United States Patent Office

3,249,547

Patented May 3, 1966

3,249,547

INHIBITION OF ACIDIC CORROSION BY USE OF A COMBINATION OF A SUGAR AND AN IODIDE OR BROMIDE SALT

Arthur Orman Fisher, Richmond Heights, Mo., assignor to Monsanto Company, a corporation of Delaware

No Drawing. Filed May 19, 1958, Ser. No. 735,973
18 Claims. (Cl. 252—136)

This invention relates to novel compositions and methods useful for inhibiting corrosion of metal by acids. More specifically, this invention relates to a corrosion inhibiting combination of ingredients, each of which by itself exhibits some corrosion-inhibiting effect, but which in combination exhibit a synergistic effect far greater than that which would be expected from such a combination.

The problems relating to corrosion of metals during the manufacture, shipment, storage and use of various acids are very well known. For example, present-day practice in large bulk shipments of phosphoric acid involves the use of rubber-lined tank cars. When such phosphoric acid is used in industrial plants or equipment, the piping and equipment contacted by the acid must be made of special corrosion-resistant metal such as type 316 or 304 stainless steels in order to withstand corrosive attack by the acid. Similar problems exist with respect to other acids, such as sulphuric, hydrochloric, nitric, citric, tartaric, oxalic, and the like. Consequently, there is a continuing demand for effective corrosion inhibitors which will allow the use of such acids in connection with the more widely available and less expensive metals, such as plain carbon steels. Accordingly, it is an object of the present invention to provide compositions and methods whereby acidic corrosion of metals is markedly decreased.

I have now found that a combination of (a) a sugar, and (b) a salt selected from the group consisting of iodides and bromides will very effectively inhibit acid corrosion of metals, such as steel, nickel, aluminum, brass, etc., and particularly ferruginous metals, such as irons or plain carbon steels.

Although the class of iodide and bromide salts generally is applicable with respect to the present invention, there are rather marked variations in effectiveness within the general class. Examples of typically useful salts are cadmium, cupric, zinc, aluminum and mercuric salts; alkaline earth metal salts, such as calcium, magnesium, and barium; and alkali metal salts, such as sodium, potassium, lithium, and ammonium. The iodides are somewhat more effective than the corresponding bromides, particularly preferred iodides being potassium iodide and magnesium iodide.

By the term "sugar" as used herein is meant a monosaccharide, e.g., fructose, glucose, xylose, arabinose, galactose, etc., or a disaccharide, e.g., sucrose, maltose, lactose, cellobiose, etc., such as are derivable either directly from plants or by hydrolysis of higher polysaccharides.

A particularly preferred embodiment of the invention involves the use of the levorotatory monosaccharides, such as fructose, or the disaccharides, such as sucrose, which hydrolyze to produce such levorotatory monosaccharides.

A further preferred embodiment of the invention comprises the introduction of the sugar in the form of molasses. The desirability of the use of molasses is illustrated by the fact that a given weight of molasses is generally at least as effective as an equal weight of sugar, even though the sugar content in the molasses is considerably under 100%. Thus, the molasses can be used at approximately the same concentrations as the sugars, with at least as effective corrosion-inhibiting results being obtained at a much more economical price. Another preferred embodiment of the invention comprises the use of corn syrup, which has many of the same advantages of molasses.

For purposes of simplicity in further describing the manner of practicing the invention, the following disclosure will be set forth in terms of a preferred corrosion inhibiting combination of molasses and potassium iodide. It should be recognized, however, that the other iodides and bromides can be used in place of potassium iodide, and that more concentrated or pure forms of sugars can be used in place of molasses, in a substantially similar manner.

