

Specification No. 96690. Application No. 96690, dated 24th November 1964. Complete specification left on 1st September 1965. (Application accepted 18th May 1966.)

Index at acceptance—70C4 [LVIII(5)].

### PROVISIONAL SPECIFICATION.

#### IMPROVEMENTS IN OR RELATING TO DIRECT PLATING OF COPPER ON ALUMINIUM AND ALUMINIUM ALLOYS.

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, RAJ MARG, NEW DELHI-1, INDIA, AN INDIAN REGISTERED BODY INCORPORATED UNDER THE REGISTRATION OF SOCIETIES ACT (ACT XXI OF 1960).

The following specification describes the nature of this invention.

This is an invention by BALKUNJE ANANTHASHENOI, Scientist, RAMACHANDRA SUBRAMANIAN, Senior Scientific Assistant; CHIDAMBARAKRISHNAIYER BALASINGH, Junior Scientific Assistant, and C. LAKSHMINARAYAN, Senior Laboratory Assistant, all of the Central Electrochemical Research Institute, Karaikudi, Madras, India, all Indian Citizens.

This invention relates to improvements in or relating to direct plating of copper on aluminium and alloys of aluminium.

Hitherto it has been proposed to deposit copper on Zincated Aluminium or Anodized Aluminium.

This is open to the objection that the processes are either time consuming involving a large number of steps or costly and requiring special treatments for different alloys.

The object of this invention is to obviate these disadvantages by electrodeposition of copper from an aqueous electrolyte directly on the aluminium surface without intermediate layer.

To these ends, the invention broadly consists in electro-depositing copper from an aqueous solution containing copper salt, ammonia and a salt of hydroxy acid with copper anodes and aluminium or aluminium alloys as cathode, just as is done for copper plating on other base metals from the conventional copper plating baths.

The following typical examples are given to illustrate the invention;

#### EXAMPLE 1.

The aqueous solution contains:

Copper	15—25 g/l
25 per cent. Ammonia	1000 ml.
Tartarate	15—30 g/l
pH	9 to 11
Current density	20 asf to 75 asf
Temperature	20°C. to 40°C.
Copper	anode.

The alloy of aluminium 2S is degreased, immersion cleaned in aqueous solution of sodium phosphate and sodium carbonate at 80° C. for 3 minutes, rinsed, dipped for 30 seconds to 120 seconds in Nitric acid, rinsed, is

made the cathode in the above solution and copper is electrodeposited.

#### EXAMPLE 2.

With the same procedure 26S, 57S, 3S and 65S aluminium alloys are plated.

The following are among the main advantages of the invention:

- (1) The deposit is very bright and smooth, requiring no buffing.
- (2) No intermediate layers of zinc or anodic oxide film are necessary.
- (3) Dispenses away with too many steps in preparing the surface to receive copper and hence saves time and labour.
- (4) Much cheaper than anodising step method.
- (5) Easily adaptable in automatic plating schedule.
- (6) Non-toxic and non-corrosive and hence the hazards encountered with cyanide or acid copper are avoided.
- (7) Requires no special care, constant attention and rigorous control.
- (8) No different treatment cycles are needed for different alloys of Aluminium.
- (9) For production of Bimetallic plates—for lithographic printing plates.

R. BHASKAR PAI,

Patent Officer,

Council of Scientific & Industrial Research.

Dated this 6th day of November 1964.

### COMPLETE SPECIFICATION.

#### IMPROVEMENTS IN OR RELATING TO DIRECT PLATING OF COPPER ON ALUMINIUM AND ALUMINIUM ALLOYS.

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, RAJ MARG, NEW DELHI-1, INDIA, AN INDIAN REGISTERED BODY INCORPORATED UNDER THE REGISTRATION OF SOCIETIES ACT (ACT XXI OF 1960).

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 ANANTHASHENOI (Scientist), RAMACHANDRA SUBRAMANIAN (Senior Scientific Assistant), CHELLIAH BALASINGH (Junior Scientific Assistant), and CHIDAMBARAKRISHNAIYER LAKSHMINARAYANAN (Senior Laboratory Assistant), Citizens of India, all of the Central Electrochemical Research Institute, Karaikudi, Madras, India.

This invention relates to improvements in or relating to direct plating of copper on aluminium and aluminium alloys.

Hitherto it has been proposed to deposit copper on aluminium or aluminium alloys previously treated either by zincate process to have a thin adherent coating of zinc or by the anodising methods to have a uniform, sufficiently thick and porous coating of aluminium oxide.

The zincate process requires different methods of treatment for different alloys of aluminium, no simple and single method being suitable for all types of alloys. Thus articles made of different alloys cannot be processed in the same cycle. Further the number of steps in the sequence of operation is inconveniently large and hence time consuming. The temperature and period of treatment in zincating is critical and any deviation from the

Price : TWO RUPEES.

optimum conditions will produce dark grey spongy deposits of zinc which will not be very adherent.

The anodised plate will enhance the cost of the processing method and will become uneconomical. Further it requires special equipments for cooling and processing.

In both the methods mentioned above, an intermediate layer is present between the plated metal and the basis aluminium surface. In some applications, as is the case with alloy printing plates, this is objectionable.

Direct plating of copper on aluminium from conventional baths like acid copper sulphate or cyanide type is not possible because a loosely adherent immersion deposit of copper is formed which weakens the strength of bonding between the deposited copper and basis metal.

The object of this invention is to obviate these disadvantages by electrodeposition of copper from a suitable aqueous electrolyte directly on the aluminium surface as done in conventional plating methods on other basis metals.

