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PROVISIONAL SPECIFICATION

"IMPROVEMENTS IN OR RELATING TO ELECTROLESS COPPER PLATING BATH CONTROL OVER ACRYLONITRILE BUTADIENE STYRENE"

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 describes the nature of this invention :—

This is an invention by Balkunje Anantha Shenoi, Scientist, and Mahalingom Ponnuthurai, Senior Laboratory Assistant both are Indian Nationals and are employed in the Central Electrochemical Research Institute, Karaikudi-3, India.

This invention relates to improvements in or relating to methods of electroless copper plating bath control over acrylonitrile butadiene styrene.

Hitherto it has been proposed to adopt the following procedures for electroless copper plating over ABS plastics which are used for preparing subsequent purposes.

As an example, bimetallic printing plates are usually prepared as follows :

The ABS plastic pieces are first sensitised and activated. And a thin coat is given from an electroless copper plating bath. If greater thickness is required, it can be done by plating from a conventional electroplating bath. Later, nickel or chromium or bath can be given.

An electroless copper plating bath, generally consists of a water-soluble copper salt, a complexing agent for cupric ion and an alkali metal hydroxide (and/or together with its carbonate) to render the required degree of alkalinity.

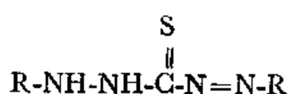
The water-soluble copper salts may be copper sulphate, copper(ic) chloride, copper(ic) nitrate, copper acetate, or copper gluconate and the complexing agent may be Rochelle salts, EDTA, sodium gluconate, sodium citrate, triethanolamine, and the like. The reducing agent, commonly used is formaldehyde or formalin or its polymerised forms.

To start the reducing action of formaldehyde, a suitable catalyser is required. For this, the surface of the substrate itself made to act like a catalyser by the well-known sensitisation activation treatments. When the thus-prepared substrate is submerged in the above mentioned electroless bath, a thin copper film is formed on the substrate by the reducing action of formaldehyde.

This is open to the objection that an electroless bath will not last long because of quick decomposition. Usually, an electroless copper plating bath will not last long even for a day or less than that.

Therefore, the main object of this invention is to stabilise the electroless copper plating bath which can be successively used for preparing copper coated ABS plastics and hence, for bimetallic printing plates. The electroless copper plating bath under consideration is stabilised by adding a suitable stabiliser which will facilitate the bath to be used for three days without the formation of copper deposit on the walls of container and without the formation of any precipitate.

To these ends, the invention broadly consists in adding small quantities of the stabilising compound having the empirical formula—



where 'R' is an aryl group. Herein the said compound which stabilises an aqueous electroless copper plating solution is diphenyl thiocarbazone.

The amount of the said stabiliser in the aqueous electroless copper plating solution ranges from 0.05 to 4 mgm per litre of the aqueous solution. The resultant bath can be used for three days without any copper deposit on the container.

The electroless copper plating bath herein used consists of a copper salt solution containing the pentahydrate of copper sulphate and a reducing agent usually formaldehyde, a reducing solution containing a nickel salt, a complexing agent for cupric ion as Rochelle salt and an alkali metal hydroxide and its carbonate. The electroless copper solution is prepared by mixing in the ratio 1 : 1 : 2 of copper salt solution, reducing solution and distilled water. The stabiliser is added to the above solution just before deposition in the quantities mentioned above.

The copper salt solution is prepared by dissolving 25 grams of copper sulphate pentahydrate in one litre of distilled water and to the above well-mixed solution of copper sulphate 250 ml of formaldehyde (37%) of formalin is added. The reducing solution is prepared by dissolving nickel chloride hexahydrate 8 grams, sodium potassium tartrate 90 grams, sodium hydroxide 20 grams and sodium carbonate 9 grams in one litre of distilled water.

The said stabiliser is dissolved in minimum amount of rectified spirit and is kept in a dark and cool place. Addition of fresh water to this, while preparing, should be avoided.

