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ELECTRODEPOSITION OF LEAD-
ANTIMONY-TIN ALLOYS

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1

The present invention relates to the method of alloy-plating and is more particularly concerned with the electrodeposition of an alloy containing lead, antimony and tin.

We have found that an alloy of lead and the two other metals above mentioned can be electrodeposited from aqueous acid baths and that the deposit is dense, smooth, adherent, and remarkably resistant to corrosion.

One of the main objects of the invention is the replacement of lead in anti-corrosive coatings; another important object is the use of the ternary alloy for bearing surfaces. While electrodeposited lead alone has been widely used as protective coating owing to its resistance against dilute sulfuric acid and cold hydrofluoric acid as well as some other corrosive agents, the addition of tin and antimony considerably adds to its usefulness in widening the range of protection against corrosion on the one hand, and in improving the physical properties of the plate such as grain structure and adherence on the other hand. As a bearing liner electrodeposition of the alloy is an improvement over lead-indium alloys hitherto in use since the antimony is effective, in a way known per se, to contribute to the hardness of the alloy, to its resistance against compression and to its corrosion resistance.

A wide variation in the composition of the deposited alloy may be obtained according to the proportion of the metal components of the bath, the acid used, and other factors, influencing electrodeposition such as current density and concentration. Addition agents also play an important part in the determination not only of the required smoothness and density of the deposit, but also in the percentage in which the components will be present in the alloy.

As already mentioned above, the electrodeposition of the alloy occurs from acid baths. Although other aqueous acids may be used, we have found it most advantageous to use fluoboric, perchloric, or sulfamic acid baths. With these acids the electrodeposition takes place rapidly, the baths can be easily controlled and the results we obtain are accurate and reproducible.

In preparing the bath we may start with the desired acid and soluble salts of the three metals; or the bath may be made with soluble electrodes and the aid of the electric current. In some cases we may use a combination of these methods. Thus we may, for instance, prepare a bath with aqueous fluoboric acid as a bath liquid, by dissolving therein basic lead carbonate, stannous sulfate, and antimony trifluoride. Another way

2

to proceed is to use a lead salt, thereby first preparing a lead bath, which is thereafter built up in tin by using a tin anode, and finally built up in antimony by the application of an antimony

5 anode. A convenient source for lead is white lead or basic lead carbonate. It also proved to be satisfactory to use commercial prepared lead plating salts or lead plating solution.

10 Tin is usually added as stannous oxide or as a stannous salt. In the latter case it is necessary, in calculating the relative amounts of lead and tin, to consider the fact, that the bath will be built up in tin at the expense of a precipitate

15 of lead sulfate. When antimony is added as a salt, soluble antimony fluoride is a convenient addition to fluoborate baths. For other baths, while not being exactly harmful, it is less useful because it limits

20 the type of container used for the bath to those not attacked by acid fluorides. It will be understood that these methods of building up the baths are given by way of

25 example only and that it is not intended to limit the invention to the use of the particular substances mentioned. As already mentioned above, we may build up the bath in part or even entirely by the use of

30 soluble anodes. The anodes may consist of any one of the three components alone, or we may use lead-tin alloys and antimony. In case we use lead or lead-tin anodes, some antimony will immersion-plate or plate by chemical displacement on the anode. We have found, however,

35 that this is not serious since the rate at which antimony immersion-plates on the anode is only about a fourth of the rate at which the antimony is electrodepositing at the cathode. The immersion-plate is adherent enough so that the

40 anode may be used two or three times and then the antimony may be scrubbed off and reclaimed. Lead-tin-antimony anodes may also be used, but in this case a greater amount of antimony

45 appears on the surface of the anode during bath operation. The bath may also be operated with insoluble

50 anodes, such as carbon or platinum anodes. In this case some lead oxide may be electrodeposited on the anodes. But as in the case mentioned

55 above, the deposition on the anode is not harmful for the process as a whole and the lead may be reclaimed after some time. The following examples will serve to illustrate the invention more specifically:

Example 1

For making a ternary alloy of lead, antimony and tin having a basis of lead and containing between 1 and 2% of antimony and between 1 and 2% of tin, we may use the following bath:

	Grams per liter
Fluoboric acid (42%)	450
Basic lead carbonate	278
Antimony trifluoride	4.4
Stannous sulfate	126
Gelatine	0.5

A current density of 20 amperes per square foot will give a good deposit; if the current density is increased, the percentage of tin in the deposit will increase and the percentage of antimony in the deposit will decrease. If the gelatine in the bath is increased, the percentage of tin in the plate will increase, but the antimony will be little affected. In this as in all other cases the temperature of the bath is maintained at room temperature (about 70° F.).

