PROCESS OF TREATING SURFACES OF METALLIC ARTICLES

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ABSTRACT OF THE DISCLOSURE

A metal surface is protected by depositing chromium oxide thereon by a process of electrolyzing between an anode surface and a cathode surface of said metal, an aqueous solution of ionic compounds of hexavalent chromium ions and an additive. The additive is selected from acids, alkali salts and oxides which form anions in solution of elements of the group consisting of zirconium, titanium, tungsten, molybdenum, selenium, tellurium, vanadium and arsenic. The additive may also be a mono-basic fatty acid or monobasic fatty acid salt.

This application is a continuation-in-part application of our copending application Ser. No. 260,886, filed Feb. 25, 1963 now abandoned.

BACKGROUND OF INVENTION

This invention relates to a process of treating metal surfaces and particularly to a process for the cathodic treatment of surfaces such as those of iron, steel and other base metals in an aqueous electrolytic bath of chromic acid including a proper additive.

In recent years various electrolytic processes have been proposed using an aqueous solution of chromic acid. For example, protective films in the form of a hydrated oxide of chromium may be produced on metallic articles having a surface of iron, or steel by treating the same as the cathode in an aqueous electrolytic bath of chromic acid and boric acid or its salts. Alternatively, protective coatings in the form of a mixture of phosphate and chromate may be formed on iron articles by treating the same as the cathode in an aqueous electrolytic bath including ions of phosphoric acid and hexavalent chromium ions. Further, anti-corrosive coatings consisting of chelate compounds of chromium were formed on articles of iron, steel or aluminum by treating the metal as the cathode in an aqueous electrolytic bath including essentially anhydrous chromic acid and a small amount of a proper organic compound. However, in view of the fact that prior art processes of the above type are based upon the formation of relatively thick oxide coatings produced by electrochemical reduction, it can hardly be said that basic improvements have been accomplished thereby, in a process of forming a coating on a metal surface.

SUMMARY OF INVENTION

The chief object of the invention, therefore, is the provision of an improved process for forming a protective coating of chromium on a surface of metals such as iron, steel and the like.

Another object of the invention is to form a protective oxide coating of chromium on a surface of metals such as iron, steel and the like.

A further object of the invention is to provide additives to an aqueous electrolytic bath of chromic acid effective for forming a protective coating having excellent anti-corrosive and paint adhering properties on surfaces of metals such as iron, steel and the like during a short interval of time.

With these objects in view, the invention resides in a process of treating a surface of a metallic article by depositing chromium oxide thereon by electrolyzing between an anode surface and a cathode surface of said metal an aqueous solution of ionic components consisting essentially of hexavalent chromium ions and an additive selected from the group consisting of alkali salts of zirconium fluoride, alkali salts of titanium fluoride, alkali salts of tungstic acid, silico-tungstic acid, molybdcic acid, alkali salts of molybdic acid, selenic acid, alkali salts of selenic acid, telluric acid, alkali salts of telluric acid, vanadic acid, alkali salts of vanadic acid, vanadium pentoxide, arsenic acid, and alkali salts of arsenic acid.

In accordance with one aspect of this invention, it has also been found that the aqueous solution of ionic components may consist essentially of monobasic fatty acids or salts of monobasic fatty acids.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The process is preferably carried out with metal surfaces of iron and steel; however other metallic surfaces such as those of aluminum and tin may also be treated in accordance with this invention. Normally the surface of the metallic article is subjected to a preliminary degreasing and acid immersion before carrying out the present process.

Preferably the aqueous electrolytic bath comprises approximately 0.1 to 1 mol of chromic acid and approximately 0.1 to 5 g./l. of the additive except for telluric acid the amount of which ranges from 10 to 200 g./l.

The cathodic treatment may be advantageously performed at a temperature of from 20° to 60° C. within about 5 seconds and with a current density of from 10 to 50 amperes/dm.².

The cathodic electrolysis of an aqueous solution including hexavalent chromium ions yields an oxide coating which consists essentially of trivalent chromium and approximates a monomolecular layer, formed on the cathode used. In this case, if a density of electric current flowing through the electrolytic bath becomes higher, then the thickness of the oxide coating is progressively increased, resulting in the formation of a black chromium layer. Under these circumstances, if anions of an additive such as those of sulfuric acid, fluorine ions or the like are added in a very small amount to the bath of chromic acid, then the electrolytic deposit on the cathode changes from black chromium (or chromium oxide) to metallic chromium exhibiting metallic luster. This appears to result from the fact that the oxide coating deposited on the surface of the cathode is an of-type compound of reticulate structure including trivalent chromium while the added anions sever the meshes in the of-type compound resulting in a variation in the velocity at which the coating is electrochemically reduced. The term "of-type compound" means a complex compound including metal atoms bonded to each other by bridging hydroxyl groups.

