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PROCESS FOR THE ELECTRODEPOSITION OF TIN ALLOYS

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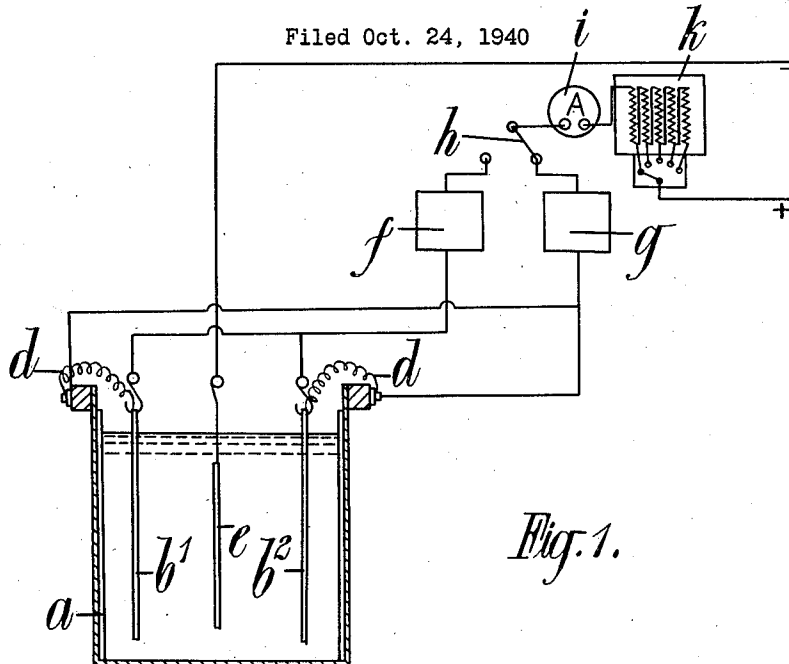


Fig. 1.

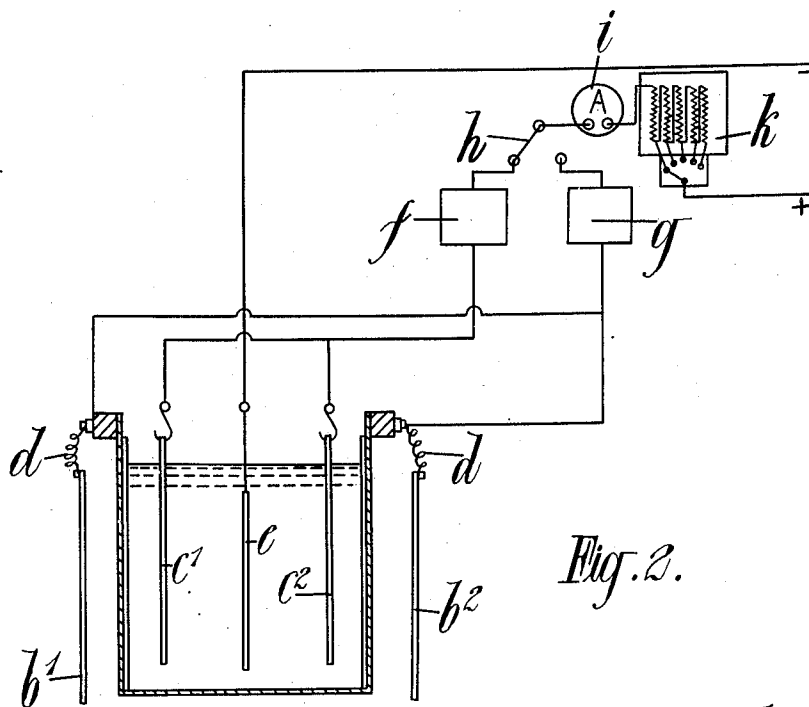


Fig. 2.

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## UNITED STATES PATENT OFFICE

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PROCESS FOR THE ELECTRODEPOSITION  
OF TIN ALLOYS

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7 Claims. (Cl. 204—44)

This invention relates to the electrodeposition of alloys of tin with such metals as copper, nickel, cobalt, cadmium, zinc, antimony and the like, which can be co-deposited with tin from alkaline solutions of suitable composition, and is more particularly directed to the deposition of high tin content alloys, for example copper-tin, containing upwards of 30% of tin.

