

March 19, 1963

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3,082,157

ELECTRODEPOSITION OF TIN

Filed June 23, 1958

2 Sheets-Sheet 1

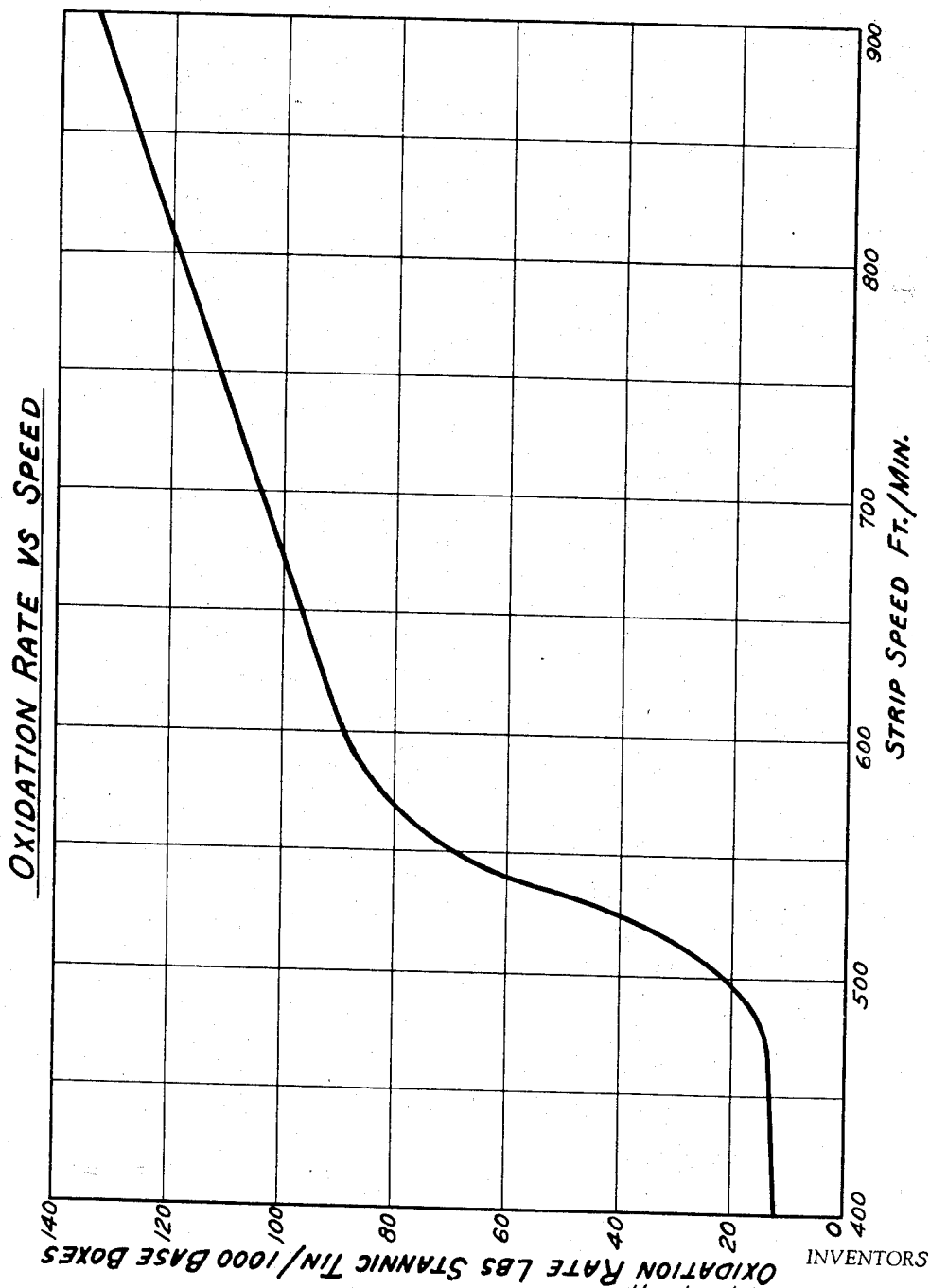


Fig. 1

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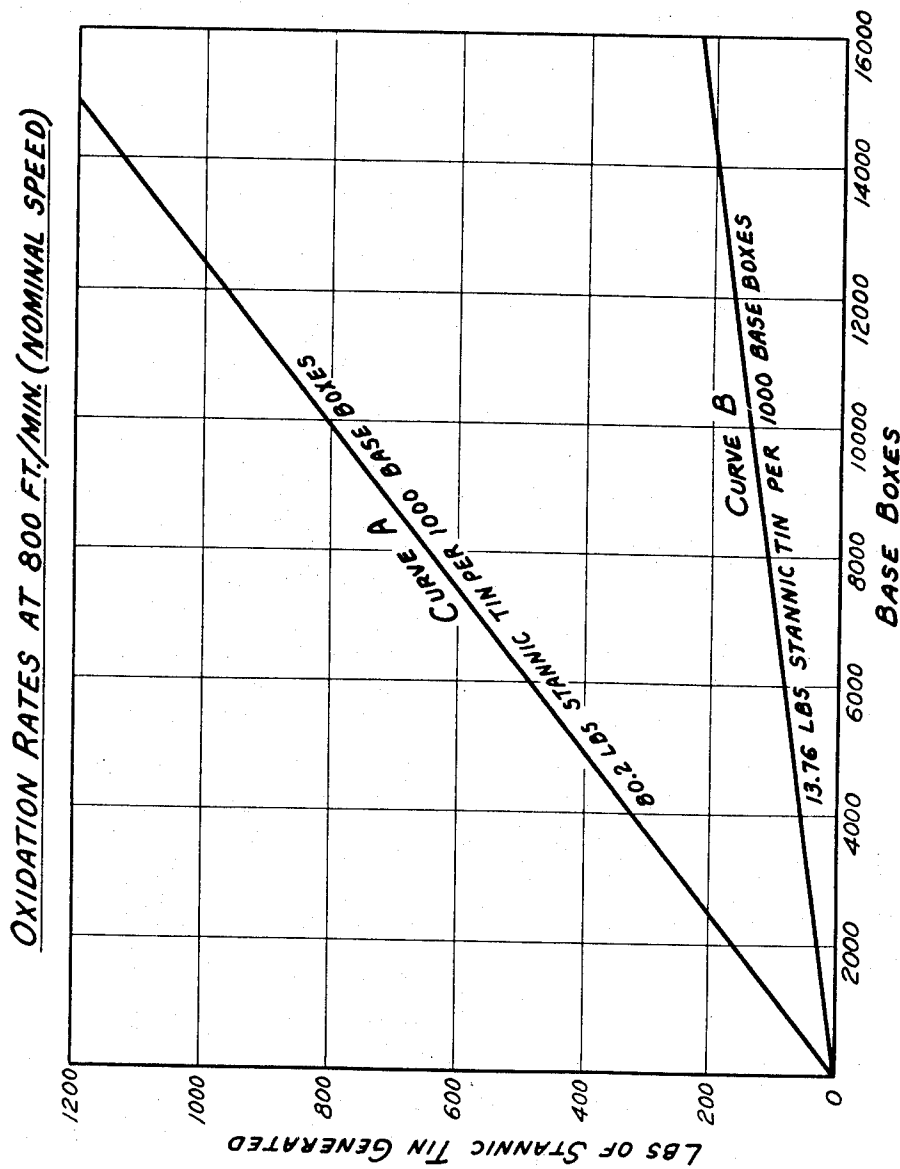


Fig. 2

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1

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ELECTRODEPOSITION OF TIN

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14 Claims. (Cl. 204—54)

This invention relates to the electrodeposition of tin from acid tinplating baths, and more particularly to electrodeposition from baths of the stannous fluoborate type.

One of the principal objects of this invention is to control the rate of oxidation in an acid tinplating bath.

Another object is to provide a bath having a low rate of oxidation.

A further object is to maintain stannic tin in the soluble form in an acid tinplating bath.

Another object is to provide a bath with a high anode limiting current density and high cathode efficiency.

In the development of high speed acid tin electroplating lines for the plating of steel strip, one of the serious drawbacks has been excessive oxidation in the plating bath.

