United States Patent Office 3,260,673 Patented July 12, 1966

3,260,673

CORROSION INHIBITED PHOSPHORIC ACID COMPOSITION

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No Drawing. Filed Jan. 27, 1964, Ser. No. 340,525
11 Claims. (Cl. 252—136)

This invention relates to novel and useful compositions and methods for inhibiting the corrosion of metals by acids.

This is a continuation-in-part of United States patent application, Serial Number 75,120, filed December 12, 1960, now abandoned.

At the present time shipments of large quantities of acids, such as phosphoric, sulfuric, hydrochloric, nitric, acetic, formic, oxalic, and the like, are usually made in rubber-lined tank cars in order to obviate the corrosion of the tanks' metal that would ordinarily take place if these acids were shipped in, for example, plain steel cars or containers. Even when these acids, such as phosphoric acid, are used in industrial plants and equipment, the equipment contacted by the acid ordinarily must be made of special corrosion-resistant metal such as type 316 and 304 stainless steels in order to withstand the corrosive attack of the acid.

Although many materials have been suggested as corrosion inhibitors for acids, the materials or compositions suggested to date are limited as to the total extent to which they actually protect the various metals from such acidic corrosion. For example, many inhibitors are available which perform fairly well when called upon to protect metals which are completely submerged in the acid but which are practically useless for any application in which there is an air-acid interface in contact with the metal. Consequently, there is a continuing demand for more effective corrosion inhibitors—particularly those which will inhibit the corrosive attack by acids not only beneath the sufaces of the liquid acids but also at the air-liquid-metal interfaces in storage, transport, and manufacturing equipment.

Accordingly, it is an object of the present invention to provide compositions and methods whereby the corrosion of metals by acids is markedly decreased.

It is another object of the present invention to provide compositions and methods for the inhibition of the corrosion of metals by phosphoric acid, whereby acidic corrosion of the metals both at and below the surface of the phosphoric acid is markedly diminished.

The above as well as other objects of the invention are achieved by including in the acids a combination of (a) an inorganic salt selected from the group consisting of iodides and bromides, (b) a primary or secondary aliphatic amine, and (c) a quaternary ammonium compound.

Although certain combinations of primary amines, for example, with iodides, as well as certain quaternary ammonium compounds, have heretofore been known to possess some corrosion inhibiting properties, the excellent over-all inhibiting abilities of the compositions contemplated by this invention are believed to be surprising because they apparently depend upon an unexpected three-component synergism or beneficial interaction which could not have been foretold from the actions in acidic systems of either the individual ingredients or any binary combination of the basic ingredients which, together, make up the inhibiting compositions of this invention.

Almost any material can be present in the acidic compositions which are inhibited by the compositions and processes of this invention without any noticeable deleterious effect on the surprising beneficial interaction (or

synergism) that results from its practice. For example, the corrosion of phosphoric acid containing practically any of the impurities often found therein (such as polyphosphoric acid, ammonium phosphate, halide, sulfate, etc.), as well as any of the usual acidic compositions containing phosphoric acid (such as fertilizer compositions, and other phosphatic solutions, etc.), can be readily inhibited by practicing this invention. The metallic corrosion caused by solutions of other non-oxidizing acids, such as hydrochloric, acetic, benzoic, butyric, maleic, oxalic, phosphorous, propionic, pyrophosphoric, tartaric, chloroacetic, and the like, either with or without most impurities, as well as in the presence of almost any other chemical compound, can be similarly inhibited by practicing the invention. There is only one notable exception to this very wide applicability of the present invention. That is that this invention is ineffective in the presence of more than about 1 weight percent of an oxidizing acid such as, for example, nitric, perchloric, bromic, hypobromous, iodic, hypochlorous, etc. An oxidizing acid is known to be an acid which can be very readily reduced by organic materials in an acidic medium.

The metals which are protected from acidic corrosion by the compositions of this invention are all of those which are normally corroded by non-oxidizing acids, and which are non-graphitic, that is, do not contain an appreciable amount of free carbon in the graphite form. For example, nickel, ferruginous metals (except for cast iron) such as cast steel, wrought iron, mild steels, certain of the various so-called stainless steels which are corroded by some nonoxidizing acids (e.g., type 316 stainless steel is attacked by hydrochloric acid under some conditions), Monel metal, the Hastalloys (containing nickel, molybdenum, sometimes chromium, etc.) and the like, are generally protected from acidic corrosion by the compositions of this invention. The reason that cast iron is not protected is believed to be that the presence of graphite flakelets act as focal points for localized cathodic corrosion. These focal points of corrosion apparently cause areas adjacent to them to corrode more readily and thus defeat the effect of the inhibitor composition. Apparently, in the absence of graphitic flakelets, as in steels, wrought iron, etc., the inhibitor can prevent the formation of most of the focal points of corrosion which ordinarily would have been formed in the absence of the inhibitor composition.

