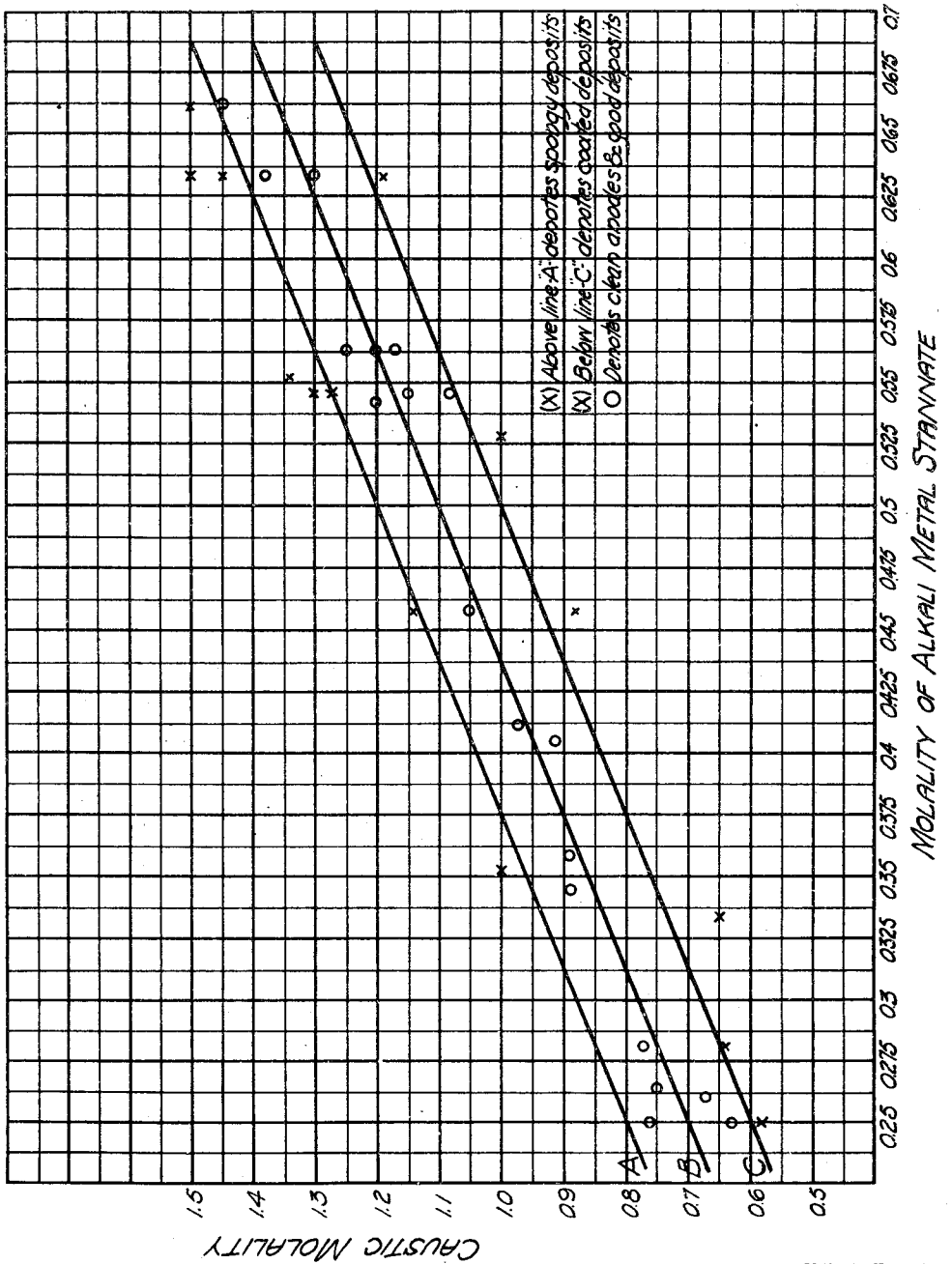
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PROCESS FOR THE ELECTRODEPOSITION OF TIN

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PROCESS FOR THE ELECTRODEPOSITION OF TIN

Application filed February 6, 1929. Serial No. 337,824.

This invention has for its object the continuous production of white, smooth and non-porous tin deposits over extended periods of time and at a high rate of speed, with practically no production of waste materials.

