

Description

This invention relates to a method for production of tin-cobalt, tin-nickel, or tin-lead binary alloy electroplating bath composition and an electroplating bath produced thereby which produces a tin-cobalt, tin-nickel, or tin-lead binary alloy coating glossy and excellent in decorative effect and permits stable plating work.

Methods for electrodepositing tin-cobalt, tin-nickel, and tin-lead binary alloy platings have been known in the art.

A method disclosed by T. L. Ramachar "Electrochemistry", 25, 573 (1957), a method disclosed by A. E. Davies and R. M. Angleo "Trans. Inst. Metal Finishing, 33, 277 (1956), and a method disclosed by A. Brenner "Electrodeposition of Alloy", vol. 2, 339 (1963) are examples. The coatings electrodeposited in a large thickness by these known methods have a disadvantage that they have no gloss, assume a grayish white color, and sustain cracks under strong stress.

For this reason, these alloy coatings can be used only for thin decorative coatings, though they possess as high a corrosionproofness as Monel (Registered Trade Mark), Metal or Inconel (Registered Trade Mark).

As tin-lead alloy electrodepositing baths, a borofluoride bath, a pyrophosphoric acid bath, etc. are available. These methods have problems relating the safety of the workers and are apt to cause water pollution. Moreover, the bath compositions are susceptible to degeneration due to oxidation because they use divalent tin.

The inventors continued a study with a view to developing a plating method which is free from the drawbacks of such conventional methods as described above and is capable of producing a glossy coating without reference to thickness. So far they have secured Japanese Patent No. 1,027,262 for an invention characterized by containing 1-hydroxyethane-1,1-phosphoric ester or a salt thereof in a plating bath, Japanese Patent No. 1,027,292 for an invention characterized by further containing aldehyde and a betaine compound, and Japanese Patent No. 1,166,434 and No. 1,180,236 for an invention characterized by containing glycol ether.

Coatings of tin-cobalt, tin-nickel, and tin-lead alloys are used in various kinds of articles. In recent years, a need has arisen for a coating of rich gloss and high decorative value. As a result, there is a need for a plating bath capable of stably forming a coating of desired composition.

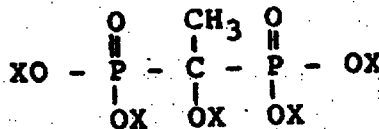
Through various studies the inventors discovered that a plating bath incorporating therein a mixture of 1-hydroxyethane-1,1-diphosphoric acid or a salt thereof with methanesulfonic acid or an alkali salt thereof permits a notable addition to the decorative value of a coating and that a bath using a stannic salt as a tin salt permits the plating work to be performed stably and easily. The present invention has been perfected on the basis of this knowledge.

To be specific, this invention is directed to a method for the production of a tin-cobalt, tin-nickel, or tin-lead binary alloy electroplating bath composition, characterized by mixing (a) a tin salt and one member selected from the group consisting of a cobalt salt, a nickel salt, and a lead salt as alloy coating-forming agents, (b) at least one member selected from the group consisting of 1-hydroxyethane-1,1-diphosphoric acid and salts thereof, (c) at least one member selected from the group consisting of methanesulfonic acid and alkali salts thereof and (d) at least one electroconductive salt, and to a tin-cobalt, tin-nickel, or tin-lead binary alloy electroplating bath composition characterized by containing the components mentioned above and produced by the method described above.

Now, the method of production mentioned above and the components used in the production of the bath will be described below.

(a) This component comprises alloy coating-forming agents which are required to account for specific concentrations, i.e. the tin salt 5 to 50 g/liter, the cobalt salt 3 to 12 g/liter, the nickel salt 3 to 13 g/liter, and the lead salt 3 to 25 g/liter respectively as metal. If the concentration of this component is higher than the range mentioned above, the components of (b) and (c) are not sufficient in supply for the plating bath to manifest its function satisfactorily. If the concentration is lower than the range, the plating bath forms the coating slowly and impairs the alloy ratio necessary for manifestation of high corrosionproofness and consequently fails to fulfil the object of plating.

(b) This component is represented by the following general formula and contributes to greatly enhancing the gloss of the coating.



wherein X stands for hydrogen, sodium or potassium. The amount of this component to be added is in the range of 20 to 140 g/liter. If the concentration of this component is larger than the range mentioned above, the bath concentration becomes unduly large. If the concentration is lower than the range, the effect of the addition of this component is lost.

