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(54) Metal plating composition for deposition of tin-zinc alloys onto a substrate

(57) A tin-zinc alloy plating bath composition comprising a quaternary ammonium polymer additive. A process for deposition of tin-zinc alloys from a plating bath composition comprising a quaternary ammonium plating additive onto a substrate.

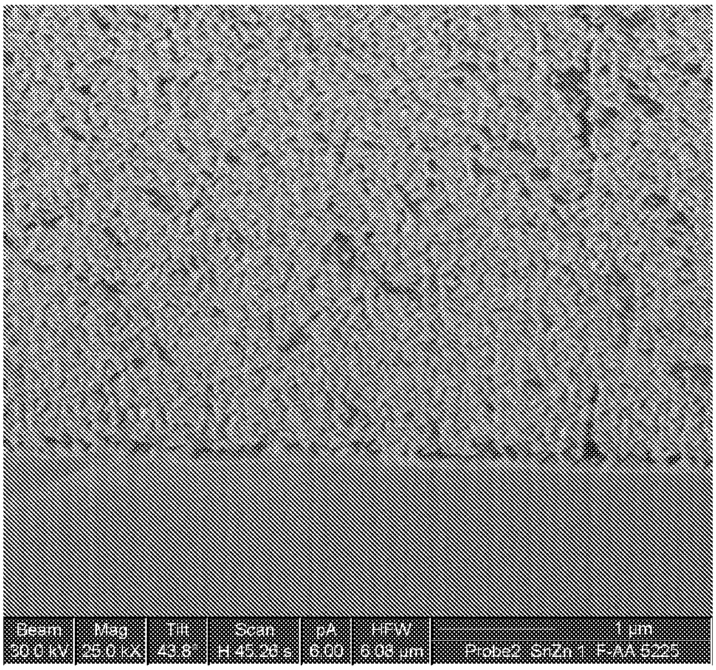

Figure 1

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Description

Field of the Disclosure

[0001] The present invention relates to electroplating bath compositions for the deposition of tin-zinc alloys useful for corrosion protection of a metal substrate. Further, the invention relates to a process for the preparation of additives and their use in said metal plating compositions.

Background of the Invention

[0002] The electrodeposition of tin-zinc alloys is used for, e.g., corrosion protection of metal substrates, especially steel substrates.

[0003] The corrosion protection capability by tin-zinc alloy deposits depends on various parameters such as small grain size of the deposit (Y.-S. Choi, P. Ganesan, S. P. Kumaraguru, B. N. Popov "Development of Sacrificial Zn-Sn Coatings by a Pulse Electrodeposition Process", Journal of Applied Surface Finishing 2 (1), 29-36 (2007)).

[0004] The deposits in most cases consist of mixtures of individual tin and zinc grains. Such deposits are referred herein as tin-zinc alloys. Mostly, no alloy particles of Sn_xZn_y type are formed. Therefore, it is important to generate a deposit with a homogeneous distribution of tin and zinc domains (i.e., grains) within the deposits in order to obtain a good corrosion protection.

[0005] Another important factor influencing the capability of corrosion protection of tin-zinc alloy deposits is a homogeneous composition distribution of said deposits. Many efforts were taken to improve the compositional homogeneity.

[0006] The above mentioned criteria, i.e., a narrow compositional homogeneity range for a tin-zinc alloy deposit to enable good corrosion protection to a metal substrate can be fulfilled by selecting appropriate additives to be added to the metal plating composition.

[0007] Polyquaternary amine compounds of different types have been suggested to deposit zinc and zinc alloy coatings possessing a good corrosion protection.

[0008] Polycondensation products obtained by reacting of di-tertiary amines with a methylene linker are disclosed in EP 1 114 206 B1. Polycondensation products derived from di-tertiary amines including an amide or thioamide functional group and ether type linkers are disclosed as additives for zinc and zinc-transition metal alloy plating compositions in US 5,405,523 and US 5,435,898, and for application in tin-zinc alloy plating compositions in EP 1 201 789 B9. Document WO 02/08497 discloses polycondensation products derived from di-tertiary amines including an amide or thioamide functional group with a linker bearing an unsaturated moiety and optionally a second di-tertiary amine with or without an unsaturated moiety as additives for zinc and zinc alloy plating compositions. Furthermore, WO 02/08497 describes another type of additive derived by polycondensation of a di-tertiary amine including an amide or thioamide functional group, a di-tertiary amine without an amide or thioamide functional group and a linker.

