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(54) ELECTROLYTIC BATHS AND ELECTROLYTIC PROCESSES

(71) We, BERGISCHE METALL-WARENFABRIK DILLENBERG & CO. KG, a body Corporate organised and existing under the laws of the Federal Republic of Germany of 5601 Gruiten, Millrather Strasse 36, Federal Republic of Germany, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to electrolytic baths and electrolytic processes for the electrolytic deposition of tin/nickel, tin/cobalt or tin/nickel/cobalt layers.

It is customary to protect objects against corrosion, such as bumpers, door or window furnishings, parts of a clockwork mechanism, metallic decorative strips, etc., by electrolytic chrome plating. Electrolytic chrome plating, however, is disadvantageous in that the control of the bath is relatively complicated and the so-called throwing power (which relates to the depth of coating thrown from the bath) is so little that hollow articles or, for example, the concave reverse side of automobile bumpers cannot be chrome plated.

It is known that tin-nickel coatings applied electrolytically, in which tin and nickel are present in approximately the same number of atoms, have a corrosion resistance that is just as good as chrome coatings and that in the case of these processes the throwing power is considerably better than in the case of chrome plating. In the article, "Electrodeposition of Tin-Nickel Alloy Plate from Chloride-Fluoride Electrolytes", Journal of Electrochemical Society, Vol. 100, No. 3, March 1953, USA, the electrolytic coating of objects with a tin/nickel layer is described in detail. There, an electrolyte made of 50 g/litre tin (II) chloride, 300 g/litre nickel chloride, 28 g/litre sodium fluoride and 35 g/litre ammonium bifluoride is proposed. The coatings produced in the case of use of such an electrolyte however, and even in the case of

deposition on a highly lustrous nickel plated base, are dull or at most semi-gloss, and in the case of hollow goods or other uneven objects the coatings on the places of the base body which are either hidden or deeper down (being in regions of lesser current density) are increasingly more dull. To this must be added that these tin/nickel coatings are strongly reddish, and for that reason these coatings, generally speaking, do not meet aesthetic requirements. Beyond that, the coatings are very brittle and, especially in the case of a larger thickness of the layer, they are inclined to chip off. Furthermore, the control of the bath is difficult, since close temperature tolerances must be maintained. Tin/nickel coatings have thus not gained ground sufficiently to replace chrome coatings, despite the fact that it is simpler to produce tin/nickel coatings.

From German Patent Specifications Nos. 1,260,915 and 1,260,916, electrolytic tin/nickel baths are known that contain 0.05 to 2 g/litre triaminotriphenylmethane, of 0.05 to 1 g/litre 1 - (p - aminophenyl) - 3 - methylpyrazole as lustre forming agents which are incorporated in the electrolytic deposition. The coatings precipitated with these known baths however are very brittle.

An object of the invention is to provide electrolytic baths with which bright (minimum or no reddishness at all) tin/nickel, tin/cobalt or tin/nickel/cobalt coatings of a high ductility are achieved, which retain the lustre of the base in an even throwing power.

According to one aspect of the invention an electrolytic bath containing a tin salt together with a nickel salt and/or cobalt salt and fluoride or fluoroborate salts for electrolytically depositing tin/nickel, tin/cobalt or tin/nickel/cobalt layers, is characterised in that the bath contains the fluoride or fluoroborate salts of one or more amines, the amine(s) being present in a total amount of at least 10 g/l and up to 100 g/l.

As detailed investigations have shown, even in the case of a small addition of amine,

e.g. the minimum of 10 grams per litre, coatings with less reddishness and higher ductility are attained and these effects become even more apparent with an increased quantity of amine, whereby in the case of amine additions of 100 g/litre, optimum values are achieved in regard to brightness and ductility. The throwing power of lustre is even at points of high and low current density. Because of their low brittleness (high ductility), the coatings can be applied at a considerable thickness of the layer without there being any danger of its chipping. The coatings are obtained with the same surface smoothness as the base previously had. The invention thus offers the possibility of depositing highly lustrous tin/nickel layers after preliminary nickel plating of the base body. Another advantage of the bath according to the invention is that the bath can also be used for coating directly on to base bodies made of iron with tin/nickel, tin/cobalt and tin/nickel/cobalt coatings, for which purpose the known tin/nickel baths cannot be used.

