⑲ Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number: **0 180 265**
B1

⑫
EUROPEAN PATENT SPECIFICATION

㊺ Date of publication of patent specification: **19.04.89**

㉛ Int. Cl.^{4}: **C 23 C 18/46**

㉑ Application number: **85201585.8**

㉒ Date of filing: **02.10.85**

㊿
Method of autocatalytically tin-plating articles of copper or a copper alloy.

㉚ Priority: **05.10.84 NL 8403033**

㊸ Date of publication of application:
07.05.86 Bulletin 86/19

㊺ Publication of the grant of the patent:
19.04.89 Bulletin 89/16

(84) Designated Contracting States:
DE FR GB IT SE

(56) References cited:
GB-A-2 039 534
US-A-2 369 620

Surface Technology, 16(1982), pp. 265-275
Autocatalytic tin deposition", A. Molenaar,
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Courier Press, Leamington Spa, England.

Description

The invention relates to a method of autocatalytically tin-plating articles of copper or of a copper alloy.

GB—PS—2 039 534 discloses an electrolessly operating tin-plating solution which consists of a strongly alkaline aqueous solution containing at least 0.20 mol/litre of bivalent tin ions. The operating temperature of said solution is between 60 and 95°C and it contains at least 1 mol/litre of alkali hydroxide.

In a preferred embodiment a small quantity of tin (IV) ions and/or a strong reduction agent, for example hypophosphite or a borazane, is or are added to the solution. As a result of this an improvement of the quality of the deposit and the deposition rate is achieved.

However, the soldering properties of tin deposited electrolessly directly on a copper surface are insufficient in practice without additions. Even with an addition of hypophosphite, which for practical reasons is rather to be avoided, the desired soldering properties are often not obtained.

In an article by A. Molenaar and J. J. C. Coumans in Surface Technology *16*, 265—275 (1982) a method is described according to which a surface of copper or a copper alloy is subjected to a pre-treatment with a tin exchanging bath. This pre-treatment is carried out by means of an alkaline solution with cyanide ion as a complex forming agent for Cu^+ and/or Cu^{++} ions and for Sn^{++} ions.

In the experiments which have led to the present invention, however, it has been found that satisfactory results are not obtained in all respects with this method. The exchanged layer which is obtained from the alkaline solution has the structure of β-tin, the same modification which is also obtained from the autocatalytic solution. In spite of the fact that the same modification is deposited, often no optimum soldering properties are obtained.

According to the invention it has been found that considerably better soldering properties are obtained if the pre-treatment for the electroless deposition of the tin is carried out with an acid reacting exchanging solution with thiourea as a complex former for Cu^{++} and/or Cu^+ ions and for Sn^{++} ions.

In spite of the fact that the exchanged layer also comprises the alloy Cu_6Sn_5, better soldering properties are nevertheless obtained after growing said layer by means of the autocatalytic method which deposits tin in the form of the β-modification, than when an alkaline exchanging solution has been used for the pre-treatment.

These improved results cannot be well explained; they are ascribed by Applicants to the fact that adsorption of tin-II-complex having disproportionating properties is promoted by the exchanging reaction in acid medium with thiourea as a complex former for Cu^{++} and/or Cu^+ ions and for Sn^{++} ions.

An advantage of the use of the acid exchanging solution which preferably comprises thiourea as a complex former, as compared with the alkaline solution with cyanide, is that this solution is not poisonous.

Various acids may be used in the exchanging solution, for example, hydrochloric acid, sulphuric acid or citric acid, but the very best results are obtained by means of a sulphuric acid solution.

One embodiment has the following composition:

0.02 mol/l $SnCl_2 \cdot 2H_2O$
0.2 mol/l H_2SO_4
0.6 mol/l thiourea.

This aqueous solution is preferably used at a temperature between 20 and 30°C, the articles being kept immersed in it for 10 minutes.

The best result as regards the quality and the adhesion of the tin deposit is obtained when the surface of copper or the copper alloy is previously cleaned. This cleaning may be done mechanically or chemically. The chemical method may be a cleaning, polishing or etching method but the surface is preferably treated by means of a chemical polishing solution.

One embodiment has the composition:

55 parts by volume of phosphoric acid (85% by weight)
25 parts by volume of acetic acid (100% by weight)
20 parts by volume of nitric acid and (65% by weight)
0.5 parts by volume of hydrochloric acid (37% by weight).