[0009] The above discussed additives for tin-zinc alloy plating compositions are suitable for tin-rich tin-zinc alloy deposits with a tin content > 50 wt.-% but suffer from higher deviations from the targeted composition for tin-zinc alloys deposits with a tin content of 30 to 50 wt.-%.

Object of the Invention

[0010] The object of the present invention is to provide a metal plating composition, which can be used to deposit a tin-zinc alloy layer with a composition of 0.1 to 99.9 wt.-% Sn, more preferred 20 to 60 wt.-% Sn and most preferred 30 to 50 wt.-% Sn on a metal substrate. The deposited tin-zinc alloy layer preferably shows the following properties:

(i) Small (< 1μm) and uniform grain size of deposited Sn and Zn particles

(ii) homogeneous distribution of Sn and Zn domains in the deposit

(iii) good corrosion protection to a substrate.

[0011] Furthermore, the tin-zinc alloy plating composition should allow to reach the above mentioned criteria in a wide range of current densities and lead to deposits of high brightness.

Summary of the Disclosure

[0012] The present invention relates to an aqueous tin-zinc alloy plating bath composition comprising a novel type of additives for deposition of tin-zinc alloy layers on metal substrates. Furthermore, the inventive plating bath composition allows the deposition of tin-zinc alloys with a tin content of 30 to 50 wt.-% in a wide current density range of 0.01 to 10 A/dm^2.

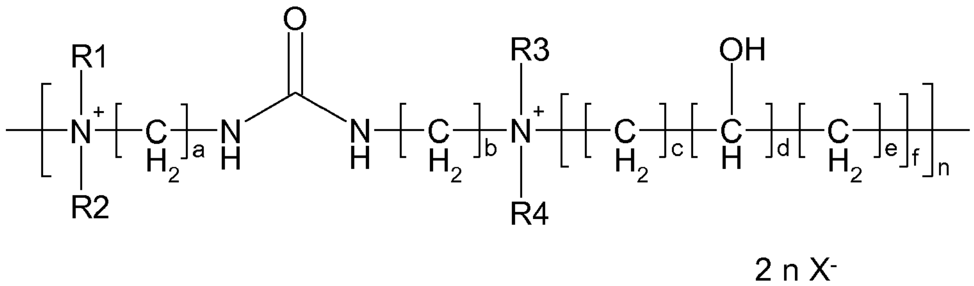
Brief Description of the Figures

[0013]

> Figure 1 shows a FIB-SEM micrograph of a tin-zinc alloy layer coated on a metal substrate derived from example 1. The additive used in the corresponding plating bath composition was the polycondensation product of N,N'-Bis (dimethylaminopropyl)urea and 1,3-Dichlor-propan-2-ol according to the present invention. The micrograph shows a uniform distribution of tin and zinc grains within the tin-zinc alloy deposit. (FIB-SEM = Focused Ion Beam-Scanning Electron Microscope)
>
> Figure 2 shows a FIB-SEM micrograph of a tin-zinc alloy layer deposited from a prior art plating bath composition on a metal substrate derived from example 2. The additive used in the corresponding plating bath was Mirapol A-15 (disclosed in example 1 of EP 1 201 789 B9). The dark spots within the tin-zinc alloy deposit are composed of tin. The distribution of tin and zinc grains is not as uniform as in the deposit derived from an plating bath containing an additive from the present invention (example 1).

Detailed Description of the Invention

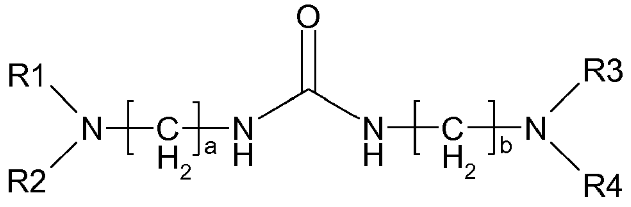
[0014] The aqueous tin-zinc plating bath composition comprises stannous ions in form of at least one water soluble stannous salt, at least one water soluble zinc salt, at least one acid and at least one quaternary ammonium polymer additive which is represented by formula I:



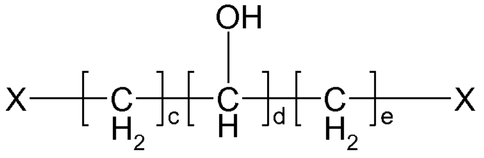
Formula I

wherein a, b, c, d, e and f are identical or different and represent an integer ranging from 1 to 5, n is an integer greater than 1, R1, R2, R3 and R4 are identical or different and represent a substituted or unsubstituted C1 to C6 alkyl or a $-CH_2CH_2(OCH_2CH_2)_y-OH$ residue, wherein y is ranging from 1 to 6, and X- is a suitable anion. The substituted or unsubstituted C1 to C6 alkyl residues R1, R2, R3 and R4 are more preferred selected independently from the group consisting of methyl, ethyl, propyl and butyl and their hydroxy derivatives.

[0015] Said quaternary ammonium polymers may be prepared by a condensation polymerization of one or more amine monomers of formula III, wherein R1, R2, R3, R4, a and b are defined as in formula I, with one or more hydroxyl functionalized aliphatic dihalogenide compound of formula IV, wherein c, d, e and X are defined as in formula I.



Formula III



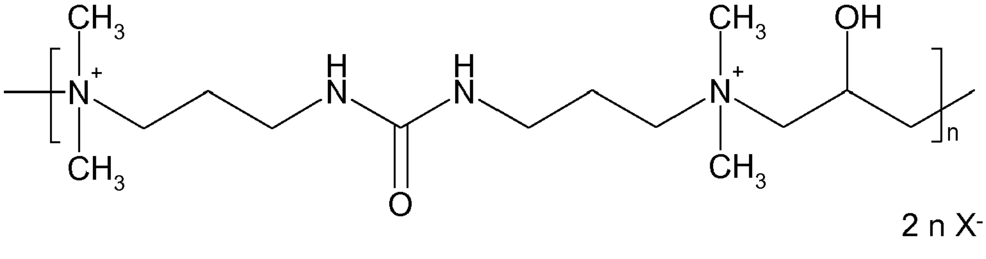
Formula IV

[0016] The molecular weight of the quaternary ammonium polymer according to formula I may range from about 500 to 100,000 Da, preferred from about 5,000 to 30,000 Da.

[0017] The amount of the quaternary ammonium polymer according to formula I included in the tin-zinc alloy plating bath composition is added in an amount sufficient to provide desired improvements in the deposited tin-zinc alloy such as reduced burning of high current density deposits, homogeneous composition of tin and zinc domains in the deposit, fine and uniform grain size and improved corrosion resistance.

[0018] Preferably, the tin-zinc alloy plating bath composition of the present invention contain from about 0.1 to 10 g/l of the quaternary ammonium polymer according to formula I, more preferred 0.2 to 6 g/l.

[0019] In one embodiment, the inventive additive is characterized by formula II.



Formula II

wherein n is greater than 10 and X- is a halogenide or pseudohalogenide ion.

[0020] Pseudohalogenide ions are selected from the group comprising -OCN, -NCO, -CNO, -SCN, -NCS, alkylsulfonates, mesitylate and triflate.

[0021] The tin-zinc alloy plating bath composition of the present invention will contain stannous ions in a concentration of about 1 to 100 g/l, more preferred 5 to 40 g/l. The one or more source of stannous tin ions is preferably selected from the group comprising tin(II) sulfate, tin(II) methanesulfonate, tin(II) chloride, tin(II) fluoride, tin(II) sulfamate, tin(II) acetate and tin(II) oxide. Further, the tin-zinc alloy plating bath composition contains zinc ions in a concentration of about 1 to 100 g/l, more preferred 5 to 50 g/l. The one or more source of zinc ions is preferably selected from the group comprising zinc sulfate, zinc methanesulfonate, zinc sulfamate, zinc chloride, zinc fluoride, zinc acetate and zinc fluoroborate. The weight ratio of tin and zinc ions in the plating bath composition is ranging from 1 : 5 to 5 : 1, more preferred 2 : 5 to 5 :

2 and is most preferred 2 : 3. Throughout this written description of the invention, the range and ratio limits may be combined.

