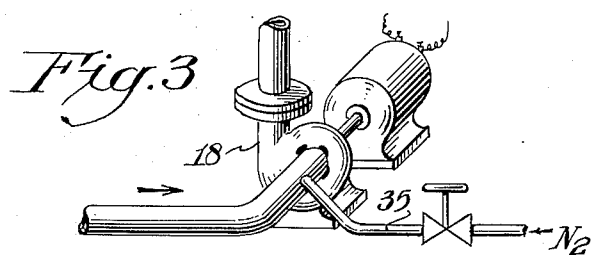
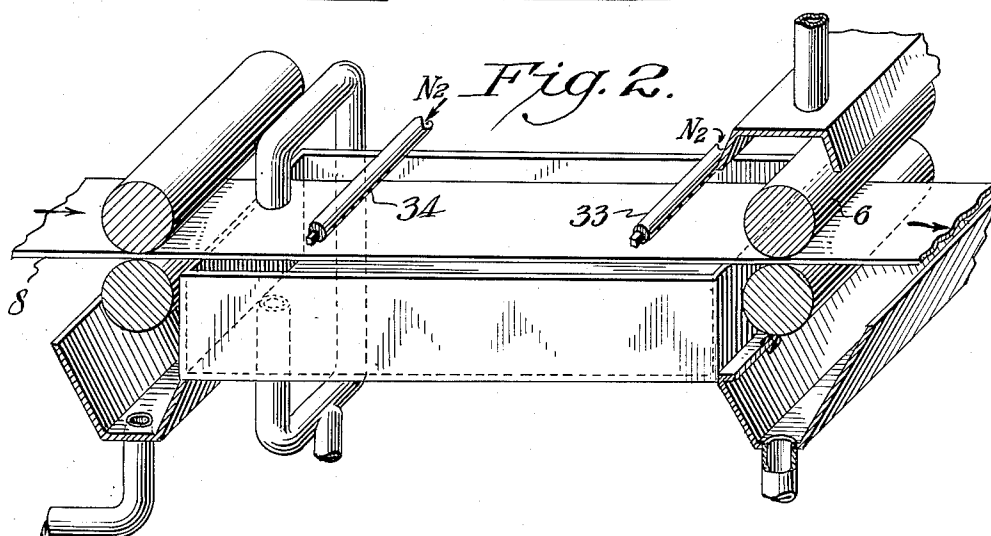
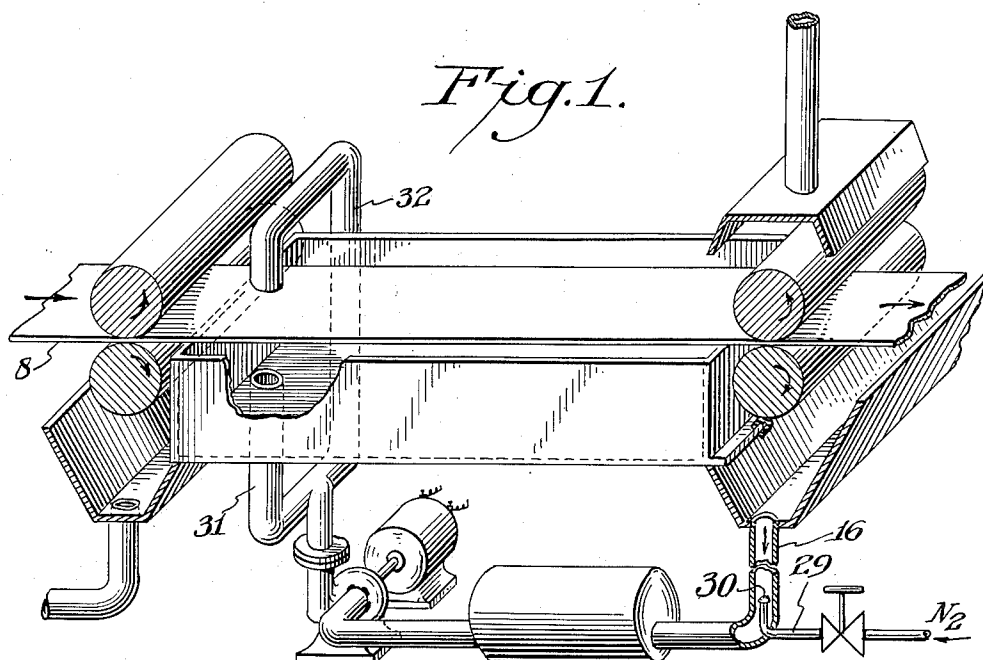


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ELECTRODEPOSITION OF TIN

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1

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ELECTRODEPOSITION OF TIN

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This invention relates to the electrodeposition of tin from stannous plating baths.