Example 2

In order to obtain a ternary alloy containing a higher amount of antimony a bath of the following ingredients may be used:

	Grams per liter
Fluoboric acid (42%)	189
Basic lead carbonate	135
Stannous sulfate	32.6
Antimony trifluoride	26.4
Gelatine	0.5

This bath at a cathode current density of 20 amperes per square foot will give a good deposit of the ternary alloy containing antimony 12.2%, tin 1.4%.

Example 3

In order to obtain an alloy containing antimony from 1½ to 2½% and tin from 4½ to 6½% we may proceed as follows, using lead and tin concentrates from previous baths to make up a fresh bath:

	Grams per liter
Lead	100-110
Tin	5-7
Antimony	.9-1.4
Fluoboric acid	15-25
(added in the concentrate)	
Excess fluoboric acid	20
Resorcinol	4-5
Gelatine	1-1.5

The current density and temperature are as in the above examples. Increase in either addition agent will result in an increase of tin in the deposit. If the tin content in the alloy should suddenly drop, we may restore the desired percentage by adding either ½ gram per liter of gelatine or 1 gram per liter of resorcinol.

Example 4

Perchloric acid (70%)	milliliters per liter	270
Basic lead carbonate	grams per liter	288
Stannous sulfate	do	100
Antimony trifluoride	do	3
Gelatine	do	0.5
Oil of cloves	drop per liter	1

is applied at a cathode current density of 20 amperes per square foot at room temperature; a good plate of the ternary alloy containing antimony 2.9%, tin 1.3% is obtained.

Example 5

Another example of bath is:

2 molar lead sulfamate solution	milliliters per liter	900
Stannous sulfate	grams per liter	100
Antimony trifluoride	do	3
Gelatine	do	0.5
Oil of cloves	drop per liter	1

This bath at a cathode current density of 20 amperes per square foot gives a very good plate of the ternary alloy containing antimony 1.3%, tin 0.8%.

While the above examples, with the exception of Example 2, illustrate the composition of ternary alloys having low contents in tin and antimony, it is possible to electrodeposit plates from the fluoboric bath containing approximately 10% of tin and 10% of antimony. We have also electro deposited ternary alloy containing tin above 20%. We are able to operate this bath at current densities as high as 70 amperes per square foot with good results.

In most cases it is desirable to operate the bath with one of the usual addition agents such as glue, gelatine, oil of cloves, resorcinol and other hydroxy aromatics. However, we have found that the sulfamic acid bath can be operated with good results even without any addition agents, but in this case a larger amount of tin must be used in the bath to obtain the same percentage in the plate.

Arsenic may be substituted for antimony, or it may be codeposited to form either an arsenic-antimony-tin-lead alloy or an arsenic-tin-lead alloy.

The following bath serves as an example:

	Grams per liter
Arsenic trioxide	5
Antimony fluoride	13
Tin	15
Lead	110
Free fluoboric acid	60
Gelatine	1
Resorcinol	5

At a current density of 20 amperes per square foot, the plate has the following analysis:

	Per cent
Arsenic	1.67
Antimony	10.6
Tin	11.8

We consider it apparent from the above specification, that the ternary alloy can be deposited over a wide composition range. The bath can be controlled within narrow limits by quantitative analytical methods familiar to those skilled in the art. The bath will not change rapidly in composition if soluble anodes are used.

Other modes of applying the principle of our invention may be employed instead of the one explained, change being made as regards the amount of the metals in the ternary alloy and the method for making the same herein disclosed, provided the ingredients or steps stated by any of the following claims or the equivalent of such stated ingredients or steps be employed.

We therefore particularly point out and distinctly claim as our invention.

1. A method of electroplating an alloy of approximately 12.2% antimony, 1%-2% tin and the balance lead which consists in electrodepositing the alloy from an aqueous bath consisting essentially of fluoboric acid (42%) 189 grams

5

per liter of bath, basic lead carbonate 135 grams per liter, antimony trifluoride 26.4 grams per liter, stannous sulfate 32.6 grams per liter, gelatin 0.5 gram per liter, the current density being not less than 20 amperes per square foot.

2. A method of electroplating an alloy of approximately 1%-2% antimony, 1%-2% tin and the balance lead, which consists in electrodepositing the alloy from an aqueous bath consisting essentially of fluoboric acid (42%) 450 grams per liter of the bath, basic lead carbonate 278 grams per liter, antimony trifluoride 4.4 grams per liter, stannous sulfate 126 grams per liter, gelatin 0.5 gram per liter, the current density being not less than 20 amperes per square foot.

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6

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