[0022] The composition of the tin-zinc alloy deposit derived from the metal plating bath contains 0.1 to 99.9 wt.-% of tin, preferred 20 to 60 wt.-% of tin and most preferred 30 to 50 wt.-% of tin.

[0023] The tin-zinc alloy plating bath composition of the invention also may contain one or more conducting salts such as sodium chloride, sodium fluoride, sodium sulfate, potassium chloride, potassium fluoride, potassium sulfate, ammonium chloride, ammonium fluoride and/or ammonium sulfate in an amount of about 50 to 300 g/l or more. In one embodiment, the conductive salt is a chloride, the stannous salt is a chloride, and the zinc salt is a chloride, thus forming an "all chloride" plating composition.

[0024] The tin-zinc alloy plating bath composition of the present invention also contains at least one acid. Suitable acids are hydroxy polycarboxylic acid and/or hydroxy carboxylic acid with about 3 to 15 carbon atoms per molecule, or a water soluble salt thereof. In one embodiment, the hydroxy polycarboxylic acids and/or hydroxy carboxylic acid contains 3 to 7 carbon atoms. Mixtures of hydroxy carboxylic acids can be utilized. Examples of hydroxy carboxylic acids which can be utilized for the tin-zinc plating bath composition of the present invention include monohydroxy and polyhydroxy carboxylic and polycarboxylic acids such as tartaric acid, malic acid, citric acid, gluconic acid and their respective salts, e. g., sodium, potassium or ammonium salts. Citric acid is a particularly useful hydroxy polycarboxylic acid for the tin-zinc plating bath composition of the present invention. Both stannous and zinc ions form complexes with hydroxy polycarboxylic acids like citric acid. The amount of hydroxy carboxylic acid ranges from about 5 to 200 g/l, more preferred from 10 to 150 g/l.

[0025] When used with one or more brightener compositions such as aromatic aldehydes and ketones, improved brightness is obtainable. Such brightener compositions are known in the art (see for example EP 1 201 789). Examples of aromatic aldehydes known as brightener additives in tin-zinc alloy plating electrolytes are benzaldehyde, o-chlorbenzaldehyde, m-chlorbenzaldehyde, p-chlorbenzaldehyde, o-hydroxybenzaldehyde, m-hydroxybenzaldehyde, p-hydroxybenzaldehyde, o-aminobenzaldehyde, verataldehyde, 2,4-dichlorbenzaldehyde, 3,4-dichlorbenzaldehyde, 3,5-dichlorbenzaldehyde, 2,6-dichlorbenzaldehyde, tolualdehyde, 3,4-dimethoxybenzaldehyde, cinnamaldehyde, anisaldehyde, 1-naphthaldehyde, 2-naphthaldehyde, 2-methoxy-1-naphthaldehyde, 2-hydroxy-1-naphthaldehyde, 2-ethoxy-1-naphthaldehyde, 4-methoxy-1-naphthaldehyde, 4-ethoxy-1-naphthaldehyde and 4-hydroxy-1-naphthaldehyde. In one embodiment, the tin-zinc alloy plating bath composition contains at least one brightener selected from aromatic carbonyl-containing compounds. The carbonyl compounds are useful for improving the brightness and luster of the deposits produced by the tin-zinc plating compositions of the present invention. The aromatic carbonyl-containing compounds act as a brightener imparting optimum leveling action over a wider plating range. The aromatic carbonyl-containing compounds may be aromatic aldehydes, ketones, or carboxylic acids or the water soluble salts thereof. The amount of aromatic aldehyde or other aromatic carbonyl-containing compounds included in the tin-zinc alloy plating compositions range from about 0.005 to 2 g/l. In one embodiment of the present invention, the aldehyde brighteners are added as a bisulfite addition product.

[0026] The tin ion sources in metal plating compositions for deposition of tin-zinc alloys are mainly salts of Sn^{2+} ions. Therefore, an antioxidant or a mixture of more than one antioxidant is preferably added to such compositions in order to prevent oxidation of Sn^{2+} to Sn^{4+} and subsequent precipitation of insoluble SnO_2. An overview of typical compounds used for this purpose is given in the textbook "The Electrodeposition of Tin and its alloys" (M. Jordan, Eugen G. Leuze Publ., 1st Ed., 1995, p. 80-84) and include hydroquinone and phenol and their respective derivatives. Heterocyclic antioxidants, e. g., amino-hydroxy substituted pyridine for tin and tin alloy plating compositions with improved properties are disclosed in the European Patent Application 08075139.9.

