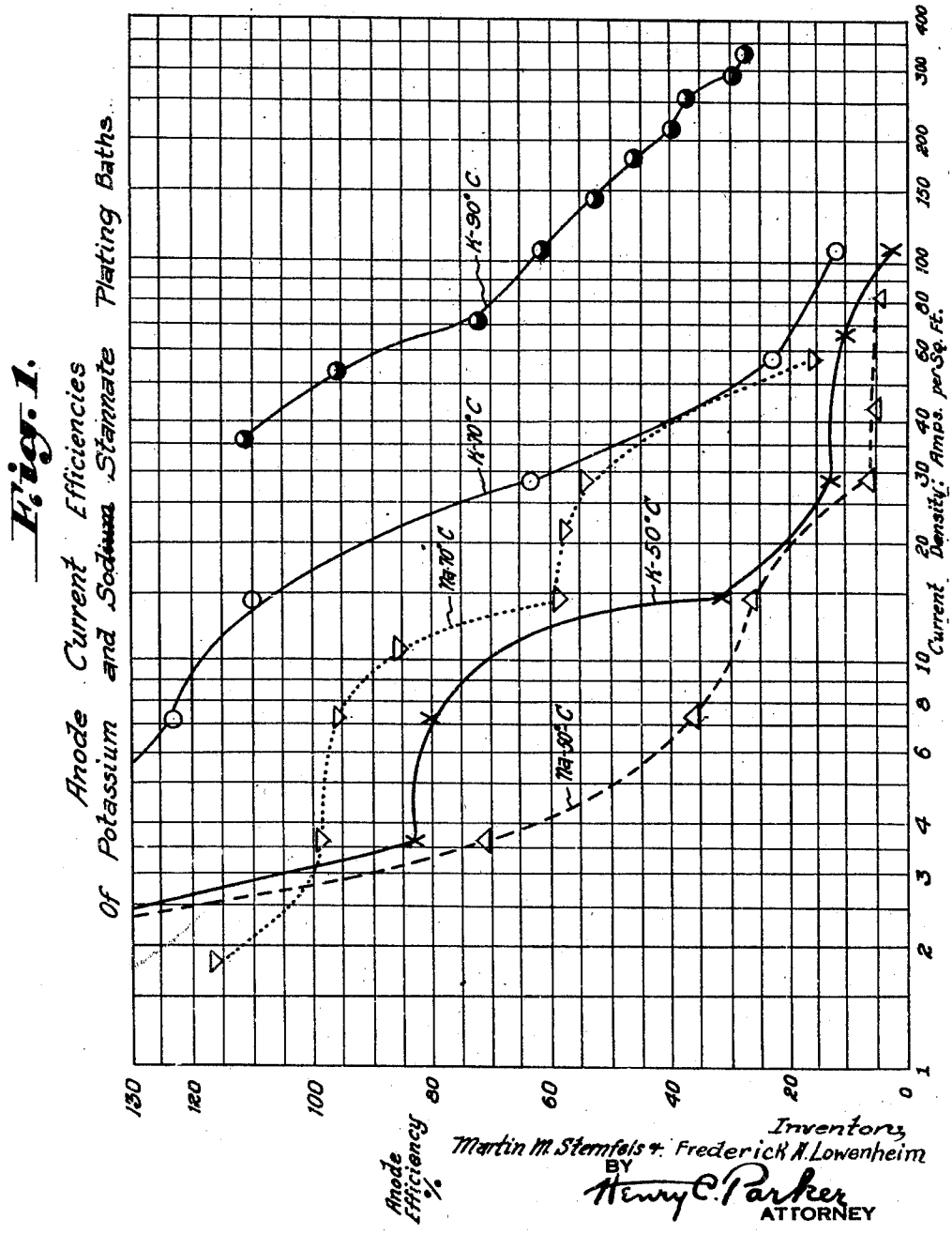
July 22, 1947. F. A. LOWENHEIM ET AL 2,424,472

