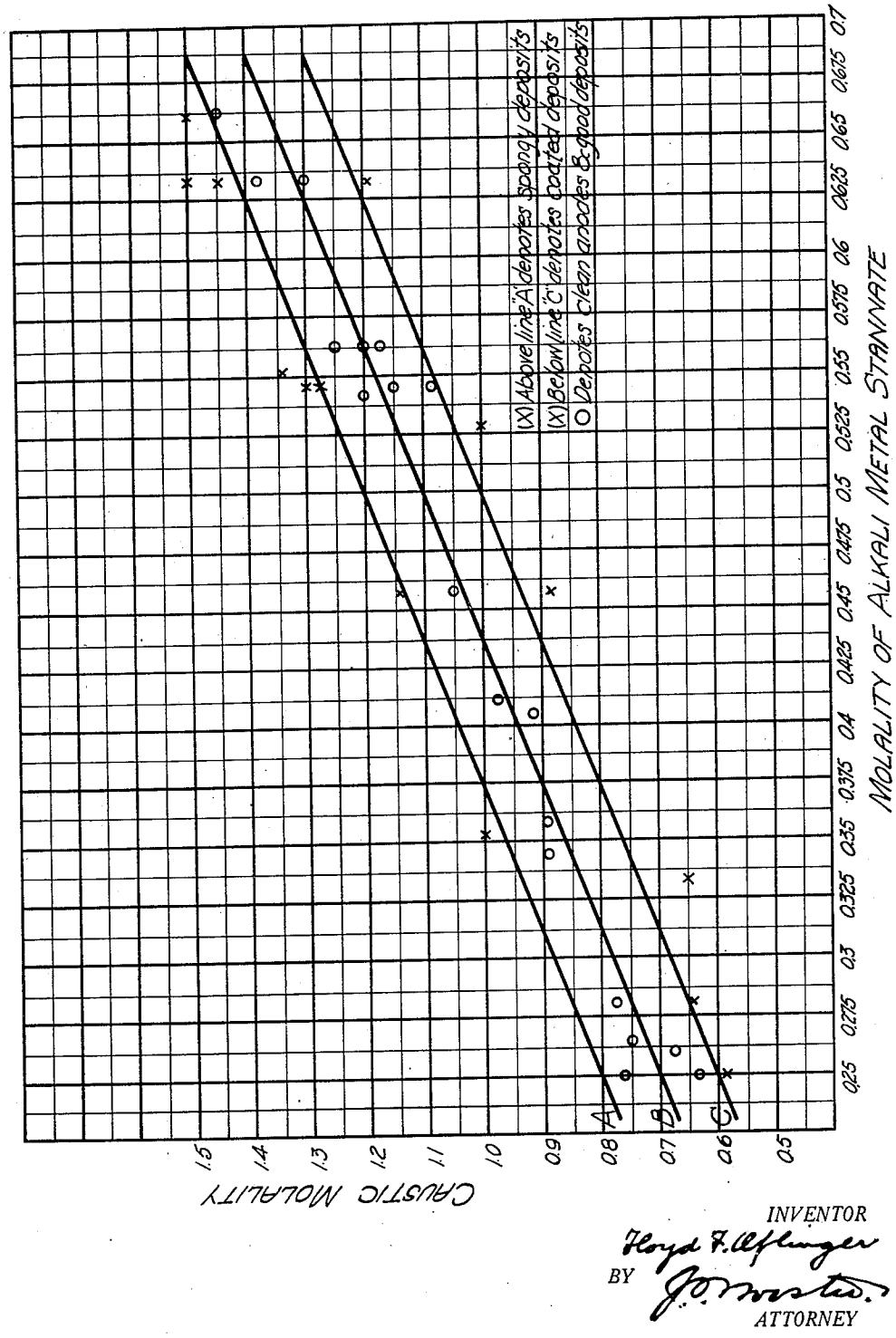
Jan. 19, 1932. F. F. OPLINGER 1,841,978

TIN PLATING

Filed Feb. 6, 1929



INVENTOR
Floyd F. Oplinger
BY J. O. Masters
ATTORNEY

Patented Jan. 19, 1932 1,841,978

UNITED STATES PATENT OFFICE

FLOYD F. OPLINGER, OF PERTH AMBOY, NEW JERSEY, ASSIGNOR, BY MESNE ASSIGNMENTS, TO THE ROESSLER & HASSLACHER CHEMICAL COMPANY, A CORPORATION OF DELAWARE

TIN PLATING

Application filed February 6, 1929. Serial No. 337,833.

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

Heretofore alkaline tin baths have been characterized by inability to continuously produce the bright, smooth deposits desired in commercial work. The majority are uneconomical in that heavy sludges, probably consisting in the main of small particles of metallic tin mixed with tin oxides or other tin compounds, are formed in the bottom of the bath after continued use. Such sludges must eventually be discarded.