[0027] In practice of the present invention, the bath is operated at temperatures in the range of about 15 to 60 °C, more preferred at 20 to 30 °C. An average cathode current density of about 0.01 to 10 A/m^2, preferred 0.5 to 5 A/dm^2, most preferred 1.5 to 2 A/m^2 is applied. The tin-zinc alloy plating bath composition can be used for barrel and rack plating.

[0028] The following examples illustrate the tin-zinc alloy plating composition of the present invention and its utility.

Examples

Preparation of polymer according to the present invention

[0029] Preparation of a polymer according to formula II with R1, R2, R3, R4 = methyl and a, b = 3 and c, d, e, f = 1 and n = 70 (approximately 25,000 Da).

[0030] 10 g (0.0434 mol) N,N'-Bis(dimethylaminopropyl)urea are dissolved in 23.6 g DI water. 5.71 g (0.0434 mol) of 1,3-Dichlor-propan-2-ol are added to this solution and held at 90 °C for 5 h.

[0031] 39.3 g of a colourless polymer solution is obtained, which contains about 40 wt.-% of a polymer according to formula II. The polymer solution was subjected directly as the additive for example 1.

Example 1

[0032] Steel substrates were degreased with standard procedures.

[0033] Next, a tin-zinc alloy plating solution was prepared, the composition is shown below:

Sn^{2+} salt	12 g/l Sn
Zn^{2+} salt	18 g/l Zn
Sodium-Gluconate	50 g/l
Citric acid	20 g/l
Inventive additive according to formula II	3.52 g/l
Anisaldehyde (brightener)	120 mg/l
Ammonium chloride	80 g/l

[0034] The above mentioned substrate was immersed in this plating bath solution and a tin-zinc alloy with a targeted composition of 40 wt.-% Sn was deposited using the following conditions:

Temperature:	20 to 25 °C
pH:	5 to 6
current density:	0.1 to 3.5 A/dm^2

Example 2 (prior art quaternary ammonium polymer additive)

[0035] Steel substrates were degreased with standard procedures.

[0036] Next, a metal plating solution was prepared, the composition is shown below:

Sn^{2+} salt	12 g/l Sn
Zn^{2+} salt	18 g/l Zn
Sodium-Gluconate	50 g/l
Citric acid	20 g/l
Mirapol A-15 (EP 1 201 789 B1; example 1;available from Rhodia)	5.87 g/l
Anisaldehyde (brightener)	120 mg/l
Ammonium chloride	80 g/l

[0037] The above mentioned substrate was immersed in this plating bath solution and a tin-zinc alloy with a targeted composition of 40 wt.-% Sn was deposited using the same conditions as in example 2.

Results and Evaluation

[0038] The tin-zinc alloy composition distribution on a substrate was evaluated with EDX for a deposit derived from a tin-zinc alloy plating composition containing an additive according to formula II (example 1 of the present invention) and a deposit derived from a tin-zinc alloy plating composition containing a prior art quaternary ammonium polymer additive disclosed in example 1 of the patent EP 1 201 789 B9 (example 2 of the present invention). The target tin-zinc alloy composition was in both cases 40 wt.-% tin and 60 wt.-% zinc. The results of the comparative experiment are summarized in Table 1. The plating bath comprising the inventive additive according to formula II leads to a more homogeneous tin-zinc alloy deposit composition compared to the deposit derived from a prior art plating bath over the entire current density range.

Table 1: deviation from the average alloy deposit composition derived from example 1 and comparative example 2.

	Absolute value of deviation from target average composition of 40 wt.-% tin and 60 wt.-% zinc (values given in %)	
current density (A/dm^2)	example 1 (inventive additive)	example 2 (prior art additive)
>> 3,5	5.47	8.64
3.5	6.56	10.01

(continued)

	Absolute value of deviation from target average composition of 40 wt.-% tin and 60 wt.-% zinc (values given in %)	
current density (A/dm^2)	example 1 (inventive additive)	example 2 (prior art additive)
2.6	6.88	10.47
1.9	6.56	9.38
1.4	6.41	9.98
1	4.54	6.80
0.7	0.80	2.26
0.4	14.54	11.94

[0039] A FIB-SEM micrograph (Figure 1) of a tin-zinc alloy deposit obtained according to example 1 shows the reduced grain size of the deposit compared to a deposit derived from a tin-zinc plating composition containing a prior art quaternary ammonium polymer additive (Figure 2, example 2). Furthermore, the grain size distribution is narrower for the deposit obtained with an inventive quaternary ammonium polymer according to formula II.