The class of iodides and bromide salts is generally applicable with respect to the present invention. However, there are some rather marked variations in effectiveness within this general class. Preferred iodide and bromide salts are those that are soluble at about 25° C. in 85 weight percent orthophosphoric acid to the extent of at least about 0.0005 weight percent. For example, while typically useful salts are cadmium, copper, zinc, aluminum and mercuric, alkaline earth metal salts (such as calcium, magnesium, and barium), and alkali metal salts (such as sodium, potassium, lithium, rubidium, and ammonium), the iodides are generally more effective than the corresponding bromides. Two particularly preferred iodides are potassium iodide and magnesium iodide.

The primary and secondary amines which can be used in the practice of this invention are those which are soluble at about 25° C. in 85 weight percent orthophosphoric acid to the extent of at least 0.02 weight percent. Generally primary and secondary aliphatic amines having between 4 and 28 carbon atoms in their molecules (depending to a slight extent upon the particular acid being inhibited) are used. In addition, amines which are unsaturated usually perform more satisfactorily than do the corresponding saturated ones. For optimum results, the

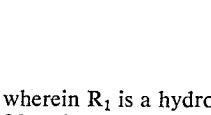
primary amines which are utilized have between 8 and 18 carbon atoms in their molecules.

Secondary aliphatic amines such as:

(wherein R_1 and R_2 are hydrocarbyl radicals having between 3 and 16 carbon atoms per radical and the sum of the total number of carbon atoms in R_1 plus R_2 is generally between 8 and 28, but preferably between 14 and 24) are often utilized in the practice of this invention. The over-all corrosion inhibiting performance of the compositions contemplated by this invention that contain primary amines in the absence of secondary amines is often slightly superior to that of compositions containing mainly secondary amines. However, the inhibiting performance by either primary or secondary amines in accordance with this invention is superior to that of the amine alone or the amine plus inorganic iodide or bromide, without the quaternary ammonium compound. Thus the three-component synergism described above can readily be seen using any of the particular amines contemplated by this invention.

Examples of typically useful amines are the saturated primary amines such as hexylamine, octylamine, dodecylamine, octadecylamine, isoamylamine, 2-ethyl hexylamine, etc.; the ethylenically unsaturated primary amines such as octadecenylamine, dodecenylamine, isooctenylamine, hexadecenylamine, decenylamine, hexenylamine, etc.; and other primary amines; the saturated secondary amines such as dibutylamine, ethylhexylamine, dioctylamine, dihexylamine, didodecylamine, octyldodecylamine, hexyloctylamine, etc.; the ethylenically unsaturated secondary amines such as hexenyloctylamine, octyldodecenylamine, dihexenylamine, butylbutenylamine, didodecenylamine, propenyloctylamine, etc.; and other secondary amines.

Although any quaternary ammonium compound that is soluble in 85 weight percent orthophosphoric acid to the extent of at least about 0.02 weight percent at about 25° C. can be used in the practice of this invention, the tetraalkylammonium halides, sulfates, acetates, etc.; which are preferred are represented structurally as:



wherein R_1 is a hydrocarbyl radical having between 6 and 30 carbon atoms, and preferably between 8 and 20 carbon atoms; R_2 is hydrogen or a saturated aliphatic hydrocarbyl radical having between 1 and 18 carbon atoms, and preferably between 1 and 13 carbon atoms; R_3 is hydrogen or a saturated aliphatic hydrocarbyl radical having between 1 and 15 carbon atoms; and preferably between 1 and 8 carbon atoms; and R_4 is hydrogen or a saturated aliphatic lower hydrocarbyl radical having between 1 and 4 carbon atoms, such as methyl-, ethyl-, propyl-, isopropyl-, butyl-, and isobutyl-; and X is an acid anion, preferably one derived from a non-oxidizing acid, such as, for example, a halogen (i.e., chloride, bromide, iodide), a mineral acid (i.e., phosphate, sulfate, etc.), acetate, and the like. These compounds perform equally well whether R is saturated or unsaturated, branched chain or straight chain. Note that R_2 can be described more simply as a saturated aliphatic hydrocarbyl radical having the empirical formula $(C_nH_{2n})+H$, where n is a whole number from 1 to 18 and preferably from 1 to 13. R_3 can be described similarly as a saturated aliphatic hydrocarbyl radical having the empirical formula $(C_bH_{2b})+H$, where b is a whole number from 1 to 15 and preferably from 1 to 8. Similarly, R_4 can be described as a saturated aliphatic lower hydrocarbyl radical having the empirical formula $(C_kH_{2k})+H$, where k is a whole number from 1 to 4. For example, especially fine performance in the inhibition of the corrosion of cold rolled steel by phosphoric acid was observed when the only quaternary ammonium compound in the inhibiting composition was didodecyl dimethyl ammonium chloride. Other examples of the preferred quaternary ammonium compounds are: hexadecylethyldimethyl ammonium chloride, trioctylmethyl ammonium chloride, dodecyltrimethyl ammonium chloride, dodecyltrimethyl ammonium acetate, didodecyldimethyl ammonium iodide, dodecylbenzyldimethyl ammonium chloride, hexadecylbenzyldimethyl ammonium iodide, hexadecylbenzyldimethyl ammonium sulfate, tridodecylmethyl ammonium chloride, cetyltrimethyl ammonium stearate, cetyltrimethyl ammonium chloride, cetyltrimethyl ammonium bromide, cetylbenzyldimethyl ammonium chloride, stearyltrimethyl ammonium sulfate, docosaneethyldimethyl ammonium iodide, octadecenyldodecenyldimethyl ammonium iodide, and the like.

The actual amounts of iodides and/or bromides, amines, and quaternary ammonium compounds (as well as their relative concentrations) which are used to inhibit acidic corrosion of metals according to the practice of this invention will depend, to some extent, upon both the acid being inhibited and the metal being protected. As a general rule, however, the effective concentration of bromide or iodide salts will range from about 0.0005 weight percent to about 1.5 weight percent, and preferably from about 0.002 to about 0.5 weight percent of the acidic composition to be inhibited, while the concentrations of both the amine and the quaternary ammonium compound respectively will range from about 0.02 weight percent to about 5 weight percent and preferably from about 0.04 to about 2 weight percent of said acid composition. Of the three clases of inhibitor ingredients in the inhibited acidic composition, the amine and quaternary ammonium compound will each almost invariably be present at a concentration considerably higher than that of the inorganic iodide or bromide salt. In this respect, the weight ratio of amine to iodide or bromide salt (as well as the weight ratio of the quaternary ammonium compound to the iodide or bromide salt) generally is greater than about 2:1, and preferably is greater than about 5:1, and usually not more than about 20:1 although the ratio of amine to iodide or bromide will not necessarily be the same as the corresponding quaternary compound to iodide or bromide ratio. The most preferred concentration of the inorganic iodides or bromides in, for example, phosphoric acid compositions being inhibited are the effective concentrations within the range of from about 0.002 to about 0.2 weight percent, based on the total weight of the acid composition, while the most preferred concentrations of amines and quaternary ammonium compounds in these same acidic compositions are for each, within the range of from about 0.02 to about 1 weight percent.

It has been found that the synergistically inhibitory benefits of this invention will accrue at most concentrations of the acids contemplated and most temperatures. Of course, limitations that are logical and will ordinarily be applied by those skilled in the art are to be observed. For example, since two of the three basic ingredients in the inhibitor compositions of this invention are organic in nature, conditions that are ordinarily destructive to organic compounds (i.e., extremely high temperatures, combined with very high acid concentrations) are generally to be avoided in the practice of this invention. In addition, it has been noted that as a general rule, more dilute acidic solutions will require higher concentrations of the respective inhibitor ingredients, in order to accomplish the best protection possible under any particular set of conditions, than will more concentrated solutions of the same acid.

It should be noted that a surprising synergistic inhibition of the acidic corrosion of metals also results from a simple combination in the acid of one of the quaternary ammonium compounds and one of the inorganic iodides or bromides, described above, even without the amine (al-

though the addition of the amine will result in still further improvement in the inhibition of the corrosion). The beneficial interaction of the quaternary ammonium compounds and inorganic iodide or bromide salts contemplated by this invention will subsequently be demonstrated in Table 1. However, it will be sufficient here to understand that by combining the quaternary ammonium compound and the inorganic iodide or bromide in proportions and at rates (in the acidic compositions to be inhibited) which are practically identical to those utilized for these materials, respectively, when the tri-component inhibitor compositions of this invention are used (as described below) to inhibit the said corrosion.