TIN PLATING FROM POTASSIUM STANNATE BATHS

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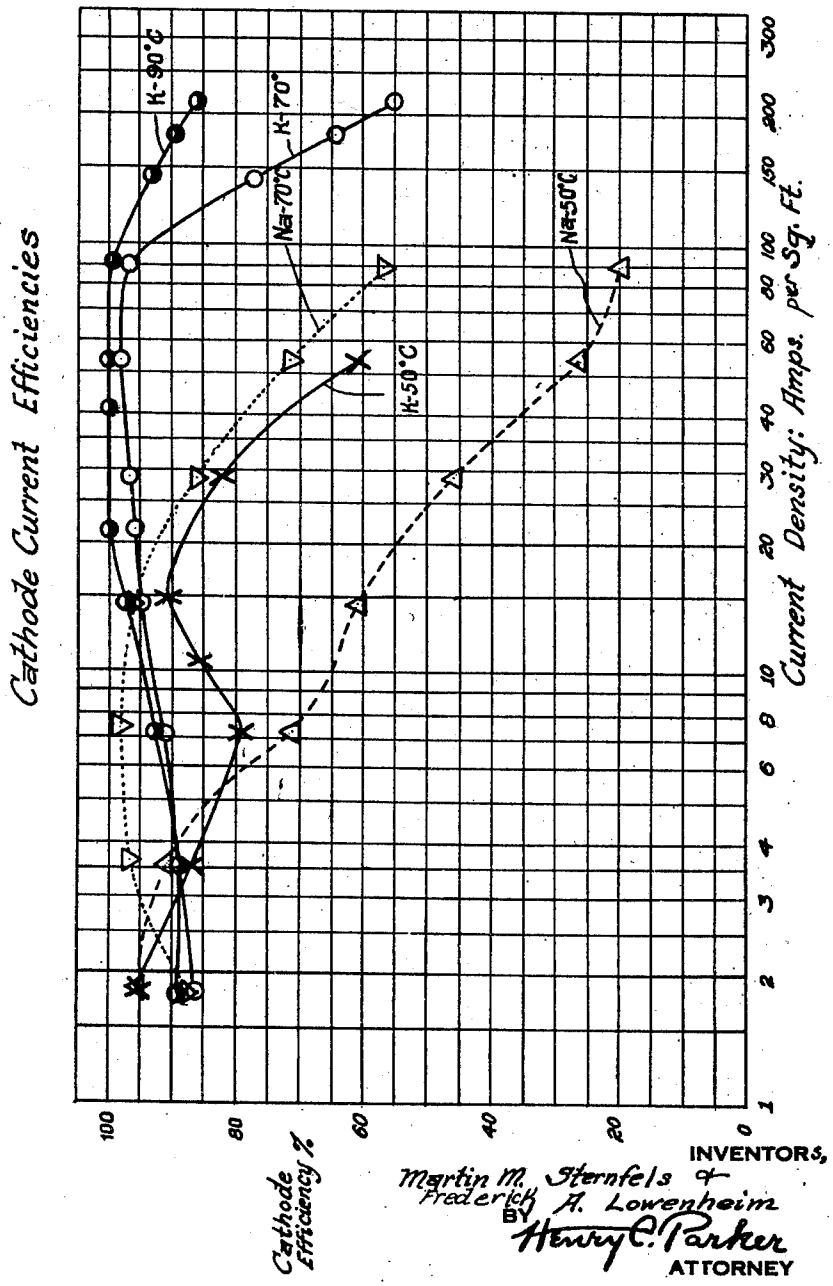
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Fig. 2.



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TIN PLATING FROM POTASSIUM STANNATE BATHS

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9 Claims. (Cl. 204—54)

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This invention relates to tin plating from potassium stannate baths; and it comprises a process wherein tin is plated electrolytically from alkaline baths containing potassium stannate and potassium hydroxide in concentrations ranging from about 0.25 to 3.0 mols per liter of the stannate and 0.15 to 3.5 mols per liter of potassium hydroxide, with cathode current densities usually ranging from about 30 to 1000 amperes per square foot and at temperatures preferably ranging from 70° C. to substantially boiling temperatures of the bath; whereby high cathode efficiencies are obtained at maximum plating speeds. The invention also includes tin plating baths having the compositions as defined; all as more fully hereinafter set forth and as claimed.

Electrolytic plating from caustic alkali-stannate baths has been known for many years. But commercial use of these baths is a rather recent development, extending over only the past ten to fifteen years. The baths used commercially have all contained sodium stannate and recently the use of these baths has expanded rapidly in spite of several rather important limitations in their operating characteristics.

