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PROVISIONAL SPECIFICATION

“IMPROVEMENTS IN OR RELATING TO COPPER ELECTROPLATING ON STAINLESS STEELS”

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 RAMACHANDRA SUBRAMANIAN, Scientist, SRINIVASAN CHAKRAPANI, Senior Laboratory Assistant, RAMASUBBU VENKATACHALAM, Senior Laboratory Assistant and BALKUNJE ANANTHA SHENOI, Scientist, all employed in Central Electrochemical Research Institute, Karaikudi and are nationals of India.

This invention relates to improvements in or relating to Copper Electroplating on Stainless Steels from Aqueous baths containing copper ions and chloride ions without any prior strike in other baths.

Hitherto it has been proposed to plate copper on stainless steel from acid copper sulphate bath after giving an initial strike at very high current densities from a nickel chloride — hydrochloric acid bath or cupric chloride — hydrochloric acid baths.

This is open to the objection that (1) the use of nickel or copper strike from chloride baths of low metal in concentration at very high current densities involving a separate tank for strike for this additional step. (2) The drag in of chloride ions into the acid copper sulphate bath causing troubles in the nature of the deposit, if proper care is not taken to prevent chloride ion impurity. (3) The deposition rate at a given current density is much lower as copper is deposited from the cupric state.

The object of this invention is to obviate these disadvantages by (1) use of a chloride bath straightaway for electroplating copper on stainless steel without an initial strike in a chloride bath and (2) use of cuprous ions in the chloride solutions so that for one Faraday of electric current passed more than 1 gm equivalent of copper is deposited thus increasing the rate of deposition nearly two-fold compared to the convention acid copper and (3) properly stabilising the cuprous chloride bath against atmospheric oxidation to cupric chloride by use of a proper inert liquid layer on the electroplating bath to prevent access of air to the electrolyte without affecting the adhesion and quality of the electrodeposited copper on stainless steels.

To these ends, the invention broadly consists in giving a desensitising etch in an aqueous solution containing hydrochloric acid with the desensitising agents chosen from polyalcohols, sugars or cellulose followed by plating stainless steel from a cuprous chloride — hydrochloric acid electrolyte covered with a layer of organic compound/s in the liquid phase, the compound/s being so chosen that they are not attacked by air or hydrochloric acid or by the electrolyte

and has a specific gravity less than that of the electrolyte so that it floats on the electrolyte and is not miscible with water or the electrolyte under the conditions of operation. The bath constituents of the electroplating bath is varied within the following limits :

Cuprous ion	0.03 M to 0.9M
Hydrochloric acid	2 N to 10N
Glue or gelatin	up to 1 gpl

This is covered by a liquid layer of organic compound or mixture of compounds in the liquid phase with properties as aforesaid, the organic compounds being chosen from saturated hydrocarbons aliphatic and/or aromatic or from mineral oils containing at least nine carbon atoms or from halogen substituted saturated aliphatic hydrocarbons.

The bath is operated under conditions varied within the limits indicated below :

Temperature	20°C to 60°C
Cathode current density	0.5 as/dm to 12 as/dm
Anodes	Electrolytic or rolled copper anodes
Anode current density	0.5 as/dm to 10 as/dm
Anode/cathode area	3:1 to 1:1

The following typical examples are given to illustrate the invention :

Example 1

The stainless steel work is cathodically cleaned in an alkaline cleaner, the operating conditions are :

Sodium carbonate	25 gpl
Sodium hydroxide	35 gpl
Temperature	70 to 80 °C
Current density	144 asf
Anode	Mild steel
Time	1 to 2 minutes

Rinsed in demineralised water, etched in desensitising etch for 2 minutes.

The composition of the etchant is

Hydrochloric acid	6N
Dextrin	15 gpl

Then transferred to plating bath.

Price : TWO RUPEES.

The work as the cathode and plating carried out to a desired thickness. The composition of the plating bath is

Cuprous oxide	20 gpl
Hydrochloric acid	500 ml/l
Temperature	30 °C
Cathode current density	1 asdm
Anode current density	1 asdm
Cathode and anode ratio	1:1

The electrolyte is covered with a layer of paraffin oil to 0.5 cm thickness.

Example 2

The stainless steel work is cathodically cleaned in an alkaline cleaner, the operating conditions are :

Sodium carbonate	25 gpl
Sodium hydroxide	35 gpl
Temperature	70-80°C
Current density	1-4 asf
Anode	Mildsteel
Time	1 to 2 minutes

Rinsed in demineralised water. Etched in desensitising etch for 2 minutes.

The composition of the etchant is

Hydrochloric acid	6N
Mannitol	20 gpl

Then transferred to plating bath.