In a copending application, Ser. No. 337,833, filed of even date herewith by one of us, F. F. Oplinger, and issued as U. S. Patent No. 1,841,978, it is shown that highly satisfactory deposits of tin may be produced from alkaline tin baths containing caustic alkali and alkali metal stannate and in which the analytically determined concentration of alkali metal stannate bears a definite relationship to the analytically determined alkalinity. The alkalinity of these baths, for each concentration of alkali metal stannate, may vary a limited amount above or below an optimum value as described more fully below.

Under ideal plating conditions, such baths will give good tin deposits continuously. But, in practical work and when operating in a large scale, the plating conditions are seldom ideal and in time it may be necessary to adjust the bath composition, as for example, by adding either caustic alkali or alkali metal stannate, in order to keep the concentration relationship within the limits specified. If one is using a bath in which the alkalinity has become so high as to exceed the relationship referred to above, the addition of alkali metal stannate, in order to increase the relative amounts of the latter and therefore decrease the relative alkalinity, may lead to serious difficulty in that the added alkali metal stannate when dissolved in the water of the solution produces an additional alkalinity of its own. The total alkalinity of the solution is often further increased, when using commercial alkali metal stannate, by the presence of free caustic in the same. Since the addition of large amounts of alkali metal stannate only slightly increases the ratio of its concentration in the solution as compared with the resulting alkalinity, it is obvious that this method of adjusting will soon fill the baths with large quantities of dissolved material and is uneconomical and impractical, particularly at higher concentrations of alkali metal stannate and at concentrations approaching saturation of the bath with this salt.

If one attempts to reduce the alkalinity of an alkaline tin plating bath containing alkali metal stannate and caustic alkali by adding acid alone, the bath becomes inoperative, since precipitates and sludges are formed and further deposition of tin will be in the form of spongy coatings.

We have now found, that the alkalinity of a tin plating bath containing caustic alkali and alkali metal stanate can be reduced, without harm to the bath, by adding to the latter an acid, preferably a weak acid, such as acetic acid, and at approximately the same time adding an oxidizing agent, such as peroxides, permanganates and persulfates of alkali metals, or hydrogen peroxide or alkali metal perborate. No precipitates or sludges are formed in the bath when the oxidizing agent is used in connection with the acid. We prefer the use of hydrogen peroxide or alkali metal perborate. The amounts of oxidizing agent added at any one time will usually be small, as for example, about 1 to 3 ounces of 25 volume hydrogen peroxide or its equivalent per gallon of plating solution. However, we do not wish to be limited to these specific amounts, since any quantity may be used as long as the solution is capable of dissolving the same. When using hydrogen peroxide, a cold solution will permit the addition of larger amounts than a hot solution, since the latter will decompose the hydrogen peroxide more rapidly and will cause violent foaming if too much is added at one time.

Although we prefer to use acid and oxidizing agent to regulate alkalinity, we have further found that the operation of alkaline tin plating baths can be improved by the addition thereto of the above mentioned oxidizing agents or per compounds alone, without the addition at the same time of any acid. We do not know what action occurs in the baths when the oxidizing agent alone is added, but we have noticed that the tendency, in baths whose alkalinity is relatively high, to deposit spongy tin at the cathode, disappears upon the addition of such oxidizing agents. We believe the action to be that of oxidizing

any alkali metal stannite which may be present to stannate, thereby slightly increasing the stannate concentration, i. e. reducing the relative alkalinity. The amount of stannite in the solution is probably small at all times, since we have found that baths having the proper relationship between alkalinity and stannate concentration for good plating results do not show the presence of any significant amounts of stannous tin.

The improvement in the operation of these tin baths, which results when adding oxidizing agent alone, sometimes disappears after about 30 minutes. This is more often the case when the caustic concentration has become too high. However, if one merely adds oxidizing agent from time to time, the baths will function continuously with the improved results.

We have also found, that baths, having had their composition regulated by adding to them an oxidizing agent or per salt, will operate for greater lengths of time without need of adjustment than baths of otherwise the same composition. Furthermore, the deposits from baths which have been so regulated appear smoother and brighter than deposits from baths which have not been so regulated. We have therefore discovered, that novel tin plating baths which plate tin even more satisfactorily than the baths of the above mentioned copending application may be produced by first adding to the latter, small amounts of the oxidizing agents or per compounds used by us in controlling the composition of alkaline tin plating baths.

Our broad invention and a specific application of the same may be explained more fully by reference to the accompanying graph, which shows the relationship between the analytically determined alkalinity and alkali metal stannate concentrations in the baths of the above mentioned copending application and which relationship also holds for our novel baths containing small amounts of oxidizing agents or per compounds, as specified above. This relationship may be maintained by the present invention for each concentration of alkali metal stannate within the limits of alkalinity shown between the lines A and C.

