PREVENTION OF CORROSION OF WET METAL ARTICLES

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The present invention relates to the prevention of corrosion of wet metal articles, and more particularly to a process for the wet preservation and corrosion protection of metal articles which are in contact with an aqueous phase and to preparations for such purposes.

The use of hydrazine as a corrosion protective agent, for example in steam boilers, hot water plants, etc., is already known. The effect of this compound is attributed to the reactivity which has long been known to exist between hydrazine and the oxygen dissolved in water. In addition, however, it is assumed that hydrazine has an effect on the formation of a protective layer on metal surfaces. In articles made of iron, this effect is explained by the formation of a very dense, firmly adhering layer of Fe₃O₄.

At normal temperature, the rate of reaction of hydrazine with oxygen is very low. The effect of hydrazine as a corrosion protective agent, especially on bare metal surfaces, leaves much to be desired, especially if chlorides or sulfates are dissolved in the water.

It has already been mentioned that the effect of hydrazine by active carbon. However, the effect of the active carbon is limited to the accelerated reaction of hydrazine with the oxygen present. In other words, this effect is limited substantially to the removal of oxygen from the water, which is used for the operation of the steam boilers, etc.

It is an object of the present invention to overcome previous drawbacks encountered in the prevention of corrosion of wet metal articles, and to provide for the more effective prevention of corrosion of wet metal articles.

A further object of the present invention is to provide a method for the wet preservation and corrosion protection of metal articles which are in contact with an aqueous phase normally corrosive therefor, especially after prolonged contact therewith, using a particular mixture of ingredients having a combined beneficial effect.

It is a further object of the present invention to provide a preparation containing a mixture of ingredients which may be added to an aqueous phase, such as an oxygen containing water and/or a salt containing water, in predetermined dosages for attaining the wet preservation and corrosion protection of such metal articles which may be in contact with the aqueous phase.

Other and further objects will become apparent from a study of the within specification and accompanying examples in which

FIGURE 1 shows the graph illustrating the reaction between hydrazine and oxygen in a closed system over an extended period of time in the presence or absence of methylene blue.

FIGURE 2 shows a graph illustrating the reduction in oxygen content by reason of the presence of hydrazine in the presence or absence of methylene blue and/or K₂[Cu(CN)₄]₂.

FIGURE 3 shows a graph illustrating the reduction in oxygen content by reason of the presence of hydrazine in the presence or absence of methylene blue and/or Na₂[Co(CN)₅]₂.

It has now been found in accordance with the present invention that a process for the wet preservation and corrosion protection of metal articles in contact with an aqueous phase may be provided by means of hydrazine in the presence of activating substances according to which hydrazine (preferably hydrazine hydrate) is added in quantities of 0.1 to 3000 mg. N₂H₄ per liter of water and methylene blue is added in quantities of 0.1 to 50 mg. per liter water optionally in addition with water-soluble complex heavy metal cyanides in quantities of 0.1 to 10 mg. per liter water calculated on the heavy metal to the aqueous phase in contact with such metal articles.

In accordance with the present invention it has been found that methylene blue especially in combination with water-soluble complex heavy metal cyanides increases the protective action of hydrazine considerably, whereby the oxygen from the aqueous phase in question is removed effectively also at normal temperatures. In addition a good corrosion protection can also be achieved on bare metal surfaces, i.e., where a protective layer is not already present. Whereas e.g., in iron systems containing water with an addition of hydrazine the corrosion amounts to about 0.1 to 0.5 g. iron per square meter per day, the average rate of corrosion is reduced by the addition of methylene blue in combination with the complex heavy metal cyanides to the very favourable value of 0.005 g. Fe per square meter per day.

For the reason of safety the hydrazine is preferably applied in aqueous solution containing about 15% by weight of N₂H₄. A solution with this hydrazine content is referred to also as 24% hydrazine hydrate. An aqueous hydrazine solution containing about 65% N₂H₄ which is obtained as azeotropic system on distilling mixtures of N₂H₄ and water is usually referred to as 100% hydrazine hydrate. Aqueous solutions containing about 15% N₂H₄ can be handled and stored without danger and specific precautions.

Hydrazine solutions with other concentrations are effective, too. Lower concentrations however are less economic and solutions with higher N₂H₄ concentrations are usually avoided as they tend to self-decomposition under certain circumstances.