The materials which, when combined in an acidic composition, yield the unexpected benefits of this invention can be added to the acid or acidic composition (the metallic corrosion by which is intended to be inhibited) in any of a number of ways. For example, the individual components of the inhibitor composition (i.e., the inorganic iodide or bromide salt, the amine and the quaternary ammonium compound) can each be simply dissolved in the acid by stirring or agitation in some conventional manner. Sometimes two or more of the components are combined by blending prior to their being dissolved into the bulk of acid being inhibited. Sometimes all of the components of the inhibitor composition are combined by blending prior to their being introduced into the acid or acid composition to be inhibited. This latter technique is particularly preferred where the ingredients for the inhibitor composition might be more readily available in bulk at one location while the acids to be inhibited might be manufactured and/or utilized at one or more different locations. In such instances it is preferred, for example, that the inhibitor compositions of this invention (i.e., the iodide or bromide salt plus primary or secondary amine plus quaternary ammonium compound) be prepared by first blending together the appropriate ingredients, then transferring or shipping the resulting mixture to any location that has need of such an extremely effective corrosion inhibiting composition. Since inorganic iodide and bromide salts are generally not directly soluble in the amines and/or quaternary ammonium compounds contemplated by this invention, uniform homogeneous blends of an inorganic iodide or bromide salt, plus an amine, plus a quaternary ammonium compound usually cannot easily be attained by simply mixing the individual ingredients together. It has been found, however, that by combining with the concentrated inhibitor mixtures at least a relatively minor amount and up to about 90 weight percent of the resulting concentrate, either of acid of the type whose corrosion is eventually to be inhibited by the inhibitor composition being prepared or of any other nonoxidizing acid, there can be made a homogeneous blend which will not separate into its individual components under normal conditions of storage and handling. Preferably, however, the acid content of these homogeneous inhibitor concentrates will contain between about 10 and about 50 weight percent of the nonoxidizing acid based upon the total weight of the inhibitor concentrate composition. Therefore, the homogeneous blends of a nonoxidizing acid, an inorganic iodide or bromide salt, a primary or secondary amine and a quaternary ammonium compound are preferred embodiments of this invention. Generally, in these preferred embodiments, the ratios of iodide or bromide salt to amine and quaternary ammonium compound will be the same as those which will be utilized for the inhibition of the acidic corrosion, described above. In addition, the concentration of the acid in the homogeneous inhibitor compositions will vary considerably. Generally, however, at least as much acid, calculated on a molar basis, as there is amine in the inhibitor concentrate, is utilized in order to facilitate the solubilization of both the amine and the inorganic iodide or bromide salt in the concentrated inhibitor system. Water can also be present in the concentrated homogeneous inhibitor compositions to any desired extent, although compositions containing as little water as possible are usually desired, because such compositions (containing a minimum of water) can be used to inhibit the corrosion caused by highly concentrated acids without unduly contributing to their dilution. Sometimes, however, the presence of a small amount of water will speed up the rate of dissolution of the iodide or bromide salt in the acid. Materials other than acids and water are sometimes used to convert the ordinarily nonhomogeneous concentrated inhibitor compositions of this invention into the homogeneous state—usually without any adverse effect whatever upon the overall ultimate performance of the inhibitor composition. For example, various mixtures of a lower alcohol such as methyl, ethyl, isopropyl, and the like, with water can be blended with the three basic inhibitor ingredients with which this invention is concerned at concentrations of up to about 30 weight percent (of alcohol) of the total homogeneous inhibitor concentrate. Usually, more than 50 weight percent of the alcohol-water mixtures utilized in this manner is water.

In spite of the fact that the above-described inhibitor concentrates considerably simplify the task of supplying high quality corrosion inhibitors to those who need them at various locations, times, etc., it is most desirable that an inhibitor concentrate be available which can inhibit acidic corrosion of the non-graphic metals in as many different acids as possible. With this goal in mind, it was found that the presence of a very small amount of phosphoric acid in almost any other acid is practically innocuous in almost every respect, while the presence of almost any other of the nonoxidizing acids is usually somewhat less widely desirable. Therefore, it is with phosphoric acid that a particularly preferred, widely applicable, embodiment of this invention is prepared. This particularly preferred homogeneous inhibitor concentrate generally contains between about 20 and about 60 and preferably between about 25 and about 40 weight percent of phosphoric acid, usually less than about 15 weight percent of water, sometimes a small amount of a lower alcohol, and the remainder one of the preferred inhibitor compositions (i.e., a blend of an inorganic iodide or bromide salt, a primary or secondary amine, and a quaternary ammonium compound). For example, a few representative particularly preferred homogeneous inhibitor concentrates are preferred as follows:

(a) To 30 parts of 75% H_3PO_4, add 32 parts of octadecenylamine, 32 parts of didodecyldimethyl ammonium chloride and 5.4 parts of potassium iodide. Mix well until the blend becomes a homogeneous liquid (usually within about 4–5 minutes).