(c) The addition of this component constitutes an important feature of this invention. It enables the produced coating to acquire an exceptionally beautiful decorative appearance. The amount of this component to be added is desired to fall in the range of 1 to 4 mols per mol of 1-hydroxyethane-1,1-diphosphoric acid or salt thereof. The total amount of the components (b) and (c) in the bath must be in the range of 40 to 180 g per liter. For use in the alloy coating-forming agent, the tin salt is desired to be a tetravalent compound such as sodium stannate, potassium stannate, or a chloride, the cobalt and nickel salts are each desired to be a chloride, sulfate, or perchlorate, and the lead salt is desired to be a water-soluble compound such as an acetate or perchlorate.

Owing to the use of a stannic (tetravalent) salt as the tin salt, the plating bath of this invention prevents otherwise possible change of the tin concentration therein due to oxidation and enables the component metals of the plating alloy, namely tin-cobalt, tin-nickel, or tin-lead, placed therein to be simultaneously chelated so that the ratio of metal concentrations in the bath coincides with that in the alloy coating to be formed by plating.

The composition of the alloy coating formed by electrodeposition, therefore, can be easily managed by maintaining the ratio of metal concentrations in the bath within a fixed range.

(d) The plating bath of this invention contains such a known electroconductive salt as sodium chloride, potassium chloride, potassium sulfate, sodium sulfate, or ammonium sulfate which is indispensable to the operation of electrodeposition. The amount of this electroconductive salt to be added is in the generally accepted range of 15 to 80 g/liter. If the amount of this salt is unduly large, the excess salt can cause coating defects such as surface streaks. If the amount is unduly small, the bath has high electric resistance.

The bath composition of the present invention is produced by mixing the aforementioned four components (a), (b), (c) and (d). The coating produced by the electroplating using this bath composition possesses heretofore unattainable excellent metallic gloss.

The electroplating bath of the present invention, when necessary, may incorporate other components therein to the extent that the bath composition is not adversely affected by the added components.

The plating operation using the electroplating bath of this invention is desired to be carried out under conditions such that the bath temperature falls in the range of 50 to 85°C, the current density at the cathode in the range of 0.5 to 5 A/dm², and the current density at the anode in the range of 0.5 to 2.5 A/dm². The pH value of the plating bath can be selected within a very wide range of 3 to 13.5.

The anode may be an ordinary insoluble anode of carbon, ferrite or 18-8 stainless steel. A variable anode may be also used. When the plating bath is acidic, for example, an anode made of the same substance as coating-forming substance, i.e. tin, cobalt, or nickel may be used. Where a tin anode is used, for example, the electroplating bath is divided by an anion-exchange membrane into a first portion containing the tin anode and a second portion containing the object to be electroplated and is electrolyzed, thereby allowing stannous ion to dissolve out of the tin anode into the first portion and, since the bath is acidic, the stannous ion is oxidized into stannic ion, which passes through the anion-exchange membrane into the second portion. In this case, since the tin is supplied from the anode, the coating-forming substance to be replenished with the progress of the plating operation may be limited to the other member of the coating-forming agent than the tin salt. Thus, the control of both compositions is very easy.

Now, the present invention will be described below with reference to working examples and comparative experiments.

EXAMPLES 1 TO 28 AND COMPARATIVE EXPERIMENTS 1 TO 11

Various bath compositions according with this invention were prepared with the components indicated in Tables 1 and 2 and they were used for plating under the conditions shown in Tables 3-1 & 3-2. The properties shown by the coatings consequently formed were as shown in Tables 3-1 and 3-2

Various bath compositions for comparison were prepared with the components indicated in Tables 4 & 5. The properties shown by the coatings formed using the bath compositions were as shown in Table 6. In the bracket (b) (c) of Tables 1 and 2, P stands for 1-hydroxyethane-1,1-diphosphoric acid, PN for sodium salt thereof, PK for potassium salt thereof, H for methanesulfonic acid, and HN for sodium salt thereof, and numerals molar ratio.