Thus the inventors have arrived at the conclusion that, if an aqueous electrolytic bath of chromic acid includes added thereto, anions, capable of serving to sever meshes in a formed oxide coating, to thereby accelerate the velocity of electrochemical reduction, as well as to form a deposit in the form of chromium oxide, rather than in the form of metallic chromium, that then chromium oxide, having excellent anti-corrosive and paint adhering properties will be formed on the surface of the cathode within a short interval of time, with the result that a process of forming chromium coating can be fundamentally improved.
The invention is based upon the conclusion just described and characterized by the cathodic electrolysis of metallic articles in an aqueous electrolytic bath including from 0.1 to 1 mol of chromic acid and a proper amount of a special additive as will be subsequently described, at a temperature within a range of from 20° to 60° C. and with a current density of from 10 to 50 amperes per square decimeter. On the surface of the metallic article serving as the cathode, chromium oxide is formed which exhibits different colors within a short interval of time, such as 5 seconds.

The concentration of the chromic acid dissolved in the aqueous electrolytic bath is preferably 0.1 mol or higher. It has been found that if the concentration of chromic acid is below the value specified above, it is difficult for a coating having good anti-corrosive properties to be formed.

The additive used is selected on the basis of the previously described conclusion. Thus acids, salts and oxides of elements selected from the group consisting of zirconium, titanium, tungsten, molybdenum, selenium, tellurium, vanadium and arsenic may be used. The acids of such elements include, for example, sclenic acid, telluric acid, arsenic acid, etc., salts of zirconium-potassium fluoride these elements include for example titanium-potassium fluoride, ammonium tungstate, ammonium molybdate, sodium vanadate, etc. Oxides of the above described elements also may be used satisfactorily, provided that the same form anions in the aqueous solution of chromic acid such as vanadium pentoxide.

Monobasic fatty acids may also be used in the present process, such as acetic acid, propionic acid, butyric acid, etc., salts thereof as sodium acetate.

The amount of the additive used should be within a range of from 0.1 to 5 g./l. except for telluric acid the amount of which should range from 1.0 to 200 g./l.

The density of current is within the range of from 10 to 50 amperes per square decimeter and preferably within a range of from 20 to 30 amperes per square decimeter. The density of current above the value just specified does not lead to any decrease in the time of electrolysis.

The optimum operating temperature has been found to be in the range of from 30° to 45° C. although it may range from 20° to 60° C. At any temperature exceeding 70° C. the coating formed has reduced anti-corrosive properties.

The time of electrolysis is preferably about 5 seconds. If the time of electrolysis exceeds 5 seconds, then the anti-corrosive properties of the deposited coating scarcely depend upon the time of electrolysis. Also the color exhibited by the coating can be adjusted by controlling the time of electrolysis.

The following examples illustrate the practice of the invention, but must not be construed as limiting the invention in any manner whatsoever.

EXAMPLE 1
Aqueous electrolytic bath:
Anhydrous chromic acid—50 g./l.
Glacial acetic acid—1 cc./l.
Temperature—45° C.
Density of current—30 amps./dm.²
Treating time—5 seconds

EXAMPLE 2
Aqueous electrolytic bath:
Anhydrous chromic acid—50 g./l.
Titanium-potassium fluoride—5 g./l.
Temperature—45° C.
Density of current—30 amps./dm.²
Treating time—5 seconds

EXAMPLE 3
Aqueous electrolytic bath:
Anhydrous chromic acid—50 g./l.
Sodium metavanadate—1 g./l.
Temperature—45° C.
Density of current—30 amps./dm.²
Treating time—5 seconds

EXAMPLE 4
Aqueous electrolytic bath:
Anhydrous chromic acid—50 g./l.
Silicotungstic acid—2 g./l.
Zirconium-potassium fluoride—3 g./l.
Treating time—5 seconds

EXAMPLE 5
Aqueous electrolytic bath:
Anhydrous chromic acid—50 g./l.
Sodium metavanadate—1 g./l.
Temperature—45° C.
Density of current—30 amps./dm.²
Treating time—5 seconds

