GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, ACHARYA JAGADISH BOSE ROAD, CALCUTTA-17.

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"IMPROVEMENTS IN OR RELATING TO BLACK CHROME PLATING"

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, RAFI MARG, NEW DELHI-1, INDIA, AN INDIAN REGISTERED BODY INCORPORATED UNDER THE REGISTRATION OF SOCIETIES ACT (ACT XXI OF 1860).

The following specification describes the nature of this invention :-

This is an invention by Balkunje Anantha Shenoi, Scientist, Miss Lakshmi Sivaswamy, Senior Laboratory Assistant and Miss Sethuraman Gowri, Senior Scientific Assistant, all of the Central Electrochemical Research Institute, Karaikudi, Tamil Nadu, India, all Indian citizens.

This invention relates to improvements in or relating to black chrome plating and has particular reference to electrodeposition of black chrome from aqueous electrolyte.

Hitherto it has been proposed to electrodeposit black chrome from (1) acetate, (2) nitrate, (3) fluoride and (4) fluoride and nitrate containing baths.

This is open to the objection that the baths (1) and (2) operate at high current density and the colour of the deposit is notsatisfactory. Baths (3) and (4) even though operate at satisfactory current density and temperature, they are sensitive to the pressence of other foreign ions and reported to be not suitable for large scale commercial operation. Deposits peel off even at low thicknesses.

The object of this invention is to obviate these disadvantages by using fluoride together with two other inorganic compounds which eliminate the disadvantages of fluoride when it is present alone.

To these ends, the invention broadly consists in electrolysing an aqueous solution of chromic acid free from sulphate (if present, removed by the addition of barium carbonate) contaning fluoride, bori acid and nitrogen containing compounds with 8% tin or antimony lead alloy as anode and copper brass etc. as cathodes.

The following typical examples are given to illustrate the invention :

EXAMPLE 1

Chromic acid :	400 g/l
Fluosilicic acid :	1 g/l
Urea :	2 g/l
Boric acid :	10 g/l
Tmperature :	20 °C
Time :	15 mts.
Current density :	23 A/dm²

EXAMPLE 2

Chromic acid :	400 g/l
Sodium Fluoride :	1 g/l
Urea nitrate :	2 g/l
Boric acid :	15 g/l
Temperature :	25°C
Time :	30 mts.
Current density :	24 A/dm²

The following are among the main advantages of the invention :

1. Shining jet black deposit is got.
2. The deposit can be grown to sufficient thickness without any change in the ductility of the deposit.
3. Life of the bath is quite considerable.
4. The deposit is easily wetted by oil.

Dated this 2nd day of May, 1972.

R. BHASKAR PAI
Patents Officer
COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH

THE PATENT ACT 1970
COMPLETE SPECIFICATION
SECTION 10
IMPROVEMENTS IN OR RELATING TO BLACK CHROME PLATING

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, RAFI MARG, NEW DELHI-1, INDIA AN INDIAN REGISTERED BODY INCORPORATED UNDER THE REGISTRATION OF SOCIETIES ACT (ACT XXI OF 1860)

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed :-

This is an invention by Balkunje Anantha Shenoi, Scientist, Miss Lakshmi Sivaswamy, Senior Laboratory Assistant and Miss Sethuraman Gowri, Senior Scientific Assistant, all of the Central Electrochemical Research Institute, Karaikudi, Tamil Nadu, India, all Indian citizens.

This invention relates to improvements in or relating to electrodepositon of black chrome from aqueous electrolyte.

Hitherto it has been proposed to electrodeposit black chrome from (1) acetate, (2) nitrate, (3) fluoride and (4) fluoride and nitrate containing baths.

This is open to the objection that the baths (1) and (2) operate at high current density leading to excessive heating and the colour of the deposit is not satisfactory. Baths (3) and (4) even though operate at satisfactory current density and temperature, they are sensitive to the presence of other foreign ions and reported to be not suitable for large scale commercial operation. Deposits peel off even at low thicknesses (greater than 3 microns).

The object of this invention is to obviate these disadvantages by using fluoride together with two other inorganic compounds which eliminate the disadvantages of fluoride when it is present alone.

According to the present invention, there is provided a process for the production of shiny corrosion resistant oil wettable black chromium plating on brass and copper by plating polished and degreased substrate comprising brass or copper wherein the plating is done by electrodepositing black chrome from an aqueous black chromium plating bath containing fluoride, chromic acid (free from sulphate) using tin or antimony lead alloy anode and the copper or brass as cathodes charactarised in that the plating is done with the bath in presence of boric acid and nitrogen containing compounds such as urea or urea nitrate in combination with fluoride.

The plating with black chromium may be done using 8% tin or antimony lead alloy anode

in an electrolyte containing chromic acid (free from sulphate) 60%, fluosilicic acid or sodium fluoride 1 %, urea or urea nitrate 2% and boric acid 10 g/1.

Fluosilicic acid may be replaced by other fluoride catalysts such as sodium fluoride, cryolite, fluoboric acid, ammonium bifluoride.