The work as the cathode and plating carried out to a desired thickness. The composition of the plating bath is

Cuprous oxide	80 gpl
Hydrochloric acid	750 ml/l
Temperature	50 °C
Cathode current density	6 asdm
Anode current density	3 asdm
Cathode and anode ratio	1:2

The electrolyte is covered with a layer of paraffin oil to 0.5 cm thickness. (Mixture of trichloroethylene and paraffin in the ratio : 1 : 5).

The following are among the main advantages of the invention :

1. No initial strike is needed.
2. Plating rate for a given current density is nearly twice that of conventional acid bath.
3. The adhesion is good since chloride ions are used in the plating bath itself and a desensitising etch is used prior to plating.
4. The bath has been completely stabilising by use of an inert layer of organic compound.

Dated this 2nd day of December, 1967.

Sd/-

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COMPLETE SPECIFICATION

"IMPROVEMENTS IN OR RELATING TO COPPER ELECTROPLATING ON STAINLESS STEELS"

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 RAMACHANDRA SUBARAMANIAN, Scientist, SRINIVASAN CHAKRAPANI, Senior Laboratory Assistant, RAMASUBBU VENKATACHALAM, Senior Laboratory Assistant and BALKUNJE ANATHA SHENOI, Scientist, all employed in Central Electro-chemical Research Institute, Karaikudi and are nationals of India.

This invention relates to improvements in or relating to Copper Electroplating on Stainless Steels from aqueous baths containing copper ions and chloride ions without any prior strike in other baths.

Hitherto it has been proposed to plate copper on stainless steels from an acid copper sulphate bath after activating the surface by one or more than one type of the following treatments to ensure proper adhesion of the electrodeposited copper.

A thin protective oxide film on stainless steel surfaces, which fortifies the surface against attack by most of the chemicals used in plating baths and which has a tendency to reform quickly after stripping, has to be removed completely before electroplating and the surface should be kept active till it is covered with the electrodeposits. This is achieved by cathodic treatments or immersion treatments in mineral acids

like sulphuric or hydrochloric acid and followed by a strike plating or by simultaneous activation and flash plating treatment :

- | | | |
|-----|--------------------------------------|--------------------------------|
| (a) | Nickel chloride | 240 g/l |
| | Hydrochloric acid | 70 ml/litre |
| | Temperature | 25-32 °C |
| | Electrode | Nickel |
| | First anodic current density | 20 asf for 2 minutes |
| | followed by cathodic current density | 20 asf for 6 minutes |
| (b) | Nickel chloride | 240 g/l |
| | Hydrochloric acid | 100 ml/litre |
| | Temperature | 25-32 °C |
| | Electrode | Nickel |
| | First cathodic current density | 50-200 asf for 2 to 4 minutes |
| | followed by cathodic current density | 15-50 asf for 15 to 30 minutes |
| (c) | Nickel chloride | 20-300 g/l |
| | Hydrochloric acid | 12-120 ml/litre |
| | Temperature | 25-32 °C |
| | Anode | Nickel |
| | Cathodic current density | 5-100 asf |
| | Time | 1/2 to 5 minutes |

(d) Copper sulphate	0.375 g/l
Hydrochloric acid (conc.)	To one litre
Temperature	25-52 °C
Anode	Nickel
Cathodic current density	40-60 asf
Time	1-5 minutes

(e) A combination of more than one type of the above treatments to secure best adhesion.

The article is then quickly rinsed and carried over to acid copper sulphate bath for plating copper and in practice, to secure best adhesion of the electrodeposit, a strike plating in any one of the baths under simultaneous activation and plating treatment is necessary to secure good adhesion.

This is open to the following objections :

1. Separate tanks and rectifiers are necessary for the simultaneous activation and strike plating and in some cases may need special reverse switches [e.g: (a)] or rectifiers of high current input capacity [e.g: (b)].
2. The simultaneous activating and flash plating of baths use hydrochloric acid as one of the constituents and the chloride ion will be carried through into the subsequent acid copper sulphate plating bath, if thorough and efficient rinsing is not carried out in between. The presence of even trace amounts of chloride ions in acid copper sulphate bath is harmful and the carrying over of chloride ion should be avoided at any cost.
3. The time that should elapse between the activating step and the subsequent plating step should be the shortest practicable so that the oxide film is not formed on the surface to be plated or the coverage of the surface by the strike should be complete.
4. The subsequent plating of copper on stainless steel after strict adherence to the above precautions is carried out in acid copper sulphate bath wherein the copper is deposited from the divalent state and hence to deposit 0.001" over one square foot of the surface 17.85 amp. hours are required, that is, if a current density of 18 asf is employed, the time required will be nearly one hour.

