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2,768,104

METHOD FOR COATING IRON

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This application relates to a new and improved process for treating metal surfaces and to coated metals produced by this process.

Throughout the years a great many different metal treatment processes have been developed, all of which have been more or less satisfactory in providing corrosion resistance to metal surfaces. These processes, while frequently acceptable, have not always been advantageous because of their cost, the time they require, or other features. Such prior processes are well known to the art and may be found by reference to any of the common texts on the subject of metal treatment.

It is an object of the present invention to provide a process for treating metal surfaces which overcomes the defects of these prior art processes and which enables a corrosion resistant surface to be quickly, easily and cheaply produced upon metals. Other objects of the invention, as well as the advantages of it, will be apparent from the following description and claims.

Essentially the present invention consists of following any of the normal metal pre-treatment steps, such as solvent and alkaline cleaning, pickling, nitric acid etching, phosphatizing, oxide coating by chemical or thermal processes, and the like, with a chromic acid-reducing agent treatment and a curing or drying step. This new treatment procedure involves wetting the metal surface with a chromic acid and then reducing part of the chromic acid upon the surface to a trivalent state with the aid of a reducing agent which is effective at the surface of the metal being treated.

The invention herein set forth is not to be limited to ferrous metals but can be applied with equal utility to aluminum, brass, copper, nickel, magnesium, tin, zinc, and the like, and their alloys. The optimum results are, however, obtained with common iron or carbon steel containing from about 0.05% to about 2% carbon. Sheets or articles of any size or shape treated in accordance with this invention can be used for a variety of applications. Perhaps its greatest utility will be in the manufacture of hot or cold rolled steel in strip, sheet or plate form.

The chromic acid and the reducing agent can be applied simultaneously to a metal surface from a common solution or they may be applied separately, as will be indicated. The application of any bath employed in this invention may be made by spraying, flooding, immersing, or with the aid of rolls such as are found in the lithographic art. In addition, the reducing agent employed with this invention can be applied directly to a metal surface while in a gaseous or vapor state.

Reducing agents which are to be employed simultaneously with the chromic acid solution should not form stable oxidation products or water soluble salts with this acid. A representative few of the many reducing agents which fall in this category are the straight chain polyalcohols such as glycol, glycerine, mannitol, sorbitol and sugars generally, as well as conventional reducing agents such as potassium iodide, phenol, hydroquinone, phos-

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phorous acid, hydroxylamine sulfate, triethanolamine, and the like. Because of its effectiveness and relatively low cost, common invert sugar is the preferred reducing agent for application with the chromic acid solution.

The foregoing and other reducing agents suggested thereby may also be applied after the chromic acid treatment. Hydrogen, methane, formaldehyde vapors, ethyl alcohol vapors, and similar gaseous reducing agents may be utilized in lieu of or supplementary to the agents mentioned previously.

At first glance it would seem that this invention is very close to many of the prior art treatment processes as mentioned above; this is not the case. Metals which have been treated in accordance with this specification exhibit much superior corrosion resistance. It is theorized that perhaps this corrosion resistance is due to the formation of a solid solution consisting partially of trivalent chromium and hexavalent chromium upon the surface treated. The wetting of the surface being treated with a chromic acid bath is believed to deposit chromates upon this surface. The reducing agent employed reduces a fraction of these chromates to a trivalent chromium compound, which, during the subsequent drying step, is thought to diffuse into the metal surface. Such a surface solid solution is not to be found in the art of record and is considered to be responsible for the improved properties obtained.

The chromic acid solution, whether applied separately or in conjunction with a reducing agent, is generally maintained at temperatures of from about 50° to about 200° F. Preferably, temperatures of from 70° to 90° F. are utilized in order to obtain the best results. The metal treated should advisably be covered with the chromic acid bath from 1 second to 5 seconds in order to produce a satisfactory chromate film. The concentration of chromic acid may vary widely, concentrations as low as ½% or as high as 30%, based upon the CrO₃ concentration, having been found to give satisfactory results. In the same manner, the concentration of reducing agent in the bath may vary widely from ¼% to 25% or higher. The amount of the reducing agent employed is normally governed by the amount of chromic acid used, and should be less than this last quantity. In general, the higher the chromate concentration the thicker the final film or solid solution.