In a vertical high speed line for the plating of strip, it is desirable to use a deep plating tank, with the strip passing through the tank in vertical skeins. The strip passes over a contact roll at the top of, and outside, the tank, down into the tank and under an idler roll at the bottom of the tank, then upward and over the next succeeding contact roll, proceeding from there to the next idler roll, and so on, in a series of skeins, numbering anywhere from two to thirty two or more. Squeegee, or back-up rolls, are usually placed adjacent the contact rolls on the side on which the strip leaves the bath. The strip passes between the squeegee and contact rolls and, when travelling rapidly, carries considerable solution with it. When the liquid strikes the juncture between squeegee and contact roll, spray is formed, and this spray entraps air, both at the point of spray formation and as the spray falls into the bath. Contact of the spray with oxygen of the air causes oxidation of the tin in the bath spray, resulting in a build-up in stannic tin in the bath, as the oxidized spray is returned to the bath.

In addition, the faces of the contact and back-up rolls are often shot-blasted, or otherwise roughened, to aid in the traction of the rolls on the strip. The resultant indentations, or cavities, in the roll surfaces carry pockets of air into the line of tangency of the two rolls. The pocketed air is compressed and then dispersed under pressure in the solution, which is carried to the rolls by the moving strip. The dispersed air results in an increased rate of oxidation of stannous tin to stannic tin.

