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" IMPROVEMENTS IN OR RELATING TO THE PRODUCTION OF
COPPER FOILS SUITABLE FOR PRINTED CIRCUITS"

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 :

PRICE: TWO RUPEES
This is an invention by BALKUNJE ANANTHA SHENOI, Scientist, Central Electrochemical Research Institute, Karaikudi, Tamil Nadu, India and is an Indian National.

This invention relates to improvements in or relating to the production of copper foils suitable for printed circuits.

Hitherto it has been proposed to produce copper foils for printed circuits, and similar components by a process of electrodeposition from a solution containing mainly copper sulphate and sulphuric acid with certain addition agents like phenol sulphonic acid, citric acid or gelatin so that the produced copper foil will have the required mechanical properties. The current density employed is of the order of 15 A/dm².

This is open to the objection that in spite of the addition agents, the current density employed is low as a result of which continuous foil formation will not be feasible.

The object of this invention is to obviate these disadvantages by making certain addition of inorganic salts which will eliminate the above defect and facilitate application of high current densities of the order of 20-50 A/dm² for agitated solutions.

To these ends, the invention broadly consists in adding alkali metal salts of nitrates, perchlorates and fluoborates or respective acids singly or in combination to the above mentioned copper sulphate sulphuric acid bath. The concentration of such salts ranges between 5 and 12.5 g/l.
The following typical examples are given to illustrate the invention:

**EXAMPLE 1**

The electroforming of copper foil was carried out using the following bath composition adopting the usual procedure:

- Copper sulphate: 220 g/l
- Sulphuric acid: 60 g/l
- Aluminium sulphate: 14 g/l
- Cl⁻ ion: 30 mg/l
- Potassium perchlorate: 3 mg/l
- Current density: 27 A/dm²
- Temperature: 40°C
- Thickness of the foil: 12.5 mil
- Time: 1 hour

The copper foil obtained from the above bath was free from pittings and perforations. The stress measurement of the foil indicated that the additions of potassium perchlorate do not have any influence on stress.

**EXAMPLE 2**

The following bath composition was used for electroforming of copper foil:

- Copper sulphate: 210 g/l
- Sulphuric acid: 60 g/l
- Hydrochloric acid: 0.05 cc/litre
- Phenol sulphonic acid: 7 g/l
- Potassium perchlorate: 36°C
- Current density: 32 A/dm²
- Thickness: 15 mil

**EXAMPLE 3**

The electroforming of copper foil was carried out using the undermentioned bath:

- Copper sulphate: 250 g/l
- Sulphuric acid: 60 g/l
- Phenol sulphonic acid: 1.2 g/l
- Citric acid: 5.2 g/l
- Potassium perchlorate: 8 g/l
Current density: $32 \text{ A/dm}^2$
Plating time 1 hour
Temperature $45^\circ \text{C}$
Thickness obtained 15 mil/hour

The copper foil obtained from the above bath was comparable with the foil obtained from the conventional bath with regard to stress.

**EXAMPLE 4**

The following bath composition was used for getting electro-formed copper foil:

- Copper sulphate: $240 \text{ g/l}$
- Sulphuric acid: $75 \text{ g/l}$
- Casein: $0.3 \text{ g/l}$
- Gelatin or animal glue: $0.03 \text{ g/l}$
- Potassium perchlorate: $3 \text{ g/l}$
- Current density: $43 \text{ A/dm}^2$
- Temperature: $45^\circ \text{C}$
- Plating time: 2 hours
- Thickness of the copper foil: 40 mil

**EXAMPLE 5**

Electroforming of copper to obtain foil was carried out using the undermentioned bath:

- Copper sulphate: $220 \text{ g/l}$
- Sulphuric acid: $60 \text{ g/l}$
- Aluminium sulphate: $14 \text{ g/l}$
- Chloride ion: $30 \text{ mg/l}$
- Sodium nitrate: $5 \text{ g/l}$
- Temperature: $40^\circ \text{C}$
- Plating time: 1 hour
- Current density: $27 \text{ A/dm}^2$
- Thickness of the foil: 12.5 mil

**EXAMPLE 6**

The following copper plating bath was used to electroform copper foil:

- Copper sulphate: $210 \text{ g/l}$
- Sulphuric acid: $60 \text{ g/l}$
- Potassium nitrate: $12 \text{ g/l}$
- Hydrochloric acid: $0.05 \text{ cc/l}$
- Temperature: $40^\circ \text{C}$
Current density: 37.5 A/dm²
Plating time: 1 hour
Thickness of the foil 17.5 mil

**EXAMPLE 7**

Electroforming of copper foil was carried out using the bath composition given in Example 3 with the addition of potassium nitrate 15 g/l instead of potassium perchlorate for a duration of one hour at 45°C at a current density of 32.5 A/dm². The copper foil obtained was 15 mil thick.

**EXAMPLE 8**

The electroforming of copper foil was carried out using the bath described in Example 4 with the addition of sodium nitrate 5 g/l instead of potassium perchlorate for a duration of one hour at 43 A/dm² current density. The thickness of the copper foil obtained was 20 mil.

**EXAMPLE 9**

Electroforming of copper foil was carried out using the bath described in Example 1 using potassium fluoride 100 g/l instead of potassium perchlorate. Duration and current density of the plating was same as in Example 1.

Smooth uniform copper foil of thickness 12.5 mil was obtained.

**EXAMPLE 10**

Electroforming of copper foil was carried out using the bath composition described in Example 1 using a mixture of nitric acid (5 cc/l) and potassium perchlorate (3 g/l), instead of potassium perchlorate above under identical condition as in Example 1. Good uniform copper foil was obtained with a thickness of 12.5 mil.

In the same experiment, instead of nitric acid, fluoboric acid (5 cc/l) of the plating bath with potassium perchlorate (3 g/l) was used under same condition and copper foil of thickness 12.5 mil was obtained.
EXAMPLE 11

Electroforming of copper foil was carried out using the composition given in Example 1 using fluoboric acid 5 cc/l of the plating bath with potassium nitrate 5 gm per litre. Electroforming was carried out for one hour at 21.5 A/dm² current density and the thickness of the foil was found to be 10 mil.

The following are among the main advantages of the invention:

1. High current densities of the order of 20 to 50 A/dm² can be employed. This facilitates fast production when continuous foil formation is contemplated.

2. The crystal orientation of the copper has been found to be lamellar which facilitates uniform etching during preparation of the printed circuits using this foil.

Dated this 21st day of February, 1974.

sd/-
Asst. Patents Officer,
Council of Scientific & Industrial Research;
"Improvements in or relating to the production of copper foils suitable for printed circuits."

Council of Scientific & 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 invention relates to improvements in or relating to the production of copper foils suitable for printed circuits.

Hitherto it has been proposed to produce copper foils for printed circuits, and similar components by a process of electro-deposition from a solution containing mainly copper sulphate and sulphuric acid with certain addition agents like phenol sulphonic acid, citric acid or gelat in so that the produced copper foil will have the required mechanical properties. The current density employed is of the order of 15 A/dm².

This is open to objection that notwithstanding the addition agents, the current density employed is low as a result of which continuous foil formation will not be feasible.

The main object of the present invention is to obviate these disadvantages by making certain addition of inorganic salts which will eliminate the above defect and facilitate the application of high current densities of the order of 20-50 A/dm² for agitated solutions.

The main finding underlying the invention consists of the process of electroforming of copper on a stainless steel
mandrel from an aqueous electrolyzing bath comprising the following:

a) Copper sulphate 150 - 300 g/l
b) Sulphuric acid 40 - 150 g/l
c) and alkali metal salts of nitrates, perchlorates and fluoborates or respective acids singly or in combination as inorganic additions agent 1 - 15 g/l

and electroforming at current densities of the order of 20-50 A/dm² at temps of 30-50°C to produce pore free copper foil.

The new result flowing from the new finding is that the use of inorganic addition agent enables the production of pore free copper foil at high current densities of the order of 20-50 A/dm² suitable for printed circuits.

The present invention consists of a process for electroforming of copper foils suitable for printed circuits which comprises the steps of mechanical polishing and buffing of the stainless steel mandrel degreasing with trichloroethylene, alkaline cleaning in 5% sodium phosphate solution, passivating in a solution of 1% chromic acid, and subsequently the said mandrel is used as cathode in the aqueous electroforming bath containing 150-300 g/l copper sulphate, 40-150 g/l sulphuric acid along with 1-15 g/l of alkali metal salts of nitrates, perchlorates and fluoborates or respective acids singly or in combination as addition agent where in the said addition agent enables the production of pore free copper foils at relatively higher current densities of the order of 20-50 A/dm² at temps of 30-50°C. The said electroformed foil is ultimately separated from the mandrel and used in the production of printed circuits.
The flow sheet of the process is given in fig. 1.

The following typical examples are given to illustrate the invention and not to limit the scope of the invention.

**EXAMPLE 1**

A stainless steel plate of the size 25 cm x 25 cm was mechanically polished and buffed, degreased with trichloroethylene, cathodically cleaned in 5% sodium phosphate solution and passivated in 1% chromic acid for about three minutes before taking to the following electroforming bath:

- Copper sulphate: 220 g/l
- Sulphuric acid: 60 g/l
- Aluminium sulphate: 14 g/l
- Cl⁻ ion: 30 mg/l
- Potassium perchlorate: 3 g/l
- Current density: 27 A/dm²
- Temperature: 40°C
- Time: 1 hour
- Thickness of the foil: 12.5 mil
- Current efficiency: 96%

The copper foil obtained from the above bath was free from pittings and perforations. The stress measurement of the foil indicated that the addition of potassium perchlorate does not have any influence on stress.

**EXAMPLE 2**

The stainless steel plate was treated as in Example 1 and the following bath composition was used for electroforming of copper foil:

- Copper sulphate: 200 g/l
- Sulphuric acid: 150 g/l
- Hydrochloric acid: 0.05 cc/litre
- Potassium perchlorate: 1 g/l
- Temperature: 36°C
- Current density: 32 A/dm²
- Thickness: 15 mil
- Current efficiency: 96.5%
EXAMPLE -3

The electroforming of copper foil was carried out using the undermentioned bath:

- Copper sulphate: 300 g/l
- Sulphuric acid: 60 g/l
- Phenol sulphonic acid: 1.2 g/l
- Citric acid: 5.2 g/l
- Potassium perchlorate: 5 g/l
- Current density: 32 A/dm²
- Plating time: 1 hour
- Temperature: 45°C
- Thickness obtained: 15 mil/hour
- Current efficiency: 97%

The copper foil obtained from the above bath was comparable with the foil obtained from the conventional bath with regard to stress.

EXAMPLE -4

The following bath composition was used for getting electroformed copper foil:

- Copper sulphate: 240 g/l
- Sulphuric acid: 40 g/l
- Casein: 0.3 g/l
- Gelatin or animal glue: 0.03 g/l
- Potassium perchlorate: 3 g/l
- Current density: 43 A/dm²
- Temperature: 45°C
- Plating time: 2 hours
- Thickness of the copper foil: 40 mil
- Current efficiency: 95%

EXAMPLE -5

 Electroforming of copper to obtain foil was carried out using the undermentioned bath:

- Copper sulphate: 300 g/l
- Sulphuric acid: 60 g/l
- Phenol sulphonic acid: 1.2 g/l
- Citric acid: 5.2 g/l
- Potassium perchlorate: 5 g/l
- Current density: 32 A/dm²
- Plating time: 1 hour
- Temperature: 45°C
- Thickness obtained: 15 mil/hour
- Current efficiency: 97%
Copper sulphate: 220 g/l
Sulphuric Acid: 100 g/l
Aluminium sulphate: 14 g/l
Chloride ion: 30 mg/l
Sodium nitrate: 2.5 g/l
Temperature: 40°C
Plating time: 1 hour
Current density: 27 A/dm²
Thickness of the foil: 12.5 mil
Current efficiency: 94%

EXAMPLE - 6

The following copper plating bath was used to electroform copper foil:

- Copper sulphate: 210 g/l
- Sulphuric acid: 60 g/l
- Potassium nitrate: 12.5 g/l
- Hydrochloric acid: 0.05 cc/l
- Temperature: 40°C
- Current density: 37.5 A/dm²
- Plating time: 1 hour
- Thickness of the foil: 17.5 mil
- Current efficiency: 95.5%

EXAMPLE - 7

Electroforming of copper foil was carried out using the bath composition given in Example 3 with the addition of potassium nitrate (15 g/l) instead of potassium perchlorate for a duration of one hour at 45°C at a current density of 32.5 A/dm². The copper foil obtained was 15 mil thick. The current efficiency of the bath was 97%.

EXAMPLE - 8

The electroforming of copper foil was carried out using the bath described in Example 4 with the addition of sodium nitrate (5 g/l) instead of potassium perchlorate for a duration of one hour at 50 A/dm² current density. The thickness of the copper foil obtained was 25 mil and the current efficiency was 95%.

EXAMPLE - 9

Electroforming of copper foil was carried out using the bath described in Example 1 using potassium fluoborate (10.0 g/l) instead of potassium perchlorate. Duration and current density of the plating was same as in Example 1. Smooth uniform copper foil of thickness (12.5 mil) was obtained and the current efficiency was 94%.
Electroforming of copper foil was carried out using the bath composition described in Example 1 using a mixture of nitric acid (5 cc/l) and potassium perchlorate (3 g/l), instead of potassium perchlorate above under identical condition as in Example 1. Good uniform copper foil was obtained with a thickness of 12.5 mil and the current efficiency was found to be 96%.

In the same experiment, instead of nitric acid, fluoroboric acid (5cc/l) of the plating bath with potassium perchlorate (3 g/l) was used under same condition and a copper foil of thickness 12.5 mil was obtained. The current efficiency of the bath was 95%.

**EXAMPLE - 11**

Electroforming of copper foil was carried out using the composition given in Example 1 using fluoroboric acid (5 cc/l) of the plating bath with potassium nitrate (5 g/l). Electroforming was carried out for one hour at 21.5 A/dm² current density and the thickness of the foil was found to be 10 mil. The current efficiency of the bath was 94%.

In all the above Example, the electroformed copper foil was found to possess a lamellar structure. The replenishment of the bath was made by visualising the surface condition of the foil. This could also be done by the usual analytical methods.

The following are among the main advantages of the invention:

1. High current densities of the order of 20 to 50 A/dm² can be employed. This facilitates fast production when continuous foil formation is contemplated.

2. The crystal orientation of the copper has been found to be lamellar which facilitates uniform etching during preparation of the printed circuits using this foil.
I CLAIM

1. A process for electroforming of copper foils suitable for printed circuits which comprises the steps of mechanical polishing and buffing of the stainless steel mandrel, degreasing with trichloroethylene, alkaline cleaning in 5% sodium phosphate solution, passivating in a solution of 1% chromic acid and subsequently the said mandrel is used as cathode in the aqueous electroforming bath containing 150-300 g/l copper sulphate, 40-150 g/l sulphuric acid along with 1-15 g/l alkali metal salts of nitrates, perchlorates and fluoborates of respective acids singly or in combination as addition agents wherein the said addition agents enables the production of pore free copper foils at relatively higher current densities of the order of 20-50 A/dm² at temps. of 30-50°C, the said electroformed foil is ultimately separated from the mandrel and used in the production of printed circuits.

Dated this 20th day of February 1975.

sd/-
(R. BHASKAR PAI)
PATENTS OFFICER
COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH.
FIG. 1

FLOW SHEET

IMPROVEMENTS IN OR RELATING TO THE PRODUCTION OF COPPER FOILS SUITABLE FOR PRINTED CIRCUITS

MANDREL PREPARATION

POLISHING AND BUFFING

DEGREASING

ALKALINE CLEANING

RINSING

PASSIVATION

RINSING

ELECTROLYSING IN THE FORMING PATH

FOIL SEPARATION

R.B. PAI
PATENTS OFFICER
C.S.I.R.