In using sodium stannate baths it is necessary to employ sufficiently high current densities together with sufficiently low free alkali contents to cause the formation of a greenish yellow film on the anode during operation. Otherwise there is a tendency to form stannite in the bath which results in the formation of spongy deposits. This places an upper practical limit of about 0.5 mol per liter (mols/l.) on the concentration of caustic soda to be used in the bath. If the content of caustic alkali falls too low there is danger that the CO_2 absorbed from the air will cause precipitation of insoluble tin salts; more important, if the alkali content is too low, the anodes become coated with an insoluble, electrically-resistant film which lowers the anode efficiency excessively, and greatly raises the voltages required to cause the desired current to flow. Hence rather careful control of the caustic content is essential.

The main disadvantage of sodium stannate baths, however, is the fact that they have reasonably high cathode current efficiencies only at low current densities, the efficiency falling rapidly as the current density is increased. This phenomenon definitely limits their plating speed, as any increase in current density is almost completely counter-balanced by a corresponding fall in cathode current efficiency, and the plating speed, i. e., the weight of deposit per unit of time, rises only slightly or even remains constant, since plating speed is proportional to the product of current density and cathode current efficiency. In general it is not practical to use cathode current densities above about 25 amperes per square foot (amps./ft.^{2}). While it is possible to increase this current density up to 60 amps./ft.^{2} or slightly higher, this can be done only at the expense of obtaining an impractically low cathode efficiency. While the cathode efficiency seemingly might be increased by the use of higher temperatures or higher stannate concentrations, the full use of these expedients is impossible owing to the fact that sodium stannate has a negative coefficient of solubility; hence there is danger of precipitating insoluble tin salts in the bath if the temperature or the concentration is raised too high. In the case of a sodium stannate plating bath containing 1.17 mols per liter of sodium stannate and 0.33 mol per liter of free caustic soda, for example, crystallization of sodium stannate from the solution starts when the temperature is raised to about 80° C. It would be impossible, therefore, to use such a bath above a temperature of about 70° C. In general the higher concentrations of sodium stannate require the lower operating temperatures.

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We have made several surprising discoveries about the operating characteristics of potassium stannate baths, which characteristics differ substantially from those of the sodium stannate baths. As a result of these discoveries, tin plating can be done at a high rate and very efficiently by the use of potassium stannate baths.

One of the important discoveries as to potassium stannate baths is that the concentration of stannate in the bath can be relatively high. Not only is potassium stannate much more soluble than sodium stannate at all temperatures both in water and in solutions of the corresponding hydroxide, but the temperature coefficient of solubility of potassium stannate is positive rather than negative. The temperature of operation and/or the concentration can, therefore, be increased substantially above the values commer-

cially usable in the operation of sodium stannate baths. Thus, while the maximum concentration of sodium stannate, which has been recommended for practical use, is about 0.75 mol per liter, we have found that our potassium stannate baths can be employed at stannate concentrations substantially above this value, that is, up to at least 3.5 mols per liter with advantages which increase as the concentration is increased.

An even more surprising fact which we have discovered is that, when the potassium stannate bath is operated at these higher concentrations and temperatures, high cathode current efficiencies are obtained over substantially any desired range of cathode current densities. The curves of cathode efficiency plotted against cathode current density in the potassium stannate bath are quite flat and their maxima occur at current densities which are far above those of the sodium stannate baths. The plating speed in the potassium baths, for a given cathode efficiency, can actually be increased more than five times that of any value obtainable with the sodium stannate bath. The potassium stannate bath has the additional advantage of providing a saving in power because of its greater conductivity. It also has a slightly higher throwing power than the sodium stannate bath.

When potassium stannate baths containing high caustic concentrations are used, there is less danger of formation of spongy deposits with slight variations in free caustic concentration than in the case of the sodium stannate bath. This has a two-fold advantage since it eliminates the necessity of close caustic control and it enables an increase in the anode efficiency. In both the sodium and the potassium stannate baths the anode efficiency is increased by increase of the caustic concentration but, as shown previously, it is impossible to take full advantage of this fact in the case of the sodium baths.

Through the range of tin concentrations, which are commonly employed in the commercial operation of sodium stannate baths, it has been found that the anode efficiencies obtained with the potassium baths are about the same as those obtained with the corresponding sodium baths. Fortunately, it is possible to increase the caustic concentration in the potassium baths up to about 3.5 mols per liter which enables the attainment of anode efficiencies substantially above those which could be obtained at the maximum caustic concentrations permissible with sodium baths.