The invented process for electrodeposition of copper directly on aluminium or alloys of aluminium consists in plating degreased and cleaned aluminium or aluminium alloy articles in the following copper plating bath:

Copper sulphate	50 to 150 gms. per litre
Ammonia solution	25 500—1000 ml. per cent.
Ammonium sulphate	0—40 gms per litre
Sodium potassium tartrate	10—30 gms. per litre.

The invention includes within its scope the aforesaid copper-plating bath for the electrodeposition of copper on aluminium or aluminium alloys.

The cleaning of the surface of the degreased articles is done by immersion in any one of the following cleaners:

- (a) Sodium phosphate . 3 per cent  
Sodium Carbonate . 3 per cent.  
Temperature . 65—80° C  
Time . 1—2 minutes.  
or
- (b) Hydrofluoric acid . 10 per cent. by volume  
Nitric acid . 10 per cent. by volume  
Temperature . 30—35° C.  
Time . 2—5 minutes.  
or
- (c) Aqueous solution of ammonium fluoride . 2—5 per cent.  
Temperature . 30—50° C.  
Time . 1—2 minutes.

The electrodeposition is carried out under the conditions specified as follows:

pH of the bath	9.5—11
Current density	20—75 asf
Temperature	20—40° C.
Anodes	Copper.

After degreasing and cleaning, the article is rinsed well in running water, and quickly transferred to the plating tank with current on as is generally done in the cyanide strike bath for plating on zinc base die-castings. After the plating is over the articles are removed, washed and dried in warm air. Adhesion of the deposit is very good. It can, if need be, further improved by heating the plated article to 300-400° C for about one hour.

The use of the sodium potassium tartrate improves the plating ranges and makes anodic dissolution of copper smooth and uniform. In the absence of sodium potassium tartrate a blue basic salt of copper is formed on the anode. Beyond 10-30 gms. per litre, the effect of sodium potassium tartrate is insignificant.

The following examples are given to illustrate the invention:

#### EXAMPLE I.

- (1) The aluminium plate is degreased in trichloroethylene.
- (2) Dip cleaned in an aqueous solution of—  
Sodium phosphate . 3 per cent. wt.  
Sodium carbonate . 3 per cent. wt.  
Temperature . 70° C  
Time . 2 minutes.

- (3) Rinse in water  
(4) Desmut in 1:1 nitric acid by dipping in for 15-30 secs.  
(5) Rinse well in running water, then in distilled water.  
(6) Make cathodic in the plating vat and introduce in the bath with current on.

The bath formulation is:

Copper sulphate	130 g/l
Ammonium 25 per cent.	1000 ml.
Sodium potassium tartrate	30 g/l
Temperature	32° C.
Anode	Copper.

#### EXAMPLE 2.

- (1) The aluminium plate is degreased in white spirit.

- (2) Dip cleaned in an aqueous solution of—  
Hydrofluoric acid . 10 per cent. vol.  
Nitric acid . 10 per cent. vol.  
Temperature . 27° C.  
Time . 3 minutes.

- (3) Rinse in water.

- (4) Make cathodic in the plating vat and introduce with current on.

The bath formulation is:

Copper sulphate	65 g/l
Ammonia (25 per cent.)	500 ml/l
Ammonium sulphate	30 g/l
Sodium potassium tartrate	30 g/l
pH	10.5
Current density	36 asf
Temperature	30° C.
Anode	Copper

The following are among the main advantages of the invention:

- (1) No immersion deposit is formed in the aluminium surface.
- (2) The deposit is bright, smooth and fine grained.
- (3) Dispenses away with too many steps in preparing the surface to receive an adherent deposit of copper and hence saves time and labour.
- (4) Much economical.
- (5) No intermediate oxide or metallic layer is required to improve adhesion.
- (6) Non-toxic and non-corrosive.
- (7) Adaptable for all common types of aluminium alloys like 2S, 3S, 26S, 65S, etc., since the preplating treatments are common.
- (8) Adhesion is good and can be used for production of Bimetallic aluminium copper printing plates for planographic printing processes.
- (9) The deposit of copper can further be plated with nickel from a Watt's type of bath or with chromium from conventional chromic acid sulphate bath.

We claim:

1. A process for electrodeposition of copper directly on aluminium or alloys of aluminium which consists in plating degreased and cleaned aluminium or aluminium alloy articles in the following copper plating bath:

Copper sulphate	50 to 150 gms. per litre
Ammonia solution	25 500—1000 ml. per cent.
Ammonium sulphate	0—40 gms. per litre
Sodium potassium tartrate	10—30 gms. per litre.

2. A process as claimed in Claim 1 wherein the surface of the degreased articles is cleaned by immersion in any one of the following cleaners:

- (a) Sodium phosphate . 3 per cent.  
Sodium Carbonate . 3 per cent.  
Temperature . 65—80° C.  
Time . 1—2 minutes.  
or
- (b) Hydrofluoric acid . 10 per cent. by volume  
Nitric acid . 10 per cent. by volume  
Temperature . 30—35° C.  
Time . 2—5 minutes.

- (c) Aqueous solution of  
 Ammonium fluoride 2—5 per cent.  
 Temperature . . . 30—50°C.  
 Time . . . . . 1—2 minutes.

3. A process as claimed in Claim 1 or 2 wherein the electrodeposition is carried out under the conditions specified as follows:

- pH of the bath . . . 9.5—11  
 Current density . . . 20—75 asf  
 Temperature . . . 20—40°C.  
 Anodes . . . . . Copper.

4. A copper plating bath for electrodeposition of

copper on aluminium or aluminium alloys as claimed in Claim 1.

5. A process of electrodeposition of copper on aluminium or aluminium alloy substantially as hereinbefore described.

R. BHASKAR PAI,

Patent Officer,

Council of Scientific & Industrial Research.

Dated this 28th day of August 1965.