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METHOD OF DE-OXIDIZING METAL SURFACES

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The present invention relates to a novel method for removing oxide from oxidized metal surfaces; and, more particularly, the invention relates to a novel chemical method which removes oxide from oxidized iron or steel surfaces leaving the underlying iron or steel surface in a condition not rapidly reoxidizable. The invention also relates to a novel bath for removing oxide from oxidized iron or steel surfaces.

As is well known, iron and steel articles rapidly oxidize, especially when subjected to conditions of high humidity. Many operations in the manufacture of steel and of iron or steel articles, such as heating procedures, and the storage of iron and steel articles result in the production of a relatively heavy layer of oxide. Even such "corrosion-resistant" steels as stainless steel, will, under certain atmospheric conditions, become oxidized slightly. Because of these oxide films, it is difficult, if not impossible, further to treat such articles in certain procedures, such as to provide thereover coatings of other metals, such as by vapor-, chemical- or electroplating. It becomes necessary, therefore, to remove this oxide layer, and this has been done in the past by the use of acid solutions.

While these acid solutions will remove the oxide, in many cases they will also attack the underlying metal, and in any event, upon removal from the de-oxidizing bath, the metal rapidly re-oxidizes. This is particularly true of hydrochloric acid. Because of the rapidity of this re-oxidization, the iron or steel articles must be almost immediately subjected to the plating operation. In many cases in industry this is not possible or convenient.

It is the principal object of the present invention to provide a novel method for removing oxide from oxidized iron or steel articles without danger of attacking the underlying metal.

It is another object of the present invention to provide a method for removing oxide from oxidized iron or steel surfaces whereby the resulting cleaned iron or steel surface will not rapidly re-oxidize.

A further object of the invention is to provide a simple and economic method of de-oxidizing oxidized iron or steel surfaces whereby the foregoing objects may be realized.

Other objects, including the provision of a novel bath for carrying out the method of the present invention, will become apparent from a consideration of the following specification and the claims.

The process of the present invention comprises immersing the oxidized iron or steel article in a bath consisting essentially of hydrochloric acid, water and ammonium chloride until the oxide has been removed from the surface of the article. In the bath employed in accordance with the present invention, the concentration of ammonium chloride will be relatively high, and, as will be discussed more in detail hereinafter, it is particularly preferred that the bath at the temperature of operation will be substantially saturated with the ammonium chloride.

Immersion of the oxidized iron or steel article in the described bath results in rapid removal of the oxide until the surface of the metal is clean and bright. The rapidity of removal of oxide is such that in most cases the oxide is completely removed in less than a minute after immersion. In spite of this rapid oxide removal, however, the bath does not rapidly attack the underlying iron or steel. Thus, the iron or steel article may be merely immersed in the bath and left there without overly careful observation, since, once the oxide is removed, the bath will not within a reasonable time, the exact time depending upon the nature of the article being treated, attack the free metal. Following removal of the oxide, the article may be removed from the bath, rinsed with water and dried. One of the most important features of the present invention is the fact that, after the described treatment, the article may be permitted to stand for periods of as long as a day or more, depending upon the humidity conditions, without any significant re-oxidation of the surface. Although the exact reason for this is not presently understood, it is believed that the nature of the metal surface resulting from the treatment is such as will not occlude or absorb moisture; whereas when, for example, hydrochloric acid alone is employed, the treated surface, possibly due to redeposition of metallic iron, appears to be of a nature which readily occludes and absorbs moisture leading to rapid re-oxidation.

The method of the present invention is, as stated, applicable to the treatment of articles prepared from iron or steel. Any iron or steel the surface of which will oxidize, including carbon steels; "stainless" steels; hardened (alloy) steels, such as molybdenum steels and tungsten steels; other alloy steels, such as chromium steels, nickel steels, chrome-vanadium steels; and the like, may be treated. Among those steels most often treated in accordance with the present process are articles prepared from cold rolled low carbon steel.