A further but relatively minor advantage of the potassium stannate baths over the sodium stannate baths is that the surface tension and viscosity of potassium hydroxide are lower than those of sodium hydroxide at equivalent concentrations, so that drag-out losses and losses due to incomplete washing are reduced.

The advantages of the present invention can be explained in more detail by reference to the following illustrative embodiments of potassium stannate plating baths which have been found satisfactory in practical tin plating operations.

The cathode efficiency values given in the following tables are subject to variation depending upon the experimental technique employed in their determination, although the relationship between the values will remain fixed. We have made all of our determinations by using 500 cc. of the given solution in a 600 cc. breaker maintained at the temperature of investigation by a thermostat. Insoluble nickel or nickel-plated anodes spaced 2 inches apart, with a copper cathode half way between them, were used for determining cathode current efficiencies. The total cathode area was 2 square inches. The time of test varied from 1 to 5 minutes depending upon the current density employed.

Plating bath No. 1

Potassium stannate, 2.44 mols/liter
Free KOH, 0.53 mols/liter
Temp., 90° C.
Cathode efficiency:
100% at 100 amps./ft.^{2}
98% at 200 amps./ft.^{2}
80% at 500 amps./ft.^{2}
70% at 1000 amps./ft.^{2}
Anode efficiency:
90% at 60 amps./ft.^{2}
80% at 75 amps./ft.^{2}
30% at 150 amps./ft.^{2}

Plating bath No. 2

Potassium stannate, 1.60 mols/liter
Free KOH, 2.14 mols/liter
Temp., 90° C.
Cathode efficiency:
95% at 50 amps./ft.^{2}
80% at 100 amps./ft.^{2}
75% at 200 amps./ft.^{2}
Anode efficiency:
85% at 160 amps./ft.^{2}
65% at 200 amps./ft.^{2}
55% at 300 amps./ft.^{2}

Plating bath No. 3

Potassium stannate, 1.21 mols/liter
Free KOH, 0.29 mols/liter
Temp., 90° C.
Cathode efficiency:
99% at 70 amps./ft.^{2}
96% at 130 amps./ft.^{2}
85% at 220 amps./ft.^{2}
Anode efficiency:
85% at 60 amps./ft.^{2}
65% at 100 amps./ft.^{2}
40% at 200 amps./ft.^{2}

It will be observed that, in the three specific examples of useful potassium stannate baths given above, the ratios of tin molarity to potassium hydroxide molarity are 4.6, 0.75 and 4.2, respectively. It is evident from these figures that no definite relationship is required between these values. The discovery of this fact was entirely unexpected, being contrary to previous opinion and teaching. It represents an important feature of our invention. Adherence to an empirically-limited range of solution compositions is unnecessary, and the plater is free to choose a plating bath tailor-made to his needs, and, by selecting the proper conditions of temperature and anode and cathode current densities, he can secure the absolute maximum in plating speed. This flexibility is absent in the case of sodium stannate baths, because of the considerably lower solubility of sodium stannate, and its negative temperature coefficient of solubility.

The important advantages which are gained by the use of potassium stannate baths at higher concentrations, temperatures and cathode current densities are made evident by consideration of the curves in the accompanying drawing. In this showing the plotted curves represent the data obtained in a direct comparison of a potassium stannate bath using the present inven-

tion with a sodium stannate bath of substantially the same concentration of tin and caustic.

In Fig. 1 the anode efficiencies in per cent are plotted as ordinates against anode current densities as abscissas, while in Fig. 2 the cathode efficiencies are plotted as ordinates against the corresponding cathode current densities.

The potassium bath used in these comparative tests corresponds to that of Plating bath No. 3 above, while the sodium stannate bath employed had the following composition:

Sodium stannate plating bath No. 3S

	Mols per liter
Sodium stannate	1.16
Free NaOH	0.37

Three temperatures were used in this comparison, namely 50°, 70° and 90° C. It will be noted that the values for the sodium bath at 90° C. are absent from the curves. This is explained by the fact that the sodium bath used in this comparison started precipitating sodium stannate when heated to a temperature of about 80° C. and, therefore, could not be operated above this temperature. In contrast the potassium bath employed was far below its saturation point at all times. But a comparison of the curves at 50° and 70° C. is sufficient to show the important advantages obtained by use of the potassium stannate baths of the present invention.