The relative concentration of molasses and potassium iodide to be used according to the present invention, as well as the total concentration of the combination, will depend to some extent upon the particular acid being inhibited and the concentration of that acid, as well as the type of metal to be protected and the degree of protection desired or required. As a general proposition, the molasses will be used in concentrations ranging between about 0.1 weight percent and about 10 weight percent, and preferably between about 0.2 weight percent and about 2 weight percent, of the acid composition to be inhibited. The concentration of potassium iodide will range from about 0.0005 weight percent and about 1 weight percent, and preferably between about 0.005 weight percent and about 0.1 weight percent, of the acid composition to be inhibited. Thus, the maximum ratio of sugar to salt in the composition of the present invention is about 20,000 to 1. This ratio is calculated as follows:

$$\frac{\text{10 weight percent of sugar}}{\text{0.0005 weight percent of salt}} = \frac{10}{0.0005} = \frac{20{,}000}{1}$$

For the preferred compositions of the present invention, the maximum ratio of sugar to salt is about 400 to 1. This ratio is calculated as follows:

$$\frac{\text{2 weight percent of sugar}}{\text{0.005 weight percent of salt}} = \frac{2}{0.005} = \frac{400}{1}$$

Of the two ingredients, the molasses will almost always be the predominant ingredient, the weight ratio of molasses to potassium iodide generally being greater than 2:1, and preferably greater than 10:1. The most preferred proportions of the two ingredients will generally be such that the potassium iodide will be present in an amount between about 0.05 weight percent and about 10 weight percent of the combination of molasses and potassium iodide.

The total concentration of the foregoing inhibitor mixture used in any particular application will, in addition to the other factors mentioned above, depend upon the concentration of acid in the mixture to be inhibited. For example, dilute aqueous acids such as 10 percent aqueous phosphoric acid or 10 percent aqueous sulphuric acid are more corrosive to plain carbon steels than are the more concentrated acids such as 77 percent phosphoric acid or 100 percent sulphuric acid. Thus, higher concentrations of inhibitors will generally be used with the more dilute aqueous acid solutions than with the more concentrated acids. Since the acids are generally manufactured, shipped and stored in the more concentrated form, a preferred embodiment of this invention involves inhibition of the more highly concentrated acids, such as phosphoric acid at concentrations greater than 40 weight percent or, more preferably, at concentrations above 75 weight percent.

It is recognized that because molasses is a natural product there will be some variation in composition thereof, depending upon the particular source of the molasses. It has been found, however, that those variations are not sufficiently great to have any substantial effect on the usefulness of the various molasses as an ingredient in the

present corrosion inhibiting composition. Thus, for example, various samples of blackstrap molasses, sugar beet molasses and citrus molasses have all been tested and found to be effective for inhibiting acidic corrosion when used in conjunction with the iodides or bromides according to the present invention. It has been found, however, that blackstrap molasses is generally more effective than the others; consequently, the use of blackstrap molasses constitutes a preferred embodiment of the invention.

Further details of specific embodiments of the invention, as well as various best modes of making and using the invention, will be readily apparent from the following examples:

EXAMPLE 1

The corrosion-inhibiting effectiveness of the combination of molasses and potassium or magnesium iodides was demonstrated by comparing the corrosiveness of 77 percent orthophosphoric acid containing (1) no inhibitor, (2) the combination inhibitor of this invention, or (3) and (4) each ingredient of that combination. This comparison was carried out by immersing test coupons (1" x 3" x 0.024") of SAE 1020 steel in the various acid solutions for a period of 72 hours at 120° F., and subsequently calculating the rate of corrosion of the immersed coupons by measuring their weight loss. The results of this comparison are set forth in the following Table I.

Table I

Additives, Wt. Percent			Corrosion Rates, Mils per Year
Molasses	KI	MgI_2	
None	None	None	ca. 1,220
1.0	None	None	77
None	0.20	None	16.4
0.25	0.05	None	2.4
None	None	None	[1] 1,055
None	None	0.01	[1] 18.9
0.50	None	0.005	[1] 2.8

[1] These tests carried out with SAE 1010 steel coupons.

From the foregoing table it can be seen that each of the individual components of the combinations of this invention has some inhibitory effect. However, the combination of two components has a marked synergistic effect—so that even greatly reduced concentrations of the additives in combination give greater inhibition than either of the components used individually.