The alkalinity is designated on the graph as caustic molality and was determined by analysis, since determinations of alkalinity by other methods will be affected by various factors, such as impurities usually present in commercial alkali metal stannate, among which are free caustic, the natural alkalinity of an aqueous solution of alkali metal stannate, etc. The alkali metal stannate content is also determined analytically for similar reasons and is designated on the graph as molality of alkali metal stannate.

To simplify further explanations of our invention, we wish wherever referring to concentrations of caustic alkali or, specifically, sodium hydroxide, whether stated in terms of normality, molality, ounces per gallon, or the like, to be understood as referring, not to concentrations of caustic added as such to the bath, but to total alkalinity, as determined by titration, using thymol phthalein as an indicator or using an equivalent procedure. Likewise, wherever referring to concentrations of alkali metal stannate, we wish it to be understood as referring to those concentrations determined either by an analysis of the solution itself or by making up the bath with a material the stannate content of which is accurately known.

In determining caustic alkali concentration, thymol phthalein is used as an indicator, since its blue color in the presence of caustic alkali and alkali metal stannate mixtures disappears upon the addition of acid, for example of hydrochloric or sulfuric acid, at the same time that insoluble tin compounds begin to precipitate. Of course, other indicators can be used instead of thymol phthalein, provided one corrects the concentration of caustic alkali so determined to give it the same value as that which would be obtained by the use of thymol phthalein. Such corrections could be made on the basis of pH values of the solution.

Referring again to the accompanying graph, the concentration of caustic for optimum plating results, as compared with the concentration of alkali metal stannate, is represented by the line B of the graph and may also be represented by the equation:

Caustic alkali (normality) = 0.4 times the alkali metal stannate (normality) + 0.3.

In this equation, a normal solution of alkali metal stannate is considered as containing ¼ mole of stannate per liter. The above equation may therefore be expressed as,

Caustic molality = 1.6 times the stannate molality + 0.3.

The range between lines A and C represents the values for ratio of caustic to stannate concentration of our alkaline tin plating baths containing oxidizing agents and of the baths of the copending application by F. F. Oplinger which do not contain these oxidizing agents. Outside of this range, less advantageous deposition of tin results. The range between lines A and C also represents values for caustic alkali concentration in the above equation when the figure 0.3 is substituted by values between 0.2 and 0.4. The figure 0.3 in the two equations denotes the concentration of 0.3 moles per liter of caustic which is always present in these baths at optimum plating compositions, regardless of the stannate concentration.

In carrying out our process of regulating the composition of alkaline tin plating baths we can apply it specifically to maintaining

the relationship shown between the lines A and C of the graph. We have found as a rough shop test, that a thin film of light greenish-yellow color exists during electrolysis on the anode when the bath contains the proper caustic concentration. When electrolysis is discontinued the anode becomes clearer and brighter under the same conditions. When too much caustic is present, the anode is clean during the electrolysis and has the ordinary dull appearance of tin in caustic solution. A whitish to yellowish coating forms on the anode when the caustic content is too low. The observations on the condition of the anodes can be followed in practical work by the addition of moderate quantities of caustic or of the oxidizing agents which we have specified, depending upon whether the solution is low or high respectively in caustic. A weak acid, such as acetic, may be added along with the oxidizing agent.

As an improvement over this more or less qualitative control, we prefer to analyze the solution for caustic as given above and also for stannate, and then to add the calculated quantity of materials such as caustic alkali, alkali metal stannate, oxidizing agent, or oxidizing agent and weak acid, in order to bring the bath composition nearer to the optimum value represented by line B of the graph.

We shall now further describe our alkaline tin plating baths containing oxidizing agents. Our preferred solution and method of operation are as follows:

Example I

Sodium stannate	0.4375 mol/l. or 12.43 oz/gal.
Sodium hydroxide	1.0 mol/l. or 5.34 oz/gal.
(Concentrations of the above 2 ingredients by analysis of solution)	
Hydrogen peroxide (25 volume)	1/15 oz/gal.
Anodes	Straits tin
Ratio of anode to cathode area	3 to 1
Cathode current density	20 to 60 A/SF
E. M. F.	4.0 to 6.0 volts
Temperature of solution	70 to 80° C. (158 to 176° F.)

A white smooth and non-porous tin deposit will be produced in a short time on a metal surface, such as clean sheet steel, by using a bath of this kind. The anode and cathode efficiencies in the above example are approximately 50% each, calculated on the basis of divalent tin.

