

UNITED STATES PATENT OFFICE

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METHOD OF PROTECTING METAL SURFACES

No Drawing.

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This invention relates to a method of protecting metal surfaces and has for its object the provision of a simple, effective and economical method of rendering metal surfaces capable of resisting the action of moisture or other influences tending to corrode such surfaces. This invention is related to that disclosed in my copending application Serial No. 227,061, filed October 18, 1927.

In accordance with the general features of the invention an article having a metal surface which it is desired to protect, is connected as a cathode in an electrolytic cell in which the bath employed contains a compound of a metallic element and an initial electric current of sufficiently low cathode current density to insure substantially no deposition of metal is passed through the cell for a short period of time, after which the article is removed from the cell and dried.

It has been found by experiment that when such metals as iron, zinc, cadmium, copper, silver, etc. are connected as cathodes in an electrolytic cell in which the bath contains a material, such as chromic acid, comprising a compound of a metallic element in which the element forms a part of an acid radical and when a current of sufficiently low cathode current density to provide conditions under which no metal is deposited, is passed through the cell for a short period of time the surfaces of the articles are rendered passive to the extent that they will resist the corrosive action of atmospheric agents for a very long period of time. The surfaces rendered passive are also quite resistant to the action of sulphur, acids, such as nitric acid and hydrogen sulphide, and numerous other corrosive substances even after the treated articles have been subjected to abrasion. This phenomenon provides a very effective method for protecting metal surfaces and it constitutes the subject matter of the present invention.

Although it is to be understood that the method of protecting metal surfaces forming the subject matter of this invention is applicable to numerous metals and that the ingredients and conditions under which the method is practiced may be varied within a wide range, a specific embodiment of the in-

vention will be described in detail in order to enable persons skilled in the art to practice the invention.

One embodiment of the invention consists in a method for protecting the surfaces of articles made of iron. In this embodiment of the invention an electrolytic cell is employed in which the bath comprises a water solution containing 22 grams per liter of chromic acid (CrO_3) in which is connected an anode of any suitable insoluble material such as iron, platinum or lead. The article to be treated is connected as a cathode in the above described electrolytic cell, an electric current of a cathode current density of 25 to 50 amperes per square foot is passed through the cell for a short period of time, and the temperature of the bath is maintained at room temperature ($20-25^\circ \text{C.}$) during the passage of the current. For rendering the surfaces resistant to the action of atmospheric agents three minutes has proven to be a satisfactory length of time for the electrolytic treatment. After this treatment the article is removed from the electrolytic cell and dried in any suitable manner. An iron article so treated will be found to have exceptional resistance to atmospheric corrosion and will not rust to any great extent even if scratched unless exposed to extreme conditions for a very long period of time.

It is believed that the embodiment of the invention just described will sufficiently illustrate how the invention may be practiced, but it is, of course, to be understood that the invention is not limited to the specific example given hereinbefore. The invention may be practiced with satisfactory results on metals other than iron, such as zinc, cadmium, copper, silver, etc. and also the conditions under which the articles are rendered passive may be varied within a wide range. For example, the bath included in the electrolytic cell need not necessarily be composed of a water solution containing 22 grams per liter of chromic acid, but the amount of the latter ingredient present in the bath may be varied within wide limits and still satisfactory results may be obtained. In fact, experiments indicate that satisfactory results may be

obtained with baths containing chromic acid in amounts varying from a very small quantity to almost saturation, but for the sake of economy the bath should preferably contain less than 50 grams per liter of chromic acid. Nor does the bath need to contain only chromic acid in water solution, but additional conducting materials may be present in order to vary the operating conditions of the bath.

It is also possible to obtain results similar to those obtained by the use of chromic acid by employing other compounds containing a metal as a part of an acid radical or an amphoteric metallic element and satisfactory results have been obtained by employing such materials as sodium, potassium, ammonium and lithium stannates, tungstates, chromates, dichromates, molybdates, etc. Some compounds, such as manganese sulphate, containing a metallic element which does not form part of an acid radical, also give results similar to those obtained by the use of the above named compounds.

Also the amount of current flowing through the cell may be varied over a wide range so long as the initial cathode current density is maintained below the range within which a metallic material would be deposited from the particular bath used in quantities more than traces. The temperature of the bath may also be varied to provide the optimum conditions of operation obtainable with the particular bath and current density employed, and also the time of treatment may be varied. Satisfactory results may be usually obtained, however, when the bath is operated at room temperature (20 to 25° C.) and the article is treated for from three to fifteen minutes in the electrolytic cell.

A satisfactory theory of the reactions which take place during the above described operations has not yet been developed, but some or all of a number of changes might possibly occur. For example, the surface of the metal which it is desired to protect may be oxidized or otherwise chemically changed. Or a physical change or displacement may be effected in the molecules comprising the surface layers of the metal so that the surface of the metal is rendered passive. Or it may be possible that the metal surface is coated with an extremely thin film composed of a compound or compounds derived from the electrolytic bath. Whatever the changes or reactions which occur may be, a treatment embodying the invention renders the surface of the treated metal resistant to corrosion, and at the same time the weight and dimensions of the treated article remain substantially unchanged. Also the appearance of the articles remains practically unchanged in most instances after treatment. For example, iron articles originally having bright,

clean surfaces usually exhibit a similar appearance with possibly a slight iridescence being noticeable after having been treated in a chromic acid bath such as has been described hereinbefore, but there is no evidence that the articles are coated with any colored or colloidal material of the types sometimes found in electroplating baths for the deposition of metallic chromium.

The method described above provides an extremely simple and inexpensive means whereby surfaces of metal articles may be protected against corrosion and abrasion without any material variation in the weight or dimensions of the article. The treatment is especially effective in treating irregular shaped articles for not only the plane surfaces of the articles are protected, but the protective effects are also obtained in corners, crevices, and the walls of holes in the articles.

By the statement employed hereinbefore in the specification and also in the appended claims, that the cathode current density is maintained at a value below those in the range within which a metal is deposited is meant a cathode current density of such value that no more than traces of a metallic material are deposited. The term "amphoteric metallic element" as used herein in the specification and claims is intended to designate those metallic elements which may form one group of compounds in which the element comprises part of an acid radical and may form another group of compounds in which it acts as a base forming element. Thus, chromium may form compounds of the nature of sodium chromate (Na_2CrO_4) in which the chromium forms part of an acid radical, or may form compounds such as chromic chloride (Cr Cl_3) in which it acts as a base forming element.

What is claimed is:

1. A process for protecting surfaces of metal articles, which consists in connecting an article as a cathode in an electrolytic cell including a bath containing chromic acid as an electrolyte, passing an electric current of a cathode current density below the range in which chromium is deposited through the cell for from three to fifteen minutes, and maintaining the temperature of the bath at room temperature.

2. A process for protecting surfaces of metal articles, which consists in connecting an article as a cathode in an electrolytic cell including a bath containing less than 50 grams per liter of chromic acid as an electrolyte, and passing an electric current of a cathode current density below the range in which chromium is deposited through the cell.

3. A process for protecting surfaces of metal articles, which consists in connecting an article as a cathode in an electrolytic cell

including a bath containing 22 grams per liter of chromic acid as an electrolyte, passing an electric current of a cathode current density below the range in which chromium is deposited through the cell for from three to fifteen minutes, and maintaining the temperature of the bath at room temperature.

In witness whereof, I hereunto subscribe my name this 30th day of September A. D., 1927.

SUMNER REDWAY MASON.