Preferably, the bath contains as amine fluorides or fluoroborates of ethylenediamine, diethylene triamine, triethylenetetramine, mono-, di- and/or triethanolamine.

Furthermore, fluorides or fluoroborates of
 2 - ethylaminoethanol
 3 - ethylamino - 1 - propylamine
 2 - ethyl - 1 - hexylamine
 N - benzyldiethanolamine
 N' - benzyl - N,N - dimethylethylenediamine
 N - benzyldimethylamine
 Bis - (2 - ethoxyethyl) - amine
 Bis - (2 - ethylhexyl) - amine
 Bis - (3 - aminopropyl) - amine
 N,N - Bis - (3 - aminopropyl) - methylamine
 N - butyldiethanolamine
 N - tert - butylethanolamine
 2 - diethylaminoethanol
 N,N - diethylcyclohexylamine
 N,N - dibenzylmethylamine
 Dicyclohexylamine
 Diisopropylamine
 Dipropylamine
 Hexadecylamine

Nickel chloride $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$
 Tin(II) chloride $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$
 Ammonium bifluoride $\text{NH}_4\text{F} \cdot \text{HF}$
 Amine

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Such a bath is produced, for example, by first of all dissolving nickel chloride, tin(II) chloride and ammonium bifluoride in the stated quantities in about 400 cc water, by then adding amine in a quantity until a pH

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Hexamethylenetetramine
 Melamine
 N - methyldiethanolamine
 N - phenyldiethanolamine
 1,3 - phenylenediamine
 Tetraethylenepentamine
 Propylamine
 Tributylamine
 Triisopropanolamine or
 Triscyanomethylamine
 may be used as derivatives.

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These amines are contained in the bath singly or in combination. In the latter case, the total concentration of all amines present is within the range 10 g/l to 100 g/l. All amines are used together with hydrofluoric acid or borohydrofluoric acid form salts, whereby naturally the limitation pertains that the pertinent amine is soluble in the bath at the operating temperature of the bath, that it is at least partly soluble and it must not be volatile.

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In practical tests, the alkylamine and benzylamine produced particularly favourable results, whereby in addition the general rule was discovered that the simply structured unbranched or only little branched amines are most suitable, while with an increasing branching or in the case of amines having additional substitution groups the ductility of the precipitated layer becomes poorer, which is due probably to the fact that in these cases carbon atoms and other foreign atoms are built into the precipitated layers and impart to them an increasing hardness and brittleness.

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According to further preferred features of the invention, tin, nickel and possibly cobalt are added during initial propagation of the bath in the form of their sulphate, sulphonate, chloride, acetate, citrate or lactate salts. The anions put into the bath thereby improve the capacity of the bath to produce coatings having the same surface smoothness as the base.

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At the same time, combinations are provided, for example, by using nickel sulphate and tin (II) chloride beside one another.

A bath suited for production of tin/nickel coatings contains per litre in aqueous solution:

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125 to 450 g
 25 to 110 g
 20 to 100 g
 40 to 100 cc
 (sufficient for a pH
 between 3.8 and 5.5).

value of between 3.8 and 5.5 is obtained, after which the remaining volume is filled with water to make up one litre bath liquid.

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In the case of the baths described previously, the amine, among others, is sup-

posed to adjust the pH value of the bath to a value between 3.8 and 5.5. As an alternative, the adjustment of the pH value can be accomplished by means of ammonia. In such a case the bath contains per litre in aqueous solution:

5	Nickel chloride $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	200 to 300 g
	Tin(II) chloride $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$	40 to 60 g
	Ammonium bifluoride $\text{NH}_4\text{F} \cdot \text{HF}$	20 to 80 g
	Solution of amine and an organic and/or inorganic nonoxidizing acid at a pH value of 3.8 to 5.5	30 to 80 cc
10	Ammonia	sufficient for 3.8 to 5.5 pH

Naturally, it is also possible to adjust the bath to the desired pH value by use partly of amine and partly ammonia. In any event, the amine concentration in the bath lies between 10 g/l and 100 g/l.

Preferably, one operates with a bath adjusted to a pH value of 4.8 by means of amine and/or ammonia.