In an acid tin plating bath the tin should be in the stannous, or bivalent state. Regardless of the nature of the tin salt which supplies the stannous tin ions to the bath, oxidation of the tin takes place to some extent, the tin being oxidized from the stannous to the stannic condition. The stannic tin has no utility insofar as producing platable tin ions is concerned, and when present in sufficient quantity will precipitate, causing sludging in the bath. The resulting precipitate must eventually be removed from the bath, and it represents a loss of tin unless reclaimed. Reclaiming the precipitated tin adds considerable cost to the plating operation. If the rate of formation of stannic tin is high, there is a serious depletion of stannous tin in the bath, requiring replenishing of the stannous tin in the form of expensive stannous compound.

The presence of precipitated matter, particularly some forms of stannic tin compounds, in the bath has a dele-

2

terious effect on submerged roll bushings, or seals, due to the somewhat abrasive nature of the precipitate.

Most acid plating lines can be operated satisfactorily, insofar as oxidation problems are concerned, if the speed of the line is held below 400 feet per minute. However, on a vertical type line, at speeds above 500 ft./min., the amount of aerated spray carried into the bath causes oxidation of the tin at such a rapid rate that the cost of operation of the plating line becomes almost prohibitive.

Another factor, in the rate of oxidation of the tin, is the amount of iron contamination in solution in the bath. Iron is introduced into the bath from the steel strip in the ferrous condition, and it apparently has a positive catalytic effect on the oxidation reaction.

In accordance with this invention, we have found that by proper selection of bath components and proper bath maintenance, we are able to control the rate of oxidation in an acid tin bath so that the bath may be operated economically on a vertical line at speeds of 900 ft./min. or greater.

We have developed a bath which is substantially non-sludging, and we define the means for controlling the anionic bath concentrations as related to the stannous tin, stannic tin and incidental iron concentrations. We have wide operating limits for a bath which will be low in oxidation rate, yet will have a high anode limiting current density, will be practically non-sludging, and will yield good tin plate.

Our bath is operable at 95% or more cathode electrochemical efficiency, provided the balance between the cathode current density, stannous tin concentration and bath temperature are maintained according to known electroplating principles. The stannous tin concentration can be varied to obtain a high cathode efficiency over a wide range of current densities. The cathode current efficiency is affected by other variables, such as free acidity, and, as is well known in the plating art, the proper conditions can be selected to obtain high cathode current efficiency.

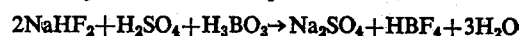
In a starting acid tinplating bath, the tin should be almost entirely in the stannous or bivalent state, and the concentration of the stannic tin is quite low. Starting, or make-up, baths can be made according to the examples given below.

Example I

This is an example of a preferred starting bath, useful in the plating of steel strip.

	G./l.
(a) Sulfuric acid (H_2SO_4) added as a water solution	35
(b) Sodium bifluoride ($NaHF_2$)	35
(c) Boric acid (H_3BO_3)	17.5
Stannous oxide (SnO) to produce stannous tin in the amount of	10
Hydroquinone	2.5
Grain refining agent (dodecyl triethyl ammonium para toluene sulfonate)	0.8

We prefer to add (a), (b) and (c) in the order shown. The quantities for (a), (b) and (c) can be varied over quite wide limits: 5 to 65 g./l. for (a) and (b), and 2.5–32.5 g./l. for (c). The ingredients (a), (b) and (c) are believed to react in the bath in the manner represented by the combined equation.



and should be added to the bath in the substantial ratio of 2 parts (a):2 parts (b):1 part (c). Sulfuric acid in excess of the stoichiometric amount required to combine with sodium bifluoride and boric acid, to form fluoboric acid, can be used up to a total sulfate (SO_4) concentration of 65 g./l., depending on the concentration of stan-

3

nic tin in the bath, as will be explained. Benefits occurring from the use of sulfuric acid in our bath within the prescribed limits are, higher reflectivity of the product, less anode sludging and less roll staining.

In Example I the fluoboric acid (HBF_4) formed by the above reaction, and as determined by the "Nitron" analytical method is equal to 18.7 g./l., or approximately 75% of the theoretical amount. Stannous tin will require $10 \times 1.48 = 14.8$ g./l. of $(\text{BF}_4)^-$ ion, therefore there is 4 g./l. excess fluoboric acid present in the bath for the given amount of tin.

In using the "nitron" method, referred to herein, we analyze for $(\text{BF}_4)^-$ ion by precipitation with nitron acetate, using essentially the procedure described by C. A. Wamser in the Journal of the American Chemical Society, vol. 73, January 1951, p. 411.

EXAMPLE II

This example is for another form of satisfactory starting bath.

	G./l.
(a) Sulfuric acid (H_2SO_4) added as a water solution	35
(b) Sodium bifluoride (NaHF_2)	35
(c) Boric acid (H_3BO_3)	17.5
Stannous tin (Sn^{++})	10
Grain refining agent	0.8

the ratio of (a), (b) and (c) should be substantially constant to conform with

$$2(a):2(b):1(c)$$

This example shows a bath similar to that of Example I without hydroquinone, the bath being applicable to those cases where maximum protection against oxidation is not required.