It is evident from the curves of cathode efficiency shown in the drawing that an increase of temperature is beneficial in increasing the efficiency in the case of both the sodium and the potassium baths. In both cases rise of temperature broadens the range of high cathode efficiencies and causes the maximum efficiencies to occur at higher values of current density. But these effects are much more marked in the case of the potassium baths. In the case of the potassium bath at 90° C., for example, the range of high current efficiency extends all the way from about 20 to 100 amps./ft.^{2}. And the cathode efficiency falls off so slowly even after its maximum point is reached that it would evidently be practical to operate this bath at cathode current densities of over 200 amps./ft.^{2}. This is far above any values possible in the case of sodium stannate baths. The cathode efficiency remains above 80% throughout the range investigated.

It will be noted from the 70° C. curve for the potassium stannate bath that a cathode current density of about 135 amps./ft.^{2} can be used while obtaining a cathode efficiency of 80 per cent—an entirely practical value. At 100 amps./ft.^{2} the cathode efficiency is 95 per cent. In contrast, in the case of the sodium stannate bath, if it is desired to obtain a cathode efficiency of at least 80 per cent, the maximum cathode current density which could be employed at 70° C. would be about 37 amps./ft.^{2}.

It will be noted that Potassium stannate bath #3 used in the comparative tests is far below saturation at 90° C., moreover as this concentration is increased the performance of the bath improves. With potassium baths more closely approaching saturation, operating at temperatures approaching their boiling points, it is possible to obtain practical cathode efficiencies at cathode current densities of 1000 amps./ft.^{2} or above. Needless to say this is a new result in the art of tin plating with alkaline stannate baths.

With respect to the anode efficiencies, it is evident from the curves of Fig. 1 that Potassium bath

#3 used in the comparison had a higher anode efficiency than the Sodium bath #3S at both 50° and 70° C. Increasing the temperature improves substantially the anode efficiencies obtained with both the sodium and the potassium baths. But while it is possible to take advantage of this fact with the potassium baths, difficulties in the form of the crystallization of tin salts prevent the use of temperatures much above 70° C. in the case of the sodium stannate baths.

It will be noted that the anode efficiency curves extend above 100 per cent. This means that the tin anodes dissolve in this region with the formation of stannite in the bath. This formation should, of course, be avoided, that is, the anode current densities employed should be sufficiently high so that the anode efficiency is below 100 per cent. The higher the temperature of the bath, the higher the current density to be employed, which emphasizes the advantages derived from the use of the higher temperatures.

While the most striking advantages of our potassium stannate baths, in comparison with sodium stannate baths, occur in baths employing concentrations of potassium stannate above 0.75 mol per liter, the advantage of obtaining a high cathode efficiency at high current densities is present even at concentrations which are conventionally employed in commercial sodium stannate baths. This is seen from the following comparison of two plating baths in which lower concentrations of stannate are employed.

Plating bath No. 4

Potassium stannate, 0.35 mols per liter
Free KOH, 0.2 mols per liter
Temp., 90° C.
Cathode efficiency:
95% at 25 amps./ft.^{2}
93% at 50 amps./ft.^{2}
90% at 75 amps./ft.^{2}
80% at 100 amps./ft.^{2}
Anode efficiency:
90% at 25 amps./ft.^{2}
60% at 50 amps./ft.^{2}
50% at 75 amps./ft.^{2}
40% at 100 amps./ft.^{2}

Sodium stannate plating bath No. 4S

Sodium stannate, 0.38 mols per liter
Free NaOH, 0.2 mols per liter
Temp., 90° C.
Cathode efficiency:
92% at 25 amps./ft.^{2}
80% at 50 amps./ft.^{2}
75% at 75 amps./ft.^{2}
65% at 100 amps./ft.^{2}
Anode efficiency:
110% at 25 amps./ft.^{2}
85% at 50 amps./ft.^{2}
65% at 75 amps./ft.^{2}
40% at 100 amps./ft.^{2}

