

[54] **ELECTROLYTIC PLATING OF
TIN-NICKEL, TIN-COBALT OR
TIN-NICKEL-COBALT ON A METAL BASE
AND ACID BATH FOR SAID PLATING**

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[56] **References Cited**
UNITED STATES PATENTS

2,658,866 11/1953 Parkinson..... 204/43 S
3,141,836 7/1964 Seyb et al..... 204/43 S

FOREIGN PATENTS OR APPLICATIONS

248,415 12/1969 U.S.S.R..... 204/43

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[57] **ABSTRACT**

A method for electrolytic plating of tin-nickel, tin-cobalt or tin-nickel-cobalt on a metal base and acid bath for said plating in which a bivalent salt of tin and nickel or tin and cobalt or tin, nickel and cobalt is dissolved in an aqueous acid bath containing an alkali metal or ammonium fluoride or fluoborate which is reacted with at least about 2 volume percent of an amine to form the fluoride or fluoborate amine salt dissolved in said bath. Preferred amines which form salts are petrylene diamine, diethylene triamine, triethylene tetramine, mono, di or tri ethanolamine and pyridine. Heavy, lustrous ductile coatings are deposited from the bath at pH 3.8 – 5.5 under current intensity of 0.1 – 5 amps/dm² and at a temperature of 40° – 90°C.

6 Claims, No Drawings

ELECTROLYTIC PLATING OF TIN-NICKEL, TIN-COBALT OR TIN-NICKEL-COBALT ON A METAL BASE AND ACID BATH FOR SAID PLATING

This invention relates to novel electrodeposition methods and novel electrodeposition baths for electrodepositing tin-nickel, tin-cobalt and tin-nickel-cobalt in the form of a bright, lustrous, ductile corrosion-resistant coating on a ferrous, copper, brass, aluminum or similar metal base.

More particularly, the invention relates to novel acid baths having a pH below 6, preferably about 3.8 - 5.5 for electroplating tin-nickel, tin-cobalt and tin-nickel-cobalt having high throwing power wherein the bivalent water-soluble salts of tin, nickel and/or cobalt are present in the aqueous bath together with a combination of alkali or ammonium fluoride or an alkali or ammonium fluoroborate with an aliphatic amine, cycloaliphatic amine or aromatic amine, the amine being present in amounts of at least about 2 volume percent per liter and up to about 120 grams per liter in order to form fluoride or fluoborate salts and to aid in adjusting the pH of the acid bath to the optimum pH range of 3.8 to 5.5.

As a result of the formation of fluoride or fluoborate salts with the amine which along or with ammonium hydroxide serves to adjust the pH value of the bath to 3.8 - 5.5 when it is added to the bivalent salts and the soluble fluoride in order to raise the pH, a new and unexpected electroplating result is achieved, namely highly lustrous coatings are achieved which are surprisingly ductile and free from brittleness so as to be capable of producing thick plate which is free from chipping and which is far superior to the tin-nickel, tin-cobalt or tin-nickel-cobalt coatings of the prior art.

In contrast to chrome plating baths which require complex formulation and control, plating baths for tin-nickel, tin-cobalt or tin-nickel-cobalt have excellent throwing power and are very attractive as a commercial improvement over chrome baths. It is known that chrome-plated clock or watch parts, decorative metal stripping, door or window hardware, automobile bumpers and other automotive accessories are expensive and difficult to produce due to the poor throwing power of the chromium plating bath and the plating of reverse concave surfaces in bumpers and hollow articles has not been uniformly successful in the hands of less skilled workers. This defect in throwing power is not shared by a tin-nickel, tin-cobalt or tin-nickel-cobalt plating bath wherein tin and the nickel or cobalt are each present in the same number of atoms, (e.g., atoms of S_n = atoms of Ni or Co or Ni + Co), so that a corrosion resistant electrodeposited coating can be achieved having equivalent corrosion resistance as the chrome coating but which can be more simply and efficiently produced.

In the article, "Electrodeposition of Tin-Nickel Alloy from Chloride-Fluoride Electrolytes," Journal of Electrochemical Society, Vol. 100, No. 3, March 1953, USA, the galvanic coating of objects with a tin-nickel layer is described in detail. There, an electrolyte made of 50 g/liter tin(II) chloride, 300 g/liter nickel chloride, 28 g/liter sodium fluoride and 35 g/liter ammonium bifluoride is proposed. The electrodeposited coatings produced in the case of this electrolyte however are not clear and bright and even in the case of electrodeposi-

sition on a highly lustrous nickel plated base, are dull or at most semiglossy, so that in the case of hollow goods or other uneven objects the coatings on the places of the base body which either are hidden or deeper down, therefore on the places of a lesser current density, are increasingly more dull and obviously inferior.