The object of this invention is to obviate these disadvantages by (1) the use of a chloride bath straightaway for electroplating copper on stainless steel without an initial strike deposit of either copper or nickel as under the simultaneous activation and strike plating treatments mentioned hitherto used and (2) the use of cuprous ions in the chloride solution so that for one ampere hour more than 2 gms of copper is deposited instead of 1.185 grams in the conventional bath; that is, if at a current density of 18 asf, the time required to deposit 0.001" over one sq.ft of surface is just 30 to 35 minutes and (3) properly protecting the cuprous chloride bath against atmospheric oxidation to cupric chloride by use of a proper inert liquid layer on the electrolyte to prevent access of air and this by its presence should not affect the adhesion of the quality of the copper deposit.

In other words, the formulation of the inert liquid layer should meet the requirements such as (1) it should be in the liquid phase, (2) it should be lighter than the electrolyte (3) should be immiscible with water or electrolyte over the range of temperature under which the bath is operated (4) should be resistant to chemical attack by air, water or the electrolyte and (5) should be hydrophobic so that when the article to be plated is put into the electrolyte through this layer, it does not form a film on the surface and affect the adhesion of the electro-deposited copper.

To these ends, the invention broadly consists in plating stainless steel objects from a cuprous chloride-hydrochloric acid electrolyte with a grain refining

agent/s added to the electrolyte, the composition and operating conditions being maintained in the range hereunder described with the surface of the electrolyte covered with an inert organic liquid layer of one or more of the compound/s being chosen from among saturated aliphatic/or aromatic hydrocarbons, mineral oils containing not less than nine carbon atoms, trichloroethylene and perchlorethylene.

The concentration of the constituents of the electrolyte lying in the range—

Cuprous ion	0.03M to 0.9M
Hydrochloric acid	2N to 10N
Glue gelatin or	to a maximum of
gum arabic	5 grams per litre

and is operated within the range

Temperature	25°C to 60°C
Anodes	Electrolytic or rolled copper
Cathodes	The work to be plated
Anodes current density	0.5 asdm to 10 asdm
Cathode current density	0.5 asdm to 2 asdm
Anode to cathode ratio	3:1 to 1:1

The electrolyte itself will activate the surface of stainless steel. However, the activating treatment in the electrolyte hereunder described is necessary to ensure very good adhesion and complete coverage by the electrodeposit. Since the work to be plated has to go through the organic layer and even though the layer is hydrophobic, at some time, there is a possibility of the film of organic liquid adhering to the surface which may cause poor adhesion or no plating. To ensure that such a film is not formed, the activating electrolyte in addition to hydrochloric acid contains a desensitizing agent, which desensitizes the surface against adsorption of the liquid film and makes the surface to completely repel the organic liquid by surface adsorption of the molecules of the desensitizing agent during activating treatment. The desensitizing agent is chosen from the compounds such as dextrin, sucrose, carboxy methyl cellulose, polyvinyl alcohol, mannitol or gum arabic. Thus, the activating and desensitizing treatment just prior to plating in the electrolyte hereinbefore described is carried out as follows :

(a) by immersion in

Hydrochloric acid	10-50 %
Desensitizing agent	1-15 gpl
Temperature	25-33 °C
Time	1 to 5 minutes

or (b) by cathodic treatment in

Hydrochloric acid	10-50%
Desensitizing agent	1-15 gpl
Temperature	25 -35 °C
Anode	Nickel or stainless steel
Cathodic current density	20-60 asf
Time	2-5 minutes

or(c) by anodic treatment in

Hydrochloric acid	10-50%
Desensitizing agent	1-51 g/l
Temperature	25-35 °C
Cathode	Nickel or stainless steel
Anodic current density	20-60 asf
Time	2-5 minutes

Because of previous metal treatment has a pronounced effect on the nature of the film on the stainless steel surface and as this film has to be removed completely to keep the surface in an active condition to receive an adherent electrodeposit, the work is given the following sequence of treatments.

The work to be plated is degreased with trichlorethylene to remove any buffing compounds and other organic films on the surface in the conventional manner by swabbing, soaking or by vapour phase degreasing treatments depending on the size and shape of the article and volume of article to be plated.

Then it is given an alkali cleaning treatment in any one of the electrolytes conventionally used for cleaning stainless steels to remove any soap residues or lubricating oil film etc. on the surface, followed by swilling and rinsing in water.

Then it is given the activating and desensitizing treatment in the said electrolyte in a manner as hereinbefore described and without rinse transferred to the plating vat.

The work is given a perfect electrical contact as cathode bearing in mind the poor electrical conductivity of stainless steel and electroplating is carried out in the said plating bath in a manner as hereinbefore described. Since the efficiency of the bath is in the range of 95 to 100% (calculated on the basis of cuprous ions) over a wide range of composition of the electrolyte and a wide range of operating conditions, the time necessary to plate a specific thickness is calculated easily and the period of plating is only half the period of plating in the conventional acid copper sulphate bath at same current densities. In effect, the production rate is increased by the process adopted substantially described above.