I have found that the characteristics of stannous plating baths can be improved by dispersing an inert gas such as nitrogen in the bath. The nitrogen displaces gaseous oxygen that is ordinarily dissolved or dispersed in the bath. Stannous plating baths containing reduced amounts of dissolved or dispersed oxygen according to the invention have improved bath characteristics over those which contain ordinary amounts of dissolved and dispersed oxygen. The baths, for example, have higher cathode efficiencies and they form less sludge than the stannous baths heretofore used.

In the drawings Figure 1 illustrates a standard type of plating equipment altered to permit bath operation according to the present invention, and

Figure 2 shows a modified method of supplying an inert gas to the bath, and

Figure 3 illustrates a still further modification.

Any stannous electrodepositing bath which contains part or all, and preferably at least a major amount, of its tin as a stannous compound may be improved according to the present invention. Prior art baths may be used in which tin is present as stannous chloride, stannous sulfate, stannous fluoride, and phenol sulfonate or other stannous salts of sulfonic acid. Baths of these types frequently include acids such as hydrochloric, hydrofluoric, sulfuric acid, or aromatic sulfonic acids. Typical stannous baths are described in Hoffman U. S. Patent 2,457,152 and in patents therein cited. Also suitable are such baths as the sulfonate baths described in Andrews 2,399,194; Harris 2,450,794; and Harris 2,450,795.

The preferred stannous baths for use according to the present invention are the so-called "halogen-tin" plating baths which are composed of an alkali fluoride-stannous chloride solution. These baths are described and claimed in Schweikher U. S. Patent 2,407,579.

In using halogen-tin baths the ratio of fluoride to stannous chloride must be carefully selected and related to the operating pH of the bath as more specifically described below, and of course as described in fuller detail in the said Schweikher Patent 2,407,579.

The baths may be made up with stannous chloride and with an alkali fluoride, say sodium, potassium, or ammonium fluoride. When reference is made hereinafter to an alkali fluoride it will be understood that sodium, potassium, or ammonium fluoride or bifluorides may be used or mixtures of any of these may be employed.

The concentration of stannous chloride may vary from about thirty-seven and one-half to one hundred and fifty grams per liter and the alkali fluoride may similarly vary from thirty-seven and one-half to one hundred and fifty grams per liter. More specifically, it is desired to maintain the concentration of the stannous chloride and the alkali fluoride between about sixty and one hundred grams per liter.

2

More important, perhaps, than the mere concentration of stannous chloride and soluble fluoride is the molar ratio of these materials as related to the pH at which the bath is operated. An empirical formula which has been found satisfactory is as follows:

$$\text{pH} = \frac{k(\text{mols MF})}{\text{mols SnCl}_2}$$

where MF is an alkali fluoride and SnCl_2 is stannous chloride.

The following conditions should be adhered to for successful use of the above formula:

(1) The constituents are used within the pH range of pH 1 to pH 5 under conditions in which they are soluble in the plating bath, the tin content being maintained within the reasonable limits of 0.05 mol to 2 mols of tin metal per liter of solution. It may additionally be noted that generally it is desirable that the concentrations of stannous chloride and alkali fluoride be more than about 25 grams per liter.

(2) The ratio of alkali fluoride to tin chloride for any given tin content is controlled by the value of k . It is then found that k is related to the pH of operation of the bath in such a way that for optimum operation at any given pH k equals 0.55. However, it will be understood that in commercial operation good results may be obtained with values of k between the broad limits of $k=0.1$ to $k=1.0$. It is more particularly preferred to stay within the limits $k=0.3$ to $k=0.7$.