(b) To 40 parts of 85% H_3PO_4, add 30 parts of hexylamine, 24 parts of octadecyl trimethyl ammonium acetate, and 4 parts of magnesium iodide. Mix well until the resulting blend forms a homogeneous fluid.

(c) To 50 parts of 75% H_3PO_4, add 30 parts of dodecylamine, 40 parts of hexadecylethyl dimethyl ammonium bromide and 3 parts of potassium iodide. Stir the resulting blend until it forms a clear, homogeneous liquid.

The amounts of such homogeneous inhibitor concentrates that are added to the acid or acidic composition (the corrosion by which is to be inhibited) will depend upon the actual concentrations of the inhibitor ingredients contained in the concentrated compositions. However, since the ratios of the various inhibitor ingredients in the concentrates will almost invariably be the same as those which are utilized to inhibit the corrosion, the correct amounts of the concentrate to be used can readily be calculated from the amount of inorganic iodide salt contained in the concentrated composition to be utilized. For example, the amount of a concentrate containing 5 weight percent of an inorganic iodide, such as magnesium iodide, which can be utilized will preferably vary between about 0.04 to about 10 weight percent of the inhibited acid composition, while the amount of a concentrate containing 10

weight percent of an inorganic iodide, such as potassium iodide which can be utilized will vary between about 0.02 and about 5 weight percent of the inhibited acid composition (to yield the preferred concentrations of between about 0.002 and 0.5 weight percent of inorganic iodide or bromide in the inhibited acid compositions).

For the utilization of the aforesaid inhibitor concentrates to inhibit corrosion, they are simply blended or stirred into the appropriate acid by conventional means until they are dissolved and well dispersed through the acid.

Various materials such as foam depressors, foaming agents, inorganic and organic diluents and bases, etc., can be added to the acids being inhibited according to this invention, in any of a number of conventional procedures or even along with the inhibitor materials themselves, without any apparently detrimental effect whatever on the surprisingly beneficial corrosion inhibition of metals by the compounds and processes of this invention. The application of some of the particularly preferred homogeneous inhibitor concentrates contemplated by this invention (such as those illustrated immediately above) to acidic systems will be demonstrated by the following examples.

EXAMPLE I

The unexpected synergistic corrosion-inhibiting effectiveness of the combination of potassium iodide, primary aliphatic amine, and a quaternary ammonium compound was demonstrated by comparing the corrosion resistance of SAE 1020 mild steel to 75% phosphoric acid containing varying concentrations of the individual ingredients, various binary compositions, and the basic three-component combination. The demonstration was carried out by contacting the steel with the appropriate acidic compositions for 72 hours at 120° F., examining a sample of the steel, and subsequently calculating the rate of corrosion of the sample by measuring its weight loss.

The corrosion attack on the steel beneath the surface of the acidic solution and at the air-metal-solution interface was noted. This was obtained by observing visually the acidic attack on the metal so exposed. Note that the most desirable inhibitor protects the metal no matter in what special contacting relationship it is with the corroding medium. Note, too, that the inhibitor composition of this invention performs best of all compostions and combinations tested. Inhibitors A and B are conventional, commercially available corrosion inhibitors for phosphoric acid, utilized at concentrations recommended by their respective manufacturer.

Table 1

Additives, Weight Percent	Corrosion Rates,[3] m.p.y.	Observations
No inhibitor	3,053	Severe over-all attack.
0.2% KI	16.4	Edge attack.
0.05% KI	14.1	Do.
0.01% KI	25.8	Do.
0.1% amine X [1]	1,049	Pitting at interface.
0.05% amine X [1]	927	Do.
0.5% quaternary Y [2]	3.0	General over-all attack.
0.1% quaternary Y [2]	2.2	Do.
0.05% quaternary Y [2]	5.0	Do.
0.01% quaternary Y [2]	19.7	Do.
0.1% amine X [1] plus 0.1% quaternary Y [2]	2.0	Interface attack.
0.05% amine X [1] plus 0.005% quaternary Y [2]	2.6	Do.
1.0% amine X [1] plus 0.1% KI	0.7	Do.
0.1% amine X [1] plus 0.01% KI	0.7	Do.
0.05% amine X [1] plus 0.105% KI	0.8	Do.
1.0% quaternary Y [2] plus 0.1% KI	0.8	Slight edge attack.
0.1% quaternary Y [2] plus 0.5% KI	0.8	Do.
0.05% quaternary Y [2] plus 0.005% KI	0.9	Do.
0.05% amine X [1] plus 0.05% quaternary Y [2] plus 0.005% KI.	0.3	No localized attack.
0.05% amine X [1] plus 0.05% quaternary Y [2] plus 0.005% MgI.	0.2	Do.
Inhibitor A at 1% (as recommended)	50.7	Pitting.
Inhibitor B at 0.1% (as recommended)	5.5	General over-all attack.