It is already known that alloys of tin and copper, nickel, zinc or cadmium may be deposited from baths containing alkaline stannates and alkaline cyanides of the second metal, together with suitable amounts of free alkali hydroxide and alkali cyanide, and that the composition of the alloy deposit may be varied by varying the proportions of stannate, metal cyanide, free alkali cyanide and hydroxide in the solution, and/or by varying the temperature of the bath or the current density used for deposition. For replenishing the plating solution with metal salts, anodes consisting of alloys of tin and the second metal in approximately the same proportions as those in the deposited alloy have been used, while it has also been proposed to employ separate anodes of tin and the second metal.

The present invention is based upon the observations that, whether alloy anodes or separate anodes are used, there is a tendency for the tin constituent to dissolve to form divalent tin salts in the bath (for example sodium stannite) instead of dissolving to form the quadrivalent tin salts (for example sodium stannate), and that the presence of divalent tin salts, even in small amounts, will cause serious roughness and at times also cracking and exfoliation of the deposited coatings, while larger amounts will cause the alloys to be deposited as loose spongy masses instead of as coherent coatings. Though the tendency to form divalent tin salts is often negligible when using alloy anodes of low tin content (say containing up to 15% of tin), it is very marked when anodes of higher tin content (say containing over 30% of tin) are used.

A satisfactory method of replenishing the plating solution with metal salts at a similar rate to that at which they are denuded at the cathode has been described in the specification of British Patent 525,364 and also in the corresponding Baier and MacNaughtan United States application, Serial No. 319,978, filed February 20, 1940, and the object of the present invention is to devise a modification of this process.

The present invention consists in a method for replenishing the metal content of alkaline tin-alloy plating baths by the employment of

suitably polarised tin anodes in alternation with anodes of a second metal, the periods of use of each type of anode being controlled so as to replenish the metals in any desired ratio. As well as controlling the relative periods of use of each type of anode, the actual periods of time of use of each type are limited so as to prevent the solution composition changing beyond any desired limits. The alternate use of the two types of anodes allows the process to be worked with a single electrical circuit instead of with two separate circuits, as referred to in the previously mentioned specification.

The accompanying drawing illustrates diagrammatically one form of apparatus in accordance with the invention:

Figure 1 shows the apparatus in use with the tin anodes, and

Figure 2 shows the same apparatus with the tin anodes removed and the anodes of the alloying metal in operation.

In carrying out the invention, the tin anodes are polarised to form an oxide film on their surface, which ensures that they dissolve to form quadrivalent salts entirely free from divalent tin salts. The polarising of the anodes may be carried out by any of the methods referred to in the previous specification.

Since it is found that on the areas of the tin anodes remote from the cathodes the current density tends to fall appreciably below the average and may cause them to lose their oxide film during plating operations, it is preferred to employ narrow tin anodes so as to obtain a more uniform distribution of current density on all surfaces.

The surface areas of the anodes of tin and the second metal anodes are chosen to suit the current required for the normal cathode load in the bath, and the area of the anodes of the metal to be alloyed with the tin is normally required to be sufficient to prevent excessive current density, with consequent polarisation. When not polarised the alloying metals dissolve at practically 100% of their theoretical efficiency while, on the other hand, the tin anodes, being polarised, dissolve at efficiencies appreciably below 100%, and the greater the current density the smaller is their efficiency. However, as the cathode efficiency in these alloy plating baths is normally also appreciably below 100% of the theoretical, it is only necessary to obtain a moderate efficiency at the tin anodes. The dissolving efficiency that is required in any particular set of conditions is dependent on the actual value

of the cathode efficiency and is obtained by adjusting the area of tin anodes to suit this. Moreover, the relative periods of immersion of each type of anode can then be calculated so that over a period of time the plating bath is replenished with the two metals at the same rate as that at which it is being denuded.

It will be understood that the use of the two types of anodes in alternation produces a fluctuation of the metallic contents of the plating solution with a consequent fluctuation in the composition of the deposited alloys. The more frequent the alternations of the anodes or the greater the volume of plating solution for any given load, the smaller will be the fluctuations. In practice it may often be permissible to vary the percentage composition of the deposited alloys within an appreciable range so that the periods of employment of each type of anode may correspond to an appreciable number of working hours or even days.