The following typical examples are given to illustrate the invention :

Example 1

The work is degreased in trichlorethylene and cathodically cleaned in the electrolyte :

Sodium carbonate	25 gpl
Sodium hydroxide	35 gpl
Temperature	70-80 °C
Current density	114 asf
Anode	mild steel
Time	2 minutes

Rinsed in water.

Activated and desensitized by immersion in

Hydrochloric acid	6N
Dextrin	15 gpl
Temperature	30-32 °C
Time	5 minutes

Transferred to the plating bath, connected to the cathode terminal and plated for 6 minutes to get a deposit of 0.0002".

Cuprous oxide	20gpl
Hydrochloric acid	500 ml/l
Water	Balance
Temperature	30 °C
Anode	Copper
Cathode current density	1.8 asdm
Anode current density	1.5 asdm

The electrolyte is covered 0.5 cm. thick layer of liquid paraffin.

Example 2

The work is degreased and cleaned cathodically as in Example 1 and then activated and desensitized in

Hydrochloric acid (onc)	200 ml/litre
Mannitol	10 gpl

and by treating it cathodically for 2 minutes at 30°C with a current density of 4 asdm. Stainless steel or graphite is used as the anode. Then transferred to

the plating bath and plated for 100 minutes to get a thickness of 0.010".

Cuprous oxide	80 gpl
Hydrochloric acid	750 ml/l
Water	Balance
Temperature	50° C
Anode	Copper
Cathode current density	6 asdm.
Anode current density	3 asdm.
Area of anode- Cathode	2 : 1

The electrolyte is covered with a 1 cm thick layer of a liquid (a mixture of trichlorethylene and liquid paraffin in the ratio 1 : 5 by volume.)

The following are among the main advantages of the invention :

1. No initial undercoat in a strike bath prior to plating step is needed.
2. The plating rate for a given current density is twice that of a conventional acid bath.
3. By the use of activating and desensitizing etch as described, and as the plating bath itself contains hydrochloric acid, the surface is kept active throughout and ensures very good adhesion.
4. The bath has been protected against atmospheric oxidation by the use of a protective liquid layer and hence the performance of the bath is as good as the conventional copper plating baths.
5. By reducing the number of pretreatment steps and increasing the plating rate, the production rate is increased.
6. The bath is cheaper and easy to make and a rough estimate for the cost of production of copper deposit of thickness 0.0002" from this process is only one fourth of the cost by the conventional nickel chloride strike-acid copper plating method.
7. As the thickness of the deposit can range from a flash coating as for example 0.0002" to substantially thicker coatings (for example 0.010") with the quality of the deposit and adhesion very good, the process can be adopted to plate copper on stainless steel for functional purposes in the place of conventional methods, as for example, in
 1. the manufacture of bi and tri metallic printing plates,
 2. the manufacture of copper coated stainless steel heating utensils, and
 3. for lubrication during cold heading, wire drawing etc.

WE CLAIM :

1. A process for electrodeposition of copper directly on stainless steels from a new electroplating bath which consists in plating the articles of stainless steels in the following copper plating bath :

Cuprous ion	.03 M to 0.9M
Hydrochloric acid	2N to 10 N
Glue or gelatin or gum arabic	upto 5 gm/litre

and operated within the following range of conditions :

Temperature	25 C to 60 C
Anodes	Electrolytic or rolled copper
Cathodes	The work to be plated
Anode current density	0.5 asdm to 10 asdm
Cathode current density	0.5 asdm to 1.2 asdm
Anode to cathode area ratio	3: 1 to 1:1

2. A process as claimed in Claim 1 wherein the electrolyte of the said electroplating bath is protected against atmospheric oxidation by a layer of an organic liquid-the organic compounds of the said liquid being chosen from saturated hydrocarbons aliphatic and/or aromatic and/or mineral oils containing at least nine carbon atoms and or trichlorethylene or perchloroethylene.

3. A process for electrodeposition of copper directly on stainless steels from the new electroplating bath as claimed under claim (1) and protected against atmospheric oxidation by an organic liquid layer as claimed under claim (2) with a preceding step of activating the surface to be plated in the electrolyte containing—

Hydrochloric acid : 10-50% by volume

Desensitizing agents chosen from dextrin, cane sugar, carboxy methyl cellulose,

polyvinyl alcohol or gum arabic : 1-15 gm/litre and the activation of the surface is effected as follows :

either (a) by immersion for 1 to 5 minutes within the range of 25°C to 35°C,

or (b) by cathodic treatment for 2 to 5 minutes within the range of 25°C-35°C and cathodic current density 20-60 asf,

or (c) by anodic treatment for 2 to 5 minutes within the range of temperature 25°C to 35°C and anodic current density 20-60 asf.

Dated this 4th day of October, 1968.

Sd./-

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