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ELECTRODEPOSITION OF TIN

Herbert H. Francisco and Homer G. Ressler, Bethlehem, and George W. Ward, Nazareth, Pa., assignors to Bethlehem Steel Company, a corporation of Pennsylvania

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This invention relates to the electrodeposition of tin from an acid plating bath, and more particularly to the formation and control of such a bath.

This application is a continuation-in-part of application Serial No. 628,546, filed December 17, 1956, now abandoned.

One of the objects of the invention is to electroplate tin on continuously moving metal parts such as steel strip at relatively high current densities.

Another object is to effect control of a tinplating bath so that it will operate at high efficiency over long periods of time.

A further object is to produce a tinplate having good reflectivity after fusing.

In the electrodeposition of tin from an acid plating bath, it is quite difficult, if not impossible, to maintain a balanced bath over long operating periods merely by adding bath components to compensate for drag out. This is true because of build-up of stannic tin, iron and silica in the bath. Furthermore, in an efficient operating bath, the desired percentage of bath components is related to the foregoing build-up ingredients.

We have found that in a stannous sulfate bath, containing sodium and fluorine and excess sulfate, it is essential to maintain the total sodium and the total fluorine within certain prescribed ranges. It is also essential in the bath of our invention to maintain the ratio of excess sulfate to sodium fluoride at approximately 1:1.

In the plating of tin we can obtain our objectives of bath component ranges and ratio by starting, as a typical example, with a bath of the following composition:

	G./l.
Stannous sulfate ($SnSO_4$)	27
Sulfate other than $SnSO_4$ (added as H_2SO_4 and calculated as SO_4)	44
Sodium fluoride (NaF)	44
Quaternary ammonium compound addition agent	0.90
Sodium bifluoride ($NaHF_2$)	5.2

This bath can be made up by adding stannous oxide in the amount of 17 g./l. and sodium fluoride in the amount of 44 g./l. to an aqueous solution of sulfuric acid containing 56.3 g./l. H_2SO_4. As a practical matter, sulfate, other than that combined as $SnSO_4$, may be calculated either as H_2SO_4 or as SO_4. All sulfate additions should be made with sulfuric acid.

A quantity of 1.05 g./l. of sodium bifluoride is added for each gram of stannous tin in excess of 10 g./l. Sodium bifluoride is added in this situation in order to supply the proper amount of fluorine to the bath without increasing the amount of sodium unduly. By this means we are able to maintain total sodium and total fluorine within certain maximum limits.

This bath will operate satisfactorily at 70° C., and at a current density of 100 amperes per square foot.

In a bath of the character above described, sodium fluoride serves as an anode control agent, i.e. it tends

to increase the maximum current density at which the anode can be operated without the formation of oxides of tin on its surface. Other alkali fluorides may be used as a source of fluorine.

When using a bath of the type shown above under proper operating conditions, we have been able to secure a satisfactory adherent, dense coating on steel strip at commercial operating speeds.

While the peak efficiency of our bath is probably reached in the preferred example given above, there need be no rigid adherence to the quantities and operating conditions given therein. Excellent results and desirable operating conditions may be obtained under widely varying conditions. The permissible range for bath conditions is shown below:

	G./l.
Stannous sulfate ($SnSO_4$)	9–55
Sulfate other than $SnSO_4$ (calculated as SO_4)	30–80
Sodium fluoride (NaF)	30–80
Sodium bifluoride ($NaHF_2$)	0–21
Addition agent	0.25–3.0

In any given bath, the amount of the bath ingredients may be varied within the broad ranges given above. Normally, stannous sulfate, sulfate (SO_4) other than stannous sulfate, and sodium fluoride will be present in more limited amounts. Some effective operating ranges for the bath components of tin (or tin sulfate), sulfate (SO_4), and sodium fluoride are shown in the following examples:

Example I

	G./l.
Stannous sulfate ($SnSO_4$)	9–30
Sulfate other than $SnSO_4$ (calculated as SO_4)	40–55
Sodium fluoride (NaF)	40–55

Example II

	G./l.
Stannous tin (Sn^{++})	5–30
Sulfate other than $SnSO_4$ (calculated as SO_4)	30–80
Sodium fluoride (NaF)	30–80