The time of electrolysis was 2 to 4 minutes for the plating with the tin-cobalt alloy or with the tin-nickel alloy and 5 to 10 minutes for the plating with the tin-lead alloy. The adhesion test was carried out in accordance with the method of JIS H8504, 3-8-a, with the results rated on a three-point scale, wherein o stands for absence of separation, Δ for 5% separation, and x for 10% separation. The results of the test for resistance to nitric acid, the test for resistance to hydrochloric acid, and the test for resistance to an alkali etchant were rated on a three-point scale, wherein o stands for absence of change, Δ for slight change, and x for appreciable change respectively in alloy coating after immersion. The results of the test for gloss were rated on a three-point scale, wherein ⊙ stands for conspicuous gloss, o for ordinary gloss, and ⊗ for rather poor gloss.

Table 1

Composition (g/l)	Example No.	1	2	3	4	5	6	7	8
(a) Component	$\text{Na}_2[\text{Sn}(\text{OH})_6]$	90				80			
	$\text{K}_2[\text{Sn}(\text{OH})_6]$		100				95		
	$\text{Sn}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$			50				50	50
	$\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$				50				
	(Sn)	40	40	17	17	36	38	17	17
	$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	40	40	17	17				
	$\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$			15	15				
	(Co)	10	10	3	3				
	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$					24		20	
	$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$						31		18
(b) (c) component						6	7	5	4
		120 IPN2H	110 IPN4H	80 IPN1H	80 IPN1HN	160 IPN4HN	100 IP3H	90 IP1H	70 IPN1HN
Electroconductive salt (d)		NaCl	KCl	$(\text{NH}_4)_2\text{SO}_4$	NH_4Cl	K_2SO_4	Na_2SO_4	KCl	NH_4Cl
Amount added		20	30	40	50	15	15	30	50

Table 2

Example No.	Composition (g/l)	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28
(a) component																					
	$\text{Na}_2[\text{Sn}(\text{OH})_6]$			30		80						75		35			25				
	$\text{K}_2[\text{Sn}(\text{OH})_6]$				35		120			80									50		60
	$\text{Sn}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$		20					50			45				90	70		45		40	
65	$\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$								30				40								
	(Sn)	22	7	13	14	36	48	17	10	32	15	33	14	16	30	24	11	15	20	14	24
	$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$							15	16	30			18								
	$\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$					16	45				33	30									
	(Co)					3	9	4	4	7	7	7	4								
	$\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$	12												20	16				30		
	$\text{Pb}(\text{CH}_3\text{COO})_4$		10		10												15	10			
	$\text{PbHCl}_2 \cdot \text{H}_2\text{O}$			15												15				10	40
	(Pb)	7	5	8	5									12	10	8	8	5	18	5	21
(b) (c) component		80	70	65	60	100	100	90	70	120	75	140	75	80	75	90	90	70	100	50	110
	IP1H	IP3H	IP1NH	IP1NH	IP1NH	IP1NH	IP1NH	IP1NH	IP1H	IP3H	IP1NH	IP1NH	IP1NH	IP1NH	IP1NH	IP1NH	IP1NH	IP1NH	IP1NH	IP3H	IP1NH
Electroconductive salt (d)	$\text{NH}_4\text{Cl}/\text{NH}_4)_2\text{SO}_4$																				
Amount added		30	20	30	25	20	15	15	50	30	60	20	50	25	65	65	30	70	40	70	50