To this defect 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 tin-nickel electrodeposited coatings are very brittle and, especially in the case of a substantially large thickness of layer, the coatings have a tendency to chip off. Furthermore, the control of the bath is difficult, since close temperature tolerances must be maintained.

Also as noted at Column 1, lines 15-20 in Seyb et al., U. S. Pat. No. 3,141,836, granted July 21, 1964, tin-nickel alloys coated in the form of an electrodeposit having a thickness greater than 6 microns is inherently cloudy, hazy and white and these defects are worsened when the base is not bright and shiny.

In German Pat. Nos. 1,260,915 and 1,260,916, galvanic tin-nickel baths are disclosed that contain 0.05 to 2 g/liter triaminotriphenylmethane, or 0.05 to 1 g/liter 1-(p-aminophenyl)-3-methylpyrazole as luster forming agents, which act as built-in substances but the electrodeposited coatings precipitated with these known baths are very brittle.

Accordingly, it is an object of the invention to provide novel tin-nickel, tin-cobalt, and tin-nickel-cobalt aqueous electroplating baths and methods for using these baths to create bright, lustrous highly ductile electrodeposited coatings adapted for a variety of shapes, hollow ware and the like with the characteristic of uniform and excellent throwing power which takes no complicated procedures to control during electroplating operations and which overcomes the strongly-reddish characteristics as well as the cloudy characteristics of the unsatisfactory prior art coatings.

A further object of the invention is to provide an acidic tin-nickel, tin-cobalt or tin-nickel-cobalt plating bath for electrodeposition which overcomes the characteristic deficiencies of alkali fluoride-stannous fluoride baths, these being commonly regarded as causing the formation of loose, crystal-lined deposits as explained in Schweikher U. S. Pat. No. 2,407,579, and leading to loss of adherence of the electrodeposited coating to the base and insufficient or inadequate density of coating.

These and other objects are accomplished, in accordance with the invention by providing a bath containing a water-soluble bivalent salt of tin, nickel and/or cobalt, such as the chloride, sulfate, sulfonate, acetate, citrate or lactate, in appropriate concentrations known in the art (e.g., 70 - 450 grams per liter of nickel, in the form of nickelous chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$) or the same concentration of cobalt chloride, and from 25 - 65 grams per liter of tin, in the form of stannous chloride) and as a critical additive to the bath the combination of an alkali or ammonium fluoride or fluoborate together with an amine reactive with said fluoride or fluoborate to form the amine salt.

As detailed investigations have shown, even in the case of a small addition of amine, *f. ex.*, only a few grams per liter, 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 about 100 g/liter and more, optimum values are achieved in regard to the brightness and ductility of the electro-deposited coating. The throwing power as well as the luster of the bath is uniform at points of high current density and at low current density. Because of the extremely low brittleness (high ductility), the coatings can be electro-deposited at considerable thickness of applied layer without there being any danger of its chipping. The coatings are obtained with the same surface smoothness as that of the underlying base.

The invention also offers the possibility of electro-depositing highly lustrous tin-nickel layers by giving first of all a highly lustrous nickel primer surface, for example, by way of nickel plating, to the base body. Another advantage of the bath according to the invention consists in the fact that the bath is especially adapted to be used for the coating of 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, so as to create a new commercial product.

According to a preferred embodiment of the invention, the bath contains as the amine salt derivatives, fluorides or fluoroborates of ethylenediamine, diethylenetriamine, triethylenetetramine, mono-, di- and/or triethanolamine or pyridine. However, many other amines have been investigated, and the fluorides or fluoroborates of the following are included.

2-ethylaminoethanol
3-ethylamino-1-propylamine
2-ethyl-1-hexylamine
N-benzyl-diethanolamine
N'-benzyl-N,N-dimethylethylenediamine
N-benzyl-dimethylamine
Bis-(2-ethoxyethyl)-amine
Bis-(2-ethylhexyl)-amine
Bis-(3-aminopropyl)-amine
N,N-Bis-(3-aminopropyl)-methylamine
N-butyl-diethanolamine
N-tert-butyl-ethanolamine
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

and

Triscyanomethylamine.