Results comparable with the above may also be obtained with the following bath:

Example II

Sodium stannate	0.634 mol/l. or 18.0 oz/gal.
Sodium hydroxide	1.3 mol/l. or 6.94 oz/gal.
(Concentrations of the above 2 ingredients by analysis of solution)	
Hydrogen peroxide (25 volume)	1/15 oz/gal.
Anodes	Straits tin
Ratio of anode to cathode area	3 to 1
Cathode current density	20 to 60 A/SF
E. M. F.	4.0 to 6.0 volts
Temperature of solution	70 to 80° C. (158 to 176° F.)

Other examples of our baths may be obtained by consulting the accompanying graph wherein symbol "0" denotes compositions from which excellent deposits were obtained; the anodes remaining clean and the anode and cathode efficiencies being equal to within about 10%. The symbol "x" on the graph above line A denotes bath compositions from which spongy deposits were obtained. Various quantities of oxidizing agents, such as peroxides, permanganates, persulfates, perborates, hydrogen peroxide, etc. were used in each of the baths shown on the graph, but these quantities were generally small.

Instead of making up our tin baths with alkali metal stannate itself, we may use any tin salt, which does not put objectionable impurities in the bath in the presence of caustic alkali and the oxidizing agent used, to form the stannate in situ.

The sodium stannate concentration of our baths may vary from practically zero to the value at saturation of the solution with the same; good results being obtained between 0.07 and 0.70 moles per liter or between about 2.0 and 20 oz. per gallon, provided the caustic soda content always bears a close relation to the stannate content as shown by the graph. Our preferred range, however, lies between about 0.25 and 0.65 moles per liter or, between about 7.0 oz/gal. and 18.5 ozs. per gallon, since experience has demonstrated that below this range of stannate concentration, too much or too little caustic, to fall in the range represented between lines A and C, is much more likely to be produced during plating as the result of accidental variations in conditions, such as changes in current density, temperature, introduced impurities, etc. Below 7 oz/gal. of sodium stannate, or its equivalent in other alkali stannate, the current efficiencies are usually lower with an attendant poor quality of deposit. On the other hand, when the stannate concentration is greater than about 18.5 oz-gal., the losses produced by the adhering of some of the solution to the plated articles as they are removed from the bath is too great for economical operation. Cyrstallization of tin salts from solutions at these higher concentrations has also been noticed.

Good results may be obtained by keeping the plating solution below 85° C., but we prefer the range of 60 to 80° C. Above 85° C. there is danger of precipitation of solids within the bath.

We have found that our tin baths operate satisfactorily with cathode current densities above about 10 amperes per square foot, good deposits having been produced at 100 A/SF. Satisfactory anode current densities lie below 20 A/SF.

Our tin plating baths may be used for plating many kinds of metal and particularly steel, copper, brass, lead, zinc, cadmium, cast iron and the like.

What we claim is:

1. Process for diminishing the ratio of caustic alkali to alkali metal stannate concentration in an aqueous tin plating solution containing these substances, comprising adding to said solution an acid and an oxidizing agent of the group consisting of hydrogen peroxide, peroxides, permanganates, persulphates, and perborates.

2. Process for diminishing the ratio of caustic alkali to alkali metal stannate concentration in an aqueous tin plating solution containing these substances, comprising adding to said solution a weak acid and an oxidizing agent of the group consisting of hydrogen peroxide, peroxides, permanganates, persulphates, and perborates.

3. Process for diminishing the ratio of caustic alkali to alkali metal stannate concentration in an aqueous tin plating solution containing these substances, comprising adding to said solution a weak acid and a per compound.

4. Process for diminishing the ratio of caustic alkali to alkali metal stannate concentration in an aqueous tin plating solution containing these substances, comprising adding to said solution a weak acid and hydrogen peroxide.

5. Process for diminishing the ratio of caustic alkali to alkali metal stannate concentration in an aqueous tin plating solution containing these substances, comprising adding to said solution acetic acid and an oxidizing agent of the group consisting of hydrogen peroxide, peroxides, permanganates, persulphates, and perborates.

6. Process for diminishing the ratio of caustic soda to sodium stannate concentration in an aqueous tin plating solution containing these substances, comprising adding to said solution a weak acid and an oxidizing agent of the group consisting of hydrogen peroxide, peroxides, permanganates, persulphates, and perborates.

7. Process for diminishing the ratio of caustic soda to sodium stannate concentration in an aqueous tin plating solution containing these substances, comprising adding to said solution acetic acid and an oxidizing agent of the group consisting of hydrogen peroxide, peroxides, permanganates, persulphates, and perborates.