If methylene blue is added to water containing hydrazine and oxygen the blue color of the solution disappears at the same rate as the oxygen is removed. Additional oxygen diffusing into the solution colors the solution blue again in case no longer excess hydrazine is present in the aqueous phase. The blue color is thus also an indicator for the presence of free oxygen and the decolorization of the aqueous phase indicates that excess hydrazine is still present.

The activating effect of methylene blue on the reaction between hydrazine and oxygen is considerably enhanced by light energy. Very small quantities of light energy are sufficient for this effect: for example after several seconds radiation with a normal electric bulb, complete decolorization, i.e., conversion of methylene blue into the leucon form occurs. Similar activation, though to a lesser extent, is obtained also by heating or by the catalytic effect of metal surfaces.

The effect of methylene blue on the speed of reaction between hydrazine and oxygen is shown in FIGURE 1. 200 mg. per liter of hydrazine in the form of a 24% hydrazine hydrate (aqueous solution containing about 15% N₂H₄) and 5 g. per liter of water of methylene blue were added to a sample of water having an O₂ content of 30 mg. per liter. The reduction in oxygen with time was then measured in comparison with a sample to which only 200 g. per liter of hydrazine hydrate had been added. The curves in FIGURE 1 show that with hydrazine activated with methylene blue—curve 2—the oxygen content falls to 1 mg. per liter at the end of 20 hours. The sample of water containing hydrazine without any addition—curve 1—on the other hand, shows only an in-
The combination of methylene blue with complex heavy metal cyanides has been found advantageous. Especially effective have been found to be the water-soluble complex cyanides of copper(I), Co(III), Ni(II), silver(I) and iron(II). The complex cyanides are used in the form of their alkali metal and/or ammonium compounds. The heavy metal cyanides must be present in a form which has no oxidizing effect on hydrazine. The complex-forming metals are therefore used in their lowest stage of oxidation, in which they are stable under normal conditions.

The effect of the combination of methylene blue and copper cyanide on the reaction between hydrazine and oxygen is indicated by the curves in FIGURE 2. When 6 mg. per liter of copper in the form of $K_2[Co(CN)_6]$—curve 2—or 5 mg. per liter of methylene blue—curve 3—are added to a solution containing 200 mg./l. of hydrazine in the form of 24% hydrazine hydrate and 50 mg. per liter of $N_2H_4$, the oxygen content is removed from the water having a temperature of about 20° C. after about 18 to 20 hours. On the other hand, when a combination of the additives is used—curve 4—the solution is already free from oxygen after one hour. Curve 1 shows the results of the blank sample, i.e. the effectiveness of hydrazine alone on the oxygen content of the water. The combination of methylene blue and the complex copper cyanides is applied advantageously, if water should be rendered free from oxygen in a very short time. Therefore the aforementioned combination of activating substances is preferably used in for example closed heating and cooling plants since in these cases the decomposition of hydrazine due to atmospheric oxygen diffusing into the water is kept within moderate limits and therefore a long lasting protection against corrosion is achieved without continuous addition of hydrazine.

The curves in FIGURE 3 show the removal of oxygen by hydrazine in the presence of the combination methylene blue/cobalt cyanide. As in the experiments with the activating mixture methylene blue/copper cyanide, the effect of 5 mg. per liter of cobalt in the form of $Na[Co(CN)_6]_2$—curve 2—and the corresponding combination with 5 mg. per liter of methylene blue—curve 3—on the speed of reaction between hydrazine and oxygen was investigated.

Whereas the methylene blue/copper cyanide combination has a potentiating effect on the removal of oxygen by hydrazine, the corresponding degradation curve obtained with the use of methylene blue and $N_2H_4[Co(CN)_6]$ lies above the degradation curve obtained with the use of methylene blue alone—curve 4. As is seen from these results, the influence of the cobalt complex is enhanced, that of methylene blue diminished. The results are similar when using a methylene blue/$N_2H_4[Ni(CN)_6]$ combination. For open systems, e.g. open cooling water circuits, it is therefore preferable to use methylene blue with the cyanide complex of nickel and cobalt, not least because these combinations of the activating substances have the most favourable effect on the formation of the protective layer on the metal surfaces. Only a very low rate of corrosion was detected, and in particular no pitting corrosion was observed.

To carry out the process, the calculated quantity of hydrazine, preferably in the form of 24% hydrazine hydrate, to produce a concentration of 0.1 mg. per liter to 3000 mg. $N_2H_4$ per liter in water is added to the supply or cooling water. In the degassed supply water, for a concentration of aboupt 0.1 mg. $N_2H_4$ per liter is sufficient whereas in cooling water circuits it is preferable to have a concentration of about 300 mg. $N_2H_4$ per liter. Higher hydrazine contents are not harmful but are avoided for economical reasons.