EXAMPLE 6
Aqueous electrolytic bath:
Anhydrous chromic acid—10 g./l.
Ammonium molybdate—5 g./l.
Temperature—45° C.
Density of current—30 amps./dm.²
Treating time—5 seconds

EXAMPLE 7
Aqueous electrolytic bath:
Anhydrous chromic acid—50 g./l.
Selenium—2 g./l.
Temperature—30° C.
Density of current—30 amps./dm.²
Treating time—5 seconds

EXAMPLE 8
Aqueous electrolytic bath:
Anhydrous chromic acid—10 g./l.
Telluric acid—20 g./l.
Temperature—30° C.
Density of current—20 amps./dm.²
Treating time—5 seconds

EXAMPLE 9
Aqueous electrolytic bath:
Anhydrous chromic acid—10 g./l.
Arsenic acid—2 g./l.
Temperature—30° C.
Density of current—20 amps./dm.²
Treating time—5 seconds

EXAMPLE 10
Aqueous electrolytic bath:
Anhydrous chromic acid—10 g./l.
Vanadium pentoxide—2 g./l.
Temperature—30° C.
Density of current—20 amps./dm.²
Treating time—5 seconds

Test pieces cut from a steel sheet were first degreased, acid immersed in the conventional manner and then subjected to the cathodic electrolysis in aqueous electrolytic baths as above described in Examples 1 through 10 under the conditions as also described in the same examples respectively.

After the completion of the cathodic electrolysis the test pieces were rinsed and dried. The coatings thus formed on the test pieces were excellent in anti-corrosive properties and gave excellent results in tests for corrosion-resistance to brine spray and for paint adhesion. More specifically the results of brine spraying test determined according to the ASTM Standard B117-61 indicated no occurrence of rust after the lapse of 6 hours. As to the paint adhering properties, the grid pattern test was conducted with a melaminealkyd resin coated upon the coat-
5ing on the test pieces. Excellent results were obtained in that the number of grids bearing the resin coated on each of the test pieces was over eighty five. The additives other than those described in the above examples also yielded excellent coatings.

While the invention has been particularly described in terms of steel articles it is to be understood that the invention is not limited to such articles and that it is equally applicable to articles of other metals such as iron, aluminum, and tin without departing from the spirit and scope of the invention.

What we claim and desire to secure by Letters Patent are:

1. A process of depositing chromium oxide on a metal surface selected from the group consisting of steel, iron, aluminum and tin, comprising electrolyzing between an anode surface and a cathode surface of said metal an aqueous solution of ionic components consisting essentially of hexavalent chromium ions and an additive selected from the group consisting of alkali salts of zirconium fluoride, alkali salts of titanium fluoride, alkali salts of tungstic acid, silico-tungstic acid, molybdic acid, alkali salts of molybdic acid, selenic acid, alkali salts of selenic acid, telluric acid, alkali salts of telluric acid, vanadic acid, alkali salts of vanadic acid, vanadium pentoxide, arsenic acid, and alkali salts of arsenic acid, the concentration of said hexavalent chromium ions corresponding to the concentration which would be produced by chromic acid in said aqueous solution in a concentration of approximately 0.1 to 1 mol per liter and the concentration of said additive being approximately from 10 to 220 grams per liter in the case of telluric acid and approximately from 0.1 to 5 grams per liter in the case of the other additives.

2. A process according to claim 1, in which said metal surface is steel.

3. A process according to claim 1, in which said metal surface is iron.

4. A process according to claim 1, in which said metal surface is aluminum.

5. A process according to claim 1, in which said metal surface is tin.

6. A process according to claim 1, in which the additive is selected from the group consisting of zirconium-potassium fluoride, titanium-potassium fluoride, selenic acid and telluric acid.

7. A process according to claim 1, in which chromic acid is in said solution whereby said hexavalent chromium ions derive from said chromic acid.

8. A process according to claim 1, in which the aqueous solution is electrolyzed with a current density of from 10 to 50 amperes per square decimeter.

9. A process according to claim 8, in which the aqueous solution is electrolyzed at a temperature of from 20 to 60 degrees centigrade.

10. A process according to claim 9, in which the aqueous solution is electrolyzed for a period of up to about 5 seconds.

11. A process according to claim 9, in which the duration of the electrolysis is about 5 seconds and the current density with which the electrolysis is performed is 20 to 30 amperes per square decimeter.

12. A process according to claim 11, in which the aqueous solution is electrolyzed at a temperature of from 30 to 45 degrees centigrade.

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