8. Process for diminishing the ratio of caustic soda to sodium stannate concentration in an aqueous tin plating solution containing these substances, comprising adding to said solution acetic acid and a per compound.

9. Process for diminishing the ratio of caustic soda to sodium stannate concentration in an aqueous tin plating solution containing these substances, comprising adding to said solution acetic acid and hydrogen peroxide.

10. A process for the electrodeposition of metallic tin, comprising conducting an electrolyzing current from a tin anode to the article to be coated as a cathode through an aqueous solution of alkali metal stannate, caustic alkali and a small amount of a per compound, the composition of which solution is limited by a caustic molality which increases at a uniform rate from 0.7 when the stannate molality is 0.25, to 1.34 when the stannate molality is 0.65, the range of caustic molality at each molality of stannate being 0.1 less to 0.1 more than the values thus defined.

11. A process for the electrodeposition of metallic tin, comprising conducting an electrolyzing current from a tin anode to the article to be coated as a cathode through an aqueous solution of alkali metal stannate, caustic alkali and a small amount of a per compound, the composition of which solution is limited by a caustic molality which increases at a uniform rate from 0.7 when the stannate molality is 0.25, to 1.34 when the stannate molality is 0.65, the range of caustic molality at each molality of stannate being 0.1 less to 0.1 more than the values thus defined and adding further quantities of said per compound from time to time.

12. A process for the electrodeposition of metallic tin, comprising conducting an electrolyzing current from a tin anode to the article to be coated as a cathode through an aqueous solution of sodium stannate, caustic soda and a small amount of a per compound, the composition of which solution is limited by a caustic molality which increases at a uniform rate from 0.7 when the stannate molality is 0.25 to 1.34 when the stannate molality is 0.65, the range of caustic molality at molality of stannate being 0.1 less to 0.1 more than the values thus defined.

13. A process for the electrodeposition of metallic tin, comprising conducting an electrolyzing current from a tin anode to the article to be coated as a cathode through an aqueous solution of sodium stannate, caustic soda and a small amount of a per compound, the composition of which solution is limited by a caustic molality which increases at a uniform rate from 0.7 when the stannate molality is 0.25 to 1.34 when the stannate molality is 0.65, the range of caustic molality at molality of stannate being 0.1 less to 0.1 more than the values thus defined and adding further quantities of said per compound from time to time.

14. An aqueous electrolyte for the electrodeposition of tin, containing 1.6 moles of caustic alkali per mole of alkali metal stannate and an additional concentration, not dependent upon the amount of said stannate, of about 0.2 to 0.4 moles of caustic alkali per liter, plus a soluble per compound.

15. An aqueous electrolyte for the electrodeposition of tin, containing 1.6 moles of caustic alkali per mole of alkali metal stannate

and an additional concentration, not dependent upon the amount of said stannate, of about 0.2 to 0.4 moles of caustic alkali per liter, plus hydrogen peroxide.

16. An aqueous electrolyte for the electrodeposition of tin, containing 1.6 moles of caustic alkali per mole of alkali metal stannate and an additional concentration, not dependent upon the amount of said stannate, of about 0.2 to 0.4 moles of caustic alkali per liter, the concentration of alkali metal stannate being 0.25 to 0.65 moles per liter, plus a soluble per compound.

17. An aqueous electrolyte for the electrodeposition of tin, containing about 1 mole of caustic alkali and about 0.4375 moles of alkali metal stannate per liter, plus a soluble per compound.

18. An aqueous electrolyte for the electrodeposition of tin, containing about 1 mole of caustic alkali and about 0.4375 moles of alkali metal stannate per liter, plus hydrogen peroxide.

19. An electrolyte for the electrodeposition of tin, comprising an aqueous solution containing 1.6 moles of caustic soda per mole of sodium stannate and an additional concentration, not dependent upon the amount of stannate, of about 0.2 to 0.4 moles of caustic soda per liter, the concentration of sodium stannate being 0.25 to 0.65 moles per liter, plus hydrogen peroxide.

20. In the process of electrodeposition of tin from a caustic alkali and alkali metal stannate bath, the step which comprises adding an oxidizing agent of the group consisting of hydrogen peroxide, peroxides, permanganates, persulphates, and perborates to said solution from time to time.

21. In the process of electrodeposition of tin from a caustic soda and sodium stannate bath, the step which comprises adding a per compound to said solution from time to time.

22. In the process of electrodeposition of tin from a caustic soda and sodium stannate bath, the step which comprises adding hydrogen peroxide to said solution from time to time.

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