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PROCESS FOR COATING METALS AND PRODUCT THEREOF

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This invention relates to the protection of metallic surfaces against corrosion. More particularly, it relates to preventing the corrosion of ferrous metals by treating the surfaces thereof with ferrates.

Among the methods available for protecting metals against corrosion are several in which active chemicals are applied to the surface of the metal to form an insulating coating thereon. Such a coating prevents contact between unreacted metal and the atmosphere or moisture and thus eliminates the major causes of corrosion. In one chemical treatment, for example, a ferrous base is coated with a layer of inorganic phosphates by immersion in a solution containing metal ions and phosphoric acid. In another chemical treatment, steel is "blued" by oxidation in a salt bath.

This invention has, as its object, provision of a novel and useful chemical method of protecting metals in general against corrosion. A specific object of the invention is provision of a new and cheap chemical treatment for protecting ferrous surfaces against corrosion.

The above-mentioned and further objects may be achieved in accordance with the principles of this invention by a process in which a protective coating is laid on a metallic workpiece by contacting the surface of the metal with an aqueous solution containing a ferrate. When the workpiece is made from a ferrous metal, such treatment produces thereon a thin, yellow, iron-containing film soluble in most acids but impervious for some time to penetration by the atmosphere and industrial gases. This film may be termed a "ferrate film" although its physical structure and chemical composition are not precisely known.

The ferrates of this invention are hexavalent iron compounds and may be prepared by the method of Thompson et al., J. Am. Chem. Soc. 73, 1379 (1951). In this procedure the iron in a trivalent iron compound is oxidized by hypochlorite to the hexavalent state. Sodium ferrate, Na_2FeO_4 , is easily prepared by the oxidation of ferric nitrate and other ferrates may be made from the sodium compound. The preferred ferrates of the invention are the alkali metal salts, particularly those of sodium and potassium.

The concentration of the ferrate employed is not particularly critical. At least 0.5% by weight should, however, be utilized for good results while up to 1% is desirable. The lower concentrations appear to give less protection than the higher but some protection may be noted at concentrations as low as 0.3%. At concentrations much higher than 1% decomposition of the ferrate becomes greatly accelerated.

Since the ferrates readily decompose with the evolution of oxygen, the solutions utilized should preferably be freshly prepared. They may, however, be stabilized for some time by the inclusion therein of an orthophosphate, non-cyclic triphosphate or tetraphosphate ion at a pH of around 9. Alternatively, stabilization may be achieved by use of a solution having a pH of 11 or above.

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A pH below 7 should be avoided since acid conditions greatly accelerate the decomposition of the ferrates.

Conventional buffers may be employed to maintain the ferrate solutions alkaline at all but very high pH's. At pH 11 the anti-corrosive effect of the solutions is surprisingly found to be greater at high buffer concentrations than at low. Thus, a ferrate solution one tenth molar in respect to both sodium carbonate and bicarbonate, adjusted to pH 11 with NaOH, is more effective in inhibiting corrosion than one containing less of the buffering compounds. Still better results are obtained from a ferrate solution almost saturated with the buffer.

Temperature seriously affects the stability of ferrates but has little influence on the speed of coating or the effectiveness of the coat produced. Temperatures above 40°–50° C. should be avoided because of the increased rate of decomposition. Normally, the solutions will be made up and utilized at ambient or room temperature but ice or even lower temperatures can beneficially be utilized.

At room temperature, for best results the time of contact between the workpiece being treated and the oxidizing solution should be about one hour.

The process of this invention is not restricted for use with ferrous metals such as cast iron or steel. It may be applied to other commercial metals such as aluminum, titanium, lead and zinc. In fact, ferrates react with many metals to form oxide films thereon and these films may afford some protection against corrosion. Since zinc and aluminum, in particular, are amphoteric, a pH within the range 9–11 is desirable in dealing with these metals.

The ferrate films of this invention can be improved to some extent by baking them. Thus, if they are heated in nitrogen for one or two hours at around 200°–300° C., their resistance to corrosion gradually increases. The optimum temperature for the heating is about 250° C. Oxygen and hydrogen may destroy the films and should be avoided during the baking period. Gases providing truly inert atmospheres such as the noble gases, argon, helium, neon and others, may, however, be substituted for the nitrogen. Ferrate films treated as described here may be referred to as "baked films."

It is generally desirable to pretreat the metal on which a ferrate coating is to be laid down. Thus, a steel workpiece may first be degreased, if necessary, pickled for a short time in hydrochloric acid, rinsed and neutralized for a few minutes in dilute caustic containing a little cyanide. The cyanide is commonly used to suppress rusting on wet ferrous surfaces exposed for short periods to the atmosphere.

