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CORROSION INHIBITOR FOR CONCENTRATED PHOSPHORIC ACID

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1

This invention is concerned with the inhibition of corrosion by concentrated phosphoric acid contained in iron and steel vessels, or applied to various ferruginous surfaces.

It is an object to make it possible by means of the new corrosion inhibitor to ship concentrated acid without the necessity of utilizing glass containers such as carboys, but instead to make it possible to ship such acid in ferruginous drums.

It is another object to inhibit the corrosion and destruction of iron and steel surfaces by phosphoric acid so as to render the storage of strong acid more economical. It is also a particular object to prevent discoloration of the acid. Such darkening and contamination of phosphoric acid in contact with iron and steel surfaces renders the acid impossible to use in many applications.

One of the handicaps which has resisted the widespread use of phosphoric acid is the difficulty of shipping this material in ferrous containers. While it is possible to employ glass carboys to hold phosphoric acid, it has not been possible heretofore to ship strong phosphoric acids in iron and steel shipping containers, nor to store such acid in other than chemically resistant and consequently expensive materials.

It has been proposed to prevent the corrosion and dissolution of steel or iron drums or containers used for the storage and transportation of phosphoric acid by dissolving in the acid a material capable of precipitating a protective coating on the steel. This precipitation may be accomplished in the presence or absence of an acid regulator. The precipitated protective coating is usually a metal below iron and above mercury in the electromotive series, such as arsenic, while the acid regulator is usually an organic substance such as pyridine bases, crude anthracene, sulfite, lye, resins, wash acids from refining hydrocarbons, etc., many of which are highly colored. In previous proposals it has been necessary to decolorize the inhibited acid, in order to obtain a water-white product. By this means appreciable amounts of the inhibitor were removed from the acid.

The present invention, however, effectively prevents the corrosion or dissolution of iron or steel surfaces, as well as the discoloration of the acid which resulted in the prior art processes. This, moreover, is accomplished without plating the surface of the containing vessel with a corrosion resistant metal. In this way a corrosion inhibitor which is cheap as well as non-poisonous, odorless and colorless is provided.

The objects of the invention are accomplished

2

as set out below. It has been found that the addition to phosphoric acid of certain nitrogen-containing organic compounds in combination with ionizable iodine compounds for all practical purposes eliminates the corrosion of iron and steel surfaces in contact with such acid. Thus it has been found that nitrogen-containing compounds of the group consisting of nitriles and primary amines containing from 6 to 20 carbon atoms are effective in the present relationship. Preferred compounds are the 6 to 14 carbon atom compounds, and in particular the twelve carbon atom radicals, such as the dodecyl and di-cyclohexyl compounds of the respective classes within the group. Both aliphatic and cyclic, i. e., aromatic and cyclo-aliphatic compounds, with and without the characteristic of unsaturation may be employed.

In addition to said nitrogen-containing compounds, the combination therewith of certain iodine-containing compounds is essential. Preferred examples are the ionizable iodine compounds, such as potassium iodide, potassium iodate or iodo-acetic acid. Such iodine-containing ingredients would of themselves discolor phosphoric acid by giving a yellowish color upon standing; but in combination with the nitrogen-containing compounds as set out above, there is obtained a non-coloring, inhibited phosphoric acid.

The desired result of inhibition of corrosion by the phosphoric acid may be accomplished by the use of 0.01–0.50% of the nitrogen-organic compound, although a preferred range is 0.03–0.10% of such compounds. Similarly the amount of iodine-containing compound may vary from 0.001–0.10% by weight, although a preferred range in this type compound is from 0.007–0.0142%. However, higher concentrations of the inhibitors are also effective, and it may be stated generally that any concentration above the threshold of inhibition may be used. This invention may be practiced as shown in the following examples which are, however, illustrative and not limitative as to the present invention.

Example 1

To a solution of 75% phosphoric acid there was added 0.03% dodecyl amine, together with 0.007% of potassium iodide, calculated upon a weight basis with respect to the phosphoric acid. Such acid was placed in contact with a sample of steel, and was found to have a negligible corrosive effect. The rate of penetration of the steel was so low as to be imperceptible.

