manganese carbonate, 0.95 part of nickel nitrate and 0.05 part of Rochelle salts. The zinc nitrate solution used above is prepared by mixing 20.7 parts of zinc oxide in 46.8 parts of 67% nitric acid and 32.5 parts of water. After placing the basket in the phosphating solution, it was withdrawn at the rate of 4 inches per minute, drained and the screws were placed on a sheet of aluminum foil to air dry.

The phosphated screws were then dip-coated in the same manner in a 30% solution (xylene) of the compositions of this invention, air-dried and subjected to a modification of the Salt Fog Corrosion Test described in ASTM procedure B 117–57 T. In this test, a waxed string is tied to each of the screws, and the free end of the string is attached to a glass rod which is then suspended in the salt fog chamber. A mist of fog of 5% aqueous sodium chloride is maintained in contact with the screws for a predetermined time at 95°±2° F. The screws are inspected for rust periodically during the test without removing them from the chamber. On completion of the test, the screws are removed from the salt fog chamber, washed with water to remove any salt deposits, and inspected to determine the number of screws which have rusted. The results of the inspections are given in Table II. It will be noted that the composition of this invention (B and D) are substantially better corrosion inhibitors than the individual components.

TABLE II.—SALT FOG CORROSION TEST

[Number of Screws Rusted*]

Coating	Close Observation in Salt Fog Cabinet				Actual Inspection, 504 hrs.
	264 hrs.	312 hrs.	432 hrs.	480 hrs.	
Product of Example 1	4	4	7	8	9
Product of Example 21	6	6	6	8	8
Composition B (1+21)	1	1	1	1	2
Product of Example 12	2	3	7	7	9
Composition D (12+21)	0	0	0	0	1

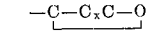
*Out of 12 screws.

The compositions of this invention are also useful as additives in lubricants intended for use in the crankcases, cylinders, transmissions, gears, chassis, torque converters, etc. of automotive equipment, industrial machinery, and marine diesel engines. Other suitable uses for the complexes are in asphalt emulsions, insecticidal compositions, stabilizing agents for plasticizers and plastics, paints, slushing oils, pesticides, foaming compositions, cutting oils, metal drawing compositions, flushing oils, textile treatment compositions, tanning compositions, metal cleaning compositions, emulsifying agents, antiseptic cleansing compositions, penetrating oils, hydraulic oils, gum solvent compositions, fat-splitting compositions, bonding agents for ceramics and asbestos, asphalt improving agents, flotation agents, improving agents for hydrocarbon fuels such as gasoline, fuel oil, gas oil, etc.

What is claimed is:

1. A composition comprising

(A) 1 part by weight of a metal-containing organic phosphate complex prepared by the process which comprises the reaction of (I) a polyvalent metal salt of an acid phosphate ester derived from the reaction of phosphorus pentoxide or phosphoric acid with a mixture of a monohydric alcohol and from about 0.25 to about 4.0 equivalents of a polyhydric alcohol per equivalent of monohydric alcohol with (II) at least about 0.1 equivalent of an organic epoxide containing at least 1



linkage where x is 0 or a small integer, and

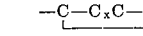
(B) from about 0.5 to about 10 parts by weight of a basic alkali or alkaline earth metal salt of a sulfonic or carboxylic acid having at least about 12 aliphatic carbon atoms, said salt having a metal ratio of at least about 1.1.

2. The composition of claim 1 wherein the acid used in the preparation of component (B) is a sulfonic acid.

3. The composition of claim 1 wherein the metal salt of component (B) is a calcium salt.

4. A composition comprising

(A) 1 part by weight of a metal-containing organic phosphate complex prepared by the process which comprises the reaction of (I) a polyvalent metal salt of the acid phosphate esters derived from the reaction of phosphorus pentoxide or phosphoric acid with a mixture of a monohydric alcohol and from about 0.25 to about 4.0 equivalents of a polyhydric alcohol per equivalent of monohydric alcohol with (II) at least about 0.1 equivalent of any organic epoxide, containing at least 1



linkage where x is 0 or a small integer and

(B) from about 0.5 to about 10 parts by weight of a carbonated basic alkaline earth metal salt of a sulfonic acid having at least about 12 aliphatic carbon atoms and a metal ratio of at least about 4.5.

5. A composition comprising the composition of claim 4 and from about 0.1 to about 40 parts by weight of a mineral oil.

6. The composition of claim 4 wherein the polyvalent metal salt of component (A) is a zinc salt.

7. The composition of claim 4 wherein the alkaline earth metal salt of component (B) is a calcium salt.

8. The composition of claim 4 wherein the organic epoxide of component (A) additionally contains a carboxylic ester group.

9. The composition of claim 4 wherein component (A) is prepare by the process which comprises the reaction of (I) the zinc salt of the acid phosphate esters derived from the reaction of phosphorous pentoxide with a mixture of isooctyl alcohol and dipropylene glycol, with (II) at least about 0.1 equivalent of butyl epoxy stearate.

10. A composition comprising

(A) 1 part by weight of a metal-containing organic phosphate complex prepared by the process which comprises the reaction of (I) a zinc salt of the acid phosphate esters derived from the reaction of phosphorous pentoxide with a mixture of isooctyl alcohol and dipropylene glycol, with (II) at least about 0.1 equivalent of butyl epoxystearate;

(B) from about 2 to about 5 parts by weight of a carbonated, basic calcium salt of an oil-soluble sulfonic acid having a metal ratio of from about 4.5 to about 20; and

(C) from about 1 to about 50 parts of mineral oil.

11. A method for inhibiting the corrosion of a metal surface which comprises applying to said surface a film of the composition of claim 5.

12. The method of claim 11 wherein the metal surface is a phosphated metal surface.

13. A metal article, the metal surface of which has

been inhibited against corrosion in accordance with the method of claim **11.**

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