Moreover, the activating substances are preferably added in the form of aqueous solutions. An adequate protective effect is achieved if methylene blue is present in quantities of 1 to 50 mg. per liter and, if desired, the heavy metal cyanide combination in quantities of 0.01 to 10 mg. per liter of water, preferably in quantities of 0.1 to 5.0 mg. per liter calculated on the metal.

In practice, it is advantageous to prepare mixtures of hydrazine hydrate and the corresponding combinations of the activating additives, these mixtures then being used in suitable doses according to the function and type of the water, i.e. its oxygen content, salt content, etc. After this initial preservation, it is then generally sufficient merely to maintain the necessary hydrazine concentration by adding subsequent doses of hydrazine hydrate. In the preservation of metal surfaces in contact with static water, a single addition of the mixture to the water is generally sufficient.

The present process can advantageously be used for the preservation under wet conditions and protection against corrosion of steam producing plants, hot water plants, circulating coolers and heat exchangers. It is especially advantageous that the preserving effect occurs already at temperatures at which only insufficient protection of the metal surfaces has hitherto been obtained by the usual methods, i.e. at temperatures of below 100° C. or more precisely below the B.P. of the water down to the freezing point. However, the temperature range given above is no limitation of the new process for the hydrazine mixed with the aforesaid activating substances is applicable also to systems containing hot water or hot water and steam.

The following examples are set forth by way of illustration and not limitation:

**Example 1**

Boiler tube rings of iron quality St. 35.29, after being annealed to remove stress and pickled, were kept for 14 days in an aqueous solution containing 200 mg. per liter of $N_2H_4$ and 100 m. per liter of NaCl in Erlenmeyer flasks closed with rubber bungs. Compared with the samples containing no methylene blue, the different samples containing increasing quantities of methylene blue of 0.1 to 0.5 mg. per liter exhibited a diminution in corrosion, especially of pitting corrosion, which disappeared completely with addition of 5 mg. per liter. At the same time, at this concentration a very thin and very stable protective layer was formed whereas the surface of the ring in water to which no methylene blue had been added showed no protective layer.

**Example 2**

The effect of the combination of heavy metal cyanides and methylene blue and of methylene blue alone was investigated under the same experimental conditions as described in Example 1. Whereas the tube ring showed strong pitting corrosion when only 200 mg. per liter of $N_2H_4$ and 100 mg. per liter of NaCl were added, the rings were still completely intact after 14 days when the hydrazine was activated with an addition of 5 mg. per liter of Co in the form of $N_2H_4[Co(CN)_6]$ and 5 mg. per liter of methylene blue or an addition of Cu in the form of $N_2H_4[Co(CN)_6]$ and methylene blue or of Ni in the form of ($N_2H_4)_{2}[Ni(CN)_6]$ and methylene blue or of methylene blue without the addition of cyanide. The strongest formation of protective coating was manifested by the ring in contact with the addition of the nickel complex.

**Example 3**

Boiler tube rings pretreated in the usual way were suspended in a condensate to which 200 mg. per liter of $N_2H_4$ had originally been added and kept to stand uncovered in the air for 14 days. The sample without addition of activator showed very strong hydroxide formation whereas the samples to which 5 mg. per liter of cobalt cyanide/methylene blue or 5 mg. per liter of nickel...
cyancide/methylene blue had been added showed practically no hydroxide formation. After 14 days, the rings still appeared as intact as at the beginning.

In the case of the combination of nickel cyanide/methylene blue, the average rate of corrosion was 0.0004 g. per square meter per day, compared with an average of 0.47 g. per square meter per day without the addition of activator. The original N$_2$H$_4$ content of 200 mg. per liter was reduced to 110 mg. per liter after 14 days if nickel cyanide/methylene blue was added. By passing air through for several days, the N$_2$H$_4$ content could then be reduced to 50 mg. per liter and the pH to 7.0. The ring was at that point still intact. This addition of activator can thus in some circumstances provide protection against corrosion even with very low quantities of N$_2$H$_4$ and at the same time it is no longer nearly so important to maintain a high pH.

**Example 4**

An open cooling circuit with fully desalted water to heavy 200 mg. per liter of N$_2$H$_4$, 5 mg. per liter of Ni in the form of Na$_2$Ni(NCN)$_3$ and 5 mg. per liter of methylene blue had been added showed no corrosion after several months of circulation if the slight consumption of hydrazine was compensated by occasional replacement and the pH maintained between 9 and 10.