Below are shown relative amounts of oxidation for several acid type tin plating baths, each containing 1 g./l. of ferrous iron.

	G./l. stannic tin
Stannous chloride bath	4.8
Stannous sulfate bath	5.6
Bath of Example II	0.2
Bath of Example I	0.1

The amounts are empirical and were attained from an accelerated laboratory test designed especially for use in measuring oxidation resistance. In this test we pass 1 liter of oxygen (dispersed by a medium porosity fritted disc) through 200 ml. of electrolyte at a constant rate of 2.2 ml./sec. The amount of oxidation is expressed in terms of stannic tin formed, where zero indicates almost complete absence of oxidation, and 0.1–0.2 g./l. of stannic tin (Sn^{++++}) represents a very low oxidation rate.

A starting bath suitable for use with high current densities, such as those used in wire plating, is shown in Example III.

EXAMPLE III

	G./l.
(a) Sulfuric acid (H_2SO_4) added as a water solution	35
(b) Sodium bifluoride (NaHF_2)	35
(c) Boric acid (H_3BO_3)	17.5
Stannous tin (Sn^{++})	80
Fluoboric acid (HBF_4) (100%)	109
Grain refining agent	0.8

To calculate the amount of fluoboric acid to be added to this bath, the "nitron" analytical method indicates that reaction between (a), (b) and (c) will yield 18.7 g./l. HBF_4 . The stannous tin will require $80 \times 1.48 = 118$ g./l. of 100% strength HBF_4 , while the desired excess of this acid is 10 g./l., or a total of 128 g./l. As the make-up bath reaction produces 18.7 g./l. HBF_4 , it is necessary to

4

add 128.0–18.7 or 109.3 g./l. HBF_4 for this high tin bath.

Most commercial fluoboric acid (HBF_4) contains free boric acid, and we prefer not to have any free boric acid in our bath. Therefore, any fluoboric acid containing free boric acid, which is used in our bath, is first treated in the following manner:

For each mol of free boric acid (H_3BO_3) present, four mols of hydrofluoric acid (HF) are added. In addition, we add up to 2% excess hydrofluoric acid.

To sample a drum of fluoboric acid for use in the plating system, we weigh 50 grams of the concentrated acid from the drum, dilute to 1000 ml. with water, and let stand 30 minutes prior to analysis. This sampling technique is applied to all strong fluoboric acids, in order to attain a knowledge of the degree of hydrolysis that pertains to the dilution of fluoboric acid, in a 10 g./l. stannous tin fluoboric acid plating bath. The technique is purely arbitrary.

Typical analyses of a drum of fluoboric acid (drum contains 520 lb. net weight), before and after addition of HF, are given below:

Before Addition of HF

Ingredient	Percent	Weight (lb.)
HF	None	None
HBF_4	40.00	203.0
$\text{HBF}_4 \cdot \text{OH}$	9.44	49.1
H_3BO_3	1.33	7.1
Total boron	6.38	33.1
Total fluorine	40.96	213.0

After Addition of 50 lbs. of HF (48–50%)

Ingredient	Percent	Weight (lb.)
HF	1.84	10.5
HBF_4	43.50	238.0
$\text{HBF}_4 \cdot \text{OH}$	3.57	20.3
H_3BO_3	None	None
Total boron	5.81	33.1
Total fluorine	41.75	238.0

The hydrofluoric acid required, for modification of any particular lot of fluoboric acid, depends on the amount of excess boric acid present. The acid prepared in the above treatment, we designate as modified fluoboric acid. This modified fluoboric acid is used for all additions of fluoboric acid to the bath.

After the above treatment, the fluoboric acid is analyzed, and the necessary additions to the bath are made on the basis of the HBF_4 found by analysis.

EXAMPLE IV

This is an example of a starting bath wherein all of the fluoboric acid is added when the bath is made up, rather than formed in the bath.

	G./l.
Stannous tin (Sn^{++})	10
Fluoboric acid (HBF_4) (100%)	20
Grain refining agent	0.8

The fluoboric acid required by the stannous tin equals 10×1.48 or 14.8 g./l., while the excess HBF_4 desired is 5.2 g./l., or a total of 20 g./l.

A practical operating bath developed in the high speed plating of steel strip will contain both iron and stannic tin. The amount of stannic tin present will depend on the degree of aeration, and the solution lost through drag-out, as well as other solution losses.

An example of the ranges of individual bath components, under which our bath was operated on a production line, is shown below.