Herein the articles are kept immersed at room temperature for 30—60 seconds.

The electroless tinplating solution, the treatment in which follows the exchange-pretreatment, comprises an aqueous solution containing at least 0.20 mol/l of a salt of bivalent tin and at least 1 mol/l of alkalihydroxide, works with these bath-constituents only. However, it is advantageous if the solution contains also a complex-forming agent for bivalent tin-ions, such as citrate or tartrate. The presence of tartrate is to be preferred as higher tin-concentrations are then attainable. The presence of citrate or tartrate moreover produces a tin-deposit of further improved solderability.

By giving an additional treatment in a solution of about pH=6 (4—8) without further constituents after the exchange-treatment and prior to the electroless Sn-plating, also the solderability and the structure of the deposited tin are favourably influenced.

In certain cases it may be advantageous to nevertheless add hypophosphite to the autocatalytic solution. The reliability of the soldered joint is further increased by the combination of pre-treatment and addition of hypophosphite to the autocatalytic solution.

US—A—2 369 620 discloses an acid tin immersion bath containing $SnCl_2$, H_2SO_4 and thiourea. With this bath only thin layers are obtained after a long time, e.g. 2.3 mg Sn/cm^2 after 24 hours. The process according to US—A—2 369 620 is based on the principle of metal exchange. It is possible to continue deposition, but the increase in the amount of deposited Sn vs time is due to the fact that the obtained tin coating is not dense, but porous. In that case tin growth continues as long as parts of the copper surface are still uncoated. The solderability of these layers is poor. There is no suggestion to use such an acid immersion bath as a pre-treatment solution for an autocatalytic tin bath.

The invention will be described in greater detail with reference to the ensuing examples.

Example 1

Copper plates having dimensions 3×1 cm^2 were subjected to the following treatments.

A dull Cu layer of 15 µm was electro-deposited on said plates by means of an acid copper sulphate bath. They were then rinsed in water and polished in the solution of the following composition for 1 minute:

55 parts by volume of H_3PO_4 (85% by weight)
25 parts by volume of acetic acid (100% by weight)
20 parts by volume of HNO_3 (65% by weight)
0.5 parts by volume of HCl (37% by weight)

and rinsed again in demineralized water for 30 seconds. One of the methods below was then used:

I no exchange

II the plates were immersed at 30°C in the following aqueous solution for 10 minutes:

0.02 mol/l $SnCl_2 \cdot 2H_2O$
0.6 mol/l thiourea
0.2 mol/l H_2SO_4

III the plates were immersed at 75°C in the following aqueous solution for 5 minutes:

0.02 mol/l $SnCl_2 \cdot 2H_2O$
0.2 mol/l NaOH
0.8 mol/l KCn

They were rinsed in demineralized water for 30 seconds. The plates were electrolessly tin-plated at 75°C for 3 hours in the following aqueous solution:

0.33 mol/l $SnCl_2 \cdot 2H_2O$
3.85 mol/l NaOH
0.66 mol/l sodium citrate

and finally rinsed in demineralized water for 30 seconds. The tin-plated plates were aged by heating them in a hot air furnace at 155°C for 16 hours. The solderability was determined by means of a so-called wetting balance ("Multicore Solders") as described *inter alia* in Circuit World *10*, No. 3, *pp*. 4—7, 1984. The forces occurring upon providing a sample in a soldering bath in accordance with time are measured by the recording apparatus coupled to said balance. The plates were immersed edge-wise while using a slightly activated flux in a liquid soldering bath. In the first instance an upward force was exerted on the plates which decreases when the surface layer of the solder has flattened along the plate. The time expiring inbetween is indicated by t_1. The wetting then causes a downward force. The fraction of said force which is measured after 3 seconds with respect to an ideally wetted plate is indicated by F_3/F_{max}.

This method of measuring is described in the IEC standard sheet 68-2-20. The value of t_1 must in practice be smaller than 1 sec and F_3/F_{max} must be larger than 50%.

