GOVERNMENT OF INDIA: THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.
Specification No. 103970. Application No. 103970, dated 21st February 1966. Complete Specification left on 16th November 1966. (Application accepted 18th November 1967.)
Index at acceptance—70C4[LVIII(5)].

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

PROVISIONAL SPECIFICATION.

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 spececification describes the nature of this invention.

This is an invention by BALKUNJE ANANTHA SHENOI, Scientist and RAMACHANDRA SUBRAMANIAN, Scientist of the Central Electrochemical Research Institute, Karaikudi, India, and SESHADRI SEETHARAMAN, Research Student at the Indian Institute of Science, Bangalore, India, all Indian Citizens.

This invention relates to improvements in or relating to direct electro-deposition of copper on aluminium from an aqueous copper plating bath.

Hitherto it has been proposed to plate copper on aluminium either zincated or anodized. Some plating baths gave direct deposits of copper on aluminium which did not give satisfactory adherent coatings.

This is open to the objection that the first two techniques were either costly or required specific treatments for different alloys. The last one was not suitable for long use. The technique patented earlier suffered from the following disadvantages—

1. Too high a concentration of ammonia, which was lost by evaporation during storage. This required a frequent addition of ammonia to keep the bath in the desired optimum pH range.

2. The pungent smell of ammonia around the plating vat is not desirable.

3. The copper anodes were chemically dissolved during idling. Even while plating the dissolution was both in the cuprous and the cupric states. The presence of cuprous ions in the bath beyond a certain limit made the bath useless.

4. Interruption of current during plating even for few seconds affected the adhesion of the deposit to the basis metal considerably.

5. Further building up of other electro-deposits like nickel, chromium or copper from other baths was not possible immediately after copper plating from the amine complex bath even though this could be achieved by heat treatment of the coated article or keeping the article stored for more than 24 hours after plating.

The object of this invention is to obviate these disadvantages by replacing the soluble copper anodes with insoluble anodes and substituting the salts of hydroxy acids with suitable inorganic salts. The amount of ammonia required is reduced to the barest minimum to form the complex. The preplating technique has also been suitably modified to improve the adhesion.

To these ends, the invention broadly consists in using a bath containing copper salt 0·1 N to 0·5 N ammonia solution to form the complex with the metal ions ; ammonium salts and salts of some divalent metals to improve the plating characteristics of the bath.

The amount of the constituents comprising the bath may be varied within the following limits—

Copper salt	0·1N to 0·5N
Ammonia	pH 8·4—9·6
Potassium, sodium and/or ammonium salt.	20 to 80 gms./lit.
Divalent metal salt	10 to 40 gms./lit.
pH	8·4— 9·6
Current density	8 asf—40 asf
Anode	Insoluble.

The following typical examples are given to illustrate the invention :

Example I

The aluminium articles are degreased, cleaned in 10% alkali solution for 2 minutes, dipped in 10% hydrochloric acid for 2 minutes, treated in 5% alkali for another 2 minutes, washed with water, desmutted in 1:1 nitric acid for 30 seconds and given a mild alkali dip (Sodium carbonate 3% solution) for 45 seconds. Then the articles are washed again quickly in water and introduced into the plating bath with current on and copper was deposited for a predetermined time.

The bath contained—

Copper	0·25N
Ammonia	to pH 9
Ammonium salt	60 gms /lit.
Cobalt sulphate	18 gms./lit.
Temperature	32°C
Anodes	Nickel

(No agitation.)

Example II

Aluminium articles were subjected to the above pretreatment cycle. After cleaning in the mild alkali cleaner they were washed in acetone or an alcohol, rinsed quickly in water and introduced into the plating vat with current on.

The bath contained—

Copper	0·38N
Ammonium	to pH 9·0
Ammonium salt	40 gms /lit.
Nickel salt	20 gms./lit.
Temperature	32°C
Anodes	Lead

(No agitation.)