The substrate, herein used is ABS (acrylonitril-butadine-styrene) plastic, which was coloured. The ABS plastic pieces 2.5 cm.x2.5 cm. dimension are immersed in 200 ml. of electroless copper plating solutions containing the said stabiliser.

The weight of copper deposited on ABS plastics by the above method after two days of the preparation of the bath are given below :

Duration of immersion is 15-20 minutes.

Concentration of the said stabiliser per litre of solution	Time in hours	Weight of copper deposited in gms.	Nature of coating
*1 ml	51	0.0020	good
*2 ml	51	0.0022	good
*4 ml	51	0.0021	good
*6 ml	50	0.0018	good
*8 ml	50	0.0020	good

*Herein 0.5 gm of the said stabiliser is dissolved in one litre of rectified spirit.

It is, therefore, seen from the above column that even higher concentration of the addition agent has no greater effect.

The ABS plastic specimens are first chemically cleaned in a conventional aqueous alkaline cleaner and the cleaned specimens are conditioned by immersing in a chromic acid phosphoric acid sulphuric acid medium. The conditioned ABS plastic pieces are then cleaned thoroughly by forcing water on its surface so as to remove any chromic acid adhering in its indentations. The thus-conditioned ABS plastic pieces are then sensitised and activated in a stannous chloride solution acidified by hydrochloric acid and chloro platinous acid solution respectively.

The following typical examples are given to illustrate the invention :

After activation and sensitisation, the ABS plastic pieces are plated in the following electroless copper plating solution :

EXAMPLE 1

Copper Salt Solution A

$CuSO_4.5H_2O$ 21-23 grams is dissolved in one litre of the solution and 250 ml of formaldehyde is added to the above solution and thoroughly mixed.

Reducing Salt Solution A

$NiCl_2.6H_2O$	8 g/l
$KNaC_4H_4O_6.4H_2O$	30 g/l
NaOH	20 g/l
Na_2CO_3	9 g/l

The electroless copper solution is prepared by mixing the copper salt solution A, Reducing Salt Solution A and distilled water in the ratio 1 : 1 : 2 and 0.05-4 mgms per litre of stabiliser sufficient to stabilise the solution. This bath can be operated for more than 70 hours.

EXAMPLE 2

Copper Salt Solution B

$Cu\ SO_4.5H_2O$ 20-23 grams of copper sulphate is dissolved in one litre of the solution and 300 ml of formaldehyde is added to the above solution and thoroughly mixed.

Reducing Salt Solution B

$NiCl_2.6H_2O$	8 g/l
$KNaC_4H_4O_6.4H_2O$	100g /l
NaOH	20 g/l
Na_2CO_3	9 g/l

Copper Salt Solution B and Reducing Salt Solution B and distilled water are mixed in the ratio 1 : 1 : 2 and 0.05-4 mgm per litre of the said stabiliser sufficient to stabilise the solution. This bath can be operated for more than 70 hours.

All these sensitisation-activation and electroless plating processes are carried out below room temperature between 20-30°C.

The thin copper-film on the ABS plastic is thickened in a conventional electrolplating copper solution which has the following composition :

Cuprous cyanide	22.5 g/l
Sodium cyanide	16 g/l
Sodium carbonate	15 g/l
pH	11.5-12.5

The temperature of the bath is maintained at room temperature. A current density of 0.5 amp/dm² is useful. Beginning with a low current density and then to increase gradually is better.

The following are the main advantages of the invention :

1. By the said stabiliser, the above said electroless copper plating bath can be operated upto 70 hours with the same rate of deposition.

2. The copper plated from the electroless bath is adherent and completely covered.

3. No copper is wasted in the form of its powder or precipitate by the addition of the stabiliser.

Dated this 30th day of December, 1971.

(Sd/-)
Scientist Incharge,
Dte. of Research Co-ordination & Industrial Liaison
Council of Scientific & Industrial Research,
Rafi Marg, NEW DELHI.
for. PATENTS OFFICER,
C. S. I. R.