A typical example of a process in accordance with the invention is the deposition of an alloy containing approximately 45% of tin and 55% of copper, and is carried out as follows:

I form a plating solution containing:

	Grams per liter
Tin (as sodium stannate)-----	42
Copper (as sodium cuprocyanide)-----	8
Free caustic soda-----	10
Free sodium cyanide-----	15
Rochelle salt-----	37

This solution has a pH value between 13 and 14 and is maintained within this range by additions of caustic soda if necessary. It is preferably used at a temperature within the range of 65 to 70° C.

For a bath *a* holding 100 gallons of the solution and capable of plating in a single load articles having a surface area of 6-10 sq. ft., I employ tin anodes *b*<sup>1</sup>, *b*<sup>2</sup> having an effective surface area of 10 sq. ft. and copper anodes *c*<sup>1</sup>, *c*<sup>2</sup> having not less than 10 sq. ft. of effective surface, and I work the plating bath with a current of 200 amperes. The tin anodes are connected to the positive side of the current supply through flexible leads *d* so that they may be inserted into the bath (as shown in Figure 1) with the current flowing, it being understood that they are lowered slowly into the solution (after inserting the cathodes *e*) for the purpose of polarising them.

The bath is then operated for 3½ hours (giving a total current of 700 ampere-hours) with the tin anodes, which are then removed from the solution and the copper anodes used in their stead (as shown in Figure 2) for a period of 3 hours (giving a current of 600 ampere-hours), after which the tin anodes are re-inserted in the manner described above and used for a period of 7 hours. Thereafter the copper and tin anodes are used in alternation in this manner for periods of 3 and 7 hours respectively.

In the course of operation the plating bath is loaded and unloaded with articles to be plated in the normal manner at any desired intervals. During the periods when the tin anodes are being used, precautions must be taken to maintain the polarising film on their surface. For this purpose they must not be left inserted in the bath except when the current is flowing, that is, they must be removed from the bath whenever it is to be completely unloaded and only re-inserted again after re-loading. The use of "dummy" cathodes to maintain a load in the bath during idle periods is resorted to when possible. During the periods

when the copper anodes are being employed, such precautions are not needed, and in fact it is preferable to immerse the copper anodes into the plating solution before switching on the current.

The periods of use of each type of anode are controlled from a knowledge of the quantities of electric current passed during each period. Such quantities may be measured by taking the product of the current passing in amperes and the time in hours, but preferably I employ ampere-hour meters for the purpose, and it is convenient to provide two of such meters *f*, *g* in the circuit arranged with a change-over switch *h* so that one can be used to measure the current passing when the tin anodes are used and the other during the employment of the copper anodes.

There may also be an ammeter *i* and a resistance board *k* in the circuit.

In the example given above the readings of the meters over a prolonged period should be in the ratio of 7:3. To simplify the control it may be useful to employ a shunt on the ampere-hour meter *g* so that it reads only ¾ of the actual current passing through the tin anodes, and in such case control can be obtained by using each type of anode for periods corresponding to readings of 600 ampere-hours. At any time the readings of the two specially adjusted ampere-hour meters should never vary from one another by more than 300 ampere-hours.

It will be understood that the periods of use of each type of anode given in the foregoing example will allow the composition of the deposited alloy to fluctuate from the average tin content of 45% to an extent not greater than 5% either up or down, and if it be desired to maintain the composition of the deposit within closer limits this can be done by decreasing the periods of use of each type of anode or by increasing the volume of the plating solution.

The invention may also be applied to the deposition of alloys of tin with any of the metals nickel, cobalt, cadmium, zinc or antimony, suitable salts of these (such as double cyanides or other salts containing the metal in an acid radicle) being employed with alkali stannates, and with appropriate anodes associated with the filmed tin anodes.

It will be understood, however, that the foregoing process is given purely by way of example, since I may vary the ingredients and proportions in the plating bath, and the temperatures, current densities and periods of operation of the respective anodes, depending upon the constitution of the particular alloy which it is required to deposit, or any practical requirements that may have to be fulfilled.

I claim:

1. A method of applying a tin alloy to an article which comprises, preparing an alkaline tin alloy plating bath containing a tin compound consisting of a stannate, arranging the article to be coated as a cathode within said bath, introducing a polarized tin anode having a surface film composed essentially of tin oxide in said bath to replenish the tin in the bath, maintaining a current flow at predetermined voltage from said tin anode during the entire time it is in said bath, removing the tin anode from the bath and introducing a second anode of another metal into the bath, passing a current at substantially said predetermined voltage from said second anode, and adjusting the time period during which the tin anode and said second anode are arranged

within the bath so as to replenish the metals in any desired ratio.