Referring specifically to the bath used in accordance with the present invention, it is prepared by dissolving ammonium chloride in aqueous hydrochloric acid. Commercial concentrated hydrochloric acid is actually a solution, in water, of 35–37%, by weight, HCl, and such commercial acid may be employed as such as the aqueous hydrochloric acid. About 37%, by weight, concentration of HCl in water is about the maximum concentration of that material obtainable in water. The concentration may be substantially lower than the above range as by adding water to the concentrated acid, and in this case the amount of water added may reach as high as about one part thereof per part of concentrated hydrochloric acid. In this case the concentration of HCl is reduced to about 16–17%. Commercial dilute hydrochloric (about 20% HCl, by weight) may also be employed. It is recommended that the hydrochloric acid employed not contain an inhibitor, such as morpholine, aniline, and the like, since it has been found that the presence of such materials results in rapid re-oxidation of the treated metal surface.

As stated, hydrochloric acid by itself results in a cleaned steel surface which rapidly re-oxidizes upon removal from the bath. The presence of the ammonium chloride in the bath prevents this rapid re-oxidation and in order to provide a bath which provides significant protection against re-oxidization, there should be at least about 10 grams ammonium chloride per 100 ml. of aqueous hydrochloric acid in the bath. The maximum amount of ammonium chloride dissolved in the bath may be that providing a saturated solution at the temperature of operation. With commercial concentrated hydrochlo-

ric acid itself, about 20 grams of ammonium chloride per 100 ml. of concentrated hydrochloric acid are required to provide saturation. In the more dilute aqueous hydrochloric acid, that is containing 16–17% HCl, about 45 grams of ammonium chloride may be dissolved in 100 ml. thereof at the temperatures of operation. In aqueous hydrochloric acid solutions near the lower end of the range of HCl concentration, it is preferred that at least about 20 grams of ammonium chloride be present per 100 ml. of solution. As stated, the aqueous hydrochloric acid solution may be saturated with ammonium chloride, and in accordance with preferred practice, concentrations of ammonium chloride substantially near saturation are employed. Of course, excess ammonium chloride over and above that providing saturation may be added to the bath to insure full saturation, such excess merely existing in solid form in the bath.

It will be seen that the bath employed in accordance with the present invention consists essentially of aqueous hydrochloric acid containing a substantial amount of ammonium chloride dissolved therein. It has been found that the bath should be substantially free of strong acid anions other than hydrochloric acid. Thus, no other strong acid or salt of a strong acid is relied upon to remove the oxide, and substantial amounts of strong acid or salt of a strong acid, or even weak acid or salt of a weak acid, the exact amount depending upon the nature of the acid or salt, in addition to the hydrochloric acid and ammonium chloride in the stated amounts may have a deleterious effect on the base metal. Accordingly, ammonium salts other than ammonium chloride, such as ammonium nitrate, ammonium sulfate, ammonium phosphate, and the like, are not relied upon to provide the ammonium chloride in solution. Of course, an ammonium salt having a volatile anion, such as ammonium carbonate, may be employed to provide some or all of the ammonium chloride in solution, since, at the temperature of operation, carbon dioxide will be evolved and released from the bath. Ammonium hydroxide may also be employed. However, in these cases, consideration must be had of the amount of hydrochloric acid required to combine with the ammonium ions to provide ammonium chloride in solution. Preferably, of course, ammonium chloride itself is added to and dissolved in the bath. While, as stated, the principal oxide-removing and re-oxidation retarding ingredients of the bath of the present invention are the hydrochloric acid and ammonium chloride, it will be understood that minor amounts of other materials not substantially deleteriously affecting the characteristics of the bath may be employed to impart or augment certain features. For example, a small amount of ferric chloride may be added to the bath to serve as an activator.

In accordance with the process of the present invention, the bath is at an elevated temperature at the time the oxide is removed from the metal articles. At temperatures below about 50 C., the time required for removal of the oxide may be too long for practical application, although, if time is not an important consideration, temperatures as low as 40° C. may be employed. At temperatures of about 50° C. and above, the oxide will be removed within a very short time, and the higher the temperature the faster the removal of the oxide. The temperature of the bath may go up to the boiling point of the solution which is in the neighborhood of about 80° C. Higher temperatures can be employed by the use of superatmospheric pressures, however, no significant advantage is to be gained by operating at such temperatures. Preferably, the bath is maintained slightly below the boiling point, especially within the range of between about 70 and about 75° C., particularly where the oxidized article has a slight greasy or oily film thereon from, for example, handling.