[1] Amine X is an octadecylamine.
[2] Quaternary Y is didodecyldimethyl ammonium chloride.
[3] Determined after exposure for 72 hours.

Synergism similar to that illustrated in Example I is observed when other of the iodides or bromides, amines, and quaternary ammonium compounds contemplated by this invention are substituted for those utilized in Example I.

EXAMPLE II

In order to observe the applicability of the present invention to various acids, the following demonstrations were made, following the procedure described in Example I, above. Data from these demonstrations are set forth in Table 2.

Table 2

CORROSION INHIBITION [1] IN VARIOUS ACIDS

Acid	Concentration, Percent	Inhibitor	Corrosion Rate, m.p.y.
H_2SO_4	10	No	916
H_2SO_4	10	Yes	9.7
H_2SO_4	65	No	28.4
H_2SO_4	65	Yes	19.2
HCl	10	No	1,400
HCl	10	Yes	28.4
HCl	35	No	3,000
HCl	35	Yes	30.2
Acetic	10	No	41.2
Do	10	Yes	16.5
H_3PO_4	105	No	540
H_3PO_4	105	Yes	0.5
Oxalic	10	No	15.2
Do	10	Yes	6.5

[1] By 0.05% of primary oleyl amine plus 0.05% didodecyldimethyl ammonium chloride plus 0.005% of potassium iodide, based on the total weight of the acid composition.

EXAMPLE III

Example III illustrates the applicability of various amines and quaternary ammonium compounds in the practice of this invention. Conditions for the data in Table 3 are the same as those described in Example I, above.

Table 3

Inhibitor:	Corrosion rate,[1] m.p.y.
(a) 0.05% of primary oleyl amine+0.05% didodecyl dimethyl ammonium chloride +0.005% KI	0.7
(b) 0.05% primary saturated octadecyl amine +0.5% dodecylbenzyl dimethyl ammonium bromide+0.005% MgI	0.7
(c) 0.05% monounsaturated primary dodecylamine+0.05% trioctyl methyl ammonium chloride+0.005% KBr	1.5

Table 3—Continued

(d) 0.05% hexadecylmethyl amine+0.05% dodecyltrimethyl ammonium chloride +0.005% KI	1.6
(e) 0.05% hexadecylamine (primary)+0.05% hexadecyltrimethyl ammonium bromide +0.008% NaBr	3.0
(f) 0.05% primary octylamine+0.05% cetyltrimethyl ammonium stearate+0.005% KI	0.4
(g) 0.05% dihexylamine+0.05% hexadecyl trimethyl ammonium acetate+0.005% MgBr	2.0
(h) 0.05% dipropylamine+0.05% cetyl ethyl dimethyl ammonium chloride+0.007% NaI	2.4
(i) 0.05% di-2-ethylhexylamine+0.05% dioctadecyl dimethyl ammonium chloride +0.01% CuI_2	17

[1] After immersion in 75% H_3PO_4 at 120° F. for 72 hours.

EXAMPLE IV

The data in Table 4 illustrate that this invention can also be used to protect metals other than steel that are corroded by acids.

Table 4

CORROSION INHIBITION[1] OF VARIOUS METALS

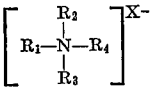
	Corrosion (m.p.y.)	
	Uninhibited	Inhibited [2]
Brass (yellow)	1.5	0.7
Monel	1.4	0.2
Nickel	4.5	1.2
Steel (mild) SAE 1010	6,770	1.2
Steel (mild) A-285	1,560	3.0
Cast Iron	2,670	5.0

[1] After immersion in 75% H_2SO_4 at 120° F. for 24 hours.
[2] 0.05% dodecylamine, 0.05% dodecyltrimethyl ammonium chloride, 0.005% KI.