(3) The mol ratio of MF/SnCl_2 should fall within the limits of 2 and 12. It is preferred that the ratio equal 6 when k equals 0.55.

(4) The pH of the formula is the maximum at which the bath is stable while the optimum pH for plating is within the range from about 1 to 5 and preferably the pH should be in the range from about 2 to 4. A bath formulation that is stable at a given pH may also be stable at a lower pH but the preferred ranges are those within which addition agents are generally most effective.

In the practical application of the formula since in ordinary use the pH of operation will be preselected, k will be fixed at the desired optimum value, and the amount of tin which it is necessary to have in the bath will be known, it may be best to express the equation in a form as shown below which may be used to calculate the amount of alkali fluoride compound required.

$$\text{MF} = \frac{\text{pH}(\text{mols SnCl}_2)}{k}$$

As an example of the use of this formula let MF equal sodium fluoride and let k equal 0.55. The conditions selected are 0.33 mol of stannous chloride to be used as a pH of 4. Then to calculate the mols of sodium fluoride using the above equation:

$$\text{Mols sodium fluoride} = \frac{(4)(0.33)}{0.55} =$$

2.4 mols of sodium fluoride required

The acidity of the bath may be that which results from the bath constituents though adjustments of the pH may be made as desired. Generally, as mentioned above, the pH will fall within the range of about pH 1 to 5 while more specifically it is desired to have the pH from about 2 to 4.

In addition to observing the above conditions it will be found desirable so to adjust the bath composition as to lead to a static solution potential within a predetermined range. The solution potential, P , should not fall outside the limits of the following two equations:

$$\begin{aligned} P &= -0.055 \text{ pH} - 0.265 \\ P &= -0.055 \text{ pH} - 0.370 \end{aligned}$$

In this formula, pH as indicated above, should have a value between 1 and 5 or, preferably, between 2 and 4.

After a solution has been prepared with constituents selected according to the methods given above in some detail, then the solution should be examined as to its potential. This can of course be done by making up a small amount of solution first and then adjusting the entire bath composition in accordance with the findings. If the solution potential is below the values given for P in the above formulae, then it may be increased (made more negative) by increasing the MF/SnCl₂ ratio; if the potential is too high it may be lowered by decreasing the MF/SnCl₂ ratio. In adjusting the potential it will be noted that the potential increases with an increase in pH and decreases with a decrease in pH. Ordinarily potential will not be adjusted by changing the pH, though this means of adjustment is available if it is preferred to use some preselected ratio of MF to SnCl₂.

The potential may be determined in any suitable manner as by connecting a potentiometer across a piece of tin metal and a calomel half cell in customary manner. The static solution potential of tin against the bath is then obtained as volts after corrections are made for the calomel half cell.

Specific examples of numerous baths of the "halogen-tin" type are given in the Schweikher Patent 2,407,579.

According to the present invention a stannous plating bath is modified by dispersing an inert gas such as nitrogen in it. An gas which is completely inert in the plating system may be used. There may be used, for example, carbon dioxide, carbon monoxide, argon, helium, hydrogen, and hydrocarbons such as methane, ethane, propane and butane. It will be understood that carbon monoxide must be very carefully handled because of its toxic effects. Hydrogen and the hydrocarbons also must be handled with great care because of their flammability. By far the preferred gas for use according to the invention is nitrogen. In the following description nitrogen will be used as illustrative of the inert gases in the discussion.

In use stannous baths ordinarily contain dissolved and dispersed air. The amounts of such dispersed air vary depending partly upon the extent of agitation of the bath. The normal practice is to effect a rather large amount of agitation and aeration so that the solutions usually contain large amounts of dispersed air.

The gases in the baths are dissolved to the extent of their solubility and then additional amounts of gas are present as finely dispersed bubbles of undissolved gas. The usual stannous plating baths will hold large amounts of dispersed gases. Halogen-tin baths, for example, if agitated with air become filled with finely dispersed air bubbles which are only slowly released. I think that this is due to the effect of salt in the bath. When water is agitated with air under similar conditions the bubbles are large in size and are rapidly released from the water.

