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PROVISIONAL SPECIFICATION

Section 4

“IMPROVEMENTS IN OR RELATING TO ELECTROPLATING OF CHROMIUM FROM AQUEOUS ELECTROLYTES

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 Namakkal Vijayam Parthasaradhy, Scientist and Thirugokarnam Ramachandran Subramanian, Senior Laboratory Assistant, both of Central Electrochemical Research Institute, Karaikudi-3, India and both Indian.

This invention relates to ELECTROPLATING OF CHROMIUM FROM TETRA CHROMATE ELECTROLYTES.

Hitherto it has been proposed to deposit chromium from:

(*a*) *Coventional Chromium Bath* : It contains chromic acid and sulphuric acid usually in the ratio of 100 : 1 and is normally employed in the temperature range of 40°—50°.C and current density range of 8-22 amp/dm², to produce bright deposit directly from the bath. The normally used basis metals are polished copper (basis or undercoat) and/or nickel undercoat etc.

(b) *Tetrachromate based electrolytes* : These have been reported in other countries. They consist of chromic acid, sulphuric acid, alkali and trivalent chromium. They are operated usually in the temperature range of 16° to 25° C and current density range of 22-100 amp/dm². The deposits are dull grey in the 'as plated' condition and are subsequently mechanically polished to obtain bright deposits.

This is open to the objection that :

(*a*)(*i*) The deposit from the convetional chrome bath generally is not uniformly bright in the 'as plated' condition, in spite of the use of appropriate current density and temperature to produce a bright deposit, because of the poor covering power and throwing power of the electrolyte. This is more often the case with complicated jobs. Further, it is not easy to polish to lustre finish the chromium deposit from this bath, since its hardness is high.

(*ii*) The corrosion resistance of the chrom deposit from the conventional bath is not high, as the deposit is somewhat porous.

(*iii*) The current efficiency of the conventional chromium bath is low and is usually of the order of 10—12%.

(*b*) The tetrachromate based electrolytes produce a dull deposit although at a higher efficiency-usually about 3 times the conventional bath-and hence use of such electrolytes involves an additional step of mechanical finishing of the deposit in order to produce a bright surface.

The object of this invention is to obviate these disadvantages by producing a bright deposit of chromium in the 'as plated' condition, from a tetrachromate based electrolyte containing an addition agent.

To these ends the invention consists in the use of a tetrachromate based electrolyte together with an addition agent for the electrodeposition of bright chromium, in the 'as plated' condition, on to polished mild steel basis, copper (basis or undercoat) and/or nickel (undercoat).

The bath composition and operational conditions are as under :

Cromic acid	2·5 to 4·5 gm. mole/l.
Hydroxides and/or Carbonates of alkali metals	0·5 to 1·6 gm./mole/l.
Trivalent chromium ..	0·03 to 0·20 gm. mole/l.
Sulphate	0·001 to 0·05 gm. mole/l.
Addition agent (Fluorine based inorganic compound of alkali metals) ..	0·001 to 0·300 gm. mole/l.
Temperature	18° to 38°C
Current density	2 to 65 am./dm².

The following typical examples are given to illustrate the invention :

Example 1

The usual preplating operations like degreasing with organic solvent and alkaline electrocleaning are given to the polished basis metal prior to actual plating.

The tetrachromate based electrolyte preferably of a composition as follows is made use of to deposit chromium.

Cromic acid	2·8 to 4·0 gm. mole/l.
Hydroxides and/or Carbonates of alkali metals	0·8 to 1·5 gm. mole/l.
Trivalent chromium ..	0·10 to 0·18 gm. mole/l.
Sulphate	0·005 to 0·030 gm. mole/l.
Addition agent ..	0·001 to 0·300 gm. mole/l.

Mild steel specimen prepared as above, is made the cathode in the above electrolyte, together with two insoluble anodes, the cathode being in the middle of the two anodes. At a temperature of 19° to 25°C, direct current from a DC source at a current density of about 9 amp/dm² is passed, when a bright chromium deposit is obtained in the 'as plated' condition.

PRICE : TWO RUPEES

Example 2

All other details as in example 1, with the difference that a polished nickel plated mild steel is the cathode used and the electrolysis is carried out at a current density of 16 amp/dm^2 at a temperature of 25° to 31° C. A bright deposit of chromium is produced straightaway from the bath.

The following are among the main advantages of the invention :

(1) The production of a bright deposit of chromium in the 'as plated' condition, for decorative applications, at a temperature of 18°—38°C and in the current density range of 2 to 65 amp/dm^2 from a tetrachromate based electrolyte.