Table 3-1

Example No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
pH	13	12.0	3.5	3.5	13	12	4	4	4	4	13	12	13	12	3.5
Current density at cathode, A/dm ²	0.5 ~ 2	0.5 ~ 2	1.0 ~ 3.0	1.0 ~ 3.0	0.5 ~ 2	0.5 ~ 2	1.0 ~ 3.0	1.0 ~ 3.0	1.0 ~ 4	1.0 ~ 4	0.5 ~ 5	0.5 ~ 5	0.5 ~ 2	0.5 ~ 2	1.0 ~ 3.0
Current density at anode, A/dm ²	0.5 ~ 1	0.5 ~ 1	0.5 ~ 1.5	0.5 ~ 1.5	0.5 ~ 1	0.5 ~ 1.5	0.5 ~ 1.5	1.8 ~ 1.5	0.5 ~ 2	0.5 ~ 2.5	0.5 ~ 2.5	0.5 ~ 2.5	0.5 ~ 1	0.5 ~ 1	0.5 ~ 1.5
Bath temperature (°C)	55 ~ 60	55 ~ 60	50 ~ 55	50 ~ 55	55 ~ 60	55 ~ 60	50 ~ 55	55 ~ 60	50 ~ 60	50 ~ 60	50 ~ 60	50 ~ 60	55 ~ 60	55 ~ 60	50 ~ 60
Anode	carbon	carbon	tin	tin	ferrite	carbon	tin	tin	tin	tin	18-8 stainless steel	carbon	carbon	carbon	18-8 stainless steel
Anion-exchange membrane	x	x	o	o	x	x	o	o	o	o	x	x	x	x	x
Stirring	x	x	airation	airation	x	x	airation	airation	airation	airation	x	x	x	x	x
Undercoating	nickel	nickel	nickel	nickel	nickel	nickel	nickel	nickel	copper	copper	copper	copper	nickel	nickel	nickel
Tin content in deposited coating (% by weight)	80.7	81.1	81.9	80.6	66.6	65.7	64.7	65.5	90.2	60.2	61.0	60.4	82.1	81.2	82.2
Resistance to nitric acid	o	o	o	o	o	o	o	o	x	x	x	x	o	o	o
Resistance to hydrochloric acid	x	x	x	x	o	o	o	o	o	o	o	o	x	x	x
Resistance to alkali etchant	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o
Adhesiveness	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o
Gloss	⊙	⊙	o	⊙	o	⊙	o	⊙	o	o	o	o	o	o	⊙

Table 3-2

Example No.	16	17	18	19	20	21	22	23	24	25	26	27	28
pH	4	12	3.5	13.0	4	13	4	4	13	4	12	4	12
Current density at cathode, A/dm ²	1.0~3.0	0.5~2	1.0~3.0	0.5~2	1.0~3.0	1.0~5	1~4	1~4	1~5	1~4	1~5	1~4	1~5
Current density at anode, A/dm ²	0.5~1.5	0.5~1	0.5~1.5	0.5~1	0.5~1.5	0.5~2.5	0.5~2	0.5~2	0.5~2.5	0.5~2	0.5~2.5	0.5~2	0.5~2.5
Bath temperature (°C)	50~55	55~60	55~55	50~60	55~55	50~60	50~60	50~60	50~60	50~60	50~60	50~60	50~60
Anode	carbon	18-8 stainless steel	tin	carbon	ferrite	carbon	carbon	tin	18-8 stainless steel	ferrite	carbon	tin	18-8 stainless steel
Anion-exchange membrane	x	x	o	x	x	x	x	o	x	x	x	o	x
Stirring	x	x	airation	x	x	x	x	airation	x	x	x	airation	x
Undercoating	nickel	nickel	nickel	nickel	nickel	copper	copper	copper	copper	copper	copper	copper	copper
Tin content in deposited coating (% by weight)	79.7	65.8	67.4	68.1	66.0	59.7	90.5	91.0	62.0	89.8	61.2	90.9	60.0
Resistance to nitric acid	o	o	o	o	o	x	x	x	x	x	x	x	x
Resistance to hydrochloric acid	x	o	o	o	o	o	o	o	o	o	o	o	o
Resistance to alkali etchant	o	o	o	o	o	o	o	o	o	o	o	o	o
Adhesiveness	o	o	o	o	o	o	o	o	o	o	o	o	o
Gloss	o	⊙	o	⊙	⊙	o	o	o	o	o	o	o	o

Table 4

Comparative Experiment No.		1	2	3	4	5	6	7	8
Composition (g/l)		75					65		
(a) Component	$\text{Na}_2[\text{Sn}(\text{OH})_6]$								
	$\text{K}_2[\text{Sn}(\text{OH})_6]$		90			70			
	$\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$			35				35	
	$\text{SnSO}_4 \cdot 2\text{H}_2\text{O}$				60				65
	(Sn)	33	36	14	21	28	29	14	22
	$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$		20	12					
	$\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$	16			20				
	(Co)	3	5	3	4				25
	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$					30			
	$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$						30	42	
Other component	(Ni)					7	7	9	6
	$\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$			50	75			50	50
	$(\text{NH}_4)_3\text{C}_6\text{H}_5\text{O}_7 \cdot \text{H}_2\text{O}$			40	55				
	$\text{K}_3\text{C}_6\text{H}_5\text{O}_7 \cdot \text{H}_2\text{O}$							60	60
	$\text{HOCH}_2\text{CO}_2\text{H}$					40	40		
	$\text{C}_{10}\text{H}_{14}\text{O}_8\text{Na}_2 \cdot 2\text{H}_2\text{O}$	50	55			30	25		
	$\text{C}_2\text{H}_3\text{O}_7\text{P}_3\text{Na}_4$	105	110						
	KCl			90		20			
	KOH	50				35		20	
	NaOH		65				42		
	K_2SO_4				30				19
	NaCl						57		