A preferred embodiment of the invention utilizing the principles noted above may be described as follows: A ferrous workpiece is carefully degreased and pickled to present a bright surface and neutralized with dilute cyanide solution. The workpiece is then immersed for at least one hour at ambient temperatures in a strongly alkaline aqueous ferrate solution preferably having a pH of 11 or above and most desirably containing a high concentration of buffer, i. e., the solution should be at least one normal in respect to buffering agents. The ferrate concentration should be about 1%. The workpiece is then withdrawn, rinsed and dried, possessing a thin yellow coat soluble in acids but affording good protection against corrosion.

The following examples illustrate operational details of this invention. All percentages given are by weight unless otherwise noted.

The potassium ferrate (VI), used throughout these examples, was prepared by the method of Thompson et al., loc. cit., modified slightly. 240 grams of sodium hydroxide was dissolved in 600 ml. of water at 5–10° C.,

a temperature maintained until the ferrate was washed with ethanol. 160 grams of chlorine was passed in, 560 grams of sodium hydroxide added and the mixture centrifuged. 200 grams of powdered iron (III) nitrate enneahydrate was added and then 200 additional grams of sodium hydroxide. The mixture was again centrifuged and 800 ml. of saturated potassium hydroxide solution added to the liquid. The precipitated potassium ferrate was filtered on coarse sintered glass and leached with twenty 20 ml. portions of 3 N aqueous potassium hydroxide. The filtrate was collected in 800 ml. of saturated potassium hydroxide solution. The ferrate was reprecipitated by this treatment and again filtered. It was slurried once with absolute ethanol, three times with 95% ethanol, each time for twenty minutes, and finally washed with ether and dried in dry air. This procedure gave 56 g. of a brownish black solid which analysis showed to contain 73% of potassium ferrate (VI).

Example 1

This example shows the corrosion inhibiting effect of a ferrate solution at pH 7.

Two 3" x 1" samples of "Weirtzin," a zinc-coated, hot-rolled mild steel, were pickled by immersion for ten seconds in concentrated hydrochloric acid to effect removal of the zinc. In order to prevent corrosion before the subsequent ferrate treatment and to remove traces of acid, the samples were then immersed for four minutes in a solution containing 0.15% each of sodium hydroxide and sodium cyanide at 75° C.

A buffer solution was also made up, at a pH of 7, containing the following ingredients: 0.4% NaOH, 1.35% KH_2PO_4 , 1% "Quadrafos," and more KH_2PO_4 to bring the pH to 7. "Quadrafos" is "sodium tetraphosphate," sold by the Heyden Chemical Corporation, and is used to stabilize the ferrate. The solution was diluted one hundred fold and two samples thereof chosen. To one sample was added 1% potassium ferrate prepared in the manner described above. The other sample was left blank, i. e., without ferrate.

One of the prepared steel strips was suspended at ambient temperature (about 23° C.) for four hours with one inch of its length immersed in the solution containing potassium ferrate. The other strip was contacted, under like conditions, with the blank solution. Both strips were removed from the solution, rinsed and dried, and suspended in the air-space of an air-tight 8 liter glass vessel. This vessel also contained 150 ml. of water carrying dissolved 0.025 g. of sodium pyrosulfite, $\text{Na}_2\text{S}_2\text{O}_5$, and two drops of concentrated sulfuric acid. The sulfur dioxide evolved passed into the air above the water and created conditions simulating those of a highly corrosive industrial atmosphere. The strips were held at 40° C. under corrosive conditions within the glass vessel for 23 hours. At the end of this period the ferrate treated sample showed heavy uniform rusting on the end not immersed in the ferrate solution and slightly less rusting on the other end. The strip immersed in the blank showed heavy over-all rusting with perhaps a greater amount on the end contacting the buffer solution. Thus ferrate, at pH 7, offers some corrosion protection.

Example 2

This example shows the effect of a ferrate solution buffered at pH 9.

The tests of Example 1 were repeated except that the buffer solution utilized in both the blank and ferrate treatments was an aqueous solution containing 1.5% NaOH, 6.25% H_3BO_3 and 1% "Quadrafos," adjusted with NaOH to pH 9 and diluted one hundred fold.

Metal strips prepared as before were immersed in the blank and ferrate solutions, rinsed and dried. They were corroded at the same time and in the same atmosphere as those of the previous example. Results were the same except that corrosion was not quite as great on the strip

treated with ferrate as it was on the one so treated at pH 7.