(2) Production of relatively pore-free and corrosion resistant chromium deposit.

(3) The use for electrodeposition of chromium, of a bath, with good covering power and throwing power, as compared to the conventional type of chromium bath, and

(4) The use of a bath for electrodeposition of chromium with high current efficiency.

Dated this 21st day of August, 1967.

Sd/-
R. BHASKAR PAI
Patents Officer
Council of Scientific & Industrial Research.

INDIAN PATENTS AND DESIGNS ACT, 1911.

COMPLETE SPECIFICATION

Section 4

IMPROVEMENTS IN OR RELATING TO ELECTROPLATING OF CHROMIUM FROM AQUEOUS ELECTROLYTES

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 ascertain the nature of this invention and the manner in which it is to be performed.

This is an invention by NAMAKKAL VIJAYAM PARTHASARADHY, Scientist and THIRUGOKARNAM RAMACHANDERAN SUBRAMANIAN, Senior Laboratory Assistant, both of the Central Electrochemical Research Institute, Karaikudi-3, India, both Indian citizens.

The invention relates to "Electroplating of Chromium From Tetra Chromate Electrolytes"

Hitherto it has been proposed to deposit chromium from :

(a) *Conventional Chromium bath* : It contains chromic acid and sulphuric acid usually in the ratio of 100 : 1 and is normally employed in the temperature range of 40°—50°C and current density range of 8-22 amp/dm^2, to produce bright deposit directly from the bath. The normally used basis metals are polished copper (basis or undercoat) and/or nickel undercoat.

(b) *Tetrachromate based electrolytes* : These have been reported in other countries. They consist of chromic acid, sulphuric acid, alkali and trivalent chromium. They are operated usually in the temperature range of 16° to 25°C and current density range of 22—100 amp/dm^2. The deposits are dull grey in the 'as plated' condition and are subsequently mechanically polished to obtain bright deposits.

Drawbacks connected with hitherto know processes/devices :

The drawbacks connected with the hitherto known processes are :

(a) (*i*) The deposit from the conventional chrome bath generally is not uniformly birght in the 'as plated' condition, in spite of the use of appropriate current density and temperature to produce a bright deposit, because of the poor covering power and throwing power of the electrolyte. This is more often the case with jobs of odd shape. Further, it is not easy to polish to lustre finish the chromium deposit from this bath, since its hardness is high.

(*ii*) The corrosion resistance of the chrome deposit from the conventional bath is not high, as the deposit is somewhat porous

(*iii*) The current efficiency of the conventional chromium bath is low and is usually of the order of 10—12%.

(*b*) The tetrachromate based electrolytes produce a dull deposit although at a higher efficiency-usually about 3 times the conventional bath-and hence use of such electrolytes involves an additional step of mechanical finishing of the deposit in order to produce a bright surface. The object of this invention is to obviate these disadvantages by producing a bright deposit of chromium in the 'as plated' condition, from a tetrachromate based electrolyte containing an addition agent.

The main object of the invention is to produce a bright deposit of chromium in the 'as plated' condition from a tetrachromate based electrolyte, by the use of an addition agent.

The other object is to develop a low and room temperature bath with better covering and throwing power, as compared to the conventional chrome bath (of the composition : Chromic acid 250 gpl, sulphuric acid 2·5 gpl, Trivalent chromium 5 gpl, maximum and operated at 50°C), for the production of bright deposit of chromium for decorative applications. Such a development is particularly suited to tropical countries like India and one can normally dispense with heating and control equipments. Also such a bath enables chromium plating feasible at low enough current density (compared to the conventional bath) which is an advantage in times of restricted electric power supply. Also the lower current density in chromium plating minimizes possible peeling of the nickel undercoat.

The invention takes the advantages of the tetrachromate based electrolyte, namely high efficiency, use of temperature around ambient temperature, wide permissible current density range, better covering power and throwing power and overcomes the defect of the bath that it produces a dull deposit in the 'as plated' condition, by the use of an addition agent, which imparts brightness to the chromium deposit.

The main finding underlying the invention is the production of a bright deposit of chromium for decorative applications, by the incorporation of a suitable addition agent in a tetrachromate based electrolyte, at a temperature of 18° to 38°C and in the current density range of 2 to 65 amp/dm^2.