COMPLETE SPECIFICATION

"IMPROVEMENTS IN OR RELATING TO ELETROLESS COPPER PLATING BATH CONTROL OVER ACRYLONITRILE BUTADIENE STYRENE"

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 is an invention by Balkunje Anantha Shenoi, Scientist and Mahalingom Ponnuthurai, Senior Laboratory Assistant, both of the Central Electrochemical Research Institute, Karaikudi-3 both Indian citizens.

This invention relates to improvements in or relating to electroless copper plating bath control over acrylonitrile butadiene styrene.

Hitherto it has been proposed to adopt the following procedures for electroless copper plating over ABS plastics.

The ABS plastic pieces are first sensitised and then activated. And then a thin coat of copper is given from an electroless copper plating bath.

An electroless copper plating bath, generally, consists of a water soluble copper salt, a complexing agent for cupric ion and an alkali metal hydroxide (and/or its carbonate) to render the required degree of alkalinity.

The water soluble copper salt may be copper sulphate, copper chloride, copper nitrate, copper acetate or copper gluconate and the complexing agent may be Rochelle salt, ethylene diamine tetra acetic acid, sodium gluconate, sodium citrate, and triethanolamine. The reducing agent commonly used is formaldehyde or formalin or one of its polymerised forms.

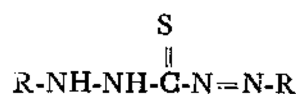
To start the reducing action of formaldehyde, a suitable catalyst is required. For this, the surface of the substrate itself is preconditioned to act like a catalyst by the well-known sensitisation-activation treatment. The activated substrate is dipped into the electroless bath when a thin film of copper is obtained on the surface by the reduction of copper ions by formaldehyde.

Drawbacks connected with the hitherto known process are that an electroless bath will not last long because of quick decomposition. Usually, an electroless copper plating bath will not last long for a day or even less than that.

Therefore, the main objective of this invention is to stabilise the electroless copper bath which can be continously used to prepare copper coated ABS plastics. The electroless copper bath under consideration is stabilised by adding a suitable stabiliser which will facilitate the bath to be used for three days without the formation of copper deposit either on the walls of the container or in the bulk of the solution.

The main finding underlying the invention broadly consists in adding small quantities of a stabilising compound which will stabilise the electroless bath to some extent.

To these ends, the invention broadly consists in adding small quantities of the stabilising compound having the empirical formula,



$$R\text{-}NH\text{-}NH\text{-}\overset{\overset{S}{\|}}{C}\text{-}N{=}N\text{-}R$$

where R is an aryl group. Herein the said compound which stabilises an aqueous electroless copper plating solution is diphenyl thiocarbazone.

The present invention consists of a process which comprises the perparation and use of an electroless copper plating bath containing pentahydrate of copper sulphate to give cupric ions, Rochelle salt as the complexing agent for cupric ions, a nickel salt, formaldehyde as the reducing agent and an alkali metal hydroxide and its carbonate to render the required degree of alkalinity; wherein diphenyl thiocarbazone acts as a stabiliser.

The electroless copper solution is prepared by mixing in the ratio 1 : 1 : 2 of copper salt solution, complexing salt solution and distilled water. The stabiliser is then added to the above solution just before deposition. The amount of the said stabiliser in the electroless copper plating solution may range from 0.05-4 mgm per litre.

The copper salt solution is prepared by dissolving 25 grams of copper sulphate pentahydrate in one litre of distilled water and to the well mixed solution of copper sulphate 250 ml of $CH_2=O$(37%) or formalin is added. The complexing salt solution is prepared by dissolving nickel chloride hexahydrate 8 grams, sodium potassium tartrate 90 grams, sodium hydroxide 20 grams, sodium carbonate 9 grams in one litre of distilled water. The said stabiliser is dissolved in a minimum amount of rectified spirit and is kept in the dark cool place.