Example III

Stannous tin (Sn^{++})	10–16
Sulfate other than $SnSO_4$ (calculated as SO_4)	40–50
Sodium fluoride (NaF)	40–50

Example IV

Stannous tin (Sn^{++})	10–20
Sulfate other than $SnSO_4$ (calculated as SO_4)	35–60
Sodium fluoride (NaF)	35–60

In the plating of steel strip the cathode current density may be varied between 25 and 400 amperes per square foot. Such variation of current density permits sudden changes in strip speed necessitated by mechanical operations imposed upon the plating line from time to time. This variation in current density also permits the coating of different weights of tin on opposing sides of the strip. The temperature of the bath may range from 50° to 90° C. Tin anodes should be used. The preferred range of pH as determined by the glass electrode, is from 2.9 to 3.5. Any of the well-known organic addition agents, which are compatible with the bath, may be used for grain refining purposes.

No special precautions are necessary in the make-up of the bath, all of the ingredients being soluble in the ranges given. To maintain a fairly uniform bath composition, ingredients should be added as needed to make up for loss through drag-out and for oxidation of stannous tin. Bath maintenance can be controlled by well-known analytical methods.

A special feature of our bath, and one which enables us to obtain high anode and cathode efficiencies, is the relationship of sulfate (other than the sulfate stoichiometrically equivalent to the tin and combined as $SnSO_4$) and sodium fluoride. We find that when the ratio of this sulfate, calculated as SO_4, to sodium fluoride is approximately 1 to 1, anode efficiencies of as high as 100% can be maintained. These high operating efficiencies, as well as bath stability, are obtained over long operating periods.

During the operation of the bath certain chemical changes of the bath occur, in addition to concentration changes caused by solution losses.

Stannous tin is slowly oxidized to stannic tin by air oxidation. The stannic compound formed is sodium fluostannate (Na_2SnF_6). Sodium fluostannate is soluble in the bath to the extent of from 10–50 g./l. depending on the bath composition and temperature of the operation. Sodium fluostannate may be removed from the solution by precipitation in an auxiliary tank by cooling the solution, or it may be allowed to reach saturation in the plating cell and precipitate as it is formed in the plating cell without deleterious effects on the plated product.

Sodium fluostannate is a heavy, dense, crystalline compound which settles readily and is amenable to removal by filtration or decantation.

Iron is brought into the bath from pretreatment solutions on the material that is to be plated. The iron compound that is formed in the bath is presumed to be sodium ferrous fluoride (Na_2FeF_4).

Silica enters the bath with the alkali fluorides. The silica compound that is presumed to be present in the bath is sodium fluosilicate (Na_2SiF_6).

Well known chemical analytical methods are employed to determine the following bath constituents: stannous tin, stannic tin, sulfate, fluorine, sodium, iron, silicon dioxide, and grain refining agent.

Deficiencies of stannous sulfate, sulfuric acid, and grain refining agent are corrected by addition to the bath of the three compounds.

In order to control our bath during operation, so that total sodium and total fluorine will be present within the prescribed ranges, and so that the ratio of excess sulfate to NaF will be approximately 1:1, we make the required additions of sodium and fluorine by calculating the sodium and fluorine demand as dictated by the formation of the above presumed sodium and fluorine containing compounds. This result is compared to the amount of sodium and fluorine found to be present in the bath by chemical analysis. The deficiency of sodium and/or fluorine is the amount to be added to re-balance the bath, and to maintain the basic requirement of sodium and fluorine for holding the 1 to 1 ratio of sulfate to sodium fluoride. The ratio of the amount of fluorine required to be added, to the amount of sodium required to be added, is called the demand ratio.

The amount of total sodium and of total fluorine, needed to maintain the 1:1 ratio and to combine with the iron, silica and stannic tin, will range from 16 to 55 g./l. for sodium, and from 14 to 55 g./l. for fluorine.

Compounds which may be used to restore the sodium and fluorine balance are: sodium fluoride, sodium hydroxide, sodium bifluoride, and hydrofluoric acid.

The demand ratio of the required amount of fluorine to the required amount of sodium determines which pair of equations, given below, should be used for calculating the additions.