5

EXAMPLE V

Stannous tin (Sn ⁺⁺)	10-19
Stannic tin (Sn ⁺⁺⁺)	0.5-24
Ferrous iron (Fe ⁺⁺)	0-1.0
Sulfate [(SO ₄) ⁻]	33-36
Total fluorine (F)	23-105
Total boron (B)	3.5-15
Fluoborate [(BF ₄) ⁻]	20-92
Grain refining agent	0.7-1.0
Organic antioxidant	2-3
pH	0.25-1.14

In maintenance of the bath, the fluoborate determined by analysis is calculated to fluoboric acid (HBF₄). The following stoichiometry is used in calculating the fluoboric acid required, based on 100% strength HBF₄:

For each gram per liter of stannous tin, 1.48 g./l. of HBF₄ is required.

For each gram per liter of stannic tin, 2.96 g./l. of HBF₄ is required.

For each gram per liter of ferrous iron, 315 g./l. of HBF₄ is required.

In addition to the above requirements, we desire an excess of from 5 to 15 g./l. of HBF₄. The bath is maintained by adding the correct amount (stoichiometric equivalent) of modified fluoboric acid, represented by the difference between calculated requirement, and the actual amount of HBF₄ present in the bath, as determined by analysis.

Laboratory tests were made using much broader ranges than those shown for the production run of Example V. These broader ranges for the individual components are given in Example VI.

EXAMPLE VI

Stannous tin (Sn ⁺⁺)	6-80 g./l.
Stannic tin (Sn ⁺⁺⁺)	0-50 or more g./l.
Ferrous iron (Fe ⁺⁺)	0-10 g./l.
Sulfate (SO ₄) ⁻	0-65 g./l.
Total fluorine (F)	13-350 g./l.
Total boron (B)	1.5-37 g./l.
Fluoborate (BF ₄) ⁻	12-300 g./l.
Grain refining agent	0.2-10 g./l.
Organic antioxidant	0-20 g./l.
Temperature	40°-90° C.
Cathode current density	25-1000 a.s.f. or above.

For efficient operation of the bath there should be at least several grams per liter excess fluoborate in the bath, over that required to combine with the tin and iron. Excess fluoborate may range as high as 100 g./l. or more.

The concentration of sulfate ion is determined analytically, and the H₂SO₄ calculated. The sulfate is preferably maintained at from 33-37 g./l., and is added in modules where the module contains H₂SO₄, NaHF₂ and H₃BO₃ in the ratio of 2:2:1 respectively. A module will yield 0.53 pound of (BF₄)⁻ ion for each pound of H₂SO₄ in the module. This yield of (BF₄)⁻ ion must be taken into account in calculating HBF₄ additions.

The amount of sulfate tolerated by our bath depends somewhat on the stannic tin content. Anode limiting current density tests, which were made at 400 a.s.f. and 70° C., proved satisfactory with a range of 0 to 30 g./l. stannic tin and 35 g./l. sulfate (SO₄), 0-20 g./l. stannic tin and 50 g./l. sulfate, and 0-10 g./l. stannic tin and 65 g./l. sulfate. Current densities other than 400 a.s.f. will tolerate more or less sulfate, e.g. increasing the current density above 400 a.s.f. will lessen the tolerance, while decreasing the current density below 400 a.s.f. will permit greater concentrations of sulfate.

Both stannous tin and stannic tin can vary within rather wide limits, provided there is present the proper amount of fluoboric acid, calculated as shown above.

In the examples which we have given for starting baths, it will be observed that sulfuric acid, sodium bifluoride

6

and boric acid, where present, are always given in the ratio of 2:2:1 respectively. This is the desired ratio, although a departure therefrom of from 5 to 10% is permissible. Starting baths which are not initially made up from sulfuric acid, sodium bifluoride and boric acid, for instance, the bath of Example IV, and operating baths which do not contain the sulfate radical, are quite effective in minimizing the rate of oxidation in the bath, but are less efficient than those baths which contain sulfate, and which are made up using the foregoing ratio.

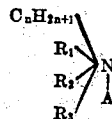
When sulfate is present in the bath, analytical control is facilitated, for a simple sulfate determination will permit the calculation of solution lost, and from this, in turn, calculation can be made of the other bath constituents which have been lost through dragout, etc. While we have selected sulfuric acid, sodium bifluoride and boric acid as the reactants to produce (BF₄)⁻ ion in the bath, other fluorides may be substituted for the sodium bifluoride, for example, ammonium bifluoride (NH₄)HF₂, and sodium fluoride-hydrofluoric acid (NaF-HF). Magnesium fluoride (MgF₂) may be substituted for sodium fluoride.

Our method of controlling an acid tin fluoborate bath, by maintaining fluoborate radical in the bath in an amount at least equal to the stoichiometric equivalent of the stannous tin, stannic tin and ferrous iron, is applicable whether the bath contains an excess of hydrofluoric acid, or fluorine ion, or a small excess of free boric acid, or borate ion.