The following results were measured:

	t_1(sec)	F_3/F_m(%)
I	>4	0
	>4	0
II	0.6	63
	0.6	64
	0.6	69
	0.8	59
III	>4	0
	1.1	47

In the same manner a test was carried out starting from copper plates without a dull electroplated copper layer. Exchange II (acid exchange with thiourea) and III (alkaline exchange with cyanide) were used. The results hereof are:

	t_1	F_3/F_m(%)
II	0.8	71
	1.0	46
III	>6	0
	>6	0

Example 2

The connection wires of glow discharge lamps consisting of copper-clad wire having a diameter of 3 and 4 millimetres were subjected to the following treatment. First of all they were immersed for 10 seconds in H_2SO_4 (48% by weight) at 90°C, then rinsed with demineralized water for 10 seconds and polished in the following solution for 30 seconds:

55 parts by volume of H_3PO_4 (85% by weight)
25 parts by volume of acetic acid (100% by weight)
20 parts by volume of HNO_3 (65% by weight)
0.5 parts by volume of HCl (37% by weight).

After rinsing with demineralized water for 30 seconds one of the two exchanging methods was used:

II the connection wires were dipped at 30°C in the following aqueous solution for 15 minutes:

0.02 mol/l $SnCl_2 \cdot 2H_2O$
0.6 mol/l thiourea
0.2 mol/l H_2SO_4,

or

III the connection wires were immersed at 75°C for 15 minutes in the following aqueous solution:

0.02 mol/l $SnCl_2 \cdot 2H_2O$
0.2 mol/l NaOH
0.8 mol/l KCN.

They were then rinsed again with demineralized water for 30 seconds and electrolessly tin-plated for 30 minutes by immersing in the following aqueous solution at 75°C:

0.33 mol/l $SnCl_2 \cdot 2H_2O$
3.85 mol/l NaOH
0.66 mol/l Na-citrate

and finally rinsed in demineralized water for 30 seconds. The tin-plated connection wires were aged either for 16 hours at 155°C in a hot air furnace (furnace test) or for 16 hours in steam of 100°C; RV 100% (steam test). The solderability was determined in the same manner as in Example 1.

	Diameter connection wires (mm)	Furnace test		Steam test	
		t_1(sec)	F_3/F_m(%)	t_1(sec)	F_3/F_m(%)
II	3	0.3	75	0.4	92
	3	0.4	75	0.3	100
	3	0.3	92	0.3	100
	3	0.3	92	0.4	75
	4	0.6	47	0.4	82
	4	0.4	47	0.4	68
	4	0.3	90	0.4	90
	4	0.3	74	0.3	68
III	3	3	0	3.5	0
	3	2	8	>6	0
	3	3	0	>6	0
	3	4	0	5.5	0
	4	3.5	0	>6	0
	4	0.5	67	>6	0
	4	4	0	>6	0
	4	2	8	>6	0

Example 3

Copper plates having dimensions of 3×1 cm^2 were subjected to the following treatments. First of all they were coated by electrodeposition with a dull copper layer of 15 μm by means of an acid copper sulphate bath, rinsed in water and subjected to one of the following cleaning treatments:

I immerse at 30°C for 1 minute in

55 parts by volume of H_3PO_4 (85% by weight)
25 parts by volume of acetic acid (100% by weight)
20 parts by volume of HNO_3 (65% by weight)
0.5 parts by volume of HCl (37% by weight)

immerse for 1 minute in HCl (20% by weight) at room temperature.

II immerse at room temperature for 1 minute in

60 ml H_2SO_4 (96% by weight)
60 ml H_2O
30 ml HNO_3 (65% by weight)
9.4 ml HCl (37% by weight)

immerse in HCl at room temperature for 1 minute.

III immerse in HNO_3 (38% by weight) at room temperature for 1 minute.

IV immerse in HCl (20% by weight) at room temperature for 1 minute.

After each of these treatments the plates were rinsed in demineralized water for 30 seconds and then the plates were immersed at 30°C for 10 minutes in the following aqueous solution:

0.02 mol/l $SnCl_2 \cdot 2H_2O$
0.2 mol/l thiourea
0.2 mol/l H_2SO_4

and again rinsed in demineralized water for 30 seconds.

The plates were finally tin-plated electrolessly at 75°C for 3 hours by immersing in the following aqueous solution:

0.33 mol/l $SnCl_2 \cdot 2H_2O$
3.85 mol/l NaOH
0.66 mol/l Na-citrate
0.90 mol/l NaH_2PO_2

and rinsed in demineralized water for 30 seconds.

The etching rates of the said cleaning treatments are as follows:

I 2.5 µm/min.
I 11 µm/min.
III 10 µm/min.
IV 0 µm/min.