Example 2

A further test of the inhibited composition of Example 1 was carried out by testing a sample of steel immersed in the inhibited acid in a 10 mm. inverted glass test tube in such a manner as to collect any liberated gas. In this arrangement the hydrogen or other gas evolved was collected and may be considered as a measure of the extent of dissolution of metal. The steel specimen used in the test measured 7 x 40 x 2 mm. and the entire test was conducted at a temperature of 100°–120° F. It was found that the amount of gas released over a period of 30 days consisted only of a very small bubble, whereas the gas liberated in a control test carried out with uninhibited acid filled the entire glass tube in three hours, as a result of the corrosive action of the steel by the 75% phosphoric acid.

Example 3

A test was conducted employing 75% phosphoric acid inhibited by 0.10% ortho-amino dicyclohexyl (the ortho-amino derivative of hydrogenated biphenyl), together with 0.007% potassium iodide. The method of test in this case consisted in immersing a steel specimen 7 x 4 x 2 mm. in a 10 mm. inverted glass test tube (about 500 mm. long), and maintaining such tube together with its contents at 120° F. The criteria of the test was again the amount of gas evolved as a result of the acid corrosion. It was found in this case that after 76 days there was evolved only 9 mm. column of released hydrogen. In contrast a similar tube tested with the same steel specimen and uninhibited 75% phosphoric acid showed the entire glass tube to fill with gas at the end of three hours.

Further test data are summarized in the table below:

Table.—Phosphoric Acid Inhibitors

[0.1% nitrogen compound and 0.007% K. I. based upon weight of acid.]

Inhibitor	Days	Gas Height
		Mm.
No inhibitor	(3 hrs.)	500
o-Amino dicyclohexyl	55	0.9
Hexadecyl amine	55	2.0
Dodecyl amine	30	bubble
Decyl amine	55	1.9
α-Naphthonitrile	212	2.5
β-Naphthonitrile	70	11.0
p-Tolunitrile	45	2.4
Benzonitrile	45	2.4
Phenylacetonitrile	240	3.5
Dodecanenitrile	96	4.0
Tetradecanenitrile	332	0.3
Octadecane nitrile	648	2.3
Melamine	2	500
Morpholine	4	500
Acetonitrile	23	500
Fumaronitrile	23	500
Chloracetoamide	2.5	500
Nitrosobenzene	2	500
Azobenzene	2	500
Succinimide	2	500
Stearamide	2	500
2-amino-pyridine	4	500
Pyridine	2	500

It is immaterial in the present process and product whether potassium iodide or the corresponding iodate compound is employed. Also equivalent in this respect is iodo acetic acid. It has been found that all of these compounds may be employed together with the nitrogen-organic compounds having from 6 to 20 carbon atoms to provide an inhibited phosphoric acid which is no longer corrosive to iron or steel and which does not discolor the acid.

In addition to the aliphatic nitrogen compounds of the group consisting of nitriles and amines, it is noted that cyclo aliphatic and aromatic radicals, as well as the corresponding alkyl aromatic compounds may be employed with the provision that the number of carbon atoms present in the molecule shall be from 6 to 20 carbon atoms. The preferred range comprises 6 to 12 carbon atoms, one being the twelve carbon atom compounds, such as the dodecyl or dicyclo hexylamines described above. However, it is desirable for superior results to employ such straight chain, or closed chain amines, and not the branched-chain alkyl radicals, since such latter class of amines gives inferior results.

While the proportions of inhibitors given above are satisfactory for ordinary service, they may be considerably varied without departing from the spirit of the invention. In general, it may be said that increasing the concentration of the inhibitor combination decreases the degree of penetration or corrosion, while decreasing the concentration of the inhibitor combination increases the penetration.