In the foregoing examples of starting baths, the boric acid is added in a quantity in which it will be completely reacted in the formation of fluoboric acid. Optimum results will be obtained when there is no unreacted boric acid in the operating bath, and to assure this condition, an excess of hydrofluoric acid should be maintained in the bath at all times. However, a small amount of boric acid can be tolerated in our system, so long as there is not enough to cause precipitation of bath ingredients, at a rate which would result in objectionable sludging. In the appended claims, the expression "substantially free of excess borate radical" means that there is insufficient excess borate radical in the bath to produce objectionable sludging.

The net result of the lowered oxidation rate, characteristic of our bath and of our method of control, is the formation of much less stannic tin than would normally be encountered in high speed plating. As only relatively small amounts of stannic tin are formed in our bath, this form of the tin is held in solution, presumably as a soluble fluoborate. The excellent results we have obtained in the reduction of the oxidation rate of the bath, can be further improved upon by the addition of an organic material having antioxidant properties, such as hydroquinone. In addition, a compatible grain refining agent should be supplied to the bath.

In selecting a compatible grain refining agent, a number of the well-known "addition agents" have been found suitable, such as polyethylene oxide 4000, phenol sulfone, cresol sulfonic acid, gelatine, glue and B-naphthol. Soluble quaternary ammonium compounds have proved especially efficient in our bath, particularly those having the general formula



where n is an integer of from 5 to 10, R₁, R₂ and R₃ are alkane radicals, each of which comprises a member of the group consisting of methyl and ethyl, and A is an anion such as toluene sulfonate, iodide, fluoborate, sulfate or the hydroxy radical. The aforesaid group includes such compounds as decyl triethyl ammonium toluene sulfonate, octyl trimethyl ammonium toluene sulfonate and decyl methyl diethyl ammonium iodide.

While our method of forming the bath has proved quite satisfactory from an operational standpoint, it is obvious that fluoborate radical may be introduced into the bath in a form other than the one described. For example, the bath may be made up with fluoboric acid (HBF₄), or with hydrofluoric acid (HF) and boric acid.

While we prefer to use hydroquinone as the material by which we obtain an additional lowered oxidation rate, other antioxidants, such as catechol, para aminophenol, 4-aminoantipyrine and para methyl aminophenolsulfate, may be substituted.

While our method of forming the bath decreases the inception of oxidation, some oxidation of the stannous tin to the stannic form is inevitable due to the continual aeration of the bath and the presence of iron, which is carried into the bath by the steel strip. As the stannic tin (Sn⁺⁺⁺) forms in an operating bath, 2.96 grams of fluoboric acid (HBF₄) are added for each gram of stannic tin. For each gram of ferrous iron introduced into the bath, 3.15 grams of fluoboric acid are added. In addition, for each gram of stannous tin (Sn⁺⁺) in the bath in excess of the make-up concentration, 1.48 grams of fluoboric acid are added. When sulfate is used in the starting bath, introduced either as H₂SO₄ or sodium sulfate (Na₂SO₄), the sulfate radical may be held at a nearly constant figure during plating operations for control purposes. To make up for drag out, tin, sulfate radical, sodium ion, hydroquinone and the grain refining agent should each be added in the proportion used for the starting bath, and in amounts necessary to keep these ingredients at a desired operating level.

For optimum operating conditions, stannous tin should be maintained at around 10 grams per liter. However, somewhat less tin, and up to about 80 grams per liter can be used without appreciably affecting the control of the oxidation.

Generally, in the operation of our bath for strip plating, we prefer to maintain the temperature around 70° C. The current density may range from 50-800 a.s.f. for strip plating. Any type of conventional tin anode may be used. When plating at our preferred operating conditions, we develop a cathode efficiency of 95% or above.

In order to prove the effectiveness of our treatment, a production run was made under typical operating conditions, in which approximately 1500 tons of tin-plated steel strip were produced. One-quarter pound plate was made in this run. The width of strip plated averaged 28.5 inches, and the plating was performed in a vertical system having an electrolyte volume of 15,000 gallons. The starting electrolyte for this test had the composition shown in Example I. Operating conditions were as follows:

Temp.....	70° C.
Current density.....	110 a.s.f.
Cathode efficiency.....	90-97%.
Speed of strip (normal).....	800 ft./min.
pH (glass electrode).....	2 or less.

While operating the bath, it is of course necessary to make periodic chemical control checks in order to maintain a fairly uniform bath composition. After determining bath requirements through such periodic checks, necessary additions of sulfuric acid, bifluoride, boric acid, grain refining agent and hydroquinone were added to compensate for drag-out. Fluoboric acid was added in amounts necessary to satisfy the stannous tin and any stannic tin or ferrous iron which developed in the bath. All of the tinplate produced in the test run was subsequently fused in a radiant tube fusing furnace, and the quality of the resultant fused plate was excellent.

