United States Patent Office 2,877,188
Patented Mar. 10, 1959

2,877,188

CORROSION INHIBITORS AND METHOD OF USING SAME

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No Drawing. Application July 27, 1956
Serial No. 600,368

12 Claims. (Cl. 252—389)

This invention relates in general to inhibiting the corrosion of ferrous metals by aqueous solutions where the metals and/or their alloys are in contact with water or aqueous solutions under circumstances where nonferrous metals may also be present and in contact with the aqueous media.

It relates in particular to a method of drastically reducing corrosion of ferrous metals in closed heating and/or cooling systems, which are usually fabricated from a multiplicity of metals and metal alloys.

The above mentioned systems have come into widespread use in modern structures, particularly in office buildings, apartment buildings, and the like, where a single closed system transporting a liquid, generally water or aqueous solutions, often serves the dual purpose of heating the building in cold weather and cooling it in warm weather.

Although temperatures and pressures within the closed system will vary depending upon the seasons of the year as well as upon operating conditions, these systems generally operate in a temperature range of from 50 to 180 degrees Fahrenheit although sometimes they may operate at temperatures above the atmospheric boiling point and at a pressure of 50 pounds gauge or even higher.

Water used in these systems whether at high, low, or intermediate temperatures generally tends to be quite corrosive to the system itself which may be constructed from as many as six or more different metals or metal alloys. For example, a single system may contain carbon steel, which of course is lower in cost than most other structural metals, aluminum, brass, copper, tin, lead (the latter two metals being found in soldered joints) as well as alloys of these well known metals. Although there are a number of reasonably satisfactory specific inhibitors to protect steel from corrosion when that metal is the only one to be considered, I have not found any of the usual inhibitors entirely satisfactory for the protection of carbon steel and its alloys in the presence of certain nonferrous metals, particularly copper and its alloys, under the conditions encountered in closed heating and/or cooling systems.

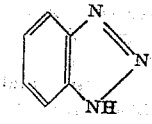
Although the mechanism is somewhat obscure, it has been known for many years that in closed systems of the type herein mentioned, the alkali metal nitrites, either potassium or sodium, particularly the latter, exhibit an inhibitive effect in the protection of carbon steel against corrosion, particularly if the pH value or alkalinity of the aqueous solutions within the system are maintained at a figure of 7 or higher. However, the alkali metal nitrites leave a great deal to be desired when used in

preventing corrosion of steel which is in contact with water that is also in contact with copper, especially if the pH value falls below 7 or if the concentration of nitrite in solution falls below 200 parts per million. A suitable additive has long been sought by workers skilled in the corrosion art but there are operational and functional problems associated with all of the additives which have been used so that the only material accepted for prevention of corrosion of steel in systems where oxygen is present and under conditions of low blowdown is chromate. This material has marked staining power when leaks occur and certain persons are also susceptible to the dermatitis it causes.

I have investigated a number of compounds which in theory should be effective in reducing the corrosivity of aqueous solutions toward steel since they reduce the attack on copper and thus cut down on the possibility of copper-steel couple formation in which the attack on the steel should be greatly increased. Such materials as potassium thiocyanate, 3-aminothiotriazole, and S-trithiane actually increased the corrosivity of the sodium nitrite solutions toward steel under the same conditions.

Additionally, I have investigated some of the well known inhibitors which are extremely effective in protecting copper and copper alloys against corrosion including the following thiols: 2-mercaptothiazole, 2-mercaptobenzoxazole, 2-mercaptobenzimidazole, and 2-mercaptobenzothiazole. These organic compounds are used quite successfully in protecting copper against corrosion but my experience has been that where sodium nitrite is employed in an alkaline environment as in closed systems, even though the thiols show protection of copper against corrosion, they have a negligible effect in protecting steel when compared to the compound I use.

I have discovered that small concentrations of the organic compound known as benzotriazole having the structural formula



exert a hitherto unobtainable inhibitory effect on steel when used in conjunction with alkali metal nitrites in an alkaline environment in the presence of copper or copper alloys. A synergistic effect seems to result from combining the nitrite, alkaline compound, and benzotriazole, since a higher degree of inhibition is obtained than the expected additive effect of the component parts of the mixture. Benzotriazole itself exhibits no inhibition of steel corrosion in aqueous solutions even in an alkaline environment.

To evaluate various inhibitors for this particular application, I prepared 500 ml. samples of Pittsburgh tap water in beakers to which I added 1000 parts per million of inhibitor. 1" x 2" cold rolled low carbon steel test specimens were carefully weighed and immersed in each beaker. Four 1" x 2" copper strips were also placed in the beakers. The solutions were continuously air-agitated at room temperature for 30 days. Makeup was approximately 75% distilled water and 25% tap water. At the end of the test, the specimens were removed, dried, and weighed.

No.	Inhibitor	Weight Loss Per Day in Milligrams Per Square Decimeter	
		Copper	Steel
1	{75% sodium nitrite {25% sodium tetraborate	0.2	10.6
2	Same as No. 1 with 1% benzotriazole added.	0.1	0.1
3	Same as No. 1 with 1% mercaptobenzothiazole added.	0.1	5.3
	(The following tests were run for 14 days)		
4	Same as No. 1 with 1% KSCN added	0.2	69.7
5	Same as No. 1 with 1% diethyldithiocarbamate added.	0.2	0.6
	(The following tests were run for 9 days)		
6	Same as No. 1 with 1% 2-thiazolinethione added.	0	58.1
7	Same as No. 1 with 1% 3-aminothiotriazole added.	0	62.4
8	Same as No. 1 with 1% S-trithiane added	0.1	59.2
9	No inhibitor used	2.3	80

It will be noted that while copper losses were negligible in a number of cases, the protection afforded the steel specimens by the benzotriazole was considerably greater than with the other materials.

While I prefer to use borax (sodium tetraborate) as the alkaline agent in my inhibitor mixtures, other alkaline compounds such as the carbonates, phosphates, bicarbonates, silicates, and the like can be added in place of borax. Borax has an added germicidal value in keeping objectionable slime growths at a minimum in certain closed systems as well as affording some protection to solder.

I prefer to use about 1% benzotriazole based on the total weight of inhibitor but I have used concentrations from as little as 0.1% to as much as 2% or more with considerable protection of the steel surfaces. In systems having considerable exposed areas of copper compared to the volume of solution, the higher concentrations are desirable.

Concentrations of inhibitor in aqueous systems may vary between 500 parts per million to upwards of 3500 parts per million. Experience generally indicates the most economical yet effective concentration of total inhibitor to be used, ranges between 1000 to 2000 parts per million.

Within the mixture itself I may vary the ratio of nitrite to alkaline salt between 9 to 1 and 1 to 4, or in other words from about 90% nitrite—10% alkaline salt to about 75% alkaline salt—25% nitrite.

Having thus described my invention, what I claim as new and desire to secure by Letters Patent is:

1. A corrosion inhibitor consisting essentially of (*a*) alkali metal nitrite (*b*) a mildly alkaline salt, and (*c*) benzotriazole, the ratio of (*a*) to (*b*) being from about 9 to 1 to about 1 to 4 and (*c*) being present in an amount which is from about 0.1 percent to about 2.0 percent of the total weight of the inhibitor mixture.

2. A corrosion inhibitor consisting essentially of (*a*) from about 90 percent by weight to about 23 percent by weight of an alkali-metal nitrite, (*b*) from about 9.9 percent by weight to about 75 percent by weight of a mildly alkaline salt, and (*c*) from about 0.1 percent by weight to about 2.0 percent by weight of benzotriazole.

3. A corrosion inhibitor as described in claim 2 where the alkali-metal nitrite is sodium nitrite and the mildly alkaline salt is a compound selected from the group consisting of alkali-metal carbonates, bicarbonates, sesquicarbonates, silicates, phosphates, and borates.

4. A corrosion inhibitor consisting essentially of (*a*) sodium nitrite, (*b*) sodium tetraborate, and (*c*) benzotriazole the amount of (*a*) and (*b*) varying between about 90 percent (*a*) and 10 percent (*b*) and about 25 percent (*a*) and 75 percent (*b*), the amount of (*c*) being from about 0.1 percent to about 2.0 percent of the inhibitor mixture.

5. A corrosion inhibitor consisting essentially of (*a*) from about 90 percent by weight to about 23 percent by weight of sodium nitrite, (*b*) from about 9.9 percent by weight to about 75 percent by weight of sodium tetraborate, and (*c*) from about 0.1 percent by weight to about 2.0 percent by weight of benzotriazole.

6. A corrosion inhibitor as described in claim 5 where (*a*) is about 74 percent by weight, (*b*) is about 25 percent by weight, and (*c*) is about 1 percent by weight.

7. A method of retarding the corrosion of ferrous metals which are in contact with water which comprises adding to the water a corrosion inhibitor consisting essentially of (*a*) about 90 percent alkali-metal nitrite, (*b*) about 9.9 percent a mildly alkaline salt, and (*c*) about 0.1 percent benzotriazole.

8. A method of retarding the corrosion of ferrous metals which are in contact with water which comprises adding to the water a corrosion inhibitor consisting essentially of (*a*) from about 90 percent to about 23 percent by weight of an alkali-metal nitrite, (*b*) from about 9.9 percent by weight to about 75 percent by weight of a mildly alkaline salt, and (*c*) from about 0.1 percent by weight to about 2.0 percent by weight of benzotriazole.

9. A method of retarding the corrosion of ferrous metals which are in contact with water which comprises adding to the water a corrosion inhibitor consisting of (*a*) from about 90 percent to about 23 percent by weight of sodium nitrite, (*b*) from about 9.9 percent to about 75 percent by weight of a mildly alkaline compound selected from the group consisting of alkali metal carbonates, bicarbonates, sesquicarbonates, silicates, phosphates, and borates, and (*c*) from about 0.1 percent to about 2.0 percent by weight of benzotriazole.

10. A method of retarding the corrosion of ferrous metals in contact with normally corrosive aqueous solutions which comprises adding to said solutions (*a*) from about 90 percent to about 23 percent by weight of sodium nitrite, (*b*) from about 9.9 percent to about 75 percent by weight of sodium tetraborate, and (*c*) from about 0.1 to about 2.0 percent by weight of benzotriazole.

11. A method of retarding the corrosion of ferrous metals in contact with normally corrosive aqueous solutions which comprises maintaining in said solution from about 500 to about 3500 parts per million of an inhibitor consisting of (*a*) from about 90 percent by weight to about 23 percent by weight of sodium nitrite, (*b*) from about 9.9 percent by weight to about 75 percent by weight of sodium tetraborate, and (*c*) from about 0.1 percent by weight to about 2.0 percent by weight of benzotriazole.

12. A method of retarding the corrosion of ferrous metals in contact with normally corrosive aqueous solutions which comprises adding to said solution (*a*) about 74 percent by weight of sodium nitrite, (*b*) about 25 percent by weight of sodium tetraborate, and (*c*) about 1 percent by weight of benzotriazole.

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