It has been found that the inhibitory combinations of the present invention are applicable to medium strong, e. g., (50% to 75% H_3PO_3) to very strong phosphoric acids (85% to 116% H_3PO_4) to accomplish the desirable corrosion-resistant results over a wide range of temperatures.

The inhibited phosphoric acid of the invention may be transported readily in iron or steel containers without corroding the same. The inhibited acid may also be used for metal cleaning operations, since the acid may be applied to clean away various deposits without corroding the underlying metal. Examples of such applications are the cleaning of boiler tubes and also steel tanks such as railway tank cars.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that the invention is not limited to the specific embodiments thereof, except as defined in the appended claims.

What is claimed as novel and is desired to be protected by Letters Patent of the United States is:

1. A process for the inhibition of corrosion of phosphoric acid essentially comprising the dissolving therein of a nitrile having from 6 to 20 carbon atoms in combination with an ionizable iodide in inhibitory concentrations to inhibit the corrosive action of the acid on iron and steel.

2. A process for the inhibition of corrosion of phosphoric acid essentially comprising the dissolving therein of a primary amine having from 6 to 20 carbon atoms in combination with an ionizable iodide in inhibitory concentrations to inhibit the corrosive action of the acid on iron and steel.

3. A process for the inhibition of corrosion of phosphoric acid essentially comprising the dissolving therein of a nitrogen-containing compound of the group consisting of primary amines and nitriles having from 6 to 20 carbon atoms, in combination with an ionizable iodide in inhibitory concentrations to inhibit the corrosive action of the acid on iron and steel.

4. A process for the inhibition of corrosion of phosphoric acid essentially comprising the dissolving therein of a nitrogen-containing compound of the class consisting of primary amines and nitriles having from 6 to 20 carbon atoms,

together with a compound of the class consisting of potassium iodide, potassium iodate, and iodo acetic acid, in inhibitory concentrations to inhibit the corrosive action of the acid on iron and steel.

5. A process for the inhibition of corrosion of phosphoric acid essentially comprising the dissolving therein of 0.01% to 0.5% of a nitrogen-containing compound of the class of primary amines and nitriles having from 6 to 20 carbon atoms, together with 0.001% to 0.1% of a compound of the group consisting of potassium iodide, potassium iodate, and iodo acetic acid, based upon the weight of phosphoric acid.

6. A composition of reduced corrosive action on iron and steel comprising phosphoric acid essentially in combination with 0.01% to 0.5% of a nitrogen-containing compound of the class of primary amines and nitriles having from 6 to 20 carbon atoms, together with 0.01% to 0.1% of a compound of the group consisting of potassium iodide, potassium iodate, and iodo acetic acid, based upon the weight of phosphoric acid.

7. An inhibited phosphoric acid comprising phosphoric acid of a concentration of at least 50% essentially in combination with approximately 0.1% of dodecylamine and 0.003% of a compound of the group consisting of potassium iodide, potassium iodate and iodo acetic acid, based upon the weight of phosphoric acid.

8. An inhibited phosphoric acid comprising phosphoric acid of a concentration of at least 75% essentially in combination with approximately 0.01% of dodecylamine and 0.003% of potassium iodate.

9. A phosphoric acid solution characterized by reduced corrosive action on iron and steel, said solution comprising phosphoric acid having dissolved therein a minor proportion of a nitrile having from 6 to 20 carbon atoms in combination with a minor proportion of an ionizable compound containing iodine.

10. A phosphoric acid solution characterized by reduced corrosive action on iron and steel, said solution comprising a major proportion of phosphoric acid in combination with relatively small amounts of an inhibitor consisting of the combination of a primary amine having from 6 to 20 carbon atoms and an ionizable compound containing iodine.

11. A phosphoric acid solution characterized by reduced corrosive action on iron and steel, said solution comprising a major proportion of phosphoric acid having dissolved therein a minor proportion of a nitrogen-containing compound of the class of primary amines and nitriles having from 6 to 12 carbon atoms, together with a minor proportion of a compound selected from the group consisting of potassium iodide, potassium iodate and iodo acetic acid.

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