What is claimed is:

1. A corrosion-inhibited phosphoric acid composition consisting essentially of said phosphoric acid and at least about 0.0405 weight percent, based on the total weight of said phosphoric acid composition, of a mixture of (a) an inorganic salt selected from the group consisting of iodides and bromides that are soluble at about 25° C. in 85 weight percent orthophosphoric acid to the extent of at least about 0.0005 weight percent; (b) an aliphatic amine selected from the group consisting of primary and secondary amines having from 4 to 28 carbon atoms in their molecules, said amine being soluble at about 25° C. in 85 weight percent orthophosphoric acid to the extent of at least about 0.02 weight percent; and (c) a quaternary ammonium compound, said quaternary ammonium compound being soluble at about 25° C. in 85 weight percent orthophosphoric acid to the extent of at least about 0.02 weight percent, the weight ratio of said amine to said salt in said composition being greater than about 2:1, and the weight ratio of said quaternary ammonium compound to said salt in said composition being greater than about 2:1.

2. A corrosion-inhibited phosphoric acid composition consisting essentially of said acid and, dissolved therein, from about 0.0005 to about 1.5 weight percent of an alkaline earth metal salt selected from the group consisting of iodides and bromides, from about 0.02 to about 5 weight percent of a primary aliphatic amine having between 4 and 28 carbon atoms in its molecule, and from about 0.02 to about 5 weight percent of a quaternary ammonium compound represented by the structure:

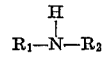


wherein R_1 is a hydrocarbyl radical having between 8 and 20 carbon atoms; R_2 is a saturated aliphatic hydrocarbyl radical having the empirical formula $(C_nH_{2n})+H$, where n is a whole number from 1 to 13; R_3 is a saturated aliphatic hydrocarbyl radical having the empirical formula $(C_bH_{2b})+H$, where b is a whole number from 1 to 8; R_4 is a saturated aliphatic lower hydrocarbyl radical having the empirical formula $(C_kH_{2k})+H$, where k is a whole number from 1 to 4; and X is an acid anion; the weight ratio of said primary aliphatic amine to said alkaline earth metal salt in said composition being greater than about 2:1, and the weight ratio of said quaternary ammonium compound to said alkaline earth metal salt in said composition being greater than about 2:1.

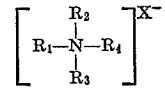
3. A composition as in claim **2**, wherein said alkaline earth metal salt is magnesium iodide.

4. A composition as in claim **3**, wherein said primary aliphatic amine is octadecylamine and said quaternary ammonium compound is didodecyldimethyl ammonium chloride.

5. A corrosion-inhibited phosphoric acid composition consisting essentially of said phosphoric acid and, dissolved therein, (a) from about 0.002 to about 0.5 weight percent of an alkali metal salt selected from the group consisting of iodides and bromides, (b) from about 0.02 to about 5 weight percent of a secondary aliphatic amine that is soluble at about 25° C. in 85 weight percent orthophosphoric acid to the extent of at least about 0.02 weight percent, and can be represented by the structure:



wherein R_1 and R_2 are hydrocarbyl radicals having between 3 and 16 carbon atoms per radical and the total number of carbon atoms in R_1 plus R_2 is between 8 and 28; and (c) from about 0.02 to about 5 weight percent of a quaternary ammonium compound which has the structure;



wherein R_1 is a hydrocarbyl radical having between 8 and 20 carbon atoms; R_2 is a saturated aliphatic hydrocarbyl radical having the empirical formula $(C_nH_{2n})+H$, where n is a whole number from 1 to 13; R_3 is a saturated aliphatic hydrocarbyl radical having the empirical formula $(C_bH_{2b})+H$, where b is a whole number from 1 to 8; R_4 is a saturated aliphatic lower hydrocarbyl radical having the empirical formula $(C_kH_{2k})+H$, where k is a whole number from 1 to 4; said quaternary ammonium compound being soluble at about 25° C. in 85 weight percent orthophosphoric acid to the extent of at least about 0.02 weight percent; and X is an acid anion; the weight ratio of said secondary aliphatic amine to said alkali metal salt in said composition being greater than about 2:1, and the weight ratio of said quaternary ammonium compound to said alkali metal salt in said composition being greater than about 2:1.

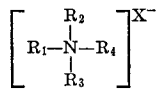
6. A composition as in claim **5**, wherein said secondary aliphatic amine is dihexylamine and said quaternary ammonium compound is hexadecylethyldimethyl ammonium chloride.