By dispersing nitrogen in the stannous bath the oxygen-containing gas is displaced, or partly displaced depending upon the amount of nitrogen used. It will also be seen that if the bath contains dispersed and dissolved nitrogen the addition of some air will result at the most in a dispersed gas with a considerably smaller oxygen content than that present in air.

The nitrogen used can be a substantially pure gas or under most practical conditions it can be a by-product gas from which a considerable part of the oxygen has been removed. The value of the nitrogen in a process of the invention will be proportional to its freedom from oxygen, but the extra advantage for extreme purity will not ordinarily justify using a pure nitrogen as compared with the various low cost by-product nitrogen gases. A typical such gas may contain three or four per cent of oxygen or even somewhat more. Generally it will be most desirable to use a nitrogen containing no more than about ten per cent of oxygen, though the advantage is proportional to the paucity of oxygen and the advantages of the

invention can be obtained in whatever measure is most economic under particular circumstances.

Plating baths for use according to the invention will generally contain dissolved and dispersed gases which contain no more than ten per cent of oxygen. Again, as will be shown later, the advantages to be derived from the processes of the invention are proportional to the paucity of oxygen and as low a figure as is attainable should be used. It is desirable, for example, to have no more than five per cent of oxygen in the dissolved and dispersed gases in the solution, and still more desirable to have as near to zero per cent of oxygen in the gases as is attainable.

The rate of nitrogen addition in a particular plating bath will depend upon the amount of aeration, the purity of the nitrogen, and upon other operating factors. The amount of nitrogen added can be adjusted to give the desired cathode efficiency and other bath properties. The effectiveness of the amount of nitrogen added in displacing oxygen can be checked in a specific instance by determining the oxygen content of the bath from time to time. In practical plating operation this can most easily be done by chemical analysis for the oxygen. The oxygen content can also be determined, though it is rather difficult for most practical electroplaters, by determining cathode efficiency which will be found to have a fairly constant relation to oxygen content for a particular plating system.

Nitrogen can be dispersed in stannous baths according to the invention in any convenient manner. It can, for instance, be bubbled through the bath to sparge out the oxygen and to leave a gas containing principally nitrogen.

As observed above, other inert gases can be used instead of nitrogen. The considerations regarding purity, oxygen content, and rate of addition and so forth, are the same as those above discussed for nitrogen.

Typical methods of introducing nitrogen, or other inert gas, into a stannous bath are illustrated in the drawings.

In Figure 1 there is shown a plating installation for depositing tin on strip steel. This equipment is of the type covered by United States patent to Hoff No. 2,490,055.

In Figure 1 it will be seen that stannous plating solution is withdrawn at pipe 16 as it overflows from the plating tank. The solution is drawn along rapidly by the moving strip 8 and some of the solution overflows.

Nitrogen can be introduced in the downcoming line 16 through pipe 29, the pipe is provided with a diffusion-head 30 so that incoming nitrogen will be dispersed through the downcoming stream of solution. The nitrogen will rise upwardly through the downcoming pipe and will be thoroughly dispersed as it passes in counter-current to the flow of the plating solution. Any air which may have been entrained or dispersed by the solution will be displaced by the countercurrent flow of nitrogen. The solution returned to the plating cell through pipes 31 and 32 will accordingly contain dispersed and dissolved nitrogen.

Other mechanical features of the equipment are not discussed but aside from a few minor changes these are shown in the above mentioned Hoff patent.

In Figure 2 there is shown a modification in which the nitrogen is introduced above the strip 8 through a pipe 33. This pipe is provided with openings so that the gas is distributed evenly over the sheet. The gas is carried rapidly along with the sheet and is beat into the solution by the roll 6. The solution "piles up" at the roll and is churned so that gases at the roll 6 near the sheet 8 are dispersed in the plating solution. A second pipe 34 for supplying a flow of nitrogen is also shown, though this may be omitted if desired.

The modification of Figure 2 may very advantageously be used jointly with the modification of Figure 1. Thus nitrogen is added both at the downcomer 16 and above the strip being plated.

In the modification of Figure 3 the nitrogen is added at a pipe 35 just prior to the time when the liquid enters the pump 18. The pump effects very thorough dispersion

5

of the nitrogen in the liquid. It will be apparent that this modification can also be used jointly with the modification of Figures 1 or 2, or that all three may be used together.