2. A method of applying a metal alloy to an article which comprises, preparing an alkaline tin alloy plating bath containing a tin compound consisting of a stannate, arranging the article to be coated in said bath, connecting the article to a negative side of an electrical source at a predetermined voltage, connecting a polarized tin electrode having a surface film composed essentially of tin oxide to the positive side of said source and introducing the tin electrode in said bath to replenish the tin in the bath, maintaining a current flow at predetermined voltage from said tin anode during the entire time it is in said bath, removing the tin electrode from the bath after a predetermined time interval, introducing an anode of a second metal in the bath at substantially the same positive potential to replenish the second metal in the bath, and adjusting the time period during which the tin electrode and said anode are alternately arranged within the bath so as to replenish the metals in a proper ratio to provide said alloy.

3. A method of applying a bronze to an article which comprises, preparing an alkaline bronze plating bath containing a tin compound consisting of a stannate, arranging the article to be coated in said bath, connecting the article to a negative side of an electrical source at a predetermined voltage, connecting a polarized tin electrode having a surface film composed essentially of tin oxide to the positive side of said source, thereafter introducing the tin electrode into said bath while the positive potential is applied to the tin electrode to replenish the tin in the bath, maintaining a current flow at predetermined voltage from said tin anode during the entire time it is in said bath, removing the tin electrode from the bath while the positive potential is applied thereto, and thereafter introducing a copper anode into the bath at substantially the same positive potential, and adjusting the time period during which the current passes from said tin anode and said copper anode to substantially different values so as to replenish the metals in a ratio to provide said bronze alloy.

4. A method for electro-deposition of an alloy of tin and another metal of the class consisting of copper, nickel, cobalt, cadmium, zinc and antimony which comprises alternately passing a current at substantially the same voltage from a polarised tin anode having a surface film composed essentially of tin oxide and from the anode of said other metal to a cathode through an alkaline tin alloy plating bath containing a tin compound consisting of a stannate, maintaining said tin anode connected to the current source during the entire time it is in contact with said

plating bath and removing said tin anode before the current is passed through said anode of the other metal.

5. A method for bronze plating comprising alternately passing a current at substantially the same voltage from a polarised tin anode having a surface film composed essentially of tin oxide and from a copper anode to a cathode through an electrolyte containing a tin compound consisting of sodium stannate, sodium cuprocyanide, free caustic soda, free sodium cyanide and Rochelle salt having a pH between 13 and 14, maintaining said tin anode connected to the current source during the entire time it is in contact with said electrolyte and removing said tin anode from the electrolyte before the current is passed through said copper anode.

6. A method for co-depositing copper and tin comprising passing a current from a copper anode to a cathode through an electrolyte containing a tin compound consisting of sodium stannate, sodium cuprocyanide, free caustic soda, free sodium cyanide and Rochelle salt having a pH between 13 and 14, disconnecting said copper anode from said current source while immersed in said electrolyte, connecting said current at substantially the same voltage to a polarised tin anode having a surface film composed essentially of tin oxide while it is out of contact with said electrolyte, introducing said polarised tin anode into said electrolyte, maintaining said tin anode connected to the current source to cause current to flow therefrom during the entire time it is in contact with said electrolyte withdrawing said tin anode after an interval of time substantially different from the interval of time of current passage from said copper anode and repeating the cycle of alternate passage of current through the copper and tin anodes respectively.

7. The method of bronze plating an alloy composed essentially of copper and tin with a tin content over 30%, comprising passing a current from a source of predetermined voltage through an alkaline electrolyte containing a soluble tin compound consisting of a stannate and containing a cuprocyanide, maintaining the concentration of said copper and tin compounds in said electrolyte by alternately passing said current at substantially the same voltage for different time intervals from a copper anode and a tin anode having a surface film of tin oxide, maintaining a current flow from said tin anode during the entire time it is in said electrolyte, measuring the amount of energy passing from the respective anodes, and adjusting said time intervals for the respective anode circuits to obtain the delivery of a predetermined ratio of energy from the respective anodes.

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