Table 5

Comparative Experiment No. Composition (g/l)		9	10	11
(a) component	$\text{SnCl}_5 \cdot 5\text{H}_2\text{O}$	60		50
	$\text{SnSO}_4 \cdot 2\text{H}_2\text{O}$		70	
	(Sn)	20	24	17
	$\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$	18		
	$\text{Pb}(\text{ClO}_4)_2$		27	
	$\text{Pb}(\text{NO}_3)_2$			19
	(Pb)	11	18	12
Other component	$\text{K}_3\text{C}_6\text{H}_5\text{O}_7 \cdot \text{H}_2\text{O}$	125		
	PEG (polymerization degree 2,000)			7
	$\text{C}_{10}\text{H}_{14}\text{O}_8\text{N}_2\text{Na}_2 \cdot 2\text{H}_2\text{O}$	46		45
	Geratin	5	1	
	CH_3COOK	100	100	100

Table 6

Comparative Experiment No.	1	2	3	4	5	6	7	8	9	10	11
pH	12~13	12~13	3~4	3~4	12~13	12~13	3~4	3~4	2~3	2~3	1.5~2.5
Current density at cathode, A/dm ²	0.5~2.0	0.5~2.0	1~4	1~4	0.5~2.0	0.5~2.0	1~4	1~4	1~5	1~5	1~5
Current density at anode, A/dm ²	0.5~1.0	0.5~1.0	0.5~2.0	0.5~2.0	0.5~1.0	0.5~1.0	0.5~2.0	0.5~2.0	0.5~2.5	0.5~2.5	1.0~2.5
Bath temperature (°C)	55~65	55~65	35~40	35~40	60~65	60~65	35~40	35~40	50~60	50~60	50~60
Anode	carbon	18-8 stainless steel	carbon	ferriite	18-8 stainless steel	carbon	carbon	carbon	carbon	carbon	ferriite
Stirring	airation	airation	airation	airation	airation	airation	airation	airation	airation	airation	airation
Undercoating	nickel	nickel	nickel	nickel	nickel	nickel	nickel	nickel	copper	copper	copper
Tin content in deposited coating (% by weight)	78.9	79.2	80.4	79.8	68.9	70.0	67.4	70.3	38.1	16.8	32.2
Resistance to nitric acid	o	o	Δ	o	o	Δ	Δ	Δ	x	x	x
Resistance to hydrochloric acid	x	x	x	x	o	o	o	o	o	o	o
Resistance to alkalii etchant	Δ	Δ	o	Δ	Δ	x	Δ	x	o	x	o
Adhesiveness	o	o	Δ	o	o	o	o	o	o	o	o
Gloss	o	o	o	⊗	o	⊗	o	o	⊗	⊗	⊗

The electroplating bath composition of the present invention contains 1-hydroxyethane-1,1-diphosphoric acid or salt thereof and methanesulfonic acid or an alkali salt thereof as mixed and the coating produced by the electroplating using the composition bath is stable and excellent in gloss. Owing to the use of a stannic salt as the tan compound as one of the two components of the coating-forming agent, the plating operation proceeds without formation of any precipitation due to such a rapid oxidation reaction as $\text{Sn}^{2+} \rightarrow \text{Sn}^{4+} + 2e$ which would occur if a stannous acid were used, the plating bath has a stable tin concentration, and the plating operation can be effectively carried out stably at a pH value selected within a wide range from acidic bath to alkaline bath.