**Example 5**

A heating circuit charged with normal salt-containing water and having a N$_2$H$_4$ concentration of 100 mg. per liter and having an activator content of 0.5 mg. per liter of cobalt in the form of K$_2$Co(CN)$_6$ and containing 0.5 mg. per liter of methylene blue showed no corrosion after the summer break and could be put into operation again with this treated water.

**Example 6**

A steam boiler which had been put out of operation and which, to preserve it against wet conditions, was completely filled with condensate to which 100 mg. per liter of N$_2$H$_4$ and 5 mg. per liter of Ni in the form of Na$_2$Ni(NCN)$_3$ and methylene blue had been added, showed no sign of corrosion after being out of operation for 8 months.

Accordingly in its broadest aspects the present invention relates to a method for the wet preservation and corrosion protection of metal articles such as those made of ferrous and nonferrous metals in contact with the aqueous phase such as water containing oxygen and/or inorganic salts such as chlorides, sulfates and/or nitrates of the alkali and alkaline earth metals etc., which comprises providing in such aqueous phase which is in contact with the particular metal article, both hydrazine in an amount substantially between about 0.1 to 3000 mg. of N$_2$H$_4$ per liter of water and methylene blue in an amount of substantially between about 0.1 to 50 mg. per liter of water. Preferably additionally a water-soluble complex heavy metal cyanide is added in an amount calculated on the heavy metal substantially between about 0.01 to 10 mg. per liter of water. Preferably the hydrazine is used in the form of hydrazine hydrate as e.g. in the form of substantially about a 15% N$_2$H$_4$ solution and the complex heavy metal cyanide is present preferably in an amount calculated on the heavy metal substantially between about 0.1 to 5 mg. per liter of water.

In accordance with the preferred embodiment of the present invention the addition of the methylene blue is combined with the addition of water-soluble complex heavy metal cyanides. The complex heavy metal cyanides are selected from the group consisting of the alkali metal mono-valent copper cyanides, the ammonium mono-valent copper cyanide, the alkali metal trivalent cobalt cyanides, the ammonium trivalent cobalt cyanide, the alkali metal divalent nickel cyanides, the ammonium divalent nickel cyanide, the alkali metal divalent iron cyanide, the ammonium divalent iron cyanide, the alkali metal mono-valent silver cyanide, the ammonium mono-valent silver cyanide and mixtures thereof. More specifically typical complex heavy metal cyanides include

\[ \text{Na}_2[\text{Cu}(\text{CN})_3]_2, \text{(NH}_3)_2[\text{Cu}(\text{CN})_3]_2, \text{K}_3[\text{Cu}(\text{CN})_3], \text{K}_2[\text{Ni}(\text{CN})_3], \text{Na}_2[\text{Ni}(\text{CN})_3]_2, \text{(NH}_3)_2[\text{Ni}(\text{CN})_3]_2, \text{K}_2[\text{Co}(\text{CN})_3], \text{Na}_2[\text{Co}(\text{CN})_3], \text{(NH}_3)_2[\text{Co}(\text{CN})_3], \text{Na}_4[\text{Fe}(\text{CN})_3]_2. \]

In another sense the present invention represents an improvement in the method for the wet preservation and corrosion protection of predominantly iron containing metals in contact with the solution containing at least one of oxygen and salt which normally cause corrosion which improvement comprises maintaining in such solution when in contact with the particular metal article a mixture of hydrazine and methylene blue preferably combined with the addition of a complex heavy metal cyanide in accordance with the foregoing.

Moreover the present invention relates to a preparation for the wet preservation and corrosion protection of metal articles in contact with the aqueous phase such preparation comprising a mixture in an aqueous solution of hydrazine and methylene blue and optionally a complex heavy metal cyanide in amounts per liter as above.

In particular preparations may be used which contain in aqueous solution a mixture of hydrazine in an amount substantially between about 0.1 to 3000 mg. N$_2$H$_4$ per liter with substantially between about 0.1 to 50 mg. of methylene blue per liter of water and optionally with an addition of complex heavy metal cyanides in an amount substantially between about 0.01 to 10 mg. per liter calculated on the particular heavy metal.