EXAMPLE 2

Further demonstrations of the effect of variations in inhibitor component concentration, as well as variations in the phosphoric acid concentration, were carried out by the same test method described in the foregoing Example 1. The results of these further tests are set forth in the following Table II.

Table II

Acid Strength, Wt. Percent H_3PO_4	Additives, Wt., Percent		Corrosion Rates, Mils per Year
	Molasses	KI	
77	0.25	0.003	2.4
77	1.0	0.003	3.5
77	1.0	0.1	5.1
41	3.0	0.05	2.1
25	10.0	0.1	0.9

EXAMPLE 3

The procedure of Example I was utilized to evaluate the effectiveness of various sugars combined with potassium iodide in inhibiting phosphoric acid. The results are set forth in the following Table III.

Table III

Additives			Corrosion Rates, Mils per Year
Sugar	Wt. Percent	KI, Wt. Percent	
Fructose	0.5	0.005	3.6
Sucrose	0.5	0.005	4.4
Glucose	0.5	0.005	9.2

EXAMPLE 4

The procedure of Example 1 was utilized to demonstrate the effectiveness of a combination of molasses (0.5 volume percent) and potassium iodide (0.005 weight percent) in inhibiting corrosion by various acids other than phosphoric acid. The results are summarized for 24 hour exposures in the following Table IV.

Table IV

Acid	Corrosion Rate, Mils per Year	
	Without Inhibitor	With Inhibitor
50% H_2SO_4	109	3.7
37% HCl	8,840	96.4
10% Oxalic	12.2	6.7
10% Tartaric	6.8	3.8

It will be noted that both the sugar or molasses and potassium iodide of the foregoing preferred corrosion inhibiting combinations have food supplement value. This gives the present invention particularly significant value with respect to use in acids (such as phosphoric, citric, tartaric, etc.) which may ultimately find their way into animal or human food. In this connection, it has been found that the combination of molasses and potassium iodide when incorporated into phosphoric acid which is to be compounded with corn gluten, alfalfa, soy bean meal, etc. and pelleted for use as animal or poultry feed considerably enhances the ease with which such feed can be pelleted. Consequently, phosphoric acid inhibited according to the present invention constitutes a further preferred embodiment of the present invention.

It should be readily apparent from the foregoing description that the various components of the present corrosion inhibiting combination may be added individually to the acid to be inhibited or, alternatively, they may be combined first and then incorporated as a mixture into the acid to be inhibited. This latter procedure has the advantage that a premixed concentrate of the inhibited combination (for example, a combination comprising 95% molasses or sugar and 5% potassium iodide) can be formulated, shipped, stored, etc., as the concentrate, and need be added to the acid only at such time as inhibition of the acid becomes necessary. As a further example of this premixing, it has been found that the addition of KI and molasses to an equal volume of 77% H_3PO_4 or of water allows easier mixing of the inhibitor ingredients to the bulk of the acid, through the lowered viscosity of the premixed components.

What is claimed is:

1. An acid corrosion-inhibiting composition consisting essentially of molasses and between about 0.05 weight percent and about 10 weight percent of an alkali metal iodide, the weight ratio of said molasses to said alkali metal iodide being at least 2:1.

2. An acid corrosion-inhibiting composition consisting essentially of molasses and between about 0.05 weight percent and about 10 weight percent of potassium iodide, the weight ratio of said molasses to said potassium iodide being at least 2:1.

3. An acid corrosion-inhibiting composition consisting essentially of molasses and between about 0.05 weight percent and about 10 weight percent of an alkali metal bromide, the weight ratio of said molasses to said alkali metal bromide being at least 2:1.

4. An acid corrosion-inhibiting composition consisting essentially of a sugar and an alkali metal iodide, the weight ratio of said sugar to said alkali metal iodide being between 2:1 and about 20,000:1.

5. An acid corrosion-inhibiting composition consisting essentially of a sugar and an alkali metal bromide, the weight ratio of said sugar to said alkali metal bromide being between 2:1 and about 20,000:1.