According to another aspect of the invention there is provided an electrolytic process for the electrolytic deposition of tin/nickel, tin/cobalt or tin/nickel/cobalt layers by use of a bath containing a tin salt together with a nickel salt and/or cobalt salt and fluoride or fluoroborate salts, characterised in that the process is performed with the bath containing the fluoride or fluoroborate salts of one or more amines, the amine(s) being present in a total amount of at least 10 g/l and up to 100 g/l.

Preferably fluorides or fluoroborates of ethylenediamine, diethylene triamine, triethylenetetramine, mono-, di and/or triethanolamine are used. Furthermore, the process according to the invention may be carried out with fluorides or fluoroborates of the following amines:

40	2 - ethylaminoethanol
	2 - ethylamino - 1 - propylamine
	2 - ethyl - 1 - hexylamine
	N - benzyldiethanolamine
	N' - benzyl - N,N - dimethylethylene-diamine
45	N - benzyldimethylamine
	Bis - (2 - ethoxyethyl) - amine
	Bis - (2 - ethylhexyl) - amine
	Bis - (3 - aminopropyl) - amine
50	N,N - Bis - (3 - aminopropyl) - methylamine
	N - butyldiethanolamine
	N - tert - butylethanolamine
	2 - diethylaminoethanol
	N,N - diethylcyclohexylamine
55	N,N - dibenzylmethylamine
	Dicyclohexylamine
	Diisopropylamine
	Dipropylamine

Hexadecylamine	
Hexamethylenetetramine	60
Melamine	
N - methyldiethanolamine	
N - phenyldiethanolamine	
1,3 - phenylenediamine	
Tetraethylenepentamine	65
Propylamine	
Tributylamine	
Triisopropanolamine or	
Triscyanomethylamine.	

Preferably, the electrolytic process is carried out at a bath temperature between 40 and 90°C and at a current density of between 0.1 and 5 ampere/dm².

In the following text a few preferred bath compositions are given, related each time to one litre of finished bath fluid, in each case the amine being present in the bath in an amount of at least 10 g/l and up to 100 g/l.

Example 1

Composition:		80
Nickel chloride $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	250 g	
Tin(II) chloride $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$	50 g	
Ammonium bifluoride $\text{NH}_4\text{F} \cdot \text{HF}$	50 g	
Diethylenetriamine	90 cc	85
	(i.e. 86.4 g)	
	(results in a pH of 4.8)	
Water	Remainder	

Example II

Composition:		90
Nickel chloride $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	250 g	
Tin(II) chloride $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$	50 g	
Ammonium bifluoride $\text{NH}_4\text{F} \cdot \text{HF}$	50 g	95
Ammonia	75 cc	
	(results in a pH of 4.8)	
Diethylenetriamine	20 cc	100
	(i.e. 19.2 g)	
Hydrochloric acid	20 cc	
Water	Remainder	

Example III

Composition:

	Nickel chloride $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	250 g
	Tin(II) chloride $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$	50 g
5	Ammonium bifluoride $\text{NH}_4\text{F} \cdot \text{HF}$	50 g
	Ammonia	75 cc
		(results in a
		pH of 4.8)
10	Diethylenetriamine	30 cc
		(i.e. 28.8 g)
	Lactic acid	50 cc
	Water	Remainder

Example IV

Composition:

15	Tin(II) chloride $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$	50 g
	Nickel sulphate $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	310 g
	Ammonium bifluoride $\text{NH}_4\text{F} \cdot \text{HF}$	60 g
20	Triethylenetetramine	95 cc
		(i.e. 92.15 g)

Example V

Composition:

	Tin acetate	50 g
25	Nickel acetate	95 g
	Ammonium bifluoride	50 cc
	N-benzyl-diethanolamine	60 cc
		(i.e. 60 g)
	Water	Remainder

- 30 These baths were operated at a bath temperature of 75°C and at an average current density of 4 ampere/dm². A sheet of nickel was used as anode. Various objects, such as
- 35 cane made of a sheet of brass, camera housings and bottle openers made of iron, door handles made of die cast tin, fruit juice presses made of aluminium, coatings of steel of electric devices, printed electric circuits,
- 40 were provided with tin/nickel coatings that had the same lustre as the objects had been given previously, for example, by nickel plating. In the case of base bodies made of iron, steel, copper, nickel and brass, it was possible to apply the coatings directly, while base
- 45 bodies made of die cast tin or aluminium had to be copper coated first. The coatings proved exceedingly corrosion resistant and highly ductile.