The substrate herein used is ABS plastic. The ABS plastic pieces of the size 6.25 sq. cm are immersed in 200 ml of electroless copper plating solutions containing the said stabiliser.

The ABS plastic specimens are first chemically cleaned in a conventional aqueous alkaline cleaner. The clean specimens are conditioned by immersing in a chromic acid-phosphoric acid-sulphuric acid medium. The conditioned ABS plastic pieces are then washed thoroughly by forcing water onto its surface. The thus conditioned ABS plastic pieces are then sensitised in a stannous chloride solution acidified by hydrochloric acid and activated in chloro-platinous acid solution.

The following typical examples are given to illustrate the invention :

After sensitisation and activation, the ABS plastic pieces are plated in the following electroless copper plating solution :

EXAMPLE 1

Copper Salt Solution A

$CuSO_4.5H_2O$ 21-23 gms is dissolved in one litre of distilled water and 250 ml of formaldehyde is added to the above solution and thoroughly mixed.

Complexing Salt Solution A

$KNaC_4H_4O_6.4H_2O$	90 gpl
NaOH	20 gpl
Na_2CO_3	9 gpl
$NiCl_2.6H_2O$	8 gpl

The electroless copper solution is prepared by mixing the copper salt solution A, complexing salt solution A and distilled water in the ratio 1 : 1 : 2 and 2.0 mgms per litre of stabiliser sufficient to stabilise the solution. This bath can be operated for more than 70 hours.

EXAMPLE 2

Copper Salt Solution B

$CuSO_4.5H_2O$ 20-23 gms is dissolved in one litre of distilled water and 300 ml of formaldehyde is added to the above solution and thoroughly mixed.

Complexing Salt Solution B

$KNaC_4H_4O_6.4H_2O$	100 gpl
NaOH	20 gpl
Na_2CO_3	9 gpl
$NiCl_2.6H_2O$	8 gpl

Copper salt solution B and complexing salt solution B and distilled water are mixed in the ratio 1 : 1 : 2, 2.0 mgm per litre of the said stabiliser is sufficient to stabilise the solution. The bath is operated for more than 70 hours.

All these sensitisation-activation, and electroless plating processes are carried out between 20-30°C.

The thin copper-film on the ABS plastic is thickened in a conventional electroplating copper solution which had the following composition :

Cuprous cyanide	22.5 gpl
Sodium cyanide	16 gpl
Sodium carbonate	15 gpl
pH	11.5-12.5

The temperature of the bath is maintained between 27 and 31 °C. A current density of 0.5 amp/dm^2 is useful. Beginning with a low current density and then to increase gradually is better.

The following are among the main advantages of the invention :

1. By using the said stabiliser, the said electroless copper plating bath can be operated upto 70 hours with the same rate of deposition.

2. The copper plated from electroless bath is adherant and uniform.

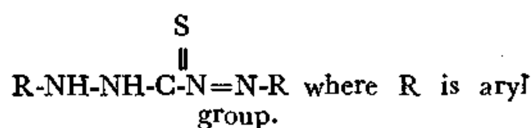
3. No copper is wasted in the form of its powdery state.

WE CLAIM :

1. A process for electroplating of copper over acrylonitrile butadiene styrene wherein copper salt solution of composition

A— Copper sulphate penta hydrate	21-23 g
Formaldehyde :	250 ml
Distilled water :	1000 ml
and a complexing salt solution B containing sodium potassium tartrate :	90 g/l
Sodium hydroxide :	20 g/l
Sodium carbonate :	9 g/l
Nickel chloride hexahydrate :	8 g/l

are mixed with distilled water in the ratio 1 : 1 : 2 with diphenyl thio carbazone as stabiliser compounds having the formula



2. A process as claimed in claim 1 wherein 2 milligrams of the stabiliser is added per litre of the bath for stabilising the electroless copper plating bath.

Dated this 1st day of January, 1973.

(Sd/-)

PATENTS OFFICER,

Council of Scientific & Industrial Research.

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