If desired, the metal sheets removed from the chromic acid treatment may be run through coarse rubber rolls in order to remove any excess solution present and distribute the solution used uniformly throughout the metal surface.

The reducing agent may be applied either with or subsequent to the chromic acid treatment as previously mentioned. When it is applied separately, the reducing agent may be more highly reactive than if it is applied with the chromic acid solution. In the same manner, higher concentrations of reducing agent may be employed for separate application than for simultaneous application.

After treatment with the chromic acid and the reducing agent, the metal surfaces produced may be converted to the desirable water insoluble film in a short period by mere exposure to air at room temperature. Alternatively, they may be converted almost instantaneously by forced drying at temperatures above the boiling point of water. For this purpose, flame drying, infra-red drying, induction heating, etc., are very useful. Drying from the inside out—as by infra-red lamps—is preferred, as the resulting product has a unique surface which is both water insoluble and water repellent.

Our invention will be more readily understood by consideration of the following comparative examples, in which the quantities stated are in parts by weight unless otherwise indicated. The corrosion resistance of surfaces

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produced both in accordance with this invention and with the prior art, as given in these examples, is based on the following scale:

- 100—excellent corrosion resistance
- 80—very good corrosion resistance
- 60—good corrosion resistance
- 40—fair corrosion resistance
- 20—poor corrosion resistance
- 0—very poor corrosion resistance

All corrosion tests consisted of immersion in tap water at 75° F. for 16 hours unless otherwise noted; full bright finish steel (Blackplate) was employed in all tests except as indicated.

Example 1

- A. Clean cathodically in a solution containing 16 g. KOH per liter using a current density of 15 amperes per square foot at 140–160° F. for 10 seconds.
- B. Cold water rinse.
- C. Clean anodically in a solution containing 16 g. KOH per liter using a current density of 15 amperes per square foot at 140–160° F. for 10 seconds.
- D. Cold water rinse.
- E. Flood with a solution containing 10% CrO₃ and 3% cane sugar, at 75° F. for 2 seconds.
- F. Roll through smooth rubber rolls wetted with the solution mentioned in "E."
- G. Dry the sheet by flaming both sides of the sheet with reducing gas flames.

Example 2

Same as Example No. 1, except in "E," a solution containing 6.5% CrO₃ and 2% glycerine was used.

Example 3

- A. Clean by immersing in an alkaline cleaner at 180° F. for 30 seconds.
- B. Cold water rinse.
- C. Immerse in a 15% HCl solution at 90° F. for 10 seconds.
- D. Cold water rinse.
- E. Immerse in a solution containing 5% CrO₃ and 3% cane sugar at 75° F. for 3–5 seconds.
- F. Roll through coarse rubber rolls.
- G. Dry between infra-red lights for 10 seconds (the metal reaching 250–300° F.).

Steel strip finished as above had a corrosion resistance of 100 as compared with steel plate finished in accordance with the same process omitting the use of the reducing agent in step "E" which had a corrosion resistance of 40.

Example 4

Same as Example No. 3, except in "C" a 5% citric acid solution at 80° F. for 10 seconds was used.

Example 5

Same as Example No. 3, except in "C" a 10% H₂SO₄ at 160° F. for 10 seconds was used.

Steel strip processed as in this example had a corrosion resistance of 100 as compared with the same steel treated in accordance with the process omitting the use of a reducing agent in step "E" which had a rating of 30.

Example 6

Same as Example No. 3, except in "C" a 3% ferric sulfate solution at 160° F. for 5 seconds was used.

Example 7

Same as Example No. 5, except a time of 5 minutes was used in step "C."

The steel strip obtained in this example had a comparative corrosion resistance of 80, whereas strip obtained by omitting the reducing agent in step "E" had a rating of 30.

Example 8

Same as Example No. 3, except in "C" a 3% oxalic acid solution at 160° F. for 10 seconds was used.

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The steel strip obtained by the process of this example had a comparative corrosion resistance of 100, while strip obtained by omitting the reducing agent in step "E" had a corrosion resistance of 50.

Example 9

Same as Example No. 3, except in "C" 39% NaOH and 2% NaNO₃ at 280° F. for 15 minutes was used.

- Steel strip obtained by stopping at step "D" in Example 3 had a corrosion resistance of 20, as compared with steel strip produced in accordance with this example which had a rating of 100.

Example 10

- A. Treat by immersing in a solution containing 1% FeCl₃, 1% HCl at 75° F. for 30 seconds.
- B. Cold water rinse.
- C. Treat by immersing in a solution containing 3% CrO₃ at 75° F. for 5 seconds.
- D. Pass through rubber rolls (coarse).
- E. Dry between infra-red lights (200–250° F.).

The steps indicated above correspond to the metal treatment process of U. S. Patent 2,288,182, and the steel sheets produced by this process had a corrosion resistance of 70. Substitution of a rinse containing 3% CrO₃ and 1.5% triethanolamine in step "C" at 75° F. for 5 seconds produced sheets having a corrosion resistance of 100.

Example 11

- A. Treat by immersing in solution containing 5% KOH at 75° C. for 5 minutes.
- B. Cold water rinse
- C. Treat by immersing in 20% HCl solution at 80° C. for 10 minutes.
- D. Cold water rinse.
- E. Treat by immersing in solution containing 1% Na₂Cr₂O₇ and .02% Na₂CO₃ at 75° F. for 5 seconds.
- F. Pass through set of rubber rolls (coarse).
- G. Dry in infra-red light for 15 seconds (200–300° F.).

This treatment corresponds to a process in U. S. Patent 2,535,794; and the steel strip prepared in accordance with the indicated process had a corrosion rating of 20. Steel strip produced by the substitution of 1% CrO₃ and .7% triethanolamine in step "E" at 75° F. for 5 seconds had a corrosion resistance rating of 70. Both of these ratings were based upon an accelerated test consisting of immersion in water (tap) at 90° C. for 5 minutes.

Example 12

- A. Treat by immersing in a solution containing 5% KOH at 75° C. for 5 minutes.
- B. Cold water rinse.
- C. Treat by immersing in a 25% H₂SO₄ solution at 75° C. for 12 minutes.
- D. Cold water rinse.
- E. Treat by immersing in a solution containing 1% Na₂Cr₂O₇ and .02% Na₂CO₃ at 75° F. for 5 seconds.
- F. Pass through rubber rolls (coarse).
- G. Dry between infra-red lights for 15 seconds (200–300° F.).

The process indicated by the above steps corresponds to a process indicated in U. S. Patent 2,535,794. A steel strip was produced having a comparative corrosion resistance of 20, whereas by the substitution of 10% CrO₃ and 3% triethanolamine in step "E" at 75° F. for 5 seconds a strip having a corrosion resistance of 90 was produced.

Example 13

Iron phosphate treatment:

- A. Treat by spraying in a solution containing 1 oz. Duridine 210B (American Chemical Paint Co.) per gallon for 96 seconds at 150° F. using a spray pressure of 12 pounds per square inch.

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- B. Same as "A" except a time of 72 seconds was used.
 C. Same as "A" except .5 oz. Duridine 210B per gallon used.
 D. Cold water rinse, 72 seconds, 12 p. s. i.
 E. Treat by spraying in a solution containing $\frac{1}{40}$ % by volume American Chemical Paint Deoxylyte #10 at 150° F. for 72 seconds, spray pressure 12 pounds per square inch.
 F.—Dry in oven at 350° F. for 2 minutes.

The corrosion resistance of sheet steel coated in this manner was 20. The above cycle was then repeated with step "E" omitted and after step "F" the steel was treated by immersing in a solution containing 2.5% CrO_3 and 2% H_3PO_3 , passed through rubber rolls (coarse) and subsequently dried between infra-red lights (200–300° F.). A corrosion resistant surface having a rating of 90 was obtained.

Example 14

Zinc phosphate treatment:

- A. Treat by immersing in a solution containing 3.5 oz. Parker Rust Proof (Parco Clean 34) for 1 minute at 170° F.
 B. Cold water rinse.
 C. Treat by immersing in a solution containing 5.34% by volume of Bonderite 32 (Parker Rust Proof Co.) for 1.5 minutes at 165° F.
 D. Cold water rinse.
 E. Treat by immersing in a solution containing .03% by volume Parcolene (Parker Rust Proof) for 45 seconds at 180° F.

This prior art treatment was then modified by substitution, in step E, of a solution containing 2.5% CrO_3 and 2% H_3PO_3 used at 75° F. for 5 seconds and the steel was passed through rubber rolls and subsequently dried between infra-red lights at 200–250° F. for 20 seconds in order to obtain superior corrosion resistance.

The surface films produced in accordance with this invention as indicated in the above examples were water insoluble, tough and durable, and showed remarkable resistance to corrosion. They were well suited for anchoring lacquer, paint, resins, enamel and the like. In many respects they were equal to or better than the more expensive tin-plate commonly used in the manufacture of food containers.

It is to be understood that the above examples are given for purposes of illustration only, and are not to be considered as limiting the invention to any of the specific conditions or materials given therein.

The products produced in accordance with the foregoing instructions may be used for a wide variety of purposes. Wherever corrosion resistance is important they are of particular value. They are likewise of great value for coating with lacquers, paints, enamels, resins and the like. Because of their low cost and unusual properties they are susceptible of many uses in the food container, construction, and other fields.

The present application is in part a continuation of prior application Serial No. 277,286, filed March 18, 1952.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope hereof, it is to be understood that it is not limited to the specific embodiments hereof except as defined in the appended claims.

What is claimed is:

1. A method for increasing the corrosion resistance

and lacquer adhesion of ferrous metal which method comprises contacting a clean surface of said ferrous metal for at least one second with an aqueous solution consisting essentially of about $\frac{1}{2}$ to about 30% chromic acid and about $\frac{1}{4}$ to 25% of a reducing agent selected from the class consisting of polyalcohols, potassium iodide, phenol, hydroquinone, phosphorous acid and hydroxylamine sulfate, the concentration of reducing agent being less than the concentration of chromic acid and the bath temperature being between about 50 and 200° F., withdrawing the contacted metal from the solution to leave a film of the solution on the surface of the metal, and then drying the film on the surface of the metal at a temperature above the boiling point of water.

2. A method for increasing the corrosion resistance and lacquer adhesion of ferrous metal which method comprises contacting a surface of said ferrous metal for at least one second with an aqueous solution consisting essentially of about $\frac{1}{2}$ to about 30% chromic acid and about $\frac{1}{4}$ to 25% of a reducing agent selected from the class consisting of polyalcohols, potassium iodide, phenol, hydroquinone, phosphorous acid and hydroxylamine sulfate, the concentration of reducing agent being less than the concentration of chromic acid and the bath temperature being between about 50 and 200° F., withdrawing the contacted metal from the solution to leave a film of the solution on the surface of the metal, and then drying the film on the surface of the metal to cause a fraction of the chromic acid to become reduced by the reducing agent.

3. The combination of claim 2 in which the ferrous metal is black plate and the reducing agent is one that does not form water-soluble salts when it is oxidized by the chromic acid.

4. The combination of claim 2 in which the ferrous metal is black plate, the reducing agent is a sugar and the drying temperature is above 250° F.

5. The combination of claim 2 in which the ferrous metal is black plate, the reducing agent is cane sugar and the drying temperature is above 250° F.

6. The combination of claim 2 in which the ferrous metal is black plate, the reducing agent is triethanolamine and the drying temperature is above 250° F.

7. The combination of claim 2 in which the ferrous metal is black plate, the reducing agent is glycerine and the drying temperature is above 250° F.

8. The combination of claim 2 in which the ferrous metal is black plate, the reducing agent is phosphorous acid and the drying temperature is above 250° F.

9. The combination of claim 2 in which the ferrous metal is black plate, the reducing agent is glycol and the drying temperature is above 250° F.

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