- 50 It was found that fluctuations in the composition of the bath, for example, brought about by consumption of the individual components, are not critical for the process and that no recognizable changes in appearance of the tin/nickel coatings occurred. From
- 55 this point of view, the addition of acid, especially hydrochloric acid, proved to be very advantageous.

- 60 Similarly, good coatings also were achieved with baths that had cobalt salts instead of nickel salts or contained additionally cobalt salts beside nickel salts.

A bath according to the invention is entirely odourless after addition of amine and no fluorine containing vapours occur at all, which represents a very important advantage for the practical use of the bath. The amine with the fluorides or fluoroborides forms salts, which exist completely dissociated in the bath and which apparently result in the special effects of the bath. The precipitated tin/nickel, tin/cobalt and tin/nickel/cobalt layers consist only of the pertinent metals.

WHAT WE CLAIM IS:—

1. An electrolytic bath containing a tin salt together with a nickel salt and/or cobalt salt and fluoride or fluoroborate salts for electrolytically depositing tin/nickel, tin/cobalt or tin/nickel/cobalt layers, characterised in that the bath contains the fluoride or fluoroborate salts of one or more amines, the amine(s) being present in a total amount of at least 10 g/l and up to 100 g/l.

2. A bath according to claim 1 and containing the fluoride or fluoroborate salts of ethylenediamine, diethylenetriamine, triethylenetetramine, mono- di- and/or triethanolamine.

3. A bath according to claim 1 and containing the fluorides or fluoroborates of

2 - ethylaminoethanol
3 - ethylamine - 1 - propylamine
2 - ethyl - 1 - hexylamine
N - benzyl-diethanolamine
N' - benzyl - N,N - dimethylethylene-diamine

N - benzyl-dimethylamine

Bis - (2 - ethoxyethyl) - amine

Bis - (2 - ethoxyhexyl) - amine

Bis - (3 - aminopropyl) - amine

N,N - bis - (3 - aminopropyl) - methyl-amine

N - butyldiethanolamine

N - tert - butylethanolamine

2 - diethylaminoethanol

N,N - diethylcyclohexylamine

N,N - dibenzylmethylamine

Dicyclohexylamine

Diisopropylamine

Dipropylamine

Hexadecylamine

Hexamethylenetetramine

Melamine

N - methyl-diethanolamine

N - phenyl-diethanolamine

1,3 - phenylenediamine

Tetraethylenepentamine

Propylamine

Tributylamine

Triisopropanolamine, or

Triscyanomethylamine.

4. A bath according to claim 1, wherein tin and nickel are added to the bath in the form of their sulphate, sulphonate, chloride, acetate, citrate or lactate salts.

5. A bath according to claim 4, where-



Example III

Composition:

	Nickel chloride $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	250 g
	Tin(II) chloride $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$	50 g
5	Ammonium bifluoride $\text{NH}_4\text{F} \cdot \text{HF}$	50 g
	Ammonia	75 cc
		(results in a pH of 4.8)
10	Diethylenetriamine	30 cc
		(i.e. 28.8 g)
	Lactic acid	50 cc
	Water	Remainder

Example IV

Composition:

15	Tin(II) chloride $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$	50 g
	Nickel sulphate $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	310 g
	Ammonium bifluoride $\text{NH}_4\text{F} \cdot \text{HF}$	60 g
20	Triethylenetetramine	95 cc
		(i.e. 92.15 g)

Example V

Composition:

	Tin acetate	50 g
25	Nickel acetate	95 g
	Ammonium bifluoride	50 cc
	N-benzyl-diethanolamine	60 cc
		(i.e. 60 g)
	Water	Remainder

- 30 These baths were operated at a bath temperature of 75°C and at an average current density of 4 ampere/dm². A sheet of nickel was used as anode. Various objects, such as
- 35 cane made of a sheet of brass, camera housings and bottle openers made of iron, door handles made of die cast tin, fruit juice presses made of aluminium, coatings of steel of electric devices, printed electric circuits,
- 40 were provided with tin/nickel coatings that had the same lustre as the objects had been given previously, for example, by nickel plating. In the case of base bodies made of iron, steel, copper, nickel and brass, it was possible to apply the coatings directly, while base
- 45 bodies made of die cast tin or aluminium had to be copper coated first. The coatings proved exceedingly corrosion resistant and highly ductile.