The foregoing amines are contained in the bath singly or they may be added in combination. All of the amines which are used together with hydrofluoric acid or borohydrofluoric acid form salts, whereby the limitation naturally pertains that the pertinent amine must be soluble in the bath at the operating temperature of the bath, or it is at least partly soluble to give an effective

amount of salt (3 g of amine per liter) and it must not be volatile.

It has turned out that the alkyl amines and benzylamines produce particularly favorable results, and in addition the general rule was discovered that the simply structured, unbranched or only slightly branched amines are most suitable for the greatest ductility and minimum embrittlement, while with increasing branching or in the case of amines having additional bulky substituted groups, the ductility of the electro-deposited 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 increasing hardness and brittleness which are undesirable.

According to a further important process characteristic of the invention, tin, nickel and cobalt are added during the first mixing of the bath in the form of the sulfate, sulfonate, chloride, acetate, citrate or lactate salts of the bivalent nickel, tin and cobalt salts. These anions put into the bath improve the capacity of the bath for maintaining the luster of the base in the electro-deposition of corrosion-resistant coatings produced according to the invention.

At the same time, the bath provides combinations for using nickel sulfate and tin (II) chloride along side one another and a bath suited for production of tin-nickel coatings contains the following ingredients per liter in aqueous solution.

TIN-NICKEL ACID BATH NEUTRALIZED WITH AMINE

Nickelchloride $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	125 to 450 g
Tin(II) chloride $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$	25 to 110 g
Ammonium bifluoride $\text{NH}_4\text{F} \cdot \text{HF}$	20 to 100 g
Amine (see listing of preferred amines)	40 to 100 cc
	(sufficient for a pH between 3.8 and 5.5).

The foregoing 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 value of 3.8 and 5.5 is adjusted, after which then the remaining volume is filled with water per one liter bath liquid.

In the case of the tin-nickel acid bath described above, the amine, serves to adjust the pH value of the bath to a range between 3.8 and 5.5.

As an alternative, the adjustment of the pH value also can be accomplished by means of ammonia. In such a case the bath is arranged as follows:

TIN-NICKEL BATH NEUTRALIZED WITH NH_3 AND AMINE

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
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.

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

METHOD OF ELECTRODEPOSITING USING BATH

The invention is also directed to a galvanization process for the precipitating of tin-nickel, tin-cobalt or tin-nickel-cobalt layers with the use of a soluble fluoride or fluoroborate salt containing bath and consists in the use of a bath which has amine derivatives at a quantity of at least several volume percent, e.g., at least 3 percent. Preferably a bath is used that is prepared with ethylenediamine, diethylenetriamine, triethylenetetramine, mono-, di- and/or triethanolamine or pyridine but the other amines mentioned hereinbefore may also be used according to the invention.

According to the invention, the electrodeposition process is accomplished at a bath temperature of about 40 to about 90° C and at a current intensity of 0.1 to 5 ampere/dm².

In the following examples a few preferred bath compositions are given, each composition being related each time to one liter of the finished aqueous bath.

EXAMPLE I

Composition:

Nickel chloride NiCl ₂ · 6H ₂ O	250 g
Tin(II) chloride SnCl ₂ · 2H ₂ O	50 g
Ammonium bifluoride NH ₄ F · HF	50 g
Diethylenetriamine	90 cc (results in a pH of 4.8)
Water	Remainder to 1 liter

EXAMPLE II

Composition:

Nickel chloride NiCl ₂ · 6H ₂ O	250 g
Tin(II) chloride SnCl ₂ · 2H ₂ O	50 g
Ammonium bifluoride NH ₄ F · HF	50 g
Diethylenetriamine	110 cc
Hydrochloric acid	20 cc
Water	Remainder to 1 liter

EXAMPLE III

Composition:

Nickel chloride NiCl ₂ · 6H ₂ O	250 g
Tin(II) chloride SnCl ₂ · 2H ₂ O	50 g
Ammonium bifluoride NH ₄ F · HF	50 g
Ammonia	75 cc (results in a pH of 4.8)
Diethylenetriamine	20 cc
Hydrochloric acid	20 cc
Water	Remainder to 1 liter

EXAMPLE IV

Composition:

Nickel chloride NiCl ₂ · 6H ₂ O	250 g
Tin(II) chloride SnCl ₂ · 2H ₂ O	50 g
Ammonium bifluoride NH ₄ F · HF	50 g
Ammonia	75 cc (results in a pH of 4.8)
Diethylenetriamine	30 cc
Lactic acid	50 cc
Water	Remainder to 1 liter