The time required for removal of the oxide will vary somewhat depending upon the thickness of the oxide film and upon the exact conditions employed during the process. In general, the oxide will be substantially completely removed within about 20 to about 50 seconds after immersion in the bath at operating temperatures above about 55° C. In the event the article has a slight greasy or oily film thereon from, for example, handling, somewhat longer times may be required.

After removal of the oxide in accordance with the present process, the article may be removed from the bath and washed, such as with water, to remove adhering bath solution. After washing, the article is preferably dried.

After the article has been removed from the bath, washed and dried, it is in proper condition for further treatment, such as vapor-, chemical- or electroplating. Following the treatment of the present invention, the article may actually stand for as long as a day, if dried, depending upon the atmospheric conditions in which the article is placed, without significant re-oxidation.

With iron or steel articles having particularly heavy oxide layers, it may be advantageous preliminarily to remove the bulk of this oxide with hydrochloric acid (preferably inhibited) itself, relying upon the procedure of the present invention to remove the remaining oxide and render the clean metal surface passive to further rapid oxidation.

The process of the present invention will be more readily understood from a consideration of the following specific example which is given for the purpose of illustration only and is not intended to limit the scope of the invention in any way.

Example

A bath is prepared by adding 20 grams of ammonium chloride to 100 ml. of commercial concentrated hydrochloric acid (35% HCl) and heating the mixture to 70–75° C.

While maintaining the bath at about 70–75° C., cold rolled steel transistor stems whose surfaces are oxidized are immersed in the bath and left therein for about 20–30 seconds. The stems are then removed, washed in water, and dried. The stems now have a clean, bright surface, ideally suited for chemical plating. The stems can be left to stand for as long as a day, except under exceptionally humid conditions, without re-oxidizing significantly.

Oxidized articles of stainless steel, wrought iron, combinations of wrought iron and hardened steel are also readily de-oxidized in this manner without any evidence of redeposition of iron on the cleaned surface and without rapid re-oxidation thereof.

Modification is possible in the selection of additives for the bath as well as in the proportion of the main ingredients, and in the exact technique followed in carrying out the process, without departing from the scope of the invention.

I claim:

1. The method of removing oxide from the surface of oxidized iron and steel articles and concurrently conditioning said surface to resist reoxidation, which comprises immersing the oxidized article in a bath consisting essentially of a solution of ammonium chloride in aqueous hydrochloric acid at a temperature between about 40° C. and the boiling point of said bath, said aqueous hydrochloric acid containing between about 16 and about 37%, by weight, of HCl and said ammonium chloride being present in an amount between about 10 grams per 100 ml. of aqueous hydrochloric acid and a mass sufficient to saturate said aqueous hydrochloric acid at said temperature, and continuing said immersion at least until oxide is removed.

2. The method of claim 1 wherein said temperature of said bath is between about 50° C. and said boiling point.

3. The method of claim 2 wherein said temperature of said bath is between about 70 and about 75° C.

4. A method for removing oxide from the surface of oxidized iron and steel articles and concurrently conditioning said surface to resist reoxidation, said method comprising the steps of: immersing the oxidized article in a bath consisting essentially of ammonium chloride in aqueous hydrochloric acid; maintaining said bath at a temperature between about 40° C. and the boiling point of said bath during said immersion of said article; and continuing said immersion at least until said oxide is removed from said article, said aqueous hydrochloric acid containing between about 20 and about 37 percent by weight of HCl and said ammonium chloride being present in an amount between about 10 grams per 100 milliliters of said aqueous hydrochloric acid and a mass sufficient to saturate said aqueous hydrochloric acid at said temperature.

5. A method according to claim 4, wherein said bath is maintained at a temperature between about 50° C.

and said boiling point during said immersion of said article.

6. A method according to claim 4, wherein said bath is maintained at a temperature between about 70° C. and about 75° C., and wherein said amount of ammonium chloride is sufficient substantially to saturate said aqueous hydrochloric acid at said temperature.

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