An outstanding characteristic of our bath is the degree to which oxidation of the tin is controlled. This oxidation control factor is very sharply illustrated by the accompanying drawing.

In the drawing, FIG. 1 is a graph representing an

oxidation rate curve wherein the pounds of stannic tin produced are plotted against strip speed.

FIG. 2 is a graph representing controlled and uncontrolled oxidation at a normal strip speed of 800 ft./min.

Referring now to FIG. 1, the data for this graph were compiled on test runs on a production bath solution made up as follows:

Tin (Sn ⁺⁺).....	g./l....	10
Sodium fluoride (NaF).....	g./l....	44
Sulfuric acid (H ₂ SO ₄).....	g./l....	52
Grain refining agent.....	g./l....	1.0
Operating conditions:		
Temp.	° C....	70
Current density.....	a.s.f....	100

These test runs were made on the same plating unit, and in the same manner, as used for the production run described above. The upswing of the curve, in the area defined by speeds of 500 to 600 ft./min., illustrates quite clearly the need for oxidation control for speeds above 500 ft./min. The sharp break in the curve, in the area referred to, is explained by the fact that above speeds of 500 ft./min. the intensity of back splashing of electrolyte from the contact and back-up rolls increases considerably.

In FIG. 2, curve A represents the oxidation rate in a bath made up as described for FIG. 1. The bath was run at a normal strip speed of 800 ft./min., and pounds of stannic tin have been plotted against base boxes of tin produced. This latter value is comparable to linear feet of strip plated. Curve B represents the oxidation rate for the bath used in the production run, the starting bath analysis of which is given in Example I. Oxidation figures were obtained from samplings of the electrolyte during the actual test run. It should be explained that while the runs represented by curves A and B were made at a normal strip speed of 800 ft./min., the strip speed was reduced to 400 ft./min. during such time as it was necessary to join one coil of strip to the next succeeding coil by welding. Thus, the strip speed was set at 400 ft./min. just prior to, and during, welding. After welding there was a certain time lag during which the strip regained its normal operating speed of 800 ft./min. It had been estimated that for any given coil, the speed was maintained at 800 ft./min. for about 70% of the coil length, the remaining 30% of its length being plated at a speed ranging between 400 and 800 ft./min. In compiling the data for both curves A and B, a series of a large number of coils were plated in each instance, so that the 70/30 length ratio for 800/400 ft./min. strip speeds is a good average.

Curve A, representing a tin bath in which no provision has been made to control the oxidation, shows a rapid rate of formation of stannic tin. Significantly, curve B, representing a bath controlled by our method, shows only a moderate rate of formation of stannic tin.

In our method, the concentration of the stannic tin reaches a point where said tin is removed from the bath, through drag-out, at a rate which is substantially equal to the rate at which it is formed in the bath, from which point thenceforth the stannic tin concentration remains constant. By maintaining the bath at this constant level, the concentration is well within the limits of economic operation.

While we have described our bath in conjunction with a vertical, or skein type, plating line, the bath has similar utility in a line of the horizontal, or tier, type.

We claim:

1. The method of controlling an aqueous electrolytic fluoboric acid tinplating bath of stannous tin in an amount of from 6-80 g./l., a grain refining agent, and containing stannic tin and ferrous iron, the plating metal of said bath consisting essentially of tin, which comprises maintaining fluoborate radical in the bath in an amount at least stoichiometrically equivalent to the stannous tin,

stannic tin and ferrous iron said bath being substantially free of excess borate radical.

2. The method of controlling an aqueous electrolytic fluoboric acid tinplating bath for the plating of a metal consisting essentially of tin, which comprises in a bath of stannous tin in an amount of from 6-80 g./l., a grain refining agent, sulfate radical in an amount not in excess of 65 g./l. and containing stannic tin and ferrous iron, maintaining fluoborate radical in the bath in an amount at least stoichiometrically equivalent to the stannous tin, stannic tin and ferrous iron and maintaining the bath substantially free of borate radical.

3. The method of controlling an aqueous electrolytic fluoboric acid tinplating bath of stannous tin in an amount of from 6-80 g./l., a grain refining agent, sulfate radical in an amount not in excess of 65 g./l., an organic antioxidant in an amount of from 0.5-8 g./l. and containing stannic tin and ferrous iron, in which bath the plating metal consists essentially of tin, which comprises maintaining fluoborate radical in the bath in an amount at least stoichiometrically equivalent to the stannous tin, stannic tin and ferrous iron and maintaining the bath substantially free of borate radical.

4. The method of controlling an aqueous electrolytic fluoboric acid tinplating bath of stannous tin in an amount of from 8-30 g./l., a grain refining agent and containing stannic tin and ferrous iron, the plating metal in said bath consisting essentially of tin, which comprises maintaining fluoborate radical in the bath in an amount at least stoichiometrically equivalent to the stannous tin, stannic tin and ferrous iron and maintaining the bath substantially free of borate radical.