The stannous baths above described may advantageously be modified with organic addition agents in accordance with practices already common in the art. They may, for example, be modified with polyethers as shown in Hoffman 2,457,152. Similarly, the other addition agents mentioned in the various patents already cited may be used.

The bath temperature is that customarily used for tinning baths. Ordinarily the baths will be used at comparatively high temperatures, that is above 50–55° C. In practical operation the problem is usually one of cooling the bath enough to keep the temperature below 75° C. This problem is particularly great when a bath, such as the halogen-tin bath, is used at very high current densities for high speed operation.

It is also to be noted that ferro- and ferri-cyanides may be used as taught in the Hull Patent 2,512,719. Thiocyanates may be used as taught in Schweikher 2,402,185.

In order that the invention may be better understood reference should be had to the following illustrative example:

A halogen-tin bath of the type covered by Schweikher 2,407,579 was made up as follows:

Stannous chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$), commercial 60 grams per liter

Sodium fluoride (NaF), 30 grams per liter

Sodium bifluoride (NaHF_2), 30 grams per liter

Sodium chloride, 15 grams per liter pH, 3.3

Temperature, 60° C.

To the bath was added 1 gram per liter of sodium ferrocyanide as taught in the Hull Patent 2,512,719.

Tin was electrodeposited from the solution onto a rotating cathode which gives agitation and cathode velocity comparable to those used in commercial practice.

A nitrogen gas containing only traces of oxygen was bubbled through the bath at a rate about 4 cubic feet per hour in five liters of solution. A cathode efficiency of 100% was obtained. Without using nitrogen and with air dispersed in the solution in accordance with normal practices the cathode efficiency was 96.5%.

Using a nitrogen gas containing five per cent of oxygen and the same feed rate the dispersed gas in the bath contained approximately five per cent of oxygen. The cathode efficiency of this solution was 99.2%. With ten per cent of oxygen in the nitrogen the cathode efficiency was 98.8%. With fifteen per cent of oxygen in the nitrogen the cathode efficiency was 98.5%. Thus even with fifteen per cent of oxygen in the nitrogen there was a considerable improvement in cathode efficiency.

Cathode efficiency was determined in the usual manner employing a copper coulometer. This is done using a copper bath made up with 150 grams per liter of copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) and 60 grams per liter of sulfuric acid of specific gravity 1.84. The cathodes were 6 x 9 inches and the temperature of the copper bath was held between 20 and 30° C. The current density was 20 amperes per square foot. The copper bath was operated in series with the stannous bath and the weight of the two cathodes was compared. The cathode efficiency was expressed taking copper as 100% in the usual way.

Similar effects were obtained using carbon dioxide and other inert gases in the same manner as in the above examples.

I claim:

1. In a process for the electrodeposition of steel strip to make tin plate, the steps comprising passing steel strip through a stannous bath while electrodepositing tin thereupon and incidentally effecting agitation and aeration of the bath so that it contains dissolved and dispersed gases, the stannous bath being an aqueous bath comprising from about 37.5 to 150 grams per liter of an alkali fluoride, and

6

from about 37.5 to 150 grams per liter of stannous chloride and satisfying the equation:

$$\text{pH} = \frac{k(\text{mols MF})}{\text{mols SnCl}_2}$$

wherein the following conditions are simultaneously true; the pH is equal to about 2 to 4, k has a value of about 0.3 to 0.7, MF is alkali fluoride, and the mole ratio

$$\frac{\text{MF}}{\text{SnCl}_2}$$

is about from 3 to 12, the static solution potential of tin in the bath being equal in volts to from

$$-0.055 \text{ pH} - 0.265 \text{ to } -0.055 \text{ pH} - 0.370$$

dispersing nitrogen which contains less than 5% of oxygen in the bath to reduce the oxygen content of gases dissolved and dispersed in the bath to below 10 per cent thus to reduce sludge formation and to maintain an increased cathode efficiency.