In another sense the present invention relates to mixtures for the wet preservation and corrosion protection of predominantly iron containing metals in contact with the solution containing at least one of oxygen and inorganic salts, which normally cause corrosion which mixtures comprise per 1 kg. of hydrazine hydrate 24% 0.1 to 20 g. of methylene blue and optionally 0.1 to 5 g. of complex heavy metal cyanides calculated on the particular heavy metal, said particular heavy metals being selected from the group consisting of copper(I), cobalt(III), nickel(II), iron(II) and silver(I).

We claim:

1. Method for the wet preservation and corrosion protection of metal articles in contact with an aqueous phase which comprises providing in such aqueous phase which is in contact with the particular metal article both hydrazine in an amount substantially between about 0.1 to 3000 mg. per liter of water and methylene blue in an amount substantially between about 0.1 to 50 mg. per liter of water.

2. Method according to claim 1, wherein in said aqueous phase is additionally provided a complex heavy metal cyanide in an amount calculated on the heavy metal substantially between about 0.1 to 10 mg. per liter of water.

3. Method according to claim 1, wherein the hydrazine is used in the form of hydrazine hydrate.

4. Method according to claim 2, wherein said hydrazine hydrate is in the form of substantially about a 24% hydrazine hydrate.

5. Method according to claim 2, wherein said cyanide is present in an amount calculated on the heavy metal substantially between about 0.1 to 5 mg. per liter of the aqueous phase.

6. Method according to claim 2, wherein said complex heavy metal cyanide is selected from the group consisting of alkali metal mono-valent copper cyanide, ammonium mono-valent copper cyanide, alkali metal trivalent cobalt cyanide, ammonium trivalent cobalt cyanide, alkali metal divalent nickel cyanide, ammonium divalent nickel cyanide, alkali metal divalent iron cyanide, ammonium divalent iron cyanide, alkali metal mono-valent silver cyanide, ammonium mono-valent silver cyanide and mixtures thereof.
7. In the method for the wet preservation and corrosion protection of predominantly iron containing metal articles in contact with a solution containing at least one of oxygen and inorganic salt which normally cause corrosion, the improvement which comprises maintaining in such solution when in contact with the particular metal articles a mixture of hydrazine in an amount substantially between about 0.1 to 3000 mg. of N₂H₄ per liter of water, methylene blue in an amount substantially between about 0.1 to 50 mg. per liter of water and a complex heavy metal cyanide in an amount calculated on the heavy metal substantially between about 0.01 to 10 mg. per liter.

8. Improvement according to claim 7, wherein the hydrazine is used in the form of substantially about a 24% hydrazine hydrate solution and said cyanide is present in an amount calculated on the heavy metal substantially between about 0.1 to 5 mg. per liter of the aqueous phase.

9. Preparation for the wet preservation and corrosion protection of metal articles in contact with an aqueous phase which comprises a mixture containing in 24% hydrazine hydrate, 0.1 to 20 g. of methylene blue per kg. of 24% hydrazine hydrate and a complex heavy metal cyanide in an amount substantially between about 0.1 to 3 g. per kg. 24% hydrazine hydrate.

10. Preparation according to claim 9, wherein said complex heavy metal cyanide is selected from the group consisting of alkali metal mono-valent copper cyanide, ammonium mono-valent copper cyanide, alkali metal trivalent cobalt cyanide, ammonium trivalent cobalt cyanide, alkali metal divalent nickel cyanide, ammonium divalent nickel cyanide, alkali metal divalent iron cyanide, ammonium divalent iron cyanide, alkali metal mono-valent silver cyanide, ammonium mono-valent silver cyanide, and mixtures thereof.

11. Preparation for the wet preservation and corrosion protection of metal articles in contact with an aqueous phase which comprises a mixture in aqueous solution of hydrazine in an amount substantially between 0.1 to 3000 mg. N₂H₄ per liter of water and 0.1 to 50 mg. of methylene blue per liter of water.

12. Preparation according to claim 11, which includes additionally an amount of a complex heavy metal cyanide in a quantity calculated on the heavy metal substantially between about 0.01 to 10 mg. per liter of water.

13. Preparation according to claim 12, wherein said heavy metal cyanide is selected from the group consisting of alkali metal mono-valent copper cyanide, ammonium mono-valent copper cyanide, alkali metal trivalent cobalt cyanide, ammonium trivalent cobalt cyanide, alkali metal divalent nickel cyanide, ammonium divalent nickel cyanide, alkali metal divalent iron cyanide, ammonium divalent iron cyanide, alkali metal mono-valent silver cyanide, ammonium mono-valent silver cyanide and mixtures thereof.

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