7. A corrosion-inhibited phosphoric acid composition consisting essentially of, in addition to said acid, from about 0.002 to about 0.2 weight percent of potassium iodide, from about 0.02 to about 1 weight percent of octadecylamine, and from about 0.02 to about 1 weight percent of didodecyldimethyl ammonium chloride.

8. A composition suitable for inhibiting the corrosion of nongraphitic metals caused by a phosphoric acid when it is dissolved in said acid in an amount equal to at least about 0.0405 weight percent, based on the weight of said acid, said composition consisting essentially of an inorganic salt soluble in 85 weight percent orthophosphoric

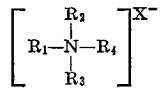
acid at about 25° C. to the extent of at least about 0.0005 weight percent selected from the group consisting of iodides and bromides; an aliphatic amine selected from the group consisting of primary and secondary aliphatic amines having from 4 to 28 carbon atoms in their molecules, said amine being soluble in 85 weight percent orthophosphoric acid at about 25° C. to the extent of at least about 0.02 weight percent; and a quaternary ammonium compound, said quaternary ammonium compound being soluble in 85 weight percent orthophosphoric acid at about 25° C. to the extent of at least about 0.02 weight percent, the weight ratio of said amine to said salt in said composition being from about 2:1 to about 20:1, and the weight ratio of said quaternary ammonium compound to said salt in said composition being from about 2:1 to about 20:1.

9. A homogeneous composition suitable for inhibiting the corrosion of nongraphic metals by a phosphoric acid when it is dissolved in said acid, said composition consisting essentially of up to about 90 weight percent of a phosphoric acid; an inorganic salt selected from the group consisting of iodides and bromides soluble at about 25° C. in 85 weight percent orthophosphoric acid to the extent of at least about 0.0005 weight percent; an aliphatic amine selected from the group consisting of primary and secondary, and having a total of between 4 and 28 carbon atoms in its molecule; and a quaternary ammonium compound having the structure:



wherein R_1 is a hydrocarbyl radical having between 6 and 30 carbon atoms; R_2 is a saturated aliphatic hydrocarbyl radical having the empirical formula $(C_nH_{2n})+H$, where n is a whole number from 1 to 18; R_3 is a saturated aliphatic hydrocarbyl radical having the empirical formula $(C_bH_{2b})+H$, where b is a whole number from 1 to 15; R_4 is a saturated aliphatic lower hydrocarbyl radical having the empirical formula $(C_kH_{2k})+H$, where k is a whole number from 1 to 4; said quaternary ammonium compound and said aliphatic amine being soluble at about 25° C. in 85 weight percent orthophosphoric acid to the extent of at least about 0.02 weight percent; and X is an acid anion; the molar ratio of said acid to said amine in said composition being greater than about 1:1, the weight ratio of said amine to said salt in said composition being greater than about 2:1, and the weight ratio of said ammonium compound to said salt in said composition being greater than about 2:1.

10. A homogeneous composition suitable for inhibiting the corrosion of nongraphitic metals by a phosphoric acid, said composition consisting essentially of, in addition to from about 10 to about 50 weight percent of phosphoric acid, an alkali metal salt soluble in 85 weight percent orthophosphoric acid to the extent of at least about 0.0005 weight percent selected from the group consisting of iodides and bromides, a primary aliphatic amine having between 8 and 18 carbon atoms in its molecule, and a quaternary ammonium compound having the structure:



wherein R_1 is a hydrocarbyl radical having between 8 and 20 carbon atoms; R_2 is a saturated aliphatic hydrocarbyl radical having the empirical formula $(C_nH_{2n})+H$, where n is a whole number from 1 to 13; R_3 is a saturated aliphatic hydrocarbyl radical having the empirical formula $(C_bH_{2b})+H$, where b is a whole number from 1 to 8; R_4 is a saturated aliphatic lower hydrocarbyl radical having the empirical formula $(C_kH_{2k})+H$, where k is a whole number from 1 to 4; said quaternary ammonium compound and said primary aliphatic amine being soluble at about 25° C. in 85 weight percent orthophosphoric acid to the extent of at least about 0.02 weight percent; and X is an acid anion; the molar ratio of said phosphoric acid to said amine in said composition being greater than about 1:1, the weight ratio of said amine to said salt in said composition being greater than about 5:1, and the weight ratio of said ammonium compound to said salt in said composition being greater than about 5:1.

11. A homogeneous composition as in claim 10, wherein said alkali metal salt is potassium iodide, said primary amine is octadecylamine, and said quaternary ammonium compound is didodecyldimethyl ammonium chloride.

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