I have now found, that highly satisfactory deposits of tin may be produced for extended periods of time from alkaline tin baths in which the analytically determined concentration of alkali metal stannate bears a definite relationship to the analytically determined alkalinity. All of my baths possess this definite relationship within certain limits of alkalinity and alkali metal stannate concentrations, described more fully below, and will therefore plate tin satisfactorily. I have further found that continuous plating will occur if the above mentioned definite relationship is maintained in my baths. One way of maintaining this relationship is to add caustic alkali when analysis shows the alkalinity of the bath to be low and to add alkali metal stannate when it shows the alkalinity of the bath to be high.

Above, I have specified alkalinity as determined by analysis, since any attempt at determination 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.

In determining the alkalinity, I use thymol phthalein as an indicator, since its blue color in the presence of 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 alkalinity 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.

The alkali metal stannate content of the solution may be determined by any satisfactory known method, such as reduction of the acidified solution and titration against standard iodine solution.

Because of the above stated reasons and for the purpose of simplifying further explanations of my baths, I 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, whenever referring to concentrations of alkali metal stannate I 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. Obviously, for a given grade of caustic alkali and of alkali metal stannate, whether these are chemically pure or of commercial quality, the actual amounts which one will use in making up my baths can be easily calculated by using the ratios obtained by dissolving weighed quantities of the two materials to a convenient volume and comparing their concentrations thus produced with the concentrations of caustic and stannate as determined from this solution by analysis, as given above.

The accompanying graph shows the relationship between the caustic alkali and alkali metal stannate concentrations in my baths. The concentration of caustic for optimum plating results, as compared with the concentration of alkali metal stannate, is represent-

ed 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 of a 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 my alkaline tin plating baths and outside of which 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 above two equations denotes the concentration of 0.3 moles per liter of caustic which is always present in my baths at optimum plating compositions, regardless of the stannate concentration.

My preferred solution and method of operation are as follows:

Example I

Sodium stannate	0.4375 mol/1. or 12.43 oz/gal.
Sodium hydroxide	1.0 mol/1. or 5.34 oz/gal.

(Concentrations of the above 2 ingredients by analysis of solution.)

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/1. or 18.0 oz/gal.
Sodium hydroxide	1.3 mol/1. or 6.94 oz/gal.

(Concentrations of the above 2 ingredients by analysis of solution.)

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	70–80° C. (158 to 176° F.)

Other examples of my baths may be obtained by consulting the accompanying graph wherein symbol ⊙ 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.

Instead of making up my tin baths with alkali metal stannate itself, I may use any tin salt, which does not put objectionable impurities in the bath in the presence of alkali, to form the stannate in situ.

The sodium stannate concentration of my 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. My preferred range, however, lies between about 0.25 and 0.65 moles per liter, that is, about a 1 normal to 2.6 normal solution 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. Crystallization 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 I prefer the range of 60 to 80° C. Above 85° C. there is danger of precipitation of solids within the bath.

I have found that my 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.

My 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 I claim is:

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

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

3. 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 of solution.

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

5. An electrolyte for the electrodeposition of tin, comprising an aqueous solution containing 1.6 moles of caustic soda per mole of sodium stannate plus 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.

6. An electrolyte for the electrodeposition of tin, which comprises 1 mole of caustic soda and 0.4375 moles of sodium stannate per liter of solution.

7. 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 and caustic alkali whose composition is limited by a caustic normality which increases at a uniform rate from 0.7 when the stannate normality is 1, to 1.34 when the stannate normality is 2.6, the range of caustic normality at each normality of stannate being 0.1 less to 0.1 more than the values thus defined.

8. 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 and sodium hydroxide whose composition is limited by a sodium hydroxide normality which increases at a uniform rate from 0.7 when the stannate normality is 1, to 1.34 when the stannate normality is 2.6, the range of sodium hydroxide normality at each normality of stannate being 0.1 less to 0.1 more than the values thus defined.

9. In a process for the continuous electrodeposition of tin from an aqueous solution of caustic alkali and alkali metal stannate, the step which comprises regulating the composition of said solution so as to maintain 1.6 moles of caustic alkali per mole of said stannate plus an additional concentration, not dependent upon the amount of stannate, of about 0.2 to 0.4 moles of caustic alkali per liter.

10. In a process for the continuous electrodeposition of tin from an aqueous solution of caustic soda and sodium stannate, the step which comprises regulating the composition of said solution so as to maintain 1.6 moles of caustic soda per mole of sodium stannate plus an additional concentration, not dependent upon the amount of stannate, of about 0.2 to 0.4 moles of caustic soda per liter.

Signed at Perth Amboy in the county of Middlesex and State of New Jersey this 5th day of January A. D. 1929.

FLOYD F. OPLINGER.