The new result flowing from the new finding is that by the use of an addition agent in the tetrachromate based electrolyte of the composition in the ranges indicated, with proper ratio of chromic acid to the hydroxides and/or carbonates of alkali metals, with appropriate ratio of sulphate to the addition agent and with a proper ratio of sulphate and addition agent with respect to the chromic acid, in the optimum range of operating conditions of temperature and current density, it is possible to produce a bright deposit of chromium in the 'as plated' condition at or below or above ambient temperature with higher cathode efficiency and hence higher rate of build up (and consequently lower duration of electrodeposition), from a bath with better covering power and throwing power, which means in practice the feasibility of electroplating chromium satisfactorily on to odd shaped jobs, with uniformly bright deposit and with less or no defects such as patches, dull or milky areas, uncovered regions etc.

To substantiate the above, the following data are given :

In the conventional chrome bath at 50°C, the current efficiency is in the range of 10 to 22% in the current density range 8 to 50 amp/dm^2. By the use of the said electrolyte as detailed in the patent, in the said composition ranges of chromic acid, alkali and/or carbonates, sulphate and addition agent etc., at 20°C one obtains a current difficiency of 18 to 39% in the current density range 8 to 30 amp/dm^2, whereas at 30°C the efficiency is 12 to 33% in the current density range 8 to 50 amp/dm^2. This does not, however, mean any significantly higher voltage requirements. An indication of this is obtained from the following data. In the conventional bath at 50°C the bath voltage, under a particular set of anode and cathode spacing, is in the range 3·4 to 10·0 volts in the current density range 8 to 70 amp/dm^2, while in the said electrolyte in the said composition ranges of chromic acid, alkali and/or carbonates, sulphate and addition agent etc., the bath voltage is 3·7—10·6 volts in the temperature range studied viz., 18° to 38°C and in the current density range of 8--70 amp/dm^2.

To produce 0·5 micron thick deposit of chromium it requires about 3 minutes at a current density of 15 amp/dm^2 in the conventional chrome bath at 50°C, whereas it needs 1·2 to 1·9 minutes at 20°C in the electrolyte covered by the patent at the above current density.

It is also to note that in practice, in view of the low covering power and throwing power of the conventional chromium bath, the plating is required to be carried out aiming 1 micron thickness (occasionally even higher, depending upon the nature of the job to be plated) to ensure that on 'significant surface' the deposit thickness is at least 0·5 micron. This difficulty is considerably reduced in the electrolyte covered by the patent, since the throwing power and the covering power of the electrolyte are high. For the same reason one can dispense with the initial strike that is normally resorted to in decorative chrome plating.

Further when the bath is operated at the optimum current density range, in the temperature range indicated, the change in current efficiency with temperature is lower than in the conventional bath. This is an added advantage in practice, particularly while electroplating big sized articles.

The throwing power of the said electrolyte covered by the patent is much better than that of the conventional bath. The sulphate content of the bath can be varied over wide range of concentration, of course maintaining its ratio with addition agent in appropriate limits.

From the view point of production of bright deposits, the electrolyte covered by this patent, can be operated any where in the range of 18°C to 38°C. Further, the finish obtained is very bright on polished copper basis (or undercoat) and/or nickel (undercoat) and mild steel basis. The electrolyte and the operating conditions are best suited for the conventional copper-nickel-chromium system.

Since the bath composition covered by the patent is capable of withstanding current interruptions, the bath can be used for barrel chrome plating without fear of producing defective deposits of chromium on to the plated samples. The improved covering and throwing power of the electrolyte are the added advantages in the use of the said electrolyte for barrel chrome plating.

The bath composition covered by the patent, can, if desired, be used for direct deposition of chromium on to aluminium and its alloys and zinc base die castings. Further, in view of the relatively low operating temperatures, the corrosion of the tank lining and of uncovered areas of the job, is rather low.

The present invention consists of a process for production of a bright deposit of chromium in the 'as plated' condition for decorative applications, which comprises in the use of tetrachromate based electrolyte with an addition agent and of the composition as under :

Chromic acid	2·5 to 4·5	gm. mole/l.
Hydroxides and/or carbonates of alkali metals	0·5 to 1·6	gm. mole/l.
Trivalent chromium ..	0·03 to 0·20	gm. mole/l.
Sulphate	0 001 to 0·05	gm. mole/l.
Addition agent (Fluorine based inorganic compound)	0·001 to 0·300	gm. mole/l.

wherein the addition agent is primarily meant for impating brightness to the deposited chromium and it should be present in optimum proportion, with respect to sulphate content, which in turn bears an appropriate relationship with chromic acid concentration in the electrolyte and the said electrolyte in the appropriate proportions in the said ranges, shall be operated at temperature of 18° to 38°C and at current density of 2 to 65 amp/dm^2.

A few typical examples to illustrate how the invention is carried out in actual practice. For process inventions, please specify quantities, conditions, yields.

