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## BLACK CHROMIUM PLATING

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The invention described in the following specification and claims may be manufactured and used by or for the Government for governmental purposes without the payment to us of any royalty thereon.

This invention relates to a process for producing a dark-gray to black, corrosion-resistant, strongly adherent, electro-deposited film or coating of chromium and oxides of chromium upon a conductive base such as a base of metal.

Heretofore, electrodeposits of this character have been produced by employing a plating bath containing chromic anhydride and acetic acid. The concentration of acetic acid in these prior art baths has been low and of the order of 5 to 10 ml. of glacial acetic acid per liter of solution. It has been necessary to operate these baths at low temperatures in the neighborhood of 50° F. and to deposit films therefrom at very high cathode current densities of the order of 1000 to 2000 amperes per square foot. Consequently, the efficiency of operation of the prior art processes has been low due, in part, to the necessity of providing refrigeration. It has also been impracticable to operate such processes on a plant scale because of the high current requirements. Moreover, the films produced have been of rather inferior quality, being generally poorly adherent and of lighter color than those attainable in accordance with the present invention.

We have found that it is possible to produce greatly improved coatings of this type at much lower cathode current densities and at room temperature or above. Our process is convenient to operate and very efficient. No refrigeration is necessary to keep the plating bath cool.

It is an object of this invention to provide a process of electrodepositing an extremely adherent dark-gray to black film upon a conductive base, which film is highly resistant to corrosion and shows excellent wear resistance and which effectively protects the base from corrosion under conditions of high humidity and temperature.

Another object is to provide a process for finishing rifle parts, artillery parts, and components of optical instruments with a coating which has low light reflectivity and which has good wearing properties.

Other objects, aims, and advantages of the invention will be in part apparent and in part pointed out in the following description.

According to the invention, the conductive base is electro-plated in a cell in which the base is cathode and in which the electrolyte comprises

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an aqueous solution of chromic anhydride ($CrO_3$) containing a non-substituted, lower aliphatic acid in a concentration of not less than 0.8 mols per liter and not more than 7.5 mols per liter. The preferred acid is acetic acid, but other homologues such as propionic acid, butyric acid, and valeric acid may he employed.

The preferred electrolyte consists of an aqueous solution containing about 275 g. of chromic anhydride and about 200 ml. of glacial acetic acid per liter of solution. It has been found that the presence of the sulfate ion in the bath is deleterious to the formation of the desirable dark-gray to black coatings. We precipitate the sulfate by the addition of small amounts of barium compounds. We preferably add about 7.5 g. of barium acetate or carbonate to each liter of solution to the freshly prepared bath. The resulting precipitate of barium sulfate may be allowed to settle to the bottom of the plating tank and remain there as a sludge, or it may be filtered from the electrolyte if desired.

The solution may be made up by dissolving the chromic anhydride in a small amount of water, adding the glacial acetic acid and, thereafter, adding water to the required volume.

An object to be plated is immersed in the bath and is made the cathode of the cell. Anodes of various materials may be employed, but we prefer to use an anode of carburized steel. Carbon anodes may be employed but with less satisfactory results. Lead cannot be used due to the corrosive action of the electrolyte upon this material. In this connection, a lead tank cannot be used to hold the electrolyte; the preferred material for a tank is mild steel. The tank may be equipped with iron pipe steam coils so that the solution may be warmed. The plating tank should be provided with an exhaust system to carry away fumes of acetic acid.

The preferred bath as hereinbefore described should be operated at a temperature of approximately 110° F. The plating should be done at a cathode current density of about 65 amperes per square foot, but satisfactory plating may be effected at a current density of as low as 15 amperes per square foot or, if practicable, as high as a thousand amperes per square foot. Very short plating times, even as low as 15 seconds, will produce a rich black film of sufficient thickness to give very satisfactory protection to the plated article. Very long plating times are less efficient, for the rate of deposition decreases rapidly after the formation of the initial film.

However, thicker films may be built up by continued deposition.

The plated article may be buffed or polished without materially affecting the blackness of the plate.

Whereas, the hereinbefore described procedure is the one which we believe to be the most effective, operations can be carried out within much wider working limits. Entirely satisfactory baths may contain from 200 g. to 500 g. of chromic anhydride and from 100 ml. to 350 ml. of glacial acetic acid per liter of solution. These solutions may be operated effectively at a temperature of from 90° F. to 115° F. and at cathode current densities of from 40 to 90 amperes per square foot.

Plating can be effected within even wider limits. The chromic anhydride concentration may range from about 167 g. per liter to saturation of the solution and the acetic acid concentration may be varied between 50 ml. and 450 ml. of the glacial acid per liter of solution. The temperature of the solution may range from about 65° F. to 180° F. However, operation of the process outside of the limits defined in the previous paragraph, while capable of producing coatings is generally not commercially desirable.

It is desirable that the anode area be kept as large as possible with reference to the cathode area in order to maintain the anode current density at a relatively low value whereby to avoid coating the anode with a film, the exact nature of which is not fully understood, but which tends to increase the resistance of the cell. The anode area should be at least as great as, and, preferably, three or four times as great as the cathode area for most efficient operation.

The precise composition of the film is not known and may vary under differing conditions, but it is believed to contain a high proportion of metallic chromium and a low proportion of oxides of chromium. Whereas the films produced according to the invention may be deposited upon all kinds of electroconductive articles, an especially fine finish may be produced upon stainless steel or may be deposited over previously electroplated chromium films.

The plating bath may be replenished by addition of chromic anhydride and acetic acid as they are consumed. In practice this may be done by adding the two compounds in the ratio of approximately 1:1 by weight. A sufficiently accurate control for plant use may be achieved by specific gravity measurements of the plating bath as by the use of a hydrometer. Should the plating bath become sluggish and exhibit poor throwing power in use, electrolytic conversion of the trivalent chromium and readjustment of the acetic acid content will generally restore the bath to proper operation. Large quantities of water should not be added to the bath.

What is claimed is:

1. The process of producing a dark-gray to black, corrosion resistant, adherent film upon a conductive base which comprises making the base the cathode of an electroplating cell in which the electrolyte comprises an aqueous solution of 275 g. of chromic anhydride and 200 ml. of glacial acetic acid per liter of solution and electrolysing at a cathode current density of from 15 to 1000 amperes per square foot.

2. The process of producing a dark-gray to black, corrosion resistant, adherent film upon a conductive base which comprises making the base the cathode of an electroplating cell in which the electrolyte comprises an aqueous solution of from 200 g. to 500 g. of chromic anhydride and from 100 ml. to 350 ml. of glacial acetic acid per liter of solution and electrolysing at a temperature of from about 90° F. to 115° F. and at a cathode current density of from 40 to 90 amperes per square foot.



3. The process of producing a dark-gray to black, corrosion resistant, adherent film upon a conductive base which comprises making the base the cathode of an electroplating cell in which the electrolyte comprises an aqueous solution of about 275 g. of chromatic anhydride and about 200 ml. of glacial acetic acid per liter of solution and electrolysing at a temperature of about 110° F. and at a cathode current density of about 65 amperes per square foot.

4. The process of producing a dark-gray to black, corrosion resistant, adherent film upon a conductive base which comprises electroplating said base in an electroplating cell in which the base is cathode and in which the electrolyte comprises an aqueous solution of from 200 g. to 500 g. of chromic anhydride containing acetic acid in a concentration of not less than 50 ml. and not more than 450 ml. of glacial acetic acid per liter of solution and electrolysing at a temperature of about 90° F. to 115° F. and at a cathode current of from 40 to 90 amperes per square foot.

5. The process of producing a dark gray to black corrosion resistant adherent film upon a conductive base which comprises electroplating said base in an electroplating cell in which the base is cathode and in which the electrolyte comprises an aqueous solution of from 167 g. to saturation of chromic anhydride containing acetic acid in a concentration of not less than 50 ml. and not more than 450 ml. of glacial acetic acid per liter of solution and electrolysing at a temperature of about 90° F. to 115° F. and at a cathode current of from 40 to 90 amperes per square foot.

6. The process of producing a dark-gray to black corrosion resistant, adherent film upon a conductive base which comprises making the base the cathode of an electroplating cell in which the electrolyte comprises an aqueous solution of about 275 g. of chromic anhydride and about 200 ml. of glacial acetic acid per liter of solution and electrolyzing at a cathode current density of about 125 amperes per square foot.

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