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ELECTROLYTIC TREATMENT OF METAL SURFACES

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This invention relates to the protective treatment of metal surfaces, and more particularly to the cathodic treatment of surfaces such as those of iron, steel, zinc, or other base metals, from a solution of chromic acid and boric acid or salts of boric acid.

The principal object of this invention is to develop a paint adhering film on the surface of base metals such as iron, steel and zinc.

Another object is to inhibit underfilm corrosion in painted metal articles.

A further object is to form a protective film on articles having base metal surfaces.

It is often desirable, before painting metal surfaces, to apply a thin intermediate film to a metal surface, such that when paint is later applied there will be an adherent bond between the paint and the metal. Frequently, when paint is applied directly to a metal surface, the paint will strip, peel or chip after short periods of wear or exposure. To enhance the adherence of paint to metal, numerous metal surface films have been developed, notably films containing phosphates, which retain the paint uniformly throughout the surface of the metal. These intermediate, paint-bonding films, are generally applied to the metal by immersion or electrolysis in aqueous solutions.

Some paint-bonding films have been found to have sufficient anti-corrosive properties in mildly corrosive atmospheres, so that the film itself may assume the nature of protective coating on metal. Even when steel or other base stock is coated with one of the so-called protective coating metals, as tin or zinc, it is oftentimes desirable to coat such tin or zinc surfaces with a non-metallic film, other than paint, to prevent incipient corrosion.

Heretofore, films have been produced on metal surfaces by cathodically electrolyzing the metal in a solution containing chromic acid (CrO_3) only. Chromium containing films formed under such conditions are produced inefficiently, being small in amount. Furthermore, such films are entirely inadequate as a corrosion resistant medium. Either a greater amount of film, or a modified and improved characteristic of protective film, is necessary to meet the requirements specified for corrosion resistance.

We have found that metal articles having a surface of iron, steel, zinc or tin, when treated as the cathode in an aqueous electrolytic bath of chromic acid and boric acid, have formed upon their surface a film, colloidal in nature, consisting of a hydrated oxide of chromium, which may be expressed by the general formula



where x , y and z may represent a whole number or any fraction thereof. This chromium bearing film has excellent paint-bonding properties and, under certain types of corrosive atmosphere, resists corrosive attack on the base metal. By our method we have increased the efficiency of film formation and altered the composite nature of the hydrated chromium oxide film.

Formation of the film of hydrated oxide of chromium

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on metals is obtained under a wide range of operating conditions. For example, when corrodible ferrous metals, or metals having a corrodible base metal surface coating such as zinc or tin, are treated cathodically with direct current in the aforementioned bath of chromic acid and boric acid, the chromic acid, calculated as CrO_3 , may range from 100–400 grams per liter, and the boric acid may be present in quantities from about 8 grams per liter to saturation (saturation is approximately 30 to 35 grams per liter). Satisfactory temperatures were found to be included in the range from 20° C. to 45° C., while the current density may be applied within the limits of 50 to 300 amperes per square foot. The time of treatment is governed by the type of film desired; i. e., whether the film is to be used for improvement in paint adhesion and inhibition of underfilm (paint film) corrosion, or as a protective film per se. A longer operating time is required for the necessarily thicker protective type of film, for the time is a function of the coating thickness.

The presence of boric acid in the electrolyte promotes the formation of the chromium bearing film. The invention is not limited to the use of boric acid, for salts of boric acid, e. g., sodium tetraborate, calcium metaborate and potassium tetraborate, have shown an equivalence of function in the promotion of film formation. As in the case of boric acid, the salts of boric acid are effective in amounts ranging from low concentrations to saturation.

Two examples of satisfactory electrolytes with normal operating conditions are given below.

Example 1

Chromic acid (CrO_3)	275 g./l.
Boric acid (H_3BO_3)	30 g./l.
Current density	200 amp./sq. ft.
Temperature	72° F.
Time	20 seconds.

Example 2

Chromic acid (CrO_3)	275 g./l.
Sodium tetraborate (borax) ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$)	15 g./l.
Current density	200 amp./sq. ft.
Temperature	72° F.
Time	20 seconds.

A study of the film formed by our invention shows a coating of two components. The first of these components, that which is nearest the basis metal, is in the form of a green layer of hydrated oxide of chromium and is covered by a second, outer, brown layer of hydrated oxide of chromium varying considerably in the ratio of Cr^{VI} to Cr^{III} from that of the first layer, the latter having a much higher proportion of trivalent chromium.