6. An acid corrosion-inhibiting composition consisting essentially of molasses and an alkali metal iodide, the weight ratio of said molasses to said alkali metal iodide being between 2:1 and about 400:1.

7. An acid corrosion-inhibiting composition consisting essentially of molasses and an alkali metal bromide, the weight ratio of said molasses to said alkali metal bromide being between 2:1 and about 400:1.

8. An acid corrosion-inhibiting composition consisting essentially of a sugar and an alkaline earth metal iodide, the weight ratio of said sugar to said alkaline earth metal iodide being between 2:1 and about 400:1.

9. An acid corrosion-inhibiting composition consisting essentially of a sugar and an alkaline earth metal bromide, the weight ratio of said sugar to said alkaline earth metal bromide being between 2:1 and about 400:1.

10. An acid corrosion-inhibiting composition consisting essentially of a sugar and a salt selected from the group consisting of iodides and bromides, the weight ratio of said sugar to said salt being between 2:1 and about 20,000:1.

11. A corrosion-inhibited acid composition containing in addition to the acid, a corrosion-inhibiting concentration of a mixture of molasses and an alkali metal iodide, the weight ratio of said molasses to said alkali metal iodide being between 2:1 and about 400:1.

12. A corrosion-inhibited phosphoric acid composition comprising at least about 20 weight percent of phosphoric acid and between about 0.1 weight percent and about 10 weight percent of molasses and between about 0.0005 weight percent and about 1 weight percent of potassium iodide, the weight ratio of molasses to iodide being greater than about 2:1.

13. A corrosion-inhibited orthophosphoric acid composition comprising at least about 40 weight percent of orthophosphoric acid, between about 0.2 weight percent and about 2.0 weight percent of molasses, and between about 0.0005 weight percent and about 0.1 weight percent of potassium iodide.

14. A corrosion-inhibited orthophosphoric acid composition comprising at least about 75 weight percent of orthophosphoric acid, between about 0.2 weight percent and about 2.0 weight percent of molasses, and between about 0.0005 weight percent and about 0.1 weight percent of potassium iodide.

15. A corrosion-inhibited acid composition containing in addition to the acid, a corrosion-inhibiting concentration of a mixture of molasses and an alkali metal bromide, the weight ratio of said molasses to said alkali metal bromide being between 2:1 and about 400:1.

16. A corrosion-inhibited phosphoric acid composition comprising at least about 20 weight percent of phosphoric acid and between 0.1 weight percent and about 10 weight percent of a sugar and between about 0.0005 weight percent and about 1 weight percent of a salt selected from the group consisting of iodides and bromides, the weight ratio of said sugar to said salt being greater than about 2:1.

17. A corrosion-inhibited acid composition containing, in addition to the acid, a corrosion-inhibiting concentration of a mixture of a sugar and a salt selected from the group consisting of iodides and bromides, the weight ratio of said sugar to said salt being between 2:1 and about 20,000:1.

18. A corrosion-inhibited phosphoric acid composition consisting essentially of at least about 20 weight percent of phosphoric acid, between about 0.2 weight percent and about 2 weight percent of molasses, and potassium iodide, the weight ratio of molasses to iodide being about 100:1.

References Cited by the Examiner

UNITED STATES PATENTS

1,809,041	6/1931	Jenkins et al.	252—389
1,948,029	2/1934	Fischer	252—396
2,005,601	6/1935	Horst	252—146
2,708,184	5/1955	Hager et al.	252—389
2,793,952	5/1957	Rawlings	99—6

OTHER REFERENCES

Wood et al.: U.S. Dispensatory, 23 ed., page 1072, pub. 1943, by J. B. Lippincott Co. of Philadelphia, Syrupus Bromidorum.

The Pharmaceutical Recipe Book, 3rd ed., published by the American Pharmaceutical Association, 1943, p. 244, Syrup of Iron and Iodide.

JULIUS GREENWALD, *Primary Examiner.*

JOSEPH R. LIBERMAN, *Examiner.*

H. B. GUYNN, R. D. EDMONDS, J. E. MOERMOND, A. T. MEYERS, *Assistant Examiners.*