Examples 3 and 4

[0040] Formation of white rust was investigated for the tin-zinc alloy deposits derived from examples 1 and 2 using standard salt spray test conditions (DIN EN ISO 9227). Prior to the salt spray test the substrates coated with Sn-Zn alloy were coated with a further passivation layer (Ecotri HC2, product of Atotech Deutschland GmbH).

Example 3

[0041] A substrate coated from a plating bath according to example 1 was subjected to a salt spray test after deposition of a passivation layer. Formation of white rust was observed after 48 h.

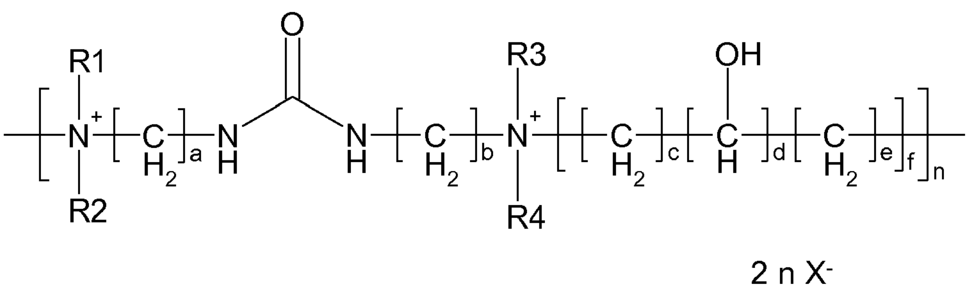
Example 4 (comparative experiment)

[0042] A substrate coated form a plating bath according to experiment 2 was subjected to a salt spray test after deposition of a passivation layer. Formation of white rust was observed after 24 h.

Claims

1. A tin-zinc alloy plating bath composition, comprising

i) at least one additive according to formula I:



$$-\left[\overset{R1}{\underset{R2}{N^{+}}}-[CH_2]_a-NH-\overset{O}{\overset{\|}{C}}-NH-[CH_2]_b-\overset{R3}{\underset{R4}{N^{+}}}-\left[[CH_2]_c[CH(OH)]_d[CH_2]_e\right]_f\right]_n- \qquad 2\,n\,X^-$$

Formula I

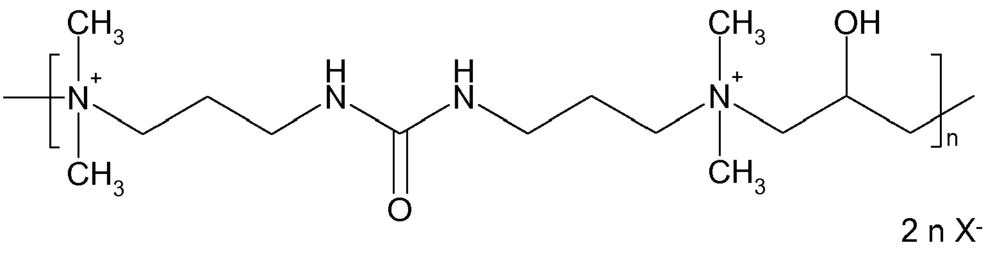
wherein a, b, c, d, e and f are identical or different and represent an integer ranging from 1 to 5,

n is an integer greater than 1,
R1, R2, R3 and R4 are identical or different and represent a substituted or unsubstituted C1 to C6 alkyl or a $-CH_2CH_2(OCH_2CH_2)_y-OH$ residue, wherein y is ranging from 1 to 6, and
X- is a suitable anion,

ii) at least one zinc ion source and
iii) at least one tin ion source and
iv) at least one acid.

2. A tin-zinc alloy plating bath composition according to claim 1, wherein R1, R2, R3 and R4 are selected independently from the group consisting of methyl, ethyl, propyl and butyl and their hydroxy derivatives.

3. A tin-zinc alloy plating bath composition according to claim 1, wherein the additive according to general formula I is represented by formula II:



Formula II

wherein n is greater than 10 and

X is a halogenide or a pseudohalogenide ion.

4. A tin-zinc alloy plating bath composition according to any of the foregoing claims, wherein 0.1 to 10 g/l of at least one additive according to formula I or II is present in the plating bath.

5. A tin-zinc alloy plating bath composition according to any of the foregoing claims, wherein 0.2 to 6 g/l of at least one additive according to formula I or II is present in the plating bath.

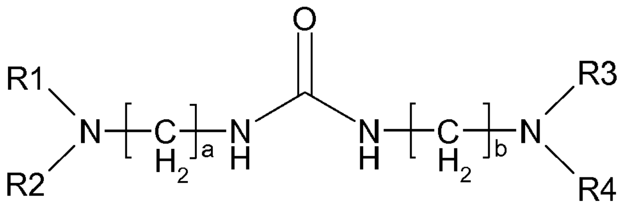
6. A tin-zinc alloy plating bath composition according to any of the foregoing claims, wherein the molecular weight of the additive according to formula I or II is between 500 Da and 100,000 Da.

7. A tin-zinc alloy plating bath composition according to any of the foregoing claims, wherein the molecular weight of the additive according to formula I or II is between 5,000 Da and 30,000 Da.

8. A tin-zinc alloy plating bath composition according to any of the foregoing claims, wherein the acid is a hydroxy carboxylic acid or a salt thereof.

9. A tin-zinc alloy plating bath composition according to any of the foregoing claims, wherein the additives according to formula I and formula II are synthesized from a N,N'-bis(dialkylaminoalkylene)urea derivative and a α,ω-dihalogenide compound.

10. A tin-zinc alloy plating bath composition according to claim 1, wherein the N,N'-bis(dialkylaminoalkylene)urea component is described by formula III:



Formula III

wherein R1 and R2 are identical or different and represent a substituted or unsubstituted C1 to C6 alkyl or $-CH_2CH_2(OCH_2CH_2)_y-OH$, wherein y is ranging from 1 to 6.

11. A tin-zinc alloy plating bath composition, wherein R1, R2, R3 and R4 of the N,N'-bis(dialkylaminoalkylene)urea component described by formula III are selected independently from the group consisting of methyl, ethyl, propyl and butyl and their hydroxy derivatives.

12. A metal alloy plating bath composition according to claim 1, wherein the α,ω-dihalogenide compound is described by formula IV:

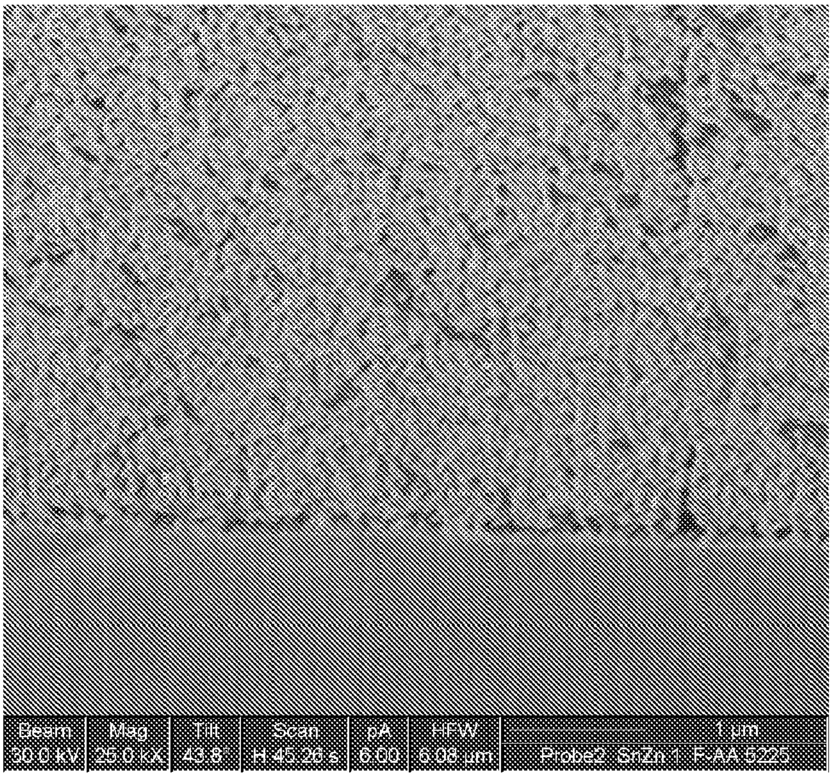

Beam
30.0 kV
Mag
25.0 kX
Tilt
43.8°
Scan
H 45.26 s
pA
6.00
HFW
6.08 µm
1 µm
Probe2 SnZn 1 F-AA 5225