After tin-plating, the plates were aged at 155°C in a hot-air furnace for 16 hours. The solderability was determined in the same manner as in Example 1.

The solderability was evaluated as follows:

	t_1(sec)	F_3/F_m(%)
I	0.8	57
	0.7	46
II	0.6	67
	0.6	72
III	0.5	78
	0.5	75
IV	0.8	58
	0.6	64

Example 4

Copper plates having dimensions 3×1 cm^2 were subjected to the following treatments.

A dull copper layer of 15 µm was electrodeposited on them by means of an acid coppersulphate bath. They were subsequently rinsed in water and during one minute polished in the solution of the following composition:

55 parts by volume of H_3PO_4 (85% by weight)
25 parts by volume of acetic acid (100% by weight)
20 parts by volume of HNO_3 (65% by weight)
0.5 parts by volume of HCl (37% by weight)

and rinsed again in demineralized water during 30 seconds.

Hereafter the plates were immersed during 10 minutes at 30°C in the following aqueous solution:

0.02 mol/l $SnCl_2 \cdot 2H_2O$
0.6 mol/l thiourea
0.2 mol/l H_2SO_4.

After rinsing with demineralized water during 30 seconds one of the following three tinplating methods were applied.

I The plates were electrolessly tin-plated during 3 hrs at 75°C in an aqueous solution of the following composition:

0.33 mol/l $SnCl_2 \cdot 2H_2O$
2.5 mol/l NaOH

II The plates were electrolessly tin-plated during 3 hours at 75°C in an aqueous solution of the following composition:

0.33 mol/l $SnCl_2 \cdot 2H_2O$
2.5 mol/l NaOH
0.66 mol/l sodiumcitrate.

This solution was prepared by dissolving the Na-citrate in about half of the volume of water and adding the $SnCl_2 \cdot 2H_2O$ (soln. 1), dissolving NaOH in about half of the volume of water (soln. 2) and combine solutions 1 and 2 while stirring vigorously.

III The plates were electrolessly tin-plated at 75°C during 3 hours in an aqueous solution of the following composition:

0.42 mol/l $SnCl_2 \cdot 2H_2O$
2.5 mol/l NaOH
0.50 mol/l Na-K-tartrate.

This solution was prepared by dissolving the Na-K-tartrate in about half of the volume of water, dissolving the NaOH in the remaining volume of water, combining the two solutions and adding thereto the $SnCl_2 \cdot 2H_2O$.

Finally, the plates were rinsed in demineralized water during 30 seconds. The tin-plated samples were aged during 16 hours at 155°C in a hot-air furnace. The solderability was determined in the same way as in Example 1.

The results are as follows:

	t_1(sec)	F_3/F_m(%)
I	1.4	36
	1.9	25
	0.6	52
	1.6	37
II	0.9	60
	1.0	45
	0.6	57
	1.0	39
	0.6	63
	0.8	50
	0.6	75
	0.6	70
	0.7	41
	1.0	52
III	0.6	79
	0.5	77
	0.8	71
	0.5	78
	0.5	77
	0.5	83
	0.5	85
	0.6	85
	0.6	89
	0.5	83

Claims

1. A method of autocatalytically tin-plating articles of copper or of a copper alloy in which the articles are first of all subjected to a pre-treatment with an aqueous solution of a bivalent tin salt and a complex former for Cu^{++} and/or Cu^{+} ions and for Sn^{++} ions, with which a layer of copper is exchanged for tin after which the article is immersed in a strongly alkaline aqueous solution which contains at least 0.20 mol/l of bivalent tin ions and at least 1 mol/l of alkalihydroxide at a temperature between 60 and 95°C, wherein the pre-treatment solution is an acid solution comprising thiourea as a complex former.

2. A method as claimed in Claim 1, characterized in that the pre-treatment is carried out in a sulphuric acid-containing solution.

3. A method as claimed in Claim 1 or 2, characterized in that the pre-treatment is carried out in an aqueous solution which contains

0.02 mol/l $SnCl_2 \cdot 2H_2O$
0.2 mol/l H_2SO_4 and
0.6 mol/l thiourea.

4. A method as claimed in any of the Claims 1 to 3, characterized in that the articles of copper or a copper alloy are cleaned mechanically or chemically before they are exposed to the exchanging solution.