If it is desired to operate at the higher current densities made possible by the present invention, it is, of course, necessary to strike a balance among the various factors of cathode and anode efficiencies, relative cathode and anode current densities and relative cathode and anode areas. It is readily seen that, in order to obtain maximum cathode current densities, that is, maximum plating speeds, it is necessary to employ anode areas which are several times the areas of the cathodes and/or to proceed with low anode efficiencies. But by studying curves corresponding to those of Figs. 1 and 2 it is a relatively simple

matter to select conditions of operation which will produce satisfactory results in a given plating problem. For example, if it is desired to operate Plating bath #3 at 90° C. at a cathode current density of 130 amps./ft.^{2}, the cathode efficiency obtained will be about 95 per cent, while an anode efficiency of 90 per cent can be obtained with an anode current density of 60 amps./ft.^{2}. This means that the anode area, under these conditions, should be roughly twice the cathode area. If it is desired to employ substantially equal cathode and anode areas, this can be accomplished by using Plating bath #2 at 90° C. with cathode and anode current densities within the range of about 150 to 200 amps./ft.^{2}. It will be seen from the data in Example 2 that under these conditions the cathode and anode current efficiencies will range from about 65 to 85%. Since it is considered practical to operate with cathode and anode efficiencies as low as 60 per cent or below, in the case of sodium stannate baths, it is evident that a wide range of operating conditions may be selected within which the potassium stannate baths can be operated economically.

The results which we have obtained with potassium stannate baths indicate that these baths can be operated at temperatures ranging from 50° C. or below up to substantially their boiling temperatures, with noteworthy advantages over the sodium bath at temperatures ranging from 70° C. to boiling, while the concentrations of potassium stannate and potassium hydroxide can be varied in practical use over the ranges of from about 0.25 to 3.0 mols per liter of stannate, and from about 0.15 to 3.5 mols per liter of potassium hydroxide. The lower practical limit of potassium stannate concentration lies at about 0.25 mol per liter, since at concentrations below this, the plating speed becomes too low to be economical.

While we have described what we consider the best embodiments of our invention, it is evident that many modifications can be made in the specific procedures and plating baths which have been described without departing from the purview of this invention. Thus, it is possible to employ any of the conventional addition agents in the potassium stannate baths. This includes the use of oxidizing agents adapted to oxidize stannites to stannates, such as hydrogen peroxide and alkali metal perborates. Foaming agents such as potassium resinate and potassium oleate can be employed if desired. The presence of carbonates in usual amounts in the bath is not harmful. The presence of small amounts of sodium ions, introduced for example as an impurity in the potassium stannate, or as a constituent of an addition agent, as e. g., sodium perborate, will not materially change the operating characteristics of the bath. The presence of excessive amounts, such as could, for example, cause the precipitation of sodium stannate, must of course be avoided. Definite limits on the permissible ratio of sodium to potassium ions cannot be set, as they depend upon the concentration of the solution, the relative proportions of stannate and hydroxide and the temperature of operation. In the preparation of the baths one may add potassium stannate as such or one may add any tin salt which will react in the bath to produce potassium stannate without introducing any harmful impurities.

While the present invention is applicable to all types of tin plating, such as still or barrel plating, it is particularly adapted for use by the manufacturer who can carefully control his operating conditions and who can therefore fully realize upon the important advantages and savings made possible by this invention. In many manufacturing plants the potassium stannate plating bath can be set up as a unit in a production line, the operating conditions being automatically controlled at the desired optimum point. Since a plating speed roughly five times that obtainable with the sodium stannate bath can be used, it would be possible to employ a plating set-up of one-fifth the size and still obtain the same production. The lower voltages required and the better throwing power obtained with the potassium bath constitute additional operating advantages. With continuous strip plating and similar operations it is possible to obtain very thin coatings having a high degree of uniformity, owing to the high throwing power of the potassium bath, and to do it at maximum plating speeds. In such installations it is possible to vary the plating speed, while still obtaining maximum plating efficiency, by the simple expedient of changing the bath temperature or concentration.

It is obvious, of course, that insoluble as well as soluble anodes can be used in our invention. If insoluble anodes are used, the tin in the bath must be replenished by the addition of tin salts.

It will be understood that our invention is not to be limited to plating baths having the compositions of the specific examples given above, which are merely by way of illustration. All baths included in the range of compositions set out in the following claims are superior to the conventional sodium stannate baths in at least one of the following respects; higher cathode current efficiency, wider range of current densities at which high current efficiencies are found, higher anode current efficiency, higher plating speed, higher conductivity and greater stability at high temperatures. Most of the baths covered by the claims are superior in several of these respects in comparison with sodium stannate baths. Other modifications of our invention, which fall within the terms of the following claims, will be immediately evident to those skilled in this art.