Example 3

This example shows the effect of ferrate solutions buffered at pH 11.

(a) The tests of the previous examples were repeated except that the buffer solution contained 10.6% Na_2CO_3 , 6.6% NaHCO_3 and 1% "Quadrafos," again adjusted with NaOH to pH 11 and diluted one hundred fold. Greatly improved corrosion resistance was noticeable in the strip treated at the higher pH.

(b) The test of (a) above was repeated with solution of pH 11 one-tenth molar in both Na_2CO_3 and NaHCO_3 and containing 0.1% "Quadrafos." The increase in concentration of the buffer improved the corrosion resistance of the steel strip treated.

(c) The test of (a) was repeated except that the buffer solution was almost saturated (one molar). Results were excellent, practically no corrosion being noticeable after the 23 hours' exposure of the sample treated.

Example 4

This example shows the effect of ferrate solutions having a very high pH.

The tests of Example 1 were repeated except that the ferrate and blank solutions utilized for the metal treatment were ten normal with respect to NaOH and contained no buffer or "Quadrafos." Results were as good in this case as in Example 3 after 23 hours' exposure to the SO_2 containing atmosphere.

Example 5

This example shows the effects of a ferrate treatment on a zinc surface.

A 1% solution of potassium ferrate buffered at pH 11 with sodium carbonate, sodium bicarbonate and sodium hydroxide was used to treat a freshly cleaned sheet of zinc. The sheet was suspended with one inch of its length extending into the solution at ambient temperature for 1 hour. At the end of this period a thin yellow film was evident on the portion of its surface contacting the ferrate solution.

The treated zinc was held within a sulfur dioxide-containing atmosphere at 40° C. for 15 hours. Less corrosion was evident on the zinc contacted with ferrate than on the untreated metal, the latter showing numerous white spots evidencing the formation of an oxide or sulfur-containing compound.

Example 6

This example shows the beneficial effects of baking a ferrate film on a steel surface.

Three steel samples were given a ferrate-coating by the method of Example 3(c). Two of these were heated at 200° in nitrogen, one for 15 minutes and the other for 100 minutes. All three were subjected to corrosion in a sulfur dioxide atmosphere for 23 hours. The unbaked "blank" was found to be somewhat corroded on the part treated; the sample baked for 15 minutes was slightly less corroded than the first; and the third sample exhibited almost no corrosion on the part treated.

Having described my invention, I claim:

1. A ferrous surface carrying a visible protective layer imparting corrosion resistance thereto formed in situ by contacting said surface with an alkaline solution containing a ferrate, thereby forming a coating on the surface, and subsequently baking said coating in an atmosphere substantially inert thereto.

2. The method of imparting corrosion resistance to a metal which comprises contacting said metal with an aqueous solution of a ferrate of an alkali metal having a pH above about 7 at a temperature between about 0° and about 50° C. and thereby forming a visible protective coating on said metal and subsequently baking the

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protective coating in an atmosphere substantially inert thereto.

3. The method of claim 2 in which the pH of the solution is between about 7 and 11.

4. The method of claim 2 in which the metal is a member of the group consisting of iron, steel, zinc and aluminum.

5. The method of claim 2 in which the concentration of the ferrate is about 1% by weight.

6. The method of claim 2 in which the time of contact between the metal and the aqueous solution is about one hour.

7. The method of claim 2 characterized in that the baking is carried out at about 200°–300° C.

8. The method of claim 2 in which the pH of the aqueous solution is maintained by means of a buffer.

9. The method of claim 8 in which the buffer is a mixture of the carbonates and bicarbonates of the alkali metals.

10. The method of claim 9 in which the buffer is a mixture of sodium carbonate and sodium bicarbonate.

11. The method of claim 10 in which the concentration of each of the components of the buffer is between about 0.1 molar and the saturation concentration.

12. The method of imparting corrosion resistance to a ferrous metal which comprises contacting the metal for at least about one hour at ambient temperature with an aqueous solution of a ferrate of an alkali metal buffered at a pH of about 7–11 by means of a sodium carbonate-bicarbonate buffer.

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13. The method of imparting corrosion resistance to aluminum which comprises contacting the metal for at least about one hour at ambient temperature with an aqueous solution of a ferrate of an alkali metal buffered at a pH of about 7–11 by means of a sodium carbonate-bicarbonate buffer.

14. The method of imparting corrosion resistance to zinc which comprises contacting the metal for at least about one hour at ambient temperature with an aqueous solution of a ferrate of an alkali metal buffered at a pH of about 7–11 by means of a sodium carbonate-bicarbonate buffer.

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