5. A method as claimed in any one of Claims 1 to 4, characterized in that the strongly alkaline, bivalent tin-ions containing aqueous solution also contains a complex-forming agent for bivalent tin-ions.

6. A method as claimed in Claim 5, characterized in that the complex-forming agent is citrate or tartrate.

7. A method as claimed in any of the Claims 1 to 6, characterized in that the strongly alkaline bivalent tin-ions containing solution also comprises a soluble hypophosphite.

Patentansprüche

1. Verfahren zur autokatalytischen Verzinnung von Gegenständen aus Kupfer oder Kupferlegierung, wobei die Gegenstände zunächst mit einer wässrigen Lösung eines zweiwertigen Zinnsalzes und eines Komplexformers für Cu^{++}- und/oder Cu^{+}-Ionen vorbehandelt werden, wodurch eine Kupferschicht gegen eine Zinnschicht ausgewechselt wird, wonach der Gegenstand in eine stark alkalische wässrige Lösung getaucht wird, die wenigstens 0,20 mol/l zweiwertige Zinnionen und wenigstens 1 mol/l Alkalihydroxide aufweist bei einer Temperatur zwischen 60 und 95°C, dadurch gekennzeichnet, dass die Vorbehandlungslösung eine saure Lösung ist mit Thioharnstoff als Komplexformer.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, dass die Vorbehandlung in einer schwefelsäurehaltigen Lösung durchgeführt wird.

3. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, dass die Vorbehandlung in einer wässrigen Lösung mit

0,02 mol/l $SnCl_2 \cdot 2H_2O$
0,2 mol/l H_2SO_4 und
0,6 mol/l Thioharnstoff

durchgeführt wird.

4. Verfahren nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, dass die Gegenstände aus Kupfer oder einer Kupferlegierung mechanisch oder chemisch gereinigt werden, bevor sie der Auswechsellösung ausgesetzt werden.

5. Verfahren nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, dass die stark alkalische, zweiwertige Zinnionen enthaltende wässrige Lösung ebenfalls ein Komlexformmittel für zweiwertige Zinnionen aufweist.

6. Verfahren nach Anspruch 5, dadurch gekennzeichnet, dass das Komplexformmittel Zitrat oder Tartrat ist.

7. Verfahren nach einem der Ansprüche 1 bis 6, dadurch gekennzeichnet, dass die stark alkalische, zweiwertige Zinnionen enthaltende wässrige Lösung ebenfalls ein lösliches Hypophosphit aufweist.

Revendications

1. Procédé pour l'étamage autocatalytique d'objets en cuivre ou en un alliage de cuivre selon lequel les objets sont d'abord soumis à un traitement préalable dans une solution aqueuse d'un sel d'étain bivalent et d'un formateur de complexes pour les ions Cu^{++} et/ou Cu^{+} et pour les ions Sn^{++}, avec laquelle une couche de cuivre est échangée contre de l'étain après quoi l'objet est immergé dans une solution aqueuse fortement alcaline contenant au moins 0,20 mole/l d'ions étain bivalent et au moins 1 mole/l d'hydroxyde alcalin à une température comprise entre 60 et 95°C, selon lequel la solution de traitement préalable est une solution acide contenant de la thiourée comme formateur de complexes.

2. Procédé selon la revendication 1, caractérisé en ce que le traitement préalable s'effectue dans une solution contenant de l'acide sulfurique.

3. Procédé selon la revendication 1 ou 2, caractérisé en ce que le traitement préalable s'effectue dans une solution aqueuse contenant

0,02 mole/l de $SnCl_2 \cdot 2H_2O$
0,2 mole/l de H_2SO_4 et
0,6 mole/l de thiourée.

4. Procédé selon l'une des revendications 1 à 3, caractérisé en ce que les objets en cuivre ou en un alliage de cuivre sont nettoyés mécaniquement ou chimiquement avant d'être exposés à la solution d'échange.

5. Procédé selon l'une des revendications 1 à 4, caractérisé en ce que la solution aqueuse fortement alcaline contenant des ions étain bivalent contient également un agent formateur de complexes pour les ions étain bivalent.

6. Procédé selon la revendication 5, caractérisé en ce que l'agent formateur de complexes est du citrate ou du tartrate.

7. Procédé selon l'une des revendications 1 à 6, caractérisé en ce que la solution fortement alcaline contenant des ions étain bivalent contient également un hypophosphite soluble.