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ELECTROPLATING CHROMIUM-NICKEL ALLOY COATINGS

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This invention relates to the process of electrodepositing chromium-nickel alloy coatings, and members produced therewith.

It has been proposed heretofore to electrodeposit chromium from certain electrolytes under such conditions that black electrodeposits are produced. However, such electrodeposited black chromium coatings are obtained with difficulty, since the conditions for producing such black coatings have to be maintained rather closely, especially the temperature, amount of impurities, and current density, etc. Furthermore, such electrodeposited black chromium coatings are not as resistant to high temperatures as desired, both in air and in a high vacuum such as exists in certain vacuum tubes. I have found that the adherence of these coatings to members is erratic and uncertain; in addition, the thermal emissivity properties are not of the type usually desired in electron tubes. Also, the throwing power of the electrolyte is low.

The object of this invention is to provide an electrolyte comprising an aqueous solution of nickel and chromium salts which deposit a silvery alloy of nickel and chromium which may be readily converted to a black coating having excellent adherence when subjected to high temperatures in vacuum tubes.

Another object of the invention is to provide an electrolyte having good throwing power, the electrolyte comprising an aqueous solution of a chromium compound, a nickel compound and a soluble organic acid.

A further object of the invention is to provide a process for electrodepositing a bright coating of a nickel-chromium alloy on members, which coating can be turned jet black by immersion in hydrochloric acid.

Other objects of the invention will, in part, be obvious and will, in part, appear hereinafter.

I have discovered that a chromium-nickel alloy plate having unusual properties may be electrodeposited from an aqueous electrolyte comprising essentially from 150 to 350 grams per liter of chromic acid (CrO_3) and from 13 to 60 grams per liter of nickel chloride ($NiCl_2$). The nickel chloride is available as the hexahydrate and each liter of the electrolyte may be prepared by adding thereto from about 25 to 115 grams per liter of the nickel chloride hexahydrate. The two metal salts may be dissolved in distilled or deionized water and the resulting solution may be employed as an electrolyte. The proportions of chromic acid to nickel chloride added to the electrolyte should be such as to maintain the ratio of chromium to nickel in the electrolyte from 4:1 to 14:1, in parts by weight. In order to secure somewhat greater latitude in bath temperature for satisfactory plating operations from the electrolyte, and to obtain more uniform coatings, it is desirable to include in each liter of the electrolyte of up to 10 milliliters of a soluble carboxylic organic acid. Glacial acetic acid is particularly satisfactory. However, propionic acid, citric acid, formic acid and oxalic acid, or mixtures of any two or more, may be added to the electrolyte in the proportions indicated.

In plating operations, the temperature of the electrolyte should not exceed 40° C. and is preferably maintained in the range of 25° C. to 35° C. Therefore, cooling coils carrying cooling water or a refrigerant should be disposed within the electrolyte during plating operations.

A member to be provided with the chromium-nickel alloy should be thoroughly cleaned in accordance with conventional preplating procedures. The member is made the cathode in the electrolyte, and bars or sheets of lead, carbon, graphite, or other insoluble material form the anode. A plating current is passed through the member at a potential of from 12 to 15 volts to provide on the member a current density of from 400 to 2,000 A. S. F. (amperes per square foot). At these current densities, there is deposited on the member a substantial thickness of chromium-nickel alloy in a period of five minutes. Longer plating times may be employed if desired, the coating deposited being proportionately thicker. The deposit comprises substantially from 4 to 6 parts by weight of chromium per part of nickel.

The resulting chromium-nickel alloy electrodeposit has a silvery finish. In order to convert the deposit to a black coating, the member with the plated chromium-nickel alloy coating on its surface is washed in water and immersed for a few seconds in a concentrated hydrochloric acid (20% and higher HCl) solution. The member is removed from the hydrochloric acid and immediately washed in running water. The treatment in the acid very quickly produces a jet black finish that is extremely adherent even when exposed to temperatures of up to 800° C. in a high vacuum. The following examples are illustrative of the practice of the invention:

Example I

An aqueous electrolyte was prepared with each liter containing 200 grams of chromic acid, 80 grams of nickel chloride hexahydrate crystals and 6.5 milliliters of glacial acetic acid. The resulting electrolyte was maintained at a temperature of between 30° C. and 35° C. by use of cooling coils supplied with water. A nickel plate was made the cathode in this electrolyte, and a lead plate was employed as the anode. A plating current of 930 A. S. F. was passed through the member. In five minutes a 0.001 inch thickness of chromium-nickel alloy was deposited on the surfaces of the nickel member. This coating was of a silvery matte appearance. The member was removed from the electrolyte, washed in cold water, and then immersed for two seconds in a 35% hydrochloric acid solution. The silvery coating turned jet black when immersed in the hydrochloric acid. After removal from the hydrochloric acid, the member was immediately washed in running water. The jet black finish was tested by exposure to temperatures of from 700° C. to 800° C., and the adherence was found to be completely unaffected by such temperatures. When immersed in cold mineral acids, such as 5% sulphuric acid, the coating resisted any attack for periods of time of an hour. The coating could be dissolved only by prolonged exposure to mineral acids. When heated in air to a dull red heat, the coating did not blister and exhibited only a slight surface oxidation.

Example II

An aqueous electrolyte was prepared by dissolving in water 200 grams per liter of chromic acid, 20 grams per liter of nickel chloride hexahydrate and 5 milliliters of glacial acetic acid per liter. A copper rod ¼ inch long was made the cathode in this electrolyte. A plating current of 1000 amperes per square foot applied for 5 minutes deposited a coating of approximately 0.001 inch

in thickness. The coating was bright and silvery in appearance, but had a matte finish.

The deposited coating of Example II when treated with concentrated hydrochloric acid as disclosed in Example I, turned jet black in approximately one second after immersion. After washing and drying, an extremely adherent jet black finish was present on the rod. This black coating could withstand elevated temperatures over prolonged periods of time.

It will be appreciated that the applied chromium-nickel alloy coating need not be treated with hydrochloric acid if it is desired to have the member with the silvery alloy coating thereon. However, for vacuum tube applications and for other purposes, the black coatings have desirable emission characteristics and for such applications the coating will be treated with hydrochloric acid.

The electrolyte disclosed herein is characterized by good throwing power. Conforming lead anodes need not be used in plating therein conventional sheets and bars or other regular geometrical-shaped members. Of course, if the member to be plated has a deep recess or cavity, it may be necessary to dispose within the recess a lead bar or other member as an anode.

The electrolyte disclosed herein is extremely stable as compared to previously known chromium plating electrolytes. The electrolytes may be employed over prolonged periods of time and they do not deteriorate on standing.

It is intended that all matter contained in the above description shall be deemed to be illustrative and not limiting.

I claim as my invention:

1. The process of depositing chromium-nickel alloy on a member comprising immersing the member in an aqueous electroplating electrolyte comprising essentially 150 to 350 grams per liter of chromic acid and from 13 to 60 grams per liter of nickel chloride ($NiCl_2$), the ratio of weight of chromium to nickel in the electrolyte being from 4:1 to 14:1, and passing a plating current through the member at a current density of from 400 to 2,000 A. S. F., the temperature of the electrolyte being maintained at below 40° C. to electrodeposit a bright plating of the chromium-nickel.

2. The process of claim 1 wherein each liter of the electrolyte further includes up to 10 milliliters of an organic acid soluble in the electrolyte.

3. The process of claim 2 wherein hydrochloric acid is applied to the plated chromium-nickel on the member for a few seconds whereby a black finish is produced.

4. The process of claim 3 wherein the organic acid is glacial acetic acid.

5. A member having on its surface an adherent black electrodeposit comprising an alloy of chromium and nickel in the proportions of from 4:1 to 14:1, the alloy being rendered black by a brief application of hydrochloric acid thereto.

6. An aqueous electroplating electrolyte comprising essentially from 150 to 350 grams per liter of chromic acid and from 13 to 60 grams per liter of nickel chloride ($NiCl_2$), the ratio of weight of chromium to nickel in the electrolyte being from 4:1 to 14:1.

7. An aqueous electroplating electrolyte comprising essentially from 150 to 350 grams per liter of chromic acid, from 13 to 60 grams per liter of nickel chloride ($NiCl_2$), the ratio of weight of chromium to nickel in the electrolyte being from 4:1 to 14:1, and up to 10 milliliters of an organic acid per liter of electrolyte.

8. An aqueous electroplating electrolyte comprising essentially from 150 to 350 grams per liter of chromic acid, from 13 to 60 grams per liter of nickel chloride ($NiCl_2$), the ratio of weight of chromium to nickel in the electrolyte being from 4:1 to 14:1, and from 3 to 10 grams per liter of glacial acetic acid.

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