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METHOD FOR COATING METALS

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The present invention relates to new and improved methods for treating metal surfaces so as to impart thereto unusual corrosion resistance and lacquer adherence, as well as the new products produced thereby. More specifically it is concerned with an improvement upon the method described in copending application Serial No. 251,450, filed October 15, 1951, whereby the time required for the desirable protective surface to form is substantially reduced and at the same time the properties of this surface are further improved.

In accordance with the teachings of the aforesaid application iron or steel articles generally are subjected to a certain sequence of treatments whereby their surfaces are profoundly altered. Briefly, these steps comprise first treating the desired article, for instance a sheet of steel, with nitric acid so as to lightly etch and slightly oxidize its surface; then wetting the etched and oxidized surface with chromic acid to produce a chromate film thereon, and finally drying and setting the surface without allowing it to come in contact with water in any form until conversion of the surface structure has been completed. By virtue of this treatment a greatly improved surface having unusual properties is produced. Articles treated in this manner exhibit excellent corrosion resistance and lacquer adherence. Sheet steel when so treated is particularly adapted for use in the manufacture of food containers.

The nitric acid treatment slightly etches the surface of the metal and oxidizes part of this surface so as to produce a thin combined ferrous and ferric oxide film. During the subsequent treatment with chromic acid, iron chromates are thought to be formed upon the so-treated surface, and part of the ferrous oxide present is considered to be oxidized to the ferric state. Simultaneously, the hexavalent chromium in the chromic acid is partially reduced to trivalent chromium at the metal surface. By this series of reactions a homogeneous solid solution is produced on the metal face.

Several days may be required for this solid solution to be converted to the desired water insoluble surface. Until this occurs the surface should be protected from water, and if this is not done the properties of the resulting product will be impaired. Needless to say, the time required for this conversion to occur and the need of protecting the surface from water while it takes place, substantially increase the cost of this method.

It is an object of the present invention to markedly reduce the conversion time necessary to produce the desired completely water insoluble surface on products produced by the foregoing and equivalent methods. A further object is to produce a water-insoluble corrosion resistant surface on steel articles by a process which is much more economical than any heretofore known. A still further object is to produce new steel articles which have surprising resistance to corrosion, and also are particularly adapted for coating with dissimilar materials of an organic or inorganic nature, such as paints, lacquers,

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plastic films, metals, etc. Additional objects will become apparent from a consideration of the following description and claims.

These and other objects are attained in accordance with the present invention, wherein chromated surfaces produced by the foregoing or equivalent methods are subjected to a reducing operation which converts the water soluble coating to a water insoluble form. To illustrate, the metal being treated is first subjected to an etching and oxidizing treatment with an agent such as nitric acid. It is then subjected to treatment with chromic acid, and either simultaneously or promptly thereafter the chromated surface is reduced to a water insoluble state by contacting it with a reducing agent. Both the chromic acid and the reducing agent may be applied simultaneously from the same solution as by dipping, spraying, flooding or using rollers of a type similar to those used in lithography. If desired, the treatment may proceed and be independent of the reducing operation. Each of said agents may be applied by the foregoing or related methods. Likewise, the reducing agent may be applied directly to the chromated surface in the form of a gas or vapor, or the like.

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, phosphorous 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.

An outstanding and surprising advantage of this invention is the fact that it permits the chromic acid treatment, and if desired the simultaneous reducing treatment, to be carried out at relatively moderate temperatures in and about room temperature, say from about 50° to about 125° F. Moreover, it is not necessary to force-dry the final product to obtain the highly desirable water insoluble film thereon, although force-drying helps to speed up the final conversion of the chromated surface. This conversion reaction takes place almost instantly at temperatures above the boiling point of water, obtained by heating the chromated surface by direct or indirect heating means.

In order to obtain optimum results, it is advisable as a general rule to start with a steel which can be etched with a mineral acid such as sulfuric or hydrochloric acid. The metal may be in the form of sheets, plates, bars, rods, or any other desired shape. Likewise, it may be hot or cold rolled.

The metal may if desired be preliminarily treated with a mineral acid such as sulfuric or hydrochloric acid in order to obtain a clean surface for subsequent treatment. A moderate etch obtained by treatment with 10% sulfuric acid at a temperature of 160° F. for a period of 15 minutes has been imparted to the metal with excellent results.

It is also possible to clean the metal surfaces either anodically or cathodically, instead of using a pickling bath for this purpose. Treatment with various alkaline clean-

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ers or solvents such as trichloroethylene, sodium phosphate, caustic soda or the like, may be employed to remove any noticeable amounts of organic material present. The presence of slight amounts of organic compounds on the article being treated generally is not harmful, as these substances are removed during the following nitric acid treatment. In most instances it is not necessary to pre-clean the material to be treated, so this step is optional.

The metal surface with or without pre-cleaning as aforesaid, is etched and oxidized by immersion in a nitric acid bath containing from about 1% to about 20% by weight of the acid, for a period of from 2 to 70 seconds at a temperature of from about 60° to about 150° F. The treatment with the nitric acid may be carried out by immersion in a tank or vat of the acid solution, or it may be satisfactorily accomplished by spraying or flooding the acid upon the metal surface or applying the acid by the use of rolls. It is to be understood that as the concentration of the acid bath is increased the time of immersion may be correspondingly decreased. Likewise, if the temperature of the bath is increased the immersion time and/or concentration of the bath may be decreased.

Following the nitric or equivalent acid treatment the metal is rinsed in water, either hot or cold, in order to avoid contamination of the succeeding chromic acid bath and to remove any residue which might be carried over by entrainment from the nitric acid treatment.

The etched and oxidized metal is then treated with chromic acid to form a chromate coating over its surface. The so-formed coating is extremely sensitive to water, as it is converted to the desirable water insoluble form by promptly subjecting it to treatment with a reducing agent. 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 1/2% 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 1/4% 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 treated with chromic acid may be run through coarse rubber rollers to remove excess solution from their surfaces and produce a uniform chromate film of satisfactory thickness.

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.

This invention may be more readily understood by a consideration of the following illustrative examples in

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which the quantities stated are in parts by weight unless otherwise noted:

Example 1

- 5 A sheet of full bright finish steel (Blackplate) was used for the following treatment:
 - A. Cathodically clean in a solution containing 16 g. KOH/l at 140–160° F., at a current density of 16 amperes per square foot for 10 seconds.
 - 10 B. Cold water rinse.
 - C. Clean anodically in a solution containing 16 g. KOH/l at 140–160° F. at a current density of 16 amperes per square foot for 10 seconds.
 - D. Cold water rinse.
 - 15 E. Flood with 2.3% HNO₃ at 80° F. for 5 seconds.
 - F. Cold water rinse (flood).
 - G. Flood with a solution containing 3.2% CrO₃ and 2% glycerine at 80° F. for 2 seconds.
 - H. Roll through smooth rubber rolls wetted with the solution mentioned in "G."
 - 20 I. Dry by flaming both sides of blackplate strip with a reducing gas flame.

Example 2

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

Example 3

- 30 Same as Example No. 1, except in "G" a solution containing 5% CrO₃ and 2% cane sugar was used.

Example 4

Same as Example No. 1, except in "G" a solution containing 10% CrO₃ and 3% cane sugar was used.

Example 5

Same as Example No. 4, except in "I," dry by flaming one side of strip with a reducing gas flame.

Example 6

- 40 A sheet of full bright finish steel (Blackplate) was used for the following treatment:

- A. Immerse in 3.0% HNO₃ 5 seconds, at 75° F.
- B. Cold water rinse.
- 45 C. Immerse in a solution containing 5.0% CrO₃ and .5% cane sugar.
- D. Roll through coarse rubber rolls.
- E. Dry between infra-red lights for 10 seconds (250–300° F.).

Example 7

Same as Example No. 6, except in "C" a solution containing 2.5% CrO₃ and .4% glycerine was used.

Example 8

- 55 Same as Example No. 6, except in "C" a solution containing 5% CrO₃, 1.3% glycerine and .5% H₂SO₄ was used.

Example 9

- 60 Same as Example No. 6, except in "C" a solution containing 5% CrO₃ and 4% mannitol was used.

Example 10

- 65 Same as Example No. 6, except in "C" a solution containing 5% CrO₃ and 2% Carbowax 1500 was used. (Carbowax 1500 is a high molecular polyethylene glycol formula CH₂OH(CH₂OCH₂)_xCH₂OH where x is about 30.)

Example 11

- 70 Same as Example No. 6, except in "C" a solution containing 5% CrO₃ and 1% glycerine was used at a temperature 180–190° F.

Example 12

- 75 Same as Example No. 11, except omit forced drying step "I"—instead dry by letting stand in air.

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Example 13

A sheet of full bright finish steel (Blackplate) was used for the following treatment:

- A. Treat by immersing in a solution containing 2.5% HNO_3 for 5 seconds at room temperature.
- B. Cold water rinse.
- C. Treat by immersing in a solution containing 2.5% CrO_3 and .7% triethanolamine for 3-5 seconds at room temperature.
- D. Pass through coarse rubber rolls.
- E. Dry between infra-red lights for 15 seconds.

Example 14

Same as Example No. 13 except in "C" 2.5% CrO_3 and 2% triethanolamine for 3-5 seconds at 180-190° F. was used.

Example 15

Same as Example 13 except in "C" 2.5% CrO_3 and 1½% hydroxylamine sulfate was used.

Example 16

Same as Example No. 13 except in "C" 2.5% CrO_3 and 2% phosphorous acid was used.

Example 17

A sheet of full bright finish steel (Blackplate) was used for the following treatment:

- A. Treat by immersing in a solution containing 2.5% HNO_3 for 5 seconds at room temperature.
- B. Cold water rinse.
- C. Treat by immersing in a solution containing 5% CrO_3 for 3-5 seconds at 180° F.
- D. Pass through coarse rubber rolls.
- E. Dry between infra-red lights for 7 seconds.
- F. Hold in fumes from boiling formaldehyde (37%) for 25 seconds.
- G. Dry between infra-red lights for 10 seconds.

Example 18

Same as Example No. 17 except in step "C" use a temperature of 75° F., and in step "F" fumes from boiling ethyl alcohol were used.

Example 19

Same as Example No. 13 except in "C" 2.5% CrO_3 and 3% potassium iodide was used.

Example 20

Same as Example No. 13 except in "C" 2.5% CrO_3 and .5% phenol was used.

Example 21

Same as Example No. 13 except in "C" 2.5% CrO_3 and .5% hydroquinone was used.

Example 22

Same as Example No. 13 except in "C" 20% CrO_3 and 10% triethanolamine at a temperature of 130° F. was employed.

In each instance, the products produced in accordance with the above examples had a water insoluble, tough, durable film on the surface which showed remarkable resistance to corrosion. These surfaces were ideal for anchoring lacquer films, and the resulting sheets in many respects were equal to or better than the well known and much more expensive tin-plate.

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Before reduction the chromated surface had a characteristic reddish color. When the reduction was complete the surface was impervious to water and had a characteristic greyish or greyish-yellow color.

It is to be understood that the above examples are given for purposes of illustration only, and are not to be considered limiting this invention to the specified reactants or conditions of treatment.

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.

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 forming a corrosion-resistant, lacquer-adhering surface on a ferrous metal, comprising etching said metal with a nitric acid bath having a concentration of from 1% to 20% HNO_3 by weight for a period of 2 to 70 seconds at a temperature of 60-150° F., the lower times being used with the higher concentrations, rinsing off the metal so treated, contacting the rinsed metal with a chromic acid solution containing from about ½% to about 30% CrO_3 for a period of at least 1 second at a temperature of about 50 to about 200° F., removing the contacted metal from the solution so that a film of the solution remains on the surface of the metal, and drying this film on the surface of the removed metal while chemically reducing a portion of the chromic acid in the film with a reducing agent as the drying is effected.
2. The process of claim 1 in which the drying is effected at a temperature above 212° F.
3. The process of claim 1 in which the reducing agent is one that does not yield water-soluble salts when it is oxidized by the chromic acid.
4. The process of claim 3 in which the reducing agent is included in the chromic acid solution film applied to the metal surface, and the drying temperature is at least as high as 250° F.
5. The process of claim 4 in which the solution film on the metal surface is an aqueous solution containing as the essential dissolved ingredients from about 2.5 to 10% chromic acid and from 0.4 to 4% of a reducing agent selected from the class of sugar, triethanolamine, glycerine and phosphorous acid.

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