Claims

1. A method for the production of a tin-cobalt, tin-nickel, or tin-lead binary alloy electroplating bath composition, said method characterised by mixing:
 - (1) tin salts, compounds of tetravalent tin, in an amount of 5 to 50 g in terms of tin metal and one member selected from the group consisting of cobalt salts in an amount of 3 to 12 g in terms of cobalt metal, nickel salts in an amount of 3 to 13 g in terms of nickel metal and lead salts in an amount of 3 to 25 g in terms of lead metal for serving as an alloy coating-forming agent;
 - (2) at least one member selected from the group consisting of 1-hydroxyethane-1, 1-diphosphoric acid and salt thereof in an amount of 20 to 140 g;
 - (3) at least one member selected from the group consisting of methanesulfonic acid and an alkali salt thereof in an amount making a total of 40 to 180 g when the amount of 1-hydroxyethane-1, 1-diphosphoric acid and/or salt thereof is added thereto; and
 - (4) at least one electroconductive salt;
 all the amounts being based on one liter of said bath composition.
2. The method according to claim 1, wherein said methane-sulfonic acid and/or salt thereof is contained in said bath composition in an amount in the range of 1 to 4 mol per mol of said 1-hydroxyethane-1, 1-diphosphoric acid and/or salt thereof.
3. A tin-cobalt, tin-nickel, or tin-lead binary alloy electroplating bath composition, characterised by containing as substantially main components thereof:
 - (1) tin salts, compounds of tetravalent, in an amount of 5 to 50 g in terms of tin metal and one member selected from the group consisting of cobalt salts in an amount of 3 to 12 g in terms of cobalt metal, nickel salts in an amount of 3 to 13 g in terms of nickel metal and lead salts in an amount of 3 to 25 g in terms of lead metal for serving as an alloy coating-forming agent;
 - (2) at least one member selected from the group consisting of 1-hydroxyethane-1, 1-diphosphoric acid and salt thereof in an amount of 20 to 140 g;
 - (3) at least one member selected from the group consisting of methanesulfonic acid and an alkali salt thereof in an amount making a total of 40 to 180 g when the amount of 1-hydroxyethane-1, 1-diphosphoric acid and/or salt thereof is added thereto; and
 - (4) at least one electroconductive salt;
 all the amounts being based on one liter of said bath composition.
4. The bath composition according to claim 3, wherein the concentration of said methanesulfonic acid and/or alkali salt thereof is in the range of 1 to 4 mols per mol of said 1-hydroxyethane-1, 1-diphosphoric acid and/or salt thereof.

Patentansprüche

1. Verfahren zur Herstellung einer Badzusammensetzung für die Elektroplattierung mit einer binären Zinn-Kobalt-, Zinn-Nickel- oder Zinn-Blei-Legierung, gekennzeichnet durch Mischen von:
 - (1) Zinnsalzen, nämlich Verbindungen von vierwertigem Zinn, in einer Menge von 5 bis 50 g bezogen auf Zinnmetall, und einem Bestandteil, der aus der Gruppe Kobaltsalze in einer Menge von 3 bis 12 g bezogen auf Kobaltmetall, Nickelsalze in einer Menge von 3 bis 13 g bezogen auf Nickelmetall und Bleisalze in einer Menge von 3 bis 25 g bezogen auf Bleimetall ausgewählt ist, um als Mittel zur Bildung des Legierungsüberzuges zu dienen;
 - (2) wenigstens einem Bestandteil, der aus der Gruppe 1-Hydroxyethan-1,1-diphosphorsäure und deren Salz ausgewählt ist, in einer Menge von 20 bis 140 g;
 - (3) wenigstens einem Bestandteil, der aus der Gruppe Methansulfonsäure und deren Alkalisalz ausgewählt ist, in einer Menge, die insgesamt 40 bis 180 g ausmacht, wenn die Menge der 1-Hydroxyethan-1,1-diphosphorsäure und/oder deren Salz hinzugefügt wird; und
 - (4) wenigstens einem Leitsalz;
 alle diese Mengen bezogen auf einen Liter der Badzusammensetzung.
2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die Methansulfonsäure und/oder deren Salz in der Badzusammensetzung in einer Menge von 1 bis 4 Mol pro Mol der 1-Hydroxyethan-1,1-diphosphorsäure und/oder deren Salz enthalten ist.