2. In a process for the electrodeposition of tin, the step comprising effecting electrodeposition from an aqueous bath comprising from about 37.5 to 150 grams per liter of an alkali fluoride, and from about 37.5 to 150 grams per liter of stannous chloride and satisfying the equation:

$$\text{pH} = \frac{k(\text{mols MF})}{\text{mols SnCl}_2}$$

wherein the following conditions are simultaneously true; the pH is equal to about 1 to 5, k has a value from 0.1 to 1.0, MF is alkali fluoride, and the mol ratio

$$\frac{\text{MF}}{\text{SnCl}_2}$$

is about from 2 to 12, the static solution potential of tin in the bath being equal in volts to from

$$-0.055 \text{ pH} - 0.265 \text{ to } -0.055 \text{ pH} - 0.370$$

continuously withdrawing portions of said bath and returning them to the bath whereby the bath is aerated so that it contains dissolved and dispersed gases, dispersing nitrogen which contains less than 10% of oxygen therein to maintain the oxygen content of gases dissolved and dispersed in the bath below 10%.

3. In a process for the electrodeposition of steel strip to make tin plate, the steps comprising effecting electrodeposition of tin upon the steel strip from an aqueous bath comprising from about 37.5 to 150 grams per liter of an alkali fluoride, and from about 37.5 to 150 grams per liter of stannous chloride and satisfying the equation:

$$\text{pH} = \frac{k(\text{mols MF})}{\text{mols SnCl}_2}$$

wherein the following conditions are simultaneously true; the pH is equal to about 1 to 5, k has a value from 0.1 to 1.0, MF is alkali fluoride, and the mol ratio

$$\frac{\text{MF}}{\text{SnCl}_2}$$

is about from 2 to 12, the static solution potential of tin in the bath being equal in volts to from

$$-0.055 \text{ pH} - 0.265 \text{ to } -0.055 \text{ pH} - 0.370$$

continuously withdrawing portions of said bath downwardly through a pipe, adding nitrogen which contains less than 5% of oxygen at a low point in the pipe to reduce the oxygen content of gases dissolved and dispersed in the bath to below 10%, passing said withdrawn portions through a pump, and returning the said portions to the said bath.

4. In a process for the electrodeposition of tin, the steps comprising effecting electrodeposition from an aqueous bath comprising from about 37.5 to 150 grams per liter of an alkali fluoride, and from about 37.5 to 150

7

grams per liter of stannous chloride and satisfying the equation:

$$\text{pH} = \frac{k(\text{mols MF})}{\text{mols SnCl}_2}$$

wherein the following conditions are simultaneously true; the pH is equal to about 1 to 5, k has a value from 0.1 to 1.0, MF is alkali fluoride, and the mol ratio

$$\frac{\text{MF}}{\text{SnCl}_2}$$

is about from 2 to 12, the static solution potential of tin in the bath being equal in volts to from

$$-0.055 \text{ pH} - 0.265 \text{ to } -0.055 \text{ pH} - 0.370$$

the bath being maintained with the gases dissolved and dispersed in said bath containing less than 10 per cent of oxygen by continuously throughout the electrodeposition process dispersing nitrogen therein which contains less than 5% of oxygen.

5. In a process for the electrodeposition of tin from a stannous bath, the steps comprising depositing tin upon a cathode, continuously withdrawing portions of the bath and returning such portions to the bath whereby the bath is aerated so that it contains dissolved and dispersed gases, and dispersing nitrogen which contains less than 5% of oxygen in the bath to maintain the oxygen content of gases dissolved and dispersed in the bath at below 10 per cent.

6. In a process for the electrodeposition of tin from a stannous bath, the steps comprising passing a cathode through the bath while electrodepositing tin thereupon

8

and incidentally effecting agitation and aeration of the bath so that it contains dissolved and dispersed gases, and dispersing nitrogen which contains less than 5% of oxygen in the bath to maintain the oxygen content of gases dissolved and dispersed in the bath at below 10 per cent.

7. In a process for the electrodeposition of tin from a stannous bath which is agitated and aerated so that it contains dissolved and dispersed gases, the steps comprising dispersing nitrogen which contains less than 10 per cent of oxygen in the bath so that the amount of oxygen in the bath comprises less than 10% of the gases dissolved and dispersed in the bath and thereafter electrodepositing tin from the bath while maintaining low oxygen content by continuous dispersing of nitrogen.

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