C_F=g./l. F shown by calculation to be required
C_{Na}=g./l. Na shown by calculation to be required

when

$$\frac{C_F}{C_{Na}}=1.65 \text{ or more}$$

the following pair of equations are used:

g./l. $NaHF_2$ to be added$=2.69\times C_{Na}$
g./l. HF to be added$=1.052\times C_F-1.74\times C_{Na}$

when

$$\frac{C_F}{C_{Na}}=.826 \text{ to } 1.65$$

the following pair of equations are used:

g./l. of NaF to be added$=3.65\times C_{Na}-2.20\times C_F$
g./l. of $NaHF_2$ to be added$=3.26\times C_F-2.70\times C_{Na}$

when

$$\frac{C_F}{C_{Na}}=.826 \text{ or less}$$

the following pair of equations are used:

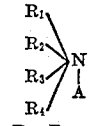
g./l. of NaF to be added$=2.21\times C_F$
g./l. of NaOH to be added$=1.74\times C_{Na}-2.1\times C_F$

The expression "other sulfate" when used in the claims, refers to the total sulfate radical, other than that combined with the stannous tin. This sulfate, which is in excess of that stoichiometrically equivalent to the tin, is calculated to SO_4.

As is well-known in the tin electroplating art, an acid electrotinning bath requires the inclusion of an addition agent, i.e. a grain refining agent, in order to produce a satisfactory tinplate. Any organic material which is compatible with our bath, and which has tin grain refining properties, will function as the addition agent in our bath. Examples of the type of material which we may use are the commonly used addition agents of cresol, beta-naphthol, phenyl sulfones, etc.

Another form of organic material, which has demonstrated outstanding grain refining properties is the type known as polyalkylene oxide. The polyalkylene oxides and terminally substituted polyalkylene oxides having a molecular weight over 400 are particularly efficacious in our bath. Included in this group of agents are the polyethylene oxides known by the trade names of Carbowax 1500, Carbowax 4000 and Igepal C.

We have also found that quaternary ammonium compounds have excellent grain refining properties in our stannous sulfate bath. Particularly useful are certain compounds of the normal and of the bis, or bisymmetrical, types. Normal compounds which we have found give exceptionally good results are those bath-soluble compounds having the general formula

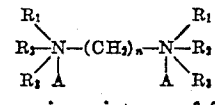


where N is nitrogen, R_1, R_2, R_3 and R_4 are alkane radicals wherein R_1 has 6 to 16 carbon atoms and R_1, R_2, R_3 and R_4 have a total of from 10 to 19 carbon atoms, and A is an anion. The anion may be toluene sulfonate, methyl sulfonate, benzene sulfonate, naphthalene sulfonate, hydroxy radical, nitrate radical, bromide, iodide, chloride, fluoride or sulfate.

Specific normal quaternary ammonium compounds which fall within the general formula given above include:

Dodecyl trimethyl ammonium p-toluene sulfonate
Decyl triethyl ammonium p-toluene sulfonate
Dihexyl diethyl ammonium p-toluene sulfonate
Decyl triethyl ammonium bromide
Hexadecyl trimethyl ammonium iodide

Among the more satisfactory bis compounds are those bath soluble compounds conforming to the general formula



where N is nitrogen, n is an integer of from 3 to 13, R_1, R_2 and R_3 are alkane radicals, each group having a total

of from 5 to 16 carbon atoms, and A is an anion of either toluene sulfonate, methyl sulfonate, benzene sulfonate, naphthalene sulfonate, hydroxy radical, nitrate radical, bromide, iodide, fluoride, chloride or sulfate.

Specific bis compounds which conform to the general formula given above are the following:

Trimethylene bis-(octyl diethyl ammonium toluene sulfonate)
Hexamethylene bis-(methyl dibutyl ammonium toluene sulfonate)
Decamethylene bis-(triethyl ammonium bromide)
Tridecamethylene bis-(decyl diethyl ammonium toluene sulfonate)

Other useful grain refining agents are lauryl ethyl methyl sulfonium iodide, alkylolamine resins and the Hercules Powder Company product known as polyethanol rosin amine D.

We claim:

1. An aqueous electrolytic tinplating bath which comprises stannous sulfate in the amount of from 9–55 g./l., sulfate radical, introduced as sulfuric acid, