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(54) METHOD OF PROTECTING METAL SURFACES AND STRUCTURES AGAINST CORROSION

(71) We, W. R. GRACE & CO., a Corporation organized and existing under the Laws of the State of Connecticut, United States of America, of: Grace Plaza, 1114 Avenue of the Americas, New York, N.Y. 10036, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:–

The present invention relates to methods of inhibiting corrosion of metal surfaces and structures which are in contact with, or likely to come into contact with, an aqueous medium of a corrosive nature.

It is well known that one can inhibit the corrosion of metal surfaces in contact with corrosive aqueous media by the inclusion of various corrosion inhibiting agents therein. For example, for many years alkali metal nitrites, especially those of potassium or sodium, have been utilized in the protection of carbon steel from corrosion by introducing an alkali metal nitrite into an aqueous solution which is maintained at an alkaline pH. The utilization of alkali metal nitrites, though, leaves much to be desired. They do not exhibit a high degree of corrosion inhibiting properties against a wide variety of corrosive agents and especially against the corrosive effect of the chlorides present in seawater and other chlorides commonly found in aqueous solutions.

Various suggestions have previously been proposed to overcome the defects encountered when using the alkali metal nitrites. Such suggestions include the utilization of alkali metal chromates, alone or in combination with the alkali metal nitrite. However, chromate solutions pose the problem of being toxic to humans and having a marked staining effect on the metal material. Zinc salts have also been used but have recently been found to adversely affect the water quality of natural water bodies in which the treated water is released. Finally, various organic compounds such as phosphonates, diazoles and thiazoles have been suggested as additives. These organic constituents have the drawback of being very expensive and are, therefore, merely useful to supplement the inorganic salts.

Consequently, compositions which are both relatively inexpensive and which effectively inhibit the corrosion of metal surfaces and structures are desired for the protection of metallic equipment.

According to the present invention there is provided a method of protecting a metal surface or structure against corrosion by an aqueous medium, usually a solution, which comprises contacting the metal structure with an aqueous solution containing calcium nitrite. Calcium nitrite has unexpectedly been found to be several times more effective as a corrosion inhibiting agent than other inorganic inhibitors, such as the alkali metal nitrites.

The present invention is effective for treating metal surfaces and metal container structures which are in contact, or liable to come into contact with, corrosive aqueous solutions. The calcium nitrite can be added to the aqueous medium in contact with the metal or it can be applied, for example as an aqueous solution, to a metal surface which is likely to be subjected to a corrosive aqueous medium.

The major corrosive ingredients of aqueous systems are dissolved oxygen and inorganic salts such as the carbonate, bicarbonate, chloride, nitrate and sulphate of sodium, calcium and magnesium. Such salts become entrained in the aqueous media which may be present in, for example, metal containers by various means.

The present invention is useful in the prevention of corrosion of metals, for example, iron, steel, galvanized steel and non-ferrous metals including copper, aluminium and their alloys which are in contact with a liquid medium which either is or contains therein an aqueous corrosive phase. It has particular utility in the prevention of the corrosion of metals used in the formation of, for example, condensers, engine blocks, cooling towers and evaporators which have water circulating through them. It is also useful in the prevention of corrosion of metal surfaces of various storage containers and especially those used in the petroleum industry. Storage containers of petroleum products are known to contain small amounts of water which almost always contain various corrosive salts. The water phase settles on the bottom of the container where it presents serious corrosion problems. This is especially true of containers which are used as oil storage tanks at refineries, domestic fuel oil tanks, oil pipe lines and cargo tanks of commercial oil tankers. Further, in the case of cargo tanks of oil tankers, it is a standard procedure to clean the inner surface of the cargo tanks with seawater. The residual seawater, with its corrosive sodium chloride, remaining in these tanks causes extensive pitting of the bottom area of the tanks where the water phase collects. The calcium nitrite can be introduced into aqueous solutions in any known convenient method. For example in a circulating water system, that is water which is moving through various types of apparatus such as condensers, engine blocks or jackets and cooling towers, solid calcium nitrite can be conveniently added to the aqueous system. Alternatively, an aqueous solution of calcium nitrite can be injected into the system as part of the initial and/or makeup feed of the system so as to maintain a sufficient amount of the agent in the system to inhibit corrosion.

In predominantly non-aqueous systems which contain small amounts of corrosive water therein, such as is found in oil storage tanks, the calcium nitrite can conveniently be added as a concentrated aqueous solution which will eventually combine with the aqueous phase present to inhibit corrosion of the metal surfaces in contact with the treated aqueous solution. Alternatively, solid calcium nitrite can be added. When the solid enters the aqueous phase, it readily goes into solution and has the desired corrosion inhibiting effect. It has been found that very small amounts of calcium nitrite act as effective corrosion inhibiting agents. Preferably, the calcium nitrite should be present in an amount of from 0.05 to 5 percent by weight of the aqueous solution, with amounts of up to about 2 percent by weight being found effective in most instances. Amounts in the upper end of the preferred range are most desirable when the process is used to protect petroleum storage vessels. Greater amounts of the corrosion inhibiting agents can be used, although this has generally been found unnecessary.

The aqueous solutions into which the calcium nitrite can be incorporated may contain non-corrosive inhibiting additives. For example, the water may contain conventional anti-freezing agents, such as ethylene glycol. The calcium nitrite has been found to be substantially unaffected by such additives.

Corrosion inhibition can also be achieved, unexpectedly, by coating a metallic surface of an article to be protected with a composition containing calcium nitrite. An aqueous composition can readily be formed by the inclusion of from, say, 0.05 to 5 percent calcium nitrite into any conventional water-based coating composition. The compositions may contain various conventional thickeners such as polyethylene oxides, hydroxyethylene oxides, hydroxyethyl cellulose, Xanthan or guar gums, alone or in combination with other conventional coating components. The coating can be done in any conventional manner, such as by spraying, brushing or dipping. The water based coating composition should generally be permitted to dry thoroughly prior to the utilization of the metal vessel. The calcium nitrite contained in such coatings exhibits corrosion inhibition over a sustained period of time.

Unexpectedly it has been found that even very small amounts of calcium nitrite exhibit superior corrosion resistance of metal pieces and surfaces against substantial amounts of sodium chloride. It is believed that calcium nitrite is also an effective corrosion inhibitor of metallic surfaces and structures which are in contact with substantial amounts of various other inorganic chlorides regardless of the cation associated therewith and other corrosive salts such as sulphates.

The following Examples further illustrate the present invention. All parts and percentages are by weight unless otherwise indicated.

EXAMPLE I

Previously weighed strips about 5 cm wide by 12.5 cm long by 0.2 cm thick of cold rolled steel commonly used in forming containers were separately immersed in salt water baths (1 percent NaCl). To one bath was added 2 percent calcium nitrite, while to the other bath was added 2 percent sodium nitrite for comparative purposes. At weekly intervals each strip was removed from the bath, washed with deionized water, dried and weighed. The results are tabulated below.

Table

	Total weight loss (in gm) of Sample in 1% NaCl water bath having	
Time (weeks)	**2% Sodium Nitrite**	**2% Calcium Nitrite**
1	0.03	0.01
2	0.05	0.01
3	0.20	0.01
4	0.21	0.01
5	0.22	0.06

The above results show that calcium nitrite is an effective corrosion inhibiting agent against a corrosive aqueous solution. Further, the above results clearly show that calcium nitrite is several times more effective than the conventional inhibitor, sodium nitrite.

EXAMPLE II

A cast iron engine block having a cooling system capacity of 18.25 ℓ is filled with a water solution containing 35 percent ethylene glycol and 0.1 percent (18.25 gms) calcium nitrite. The engine is periodically run over a 16 week period. Substantially no corrosion is observed.

EXAMPLE III

The liquid media contained in an oil storage tank of a refinery is periodically injected with a sufficient amount of a concentrated aqueous solution of calcium nitrite to maintain the calcium nitrite concentration in the water phase at the bottom of the tank at about 3 percent. Corrosion of the steel tank walls is substantially eliminated.

WHAT WE CLAIM IS:

1. A method of inhibiting corrosion of a metal surface or structure in contact with , or likely to come into contact with, an aqueous medium which comprises contacting the metal surface or structure with calcium nitrite.

2. A method according to claim 1 wherein the calcium nitrite is incorporated in the corrosive aqueous solution in contact with said metal.

3. A method according to claim 2 wherein the metal structure is a storage tank and the calcium nitrite is incorporated in the water containing liquid media therein.

4. A method according to claim 2 wherein the metal structure is an engine block and the calcium nitrite is present in the aqueous coolant contained in said engine block.

5. A method according to any one of claims 2 to 4 wherein the calcium nitrite is present in the aqueous solution in an amount from 0.05 to 5 percent by weight based on the aqueous solution.

6. A method according to claim 1 wherein the metal surface is coated with an aqueous coating composition containing calcium nitrite.

7. A method according to claim 6 wherein the calcium nitrite is present in the coating composition in an amount from 0.05 to 5 percent by weight based on the weight of the composition.

8. A method according to claim 6 or 7 wherein the coating composition comprises a thickening agent to increase the viscosity thereof.

9. A method according to claim 1 substantially as hereinbefore described.

10. A metal surface or structure whenever corrosion-inhibited by a method as claimed in any one of the preceding claims.

11. A coating composition which comprises calcium nitrite and a thickening agent.

12. A composition according to claim 11 wherein the calcium nitrite is present in an amount from 0.05 to 5 percent by weight.

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