5. A fluoboric acid electrolyte for depositing a metal consisting essentially of tin which comprises an aqueous solution of stannous tin in an amount of from 6-80 g./l., sulfate ion in an amount not in excess of 65 g./l., a grain refining agent, stannic tin, ferrous iron and substantially free of excess borate radical, and fluoborate radical in an amount at least stoichiometrically equivalent to the stannous tin, stannic tin and ferrous iron.

6. A method of preparing an aqueous electrolytic fluoboric acid tinplating bath of stannous tin in an amount of from 6 to 80 g./l., a grain refining agent and stannic tin, the plating metal from said bath consisting essentially of tin, which comprises introducing at least part of the required fluoboric acid into the bath by adding sulfuric acid up to 65 g./l., sodium bifluoride and boric acid in stoichiometric quantities necessary to produce fluoboric acid, adjusting the total fluoborate radical in the bath to an amount stoichiometrically equivalent to the tin plus an excess of at least 2 g./l. of the fluoborate radical by the addition of fluoboric acid said bath being substantially free of excess borate radical.

7. A method according to claim 4 in which the grain refining agent is decyl triethyl ammonium para toluene sulfonate.

8. A method according to claim 3 in which the organic antioxidant is hydroquinone.

9. A fluoboric acid electrolyte for depositing a metal consisting essentially of tin made by forming an aqueous solution of the reaction products of 5 to 65 g./l. of sulfuric acid, 5 to 65 g./l. of sodium bifluoride, and 2.5

to 32.5 g./l. of boric acid in the ratio of about 2:2:1 respectively with 8 to 25 g./l. of stannous oxide, in which the fluoborate radical in the bath is present in an amount stoichiometrically equivalent to the stannous tin plus an excess of at least 2 g./l. fluoborate, and containing 2 to 10 g./l. of hydroquinone and 0.3 to 10 g./l. of a grain refining agent, said electrolyte being substantially free of borate radical.

10. An aqueous fluoboric acid electrolyte for depositing a metal consisting essentially of tin which contains from 10 to 20 g./l. stannous tin, 30 to 40 g./l. sulfate radical, 17 to 104 g./l. total fluorine, 2.5 to 15 g./l. total boron, 20 to 120 g./l. fluoborate radical, 0.5 to 25 g./l. stannic tin, 0.1 to 1.0 g./l. ferrous iron, 0.2 to 10 g./l. of an organic grain refining agent and 0.2 to 8 g./l. of an organic antioxidant, said electrolyte being substantially free of borate radical.

11. An aqueous fluoboric acid electrolyte for depositing a metal consisting essentially of tin which contains from 6 to 80 g./l. stannous tin, 1 to 65 g./l. sulfate radical, 13 to 350 g./l. total fluorine, 1.5 to 3.7 g./l. total boron, 12 to 300 g./l. fluoborate radical, 0.3 to 50 g./l. stannic tin, 0.1 to 10 g./l. ferrous iron, 0.2 to 10 g./l. of an organic grain refining agent and 0.2 to 20 g./l. of an organic antioxidant, said electrolyte being substantially free of excess borate radical.

12. The method of controlling an aqueous electrolytic fluoboric acid tinplating bath of stannous tin in an amount of from 6-80 g./l., sulfate radical in an amount not in excess of 65 g./l., a grain refining agent, stannic tin and ferrous iron, and substantially free of excess borate radical, the plating metal of said bath consisting essentially of tin, which comprises maintaining fluoborate radical in the bath in an amount at least stoichiometrically equivalent to the stannous tin, stannic tin and ferrous iron.

13. An aqueous fluoboric acid electrolyte for depositing a metal consisting essentially of tin comprising 6-80 g./l. of stannous tin and a grain refining agent, and containing stannic tin and ferrous iron as impurities, said bath containing fluoborate radical in an amount at least stoichiometrically equivalent to the stannic tin, stannous tin and ferrous iron and being substantially free of borate radical.

14. The method of controlling an aqueous electrolytic fluoboric acid tinplating bath of stannous tin in an amount of from 6-80 g./l., a grain refining agent, and containing stannic tin and ferrous iron, the plating metal of said bath consisting essentially of tin, which comprises maintaining fluoborate radical in the bath in an amount at least stoichiometrically equivalent to the stannous tin, stannic tin and ferrous iron, said bath being substantially free of borate radical.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,082,157

March 19, 1963

Herbert H. Francisco et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 33, strike out "two", second occurrence; line 69, for "compoud" read -- compound --; column 3, lines 1 and 2, for "occurring" read -- accruing --; column 5, line 21, for "315 g./l." read -- 3.15 g./l. --; column 10, line 21, for "3.7 g./l." read -- 37 g./l. --.

Signed and sealed this 8th day of October 1963.

(SEAL)

Attest:

ERNEST W. SWIDER
Attesting Officer

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Acting Commissioner of Patents