The following are among the main advantages of the invention :—

1. Can be adapted to a regular plating cycle for further build up of other electro-deposits from conventional baths of copper, nickel and chromium.

2. Can be used as a strike bath for plating on mild steel and other ferrous metals instead of toxic and poisonous cyanide strike baths.

3. Depletion of copper can be made up easily by incorporating an ampere hour meter in the plating circuit to determine the amount of copper deposited.

4. The bath maintains well for very long periods without any loss of ammonia.

R. BHASKAR PAI,
Patents Officer,

COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH.

Dated this 10th day of February 1966.

Price: TWO RUPEES.

COMPLETE SPECIFICATION.

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 and RAMACHANDRA SUBRAMANIAN, Scientist of the Central Electrochemical Research Institute, Karaikudi, Inidia and SESHADRI SEETHARAMAN, Research Student at the Indian Institute of Science, Bangalore, India, all Indian Citizens.

This invention relates to improvements in or relating to direct plating copper on aluminium and has particular reference to the direct electro-deposition of copper on aluminium or aluminium alloys from an aqueous copper plating bath.

Hitherto it has been proposed to plate copper on aluminium either zincated or anodised. Some plating baths gave direct deposits of copper on aluminium, which did not give satisfactory adherent coatings.

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 proceeded 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 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 in bimetallic 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 process patented earlier (Ref. : Indian Patent No. 96690) suffered from the following disadvantages—

1. Too high a concentration of ammonia, which was lost by evaporation during storage. This required a frequent addition of ammonia to keep the bath in the desired optimum pH range.

2. The pungent smell of ammonia around the plating vat is not desirable.

3. The copper anodes were chemically dissolved during idling. Even while plating, the dissolution was both in the cuprous and the cupric states. The presence of cuprous ions in the bath beyond a certain limit made the bath useless.

4. Interruption of current during plating even for few seconds affected the adhesion of the deposit to the basis metal considerably.

5. Further building up of other electro-deposits like nickel, chromium or copper from other baths was not possible immediately after copper plating from the amine complex bath even though this could be achieved by heat treatment of the coated article or keeping the article stored for more than 24 hours after plating.

The object of this invention is to obviate these disadvantages by replacing the soluble copper anodes with insoluble anodes and substituting the salts of hydroxy acids with suitable inorganic salts. The amount of ammonia required is considerably reduced to the barest minimum to form the complex and control the pH at the optimum level. The pre-plating sequence has also been suitably modified to improve the adhesion of the electro-deposited copper to the basis metal.

To these ends, the invention broadly consists in using a bath containing copper salt 0·1N to 0·5N, ammonia solution to form the complex with the metal ions, ammonium salts and salts of some divalent metals to improve the plating characteristics of the bath.

The present invention consists in directly depositing copper on aluminium or aluminium alloys from the following bath :—

Ingredient	Range
Copper salt	0·1N to 0·5N
Ammonia solution (28%) added to bring the pH of the bath in the range.	8·4 to 9·6
Potassium, sodium and/or ammonium salts.	20 to 80 gms./litre
Nickel or cobalt salts.	10 to 40 gms./litre

under the following conditions:—

Cathode current density 0·8 amp./sq. dm. to 4 am./sq. dm. using insoluble anodes of nickel or lead or stainless steel.

Prior to electro-deposition of copper on aluminium-surface from the aforesaid bath, the surface of aluminium is given a pretreatment sequence as follows :—

The surface to be plated with copper is degreased in an organic solvent and cleaned in an aqueous 10% solution of $NaOH$ by immersion for about 1 or 2 minutes at room temperature. Rinsed thoroughly in deionised water and is given an immersion treatment in aqueous solution (10% of CP grade HCl at room temperature for about 2 minutes and rinsed in deionised water. This is followed by a desmutting dip in an aqueous solution containing nitric acid or nitric acid and hydrofluoric acid for 30 seconds at room temperature and rinsed well. Finally, a neutralising dip is given in a 3% solution of sodium carbonate and/or sodium phosphate at 30-80°C for 45 seconds. Rinsed quickly in water or a mixture of water and an organic liquid which may be acetone or isopropyl alcohol and then transferred to the plating bath with circuit on. These steps are carried out in such a way that surface to be plated, is kept active to receive the deposit in a good condition.