- 50 It was found that fluctuations in the composition of the bath, for example, brought about by consumption of the individual components, are not critical for the process and that no recognizable changes in appearance of the tin/nickel coatings occurred. From
- 55 this point of view, the addition of acid, especially hydrochloric acid, proved to be very advantageous.

- 60 Similarly, good coatings also were achieved with baths that had cobalt salts instead of nickel salts or contained additionally cobalt salts beside nickel salts.

A bath according to the invention is entirely odourless after addition of amine and no fluorine containing vapours occur at all, which represents a very important advantage for the practical use of the bath. The amine with the fluorides or fluoroborides forms salts, which exist completely dissociated in the bath and which apparently result in the special effects of the bath. The precipitated tin/nickel, tin/cobalt and tin/nickel/cobalt layers consist only of the pertinent metals.

WHAT WE CLAIM IS:—

1. An electrolytic bath containing a tin salt together with a nickel salt and/or cobalt salt and fluoride or fluoroborate salts for electrolytically depositing tin/nickel, tin/cobalt or tin/nickel/cobalt layers, characterised in that the bath contains the fluoride or fluoroborate salts of one or more amines, the amine(s) being present in a total amount of at least 10 g/l and up to 100 g/l.
2. A bath according to claim 1 and containing the fluoride or fluoroborate salts of ethylenediamine, diethylenetriamine, triethylenetetramine, mono- di- and/or triethanolamine.
3. A bath according to claim 1 and containing the fluorides or fluoroborates of
 - 2 - ethylaminoethanol
 - 3 - ethylamine - 1 - propylamine
 - 2 - ethyl - 1 - hexylamine
 - N - benzyl-diethanolamine
 - N' - benzyl - N,N - dimethylethylendiamine
 - N - benzyl-dimethylamine
 - Bis - (2 - ethoxyethyl) - amine
 - Bis - (2 - ethoxyhexyl) - amine
 - Bis - (3 - aminopropyl) - amine
 - N,N - bis - (3 - aminopropyl) - methylamine
 - N - butyldiethanolamine
 - N - tert - butylethanolamine
 - 2 - diethylaminoethanol
 - N,N - diethylcyclohexylamine
 - N,N - dibenzylmethylamine
 - Dicyclohexylamine
 - Diisopropylamine
 - Dipropylamine
 - Hexadecylamine
 - Hexamethylenetetramine
 - Melamine
 - N - methyl-diethanolamine
 - N - phenyl-diethanolamine
 - 1,3 - phenylenediamine
 - Tetraethylenepentamine
 - Propylamine
 - Tributylamine
 - Triisopropanolamine, or
 - Triscyanomethylamine.
4. A bath according to claim 1, wherein tin and nickel are added to the bath in the form of their sulphate, sulphonate, chloride, acetate, citrate or lactate salts.
5. A bath according to claim 4, where-



in cobalt is additionally added to the bath in the form of its sulphate, sulphonate, chloride, acetate, citrate or lactate salt.

- 5 6. An electrolytic process for the electrolytic deposition of tin/nickel, tin/cobalt or tin/nickel/cobalt layers by use of a bath containing a tin salt together with a nickel salt and/or cobalt salt and fluoride or fluoroborate salts, characterised in that the process
- 10 is performed with the bath containing the fluoride or fluoroborate salts of one or more amines, the amine(s) being present in a total amount of at least 10 g/l and up to 100 g/l.

- 15 7. A process according to claim 6, wherein fluorides or fluoroborates of ethylenediamine, diethylenetriamine, triethylenetetramine, mono- di- and/or triethanolamine are used for the electrolytic deposition.

8. A process according to claim 6, wherein one or more of the amines mentioned in claim 3 are used for the electrolytic deposition. 20

9. A process according to claim 6, wherein the electrolytic deposition is carried out at a bath temperature between 40 and 90°C and at a current density between 0.1 and 5 ampere/dm². 25

10. An electrolytic bath substantially as herein particularly described with reference to any of the foregoing Examples. 30

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