Figure 1

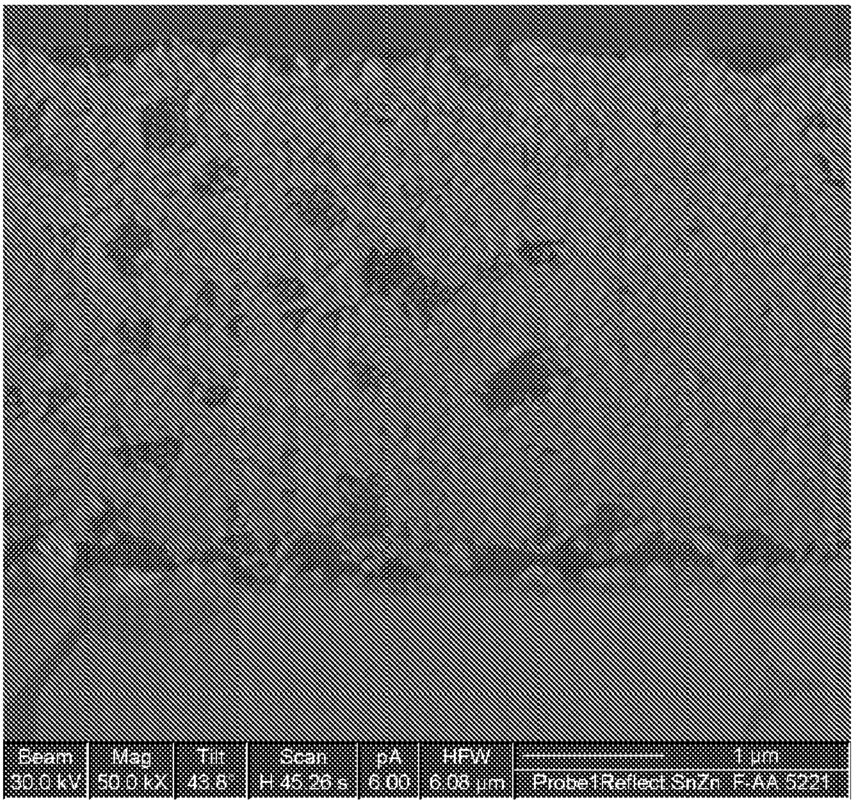

Beam
30.0 kV
Mag
50.0 kX
Tilt
43.8°
Scan
H 45.26 s
pA
6.00
HFW
6.08 µm
1 µm
Probe1Reflect.SnZn F-AA 5221

Figure 2

Europäisches
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EUROPEAN SEARCH REPORT

Application Number
EP 08 16 6465

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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X Y	WO 2007/045650 A (BASF AG [DE]; HEIDENFELDER THOMAS [DE]; NEUMANN JESSICA [DE]; WITTELER) 26 April 2007 (2007-04-26) * claims 1,2,4,9-12 * * page 1, lines 6-25 * * page 4, lines 1-8 * * page 5, line 1 - page 6, line 35 * * page 9, lines 1-32 * * page 10, lines 5-8,33-35 * * page 11, lines 5-29 * * page 14 - page 18; examples 1,2; tables 1,2 * -----	12 1-10	
Y	US 4 163 700 A (FUJISAWA YOSHIKAZU [JP] ET AL) 7 August 1979 (1979-08-07) * claim 1 * -----	8	
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A	WO 2005/093132 A (TASKEM INC [US]; ECKLES WILLIAM E [US]; KUEHLER THORSTEN [DE]) 6 October 2005 (2005-10-06) * page 9, line 5 - page 10 * -----	1-12	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	9 March 2009	Gault, Nathalie

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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4

EPO FORM 1503 03.82 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 08 16 6465

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
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09-03-2009

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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