Our chromium bearing film, when produced on steel and zinc surfaces, has been found to give excellent paint adherence. Furthermore, when paint is applied to metals previously treated with this film there is a substantial reduction in underfilm corrosion incident to scratching of the paint surface. Steel sheets (blackplate) developed good corrosion resistance in mildly corrosive atmospheres when treated with our chromium bearing film in the absence of any subsequent paint treatment. Our process can also be used successfully on tinplated steel articles, and on aluminum, magnesium, cadmium, or any other base metal surface. The term base metal, as used herein, applies to any metal which corrodes readily, as distinguished from the noble metals and the non-corrodible alloys such as stainless steel. When films of this hydrated oxide of chromium are applied to zinc-coated steel articles, the adherence of the film to the base metal is such that cold working is permissible. In the case of steel articles our process is most satisfactory when there is substantially

no deformation of the steel surface after film application; however, if a steel article is first coated with an extremely thin coating of zinc, e. g., about 0.01 oz./sq. ft., and the chromium bearing film then applied to the zinc surface, said steel article may then be elongated or extruded in the same fashion as the more conventional zinc-coated article, without any deleterious effect to the film.

When light weight, or flash, coatings of zinc in a range of the order of magnitude of 0.01 to 0.1 oz./sq. ft. are applied to steel or other metals, the zinc coating by itself has little useful purpose; however, when treated with our colloidal chromium containing film, a useful product is obtained. Because of the fact that zinc affords an excellent bonding surface for our film, many applications can be anticipated wherein a basis material can be given a flash coating of zinc, the zinc surface being subsequently treated with the hydrated oxide of chromium film.

We claim:

1. A process of forming a non-metallic coating on the surface of a metal article which comprises electrolyzing a metal article having a surface material of corrodible base metal in an aqueous solution consisting essentially of chromic acid (100 to 400 grams per liter) and a compound of the class consisting of boric acid and the alkali metal and alkaline earth metal salts of boric acid, said compound being present in an amount of from 8 grams per liter to saturation with said metal article acting as the cathode.

2. The process of forming a non-metallic coating on zinc surfaces which comprises electrolyzing a zinc-coated metal article in an aqueous solution consisting essentially of chromic acid (100 to 400 grams per liter) and a compound of the class consisting of boric acid and the alkali metal and alkaline earth metal salts of boric acid, said compound being present in an amount of from 8 grams per liter to saturation with said metal article acting as the cathode.

3. The process of forming a non-metallic coating on ferrous surfaces which comprises electrolyzing a corrodible ferrous article in an aqueous solution consisting essentially of chromic acid (100 to 400 grams per liter) and a compound of the class consisting of boric acid and salts of boric acid, said compound being present in an amount of from 8 grams per liter to saturation with said ferrous article acting as the cathode.

4. The process of forming a non-metallic coating on tin surfaces which comprises electrolyzing a tin coated metal article in an aqueous solution consisting essentially of chromic acid (100 to 400 grams per liter) and a compound of the class consisting of boric acid and salts of boric acid, said compound being present in an amount of from 8 grams per liter to saturation with said metal article acting as the cathode.

5. The process of forming a non-metallic coating on zinc surfaces which comprises electrolyzing a zinc-coated metal article in an aqueous solution consisting essentially of chromic acid (100 to 400 grams per liter) and boric

acid (8 grams per liter to saturation), said metal article acting as the cathode.

6. The process of forming a non-metallic coating on zinc surfaces which comprises electrolyzing a zinc-coated metal article in an aqueous solution consisting essentially of chromic acid (100 to 400 grams per liter) and sodium tetraborate (8 grams per liter to saturation), said metal article acting as the cathode.

7. The process of forming a non-metallic coating on zinc surfaces which comprises electrolyzing a zinc-coated metal article in an aqueous solution consisting essentially of chromic acid (100 to 400 grams per liter) and a compound of the class consisting of boric acid and the alkali metal and alkaline earth metal salts of boric acid, said compound being present in an amount of from 8 grams per liter to saturation, at a current density of from 50 to 300 amperes per square foot, said metal article acting as the cathode.

8. The process of forming a non-metallic coating on zinc surfaces which comprises electrolyzing a zinc-coated metal article in an aqueous solution consisting essentially of chromic acid (100 to 400 grams per liter) and boric acid (10 grams per liter to saturation) at a current density of from 50 to 300 amperes per square foot and at a temperature of not less than 70° F. for not less than one minute, said zinc-coated article acting as the cathode.

9. A process of forming a non-metallic coating on ferrous surfaces which comprises electrolyzing a corrodible ferrous article in an aqueous solution consisting essentially of chromic acid (100 to 400 grams per liter) and boric acid (10 grams per liter to saturation) at a current density of from 100 to 300 amperes per square foot and at a temperature of not less than 70° F. for not less than 30 seconds, said ferrous article acting as the cathode.

10. The process of treating a ferrous article having a uniform surface film of zinc, said zinc film having a coating weight not in excess of 0.1 oz./sq. ft., which comprises electrolyzing said zinc-surfaced ferrous article in an aqueous solution consisting essentially of chromic acid (100 to 400 grams per liter) and a compound of the class consisting of boric acid and the alkali metal and alkaline earth metal salts of boric acid, said compound being present in an amount of from 8 grams per liter to saturation with said ferrous article acting as the cathode.

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