Thus, black chrome may be deposited over current density 6.4 to 53 A/dm² with lead tin or lead antimony anode and copper, brass as cathodes to obtain black chrome deposit containing 54 to 56% metalic chromium.

The plating may be done for 5-10 minutes to obtain a black chrome deposit which withstands 40 days of immersion in 5% NaCl adjusted to pH 3.2 with HAC without basis metal failure.

In the invented process, an aqueous solution of chromic acid free from sulphate (if present) removed by the addition of barium (carbonate) containing fluoride, boric acid and nitrogen containing compounds is electrolysed with 8% tin or antimony lead alloy as anode and copper and brass as cathodes.

The following typical examples are given to illustrate the invention :

EXAMPLE 1

Chromic acid :	400 g/1
Fluosilicic acid :	1 g/1
Urea	2 g/1
Boric acid	10 g/1
Temperature	20°C
Time :	15 minutes
Current density :	23 A/dm²

EXAMPLE 2

Chromic acid :	400 g/1
Sodium fluoride :	1 g/1
Urea nitrate :	2 g/1
Boric acid :	15 g/1
Temperature :	25°C
Time :	30 minutes
Current density :	35 A/dm²

Quality black chrome coatings are obtained from the new formulation. As in other black chrome formulation here too chromic acid should be free from SO_4—and SO_4—presence is removed by adding 7.5 g/1 barium carbonate. Higher concentrations of urea or urea nitrate are required to get desired finish when they are used alone. In presence of fluoride smaller amounts give satisfactory coatings. Different fluorine containing inorganic compounds such as fluosilicic acid, sodium fluoride, cryolite, fluoboric acid are tried in combination with urea or urea nitrate. The jet black chrome deposits were got over wide range of current density when the catalysts are used together. For example, when fluoride was used alone, the favourable current density range was 12.4 to 53 A/dm². When calculated quantity of urea or urea nitrate was added, the favourable current density was shifted to 6.4 to 53 A/dm². Boric acid to the extent of 10 g/1 is essential to build up the thickness, to improve the quality and uniformity of black chrome. At concentrations greater than 20 g/1, boric acid crystallises at the working temperature (20°C). 1-3 g/1 sucrose may be added, if the trivalent content of the bath is less than 7.5 g/1.

The temperature of the bath should be controlled at 20°C±1° C by external cooling.

The current efficiency of deposition is the same as that with other catalysts (8—10%). Analysis of the deposit showed that just like the other black chrome deposits, deposit from this formulation also contains 54—56% metallic chromium. The deposit is quite resistant to immersion in 5% NaCl solution the pH of which is adjusted to 3.2 with acetic acid. A 5-10 minutes' coating withstands 40 days of immersion without basis metal failure. Lead-tin anode is used.

The main advantages of the invention are as follow :

1. Shining jet black deposit is got.
2. The deposit can be grown to sufficient thickness without any change in the ductility of the deposit (upto 10 microns).
3. Life of the bath is quite comparable with that of existing baths.
4. The deposit is easily wetted oil.

To sum up, this new formulation comprises chromic acid, fluosilicic acid, urea or urea nitrate and boric acid. The catalysts when used together make the bath to be operated over wide range of current density and improve the quality of the deposit and increase the impurities tolerance of the bath. The black chrome deposit from this new formulation is quite adherent uniform and is completely wetted by oil. It contains 54—56% metallic chromium and is quite resistant to immersion in 5% sodium chloride adjusted to pH 3.2 with HAC over 40 days without basis metal failure.

WE CLAIM :—

1. A process for the production of shiny corrosion resistant oil wettable black chromium plating on brass and copper by plating polished and degreased substrate comprising brass or copper wherein the plating is done by electrodepositing black chrome from an aqueaus black chromium plating bath containing fluoride, chromic acid (free from sulphate) using tin or antimony lead alloy anode and the copper or brass as cathodes characterised in that the plating is done with the bath in presence of boric acid and nitrogen containing componuds such as urea or urea nitrate in combination with fluoride.

2. A process as claimed in Claim 1 wherein the plating with black chromium is done using 8% tin or antimony lead alloy anode in an electrolyte containing chromic acid (free from sulphate) 60%, fluosilicic acid or sodium flouride 1%, urea or urea nitrate 2% and boric acid 10 g/1.

3. A process as claimed in Claim 1 or 2 wherein fluosilicic acid is replaced by other fluoride catalysts such as sodium fluoride, cryolite, fluoboric acid, ammonium bifluoride.

4. A process as claimed in any of the preceding claims wherein black chrome is deposited over current density 6.4 to 53 A/dm² with lead tin or lead antimony anode and copper, brass as cathodes to obtain black chrome deposit containing 54 to 56 % metallic chromium.

5. A process as claimed in any of the preceding claims wherein the plating is done for 5-10 minutes to obtain a black chrome deposit which withstands 40 days of immersion in 5% NaCl adjusted to pH 3.2 with HAC without basis metal failure.

6. A process for the production of shiny corrosion resistant oil wettable black chromium plating on brass and copper substantially as hereinbefore described.

Dated this 11th day of July, 1973

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