The concentrations of the various solutions herein described and the operating conditions can be varied in the following limits:—

1. NaOH solution in water	5—10%
Temperature	30—60°C
Time	1—2 minutes
2. HCl solution in water	7—12%
Temperature	30—45°C
Time	1—2 minutes
3. Desmutting solution—	
(*a*) HNO_3 in water	30—50% by volume
Temperature	25—32°C
Time	30—45 seconds
or	
(*b*) HNO_3	5—10% by volume
HF	5—10% by volume
Temperature	25—32°C
Time	30—45 seconds
4. Neutralizing solution—	
Na_2CO_3	3%
Na_3PO_4	3%
Temperature	30—80°C
Time	30—40 seconds

The following typical examples are given to illustrate and describe the method of performing the operation:—

Example I

The aluminium articles are degreased, cleaned in 10% alkali solution for 2 minutes, dipped in 10% HCl for 2 minutes, treated in 5% alkali for another 2 minutes, washed with water, desmutted in 1:1 HNO_3 for 30 seconds and given a mild alkali dip (3% Sodium carbonate solution) for 45 seconds. Then the articles are washed again quickly in water and introduced into the plating bath with current on and copper was deposited for a predetermined time.

The bath contained—

Copper . . .	0·25N
Ammonia . . .	to pH 9
Ammonium salt . . .	60 gms./litre
Cobalt sulphate . . .	18 gms./litre
Temperature . . .	32°C
Anodes . . .	Nickel

(No agitation.)

Example II

Aluminium articles were subjected to the above pretreatment cycle. After cleaning in the mild alkali cleaner, they were washed in acetone or an alcohol, rinsed quickly in water and introduced into the plating vat with current on.

The bath contained—

Copper . . .	0·38N
Ammonia . . .	to pH 9.0
Ammonium salt . . .	40 gms./litre
Nickel salt . . .	20 gms./litre
Temperature . . .	32°C
Anodes . . .	Lead

(No agitation.)

The following are among the main advantages of the invention :—

1. No immersion deposit is formed on the aluminium surface.

2. The deposit is bright, smooth and fine grained.

3. Compared to the anodising process and the zincate process, this process is much economical.

4. No intermediate oxide or metallic layer is required to improve adhesion.

5. As the bath does not contain any cyanides, this bath is less hazardous and less poisonous.

6. Adaptable for all common types of aluminium alloys like 2S, 3S 26S, 65S since the pre-plating treatments are common.

7. Adhesion is good and can be used for production of bimetallic aluminium copper printing plates for planographic printing processes as shown qualitatively by bend tests, punch-out tests and heating for 2 hours at 200°C in an air oven.

8. 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.

9. The bath maintains well for weeks without any loss of ammonia.

We claim :

1. A process for the production of copper plated aluminium or aluminium alloys which consists in directly depositing copper on aluminium or aluminium alloys from the following bath :—

Ingredient	Range
Copper salt . . .	0·1N to 0·5 N
Ammonia solution (28%) to bring the pH of the bath in the range.	8·4 to 9·6
Potassium, sodium and/or ammonium salts.	20—80 gms. per litre
Nickel or cobalt salts . .	10—40 gms. per litre

under the following conditions:—

Cathode current density 0·8 amp./sq. dm. to 4 amp./sq. dm. using insoluble anodes of nickel or lead or stainless steel.

2. A process for the production of copper plated aluminium as claimed in Claim 1 above wherein the surface of the aluminium is pretreated substantially as hereinbefore described.

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Dated this 9th day of November 1966.

MGIP Sant—SL—22 Patent/69—28-8-73—100.