EXAMPLE V

Composition:

Tin(II) chloride SnCl ₂ · 2H ₂ O	50 g
Nickel sulfate NiSO ₄ · 7H ₂ O	310 g
Ammonium fluoroborate NH ₄ BF ₄	60 g
Triethylenetetramine	95 cc
water	Remainder to 1 liter

EXAMPLE VI

Composition:

Tin acetate
Nickel acetate
Ammonium bifluoride
N-benzyl-diethanolamine
Water

50 g
95 g
50 cc
60 cc
Remainder to 1 liter

OPERATION

Each of these baths of Examples I – VI were operated at a bath temperature of 75° C and at an average current intensity of 4 ampere/dm². A sheet of nickel was used as anode. Various objects, such as cans made of a sheet of brass, camera housings and bottle openers made of iron, door handles made to die cast tin, fruit juice presses made of aluminum, coatings of steel of electric devices, printed electric circuits, were provided with tin-nickel coatings that had the same luster 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 bodies made of die cast tin or aluminum had to be copper coated first. The coatings proved exceedingly corrosion resistant and highly ductile.

In all this it likewise turned out 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 this point of view, the addition of strong mineral acid, especially hydrochloric acid, proved to be very advantageous.

Similarly, excellent electrodeposited coatings were also achieved with baths that had cobalt salts instead of nickel salts and with other baths that contained additionally cobalt salts besides nickel salts to give a Sn-Ni-Co coating.

It should be pointed out that the baths according to the invention are entirely odorless after addition of amine and that particularly no fluorine containing vapors 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 is claimed is:

1. An electrolytic method for depositing corrosion resistant tin-nickel, tin-cobalt and tin-nickel-cobalt coatings on a metal base comprising:

providing an aqueous acid bath at pH 3.8 to about 5.5 containing bivalent water soluble salts of nickel, tin and cobalt in amounts for nickel and cobalt equivalent to 125 to 450 grams per liter as bivalent nickel chloride and 25 to 110 grams per liter as stannous chloride, there being also present in said bath the combination of 20 to 100 grams per liter (1) alkali or ammonium fluoride or (2) alkali or ammonium fluoroborate with a non-volatile amine derivative reactive with said fluoride or fluoroborate to form the amine salt thereof, the amine of said amine salt being present in an amount of from 40 to 100 cubic centimeters per liter;

maintaining said bath at a temperature of about 40° to 90° C; and,
passing current through said bath at an average current intensity between 0.1 to 5 amperes per square

decimeter using a nickel anode and providing said metal base as the cathode.

2. A method as claimed in claim 1 wherein said bath contains ammonium hydroxide in addition to said amine.

3. A method as claimed in claim 1, wherein said fluoride or fluoroborate salt is formed from an amine selected from the class consisting of

ethylenediamine,
diethylenetriamine,
triethylenetetramine,
monoethanolamine,
diethanolamine,
triethanolamine,
N-benzyl-diethanolamine,
N'-benzyl-N, N-dimethylethylenediamine,
N, N-diethylcyclohexylamine,
dicyclohexylamine, and
tetraethylenepentamine.

4. A method as claimed in claim 1, wherein said bivalent tin, nickel, cobalt salt are in the bath in the form of their sulfate, sulfonate, chloride, acetate, citrate, or

lactate salts.

5. A method as claimed in claim 1 wherein said pH is 4.8.

6. An aqueous acid bath at pH 3.8 to about 5.5 containing bivalent water soluble salts of nickel, tin and cobalt in amounts for nickel and cobalt equivalent to 125 to 450 grams per liter as bivalent nickel chloride and 25 to 110 grams per liter as stannous chloride there being also present in said bath the combination of 20 to 100 grams per liter (1) alkali or ammonium fluoride or (2) alkali or ammonium fluoroborate with a non-volatile amine derivative reactive with said fluoride or fluoroborate to form the amine salt thereof, the amine of said amine salt being present in an amount of from 40 to 100 cubic centimeters per liter, said bath adapted for the electrolytic deposition of corrosion resistant tin-nickel, tin-cobalt and tin-nickel-cobalt coatings on a metal base providing by passing current through said bath at an average current intensity between 0.1 to 5 amperes per square decimeter using a nickel anode and providing said metal base as the cathode.

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