What we claim is:

1. A process for the electrolytic deposition of metallic tin, which comprises immersing an article to be plated in an aqueous plating bath of potassium stannate and free potassium hydroxide, and connecting said article as a cathode in an electric circuit, supplying plating current to said bath, said bath having a composition comprising essentially from about 0.75 to 3.0 mols per liter of potassium stannate, from about 0.15 to 3.5 mols per liter of potassium hydroxide, and water, while maintaining the temperature of said bath within the range of about 70° C. to substantially the boiling point of said bath and while using a cathode current density ranging from about 100 to 1000 amperes per square foot.

2. A process for the electrolytic deposition of metallic tin, wherein substantially equal anode and cathode current efficiencies are obtained, said process comprising immersing an article to be plated in an aqueous plating bath of potassium stannate and free potassium hydroxide, and connecting said article as a cathode in an electric circuit with a soluble metallic tin anode, supplying plating current to said bath, said bath having a composition comprising essentially about 1.6 mols per liter of potassium stannate, 2.1 mols per liter of free potassium hydroxide, and water, while maintaining said bath at substantially 90° C. and while using a cathode current density and anode

current density of about 150 to 200 amperes per square foot.

3. A process for the electrodeposition of metallic tin which comprises passing electric current from an anode to a cathode and through an electrolytic bath comprising essentially water, potassium stannate at a concentration between about 0.25 and about 3.0 mols per liter and free potassium hydroxide at a concentration between about 0.15 an about 3.5 mols per liter, maintaining the temperature of said bath within the range of about 70° C. to substantially the boiling point thereof, maintaining the cathode current density between about 30 to 1,000 amperes per square foot, and operating said process at a cathode efficiency of about 60 to 100 per cent.

4. A process for the electrodeposition of metallic tin which comprises passing an electric current from an anode to a cathode through an electrolytic bath comprising essentially water, potassium stannate at a concentration between about 0.75 and about 3.0 mols per liter and free potassium hydroxide at a concentration between about 0.15 and about 3.5 mols per liter, maintaining the temperature of said bath between about 70° C. and the boiling point thereof, maintaining the cathode current density between about 100 and 1,000 amperes per square foot, and adjusting the said values to produce a cathode efficiency between about 60 and 100 per cent.

5. A process for the electrodeposition of metallic tin which comprises passing an electric current from an anode to a cathode through an electrolylic bath comprising essentially water, potassium stannate at a concentration of about 2.44 mols per liter, free potassium hydroxide at a concentration of about 0.53 mol per liter, at a temperature of about 90° C. and maintaining the cathode current density between about 100 and 1,000 amperes per square foot.

6. A process for the electrodeposition of metallic tin which comprises passing an electric current from an anode to a cathode through an electrolytic bath comprising essentially water, potassium stannate at a concentration of about 1.21 mols per liter, free potassium hydroxide at a concentration of about 0.29 mol per liter, at a temperature of about 90° C. and maintaining the cathode current density between about 70 and 220 amperes per square foot.

7. A process for the electrodeposition of metallic tin which comprises passing electric current from an anode to a cathode and through an electrolytic bath comprising essentially water, potassium stannate at a concentration between about 0.25 and about 3.0 mols per liter and free potassium hydroxide at a concentration between about 0.15 and about 3.5 mols per liter, maintaining the temperature of said bath from above about 85° C. to substantially the boiling point thereof, maintaining the cathode current density between about 30 to 1,000 amperes per square foot, and adjusting the said values to produce a cathode efficiency between about 60 and about 100 per cent.

8. A process of tin plating which comprises passing a continuous metal strip as a cathode through an electroplating bath having an anode, said bath comprising essentially water, potassium stannate at a concentration between about 0.25 and about 3.0 mols per liter and free potassium hydroxide at a concentration between about 0.15 and about 3.5 mols per liter, maintaining the temperature of said bath from above about 85° C. to substantially the boiling point thereof, maintaining the cathode current density between about 30 to 1,000 amperes per square foot, and adjusting the said values to produce a cathode efficiency between about 60 and about 100 per cent.

9. A process for the electrodeposition of metallic tin which comprises passing an electric current from an anode to a cathode through an electrolytic bath comprising essentially water, potassium stannate at a concentration between about 0.75 and about 3.0 mols per liter and free potassium hydroxide at a concentration between about 0.15 and about 3.5 mols per liter, maintaining the temperature of said bath between about 70° C. and the boiling point thereof, maintaining the cathode current density between about 30 and 1,000 amperes per square foot.

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