Example 1

The usual preplating operations like degreasing with organic solvent and alkaline electrocleaning are given to the polished basis metal prior to actual plating. The tetrachromate based electrolyte of a composition as follows is made use of to deposit chromium :

Chromic acid ..	2·8 to 4.0	gm. mole/l.
Hydroxides and/or carbonates of alkali metals	0·8 to 1·5	gm. mole/l.
Trivalent chromium .	0·10 to 0·18	gm. mole/l.
Sulphate	0·005 to 0·030	gm. mole/l.
Addition agent ..	0·001 to 0·300	gm. mole/l

Copper specimen prepared as above, is made the cathode in the above electrolyte, together with two insoluble anodes of 93% lead—7% tin alloy, the cathode being in the middle of the two anodes. At a temperature of 19° to 25°C, direct current from a DC source at a current density of about 9 amp/dm^2 is passed, when a bright chromium deposit is obtained in the 'as plated' condition, at a current efficiency of 17—22%.

Example 2

All other details as in example 1, with the difference that a polished nickel plated mild steel is the cathode used and the electrolysis is carried out at a current density of 16 amp/dm^2 at a temperature of 25° to 31°C. A bright of deposit of chromium is produced straightway from the bath, at a current efficiency of 16—21%.

The following are the main advantages of the invention :

(1) The production of a bright deposit of chromium in the 'as plated' condition, for decorative applications, at a temperature of 18°—38°C and in the current density range of 2 to 65 amp/dm^2 from a tetrachromate based electrolyte,

(2) Production of relatively pore free and corresion resistant chromium deposit,

(3) The use for electrodeposition of chromium, of a bath with good covering power and thorwing power, as compared to the conventional type of chromium bath, and

(4) The use of a bath for electrodeposition of chromium with a relatively high current efficiency.

Summarising, the invention provides a process for the electrodeposition of bright chromium in the 'as plated' condition, for decorative applications, from a tetrachromate based electrolyte over polished mild steel, copper (basis or undercoat) and/or nickel (undercoat) with the advantages of :

(*i*) Higher efficiency ;

(*ii*) Better covering power and throwing power ;

(*iii*) Operatable at low enough current densities and at temperatures around the ambient temperatures : and

(*iv*) Capacity to withstand current interruptions as compared to the conventional bath.

Aspect (1) results in lowering the time of deposition for a given thickness, which means an increased production from a given chrome vat. The advantage (*ii*) means not only relatively uniform deposition of chromium on to the job (which will be particularly evident on complicated shapes) but also minimises or eliminates the need for increased duration of plating to ensure the minimum thickness of deposit on "significant areas."

Merit (*iii*) results in the elimination of heating and control equipments and also enables the use of the chromium bath even in times of restricted electric power supply.

The benefit (*iv*) is specifically suited for barrel chrome plating. The merits (*i*) and (*iii*) result in decreased spray from the chrome vat—an advantage both from operators' view point and from the view point of loss of chromic acid.

Further the electrolyte is quite suitable for chrome deposition, if desired, directly on to aluminium and its alloys and zinc base die castings.

We Claim :

1. A process, for the production of abright deposit of chromium in the "as plated" condition, for decorative applications which comprises in the use of tetrachromate based electrolyte with an addition agent with better covering power and throwing power compared to the conventional chromium bath and of the composition as under :

Chromic acid	2·5 to 4·5 gm. mole/l.
Hydroxides and/or carbontes of alkali metals	0·5 to 1·6 gm. mole/l.
Trivalent chromium ..	0·03 to 0·20 gm. mole/l.
Sulphate	0·001 to 0·05 gm. mole/l.
Addition agent (fluorine based inorganic compound)	0·001 to 0·300 gm. mole/l.

wherein the addition agent is primarily meant for imparting brightness to the deposited chromium and it should be present in optimum proportion, with respect to sulphate content, which in turn bears an appropriate relationship with chromic acid concentration in the electrolyte, and the said electrolyte in the appropriate proportions in the said ranges, shall be operated at temperature of 18° to 38°C and at current density of 2 to 65 amp/dm^2.

2. A process, for the production of a bright deposit of chromium in the 'as plated' condition for decorative applications, wherein the basis metals or undercoat to be plated are :

(*a*) polished nickel (basis or undercoat) ; (*b*) polished copper (basis or undercoat); (*c*) polished copper (basis or undercoat) and/or nickel (undercoat) ; and (*d*) polished mild steel.

Dated this 19th day of June, 1968.

Sd/-
R. BHASKAR PAI
Patents Officer,
Council of Scientific & Industrial Research

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