3. Badzusammensetzung zur Elektroplattierung mit einer binären Zinn-Kobalt-, Zinn-Nickel- oder Zinn-Blei-Legierung, dadurch gekennzeichnet, daß darin im wesentlichen als Hauptkomponenten enthalten sind:

- (1) Zinnsalze, nämlich Verbindungen von vierwertigem Zinn, in einer Menge von 5 bis 50 g bezogen auf Zinnmetall, und ein Bestandteil, der aus der Gruppe Kobaltsalze in einer Menge von 3 bis 12 g bezogen auf Kobaltmetall, Nickelsalze in einer Menge von 3 bis 13 g bezogen auf Nickelmetall und Bleisalze in einer Menge von 3 bis 25 g bezogen auf Bleimetall ausgewählt ist, um als Mittel zur Bildung des Legierungsüberzuges zu dienen;
 - (2) wenigstens ein Bestandteil, der aus der Gruppe 1-Hydroxyethan-1,1-diphosphorsäure und deren Salz ausgewählt ist, in einer Menge von 20 bis 140 g;
 - (3) wenigstens ein Bestandteil, der aus der Gruppe Methansulfonsäure und deren Alkalisalz ausgewählt ist, in einer Menge, die insgesamt 40 bis 180 g ausmacht, wenn die Menge der 1-Hydroxyethan-1,1-diphosphorsäure und/oder deren Salz hinzugefügt wird; und
 - (4) wenigstens ein Leitsalz;
- alle diese Mengen bezogen auf einen Liter der Badzusammensetzung.

4. Badzusammensetzung nach Anspruch 3, dadurch gekennzeichnet, daß die Konzentration der Methansulfonsäure und/oder deren Alkalisalz im Bereich von 1 bis 4 Mol pro Mol der 1-Hydroxyethan-1,1-diphosphorsäure und/oder deren Salz beträgt.

Revendications

1. Procédé de production d'un bain électrolytique d'alliage binaire étain-cobalt, étain-nickel ou étain-plomb, ledit procédé étant caractérisé en ce qu'on mélange :
 - (1) des sels d'étain, des composés d'étain tétravalents en une quantité de 5 à 50 grammes en termes d'étain métal et un membre choisi dans le groupe constitué par les sels de cobalt en une quantité de 3 à 12 grammes en termes de cobalt métal, des sels de nickel en une quantité de 3 à 13 g en termes de nickel métal et des sels de plomb en une quantité de 3 à 25 g en termes de plomb métal pour servir d'agent formateur de revêtement d'alliage ;
 - (2) au moins un membre choisi dans le groupe constitué par l'acide 1-hydroxyéthane-1,1-diphosphorique et un de ses sels en une quantité de 20 à 140 g ;
 - (3) au moins un membre choisi dans le groupe constitué par l'acide méthanesulfonique et un de ses sels alcalins en une quantité constituant un total de 40 à 180 g lorsque la quantité d'acide 1-hydroxyéthane-1,1-diphosphorique et/ou de son sel y est ajoutée et
 - (4) au moins un sel conducteur de l'électricité ;
 toutes les quantités étant données sur la base d'un litre de ladite composition de bain.
2. Procédé selon la revendication 1, dans lequel ledit acide méthanesulfonique et/ou son sel est contenu dans ladite composition de bain en une quantité située dans un intervalle allant de 1 à 4 moles par mole dudit acide 1-hydroxyéthane-1,1-diphosphorique et/ou son sel.
3. Composition de bain de dépôt électrolytique d'un alliage étain-cobalt, étain-nickel ou étain-plomb, caractérisée en ce qu'elle contient comme composants principaux :
 - (1) des sels d'étain, composés tétravalents, en une quantité de 5 à 50 g en termes d'étain métal et un membre choisi dans le groupe constitué par les sels de cobalt en une quantité de 3 à 12 g en termes de cobalt métal, des sels de nickel en une quantité de 3 à 13 g en termes de nickel métal et des sels de plomb en une quantité de 3 à 25 g en termes de plomb métal pour servir comme agent de formation de revêtement d'alliage ;
 - (2) au moins un membre choisi dans le groupe constitué par l'acide 1-hydroxyéthane-1,1-diphosphorique et ses sels en une quantité de 20 à 140 g ;
 - (3) au moins un membre choisi dans le groupe constitué par l'acide méthanesulfonique et un de ses sels alcalins en une quantité constituant un total de 40 à 180 g lorsqu'on y ajoute la quantité d'acide 1-hydroxyéthane-1,1-diphosphorique et/ou son sel ; et
 - (4) au moins un sel conducteur de l'électricité ;
 toutes les quantités étant fondées sur un litre de ladite composition de bain.
4. Composition de bain selon la revendication 3, dans laquelle la concentration dudit acide méthanesulfonique et/ou de son sel alcalin est dans un intervalle de 1 à 4 moles par moles dudit acide 1-



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hydroxyéthane-1,1-diphosphorique et/ou de son sel.

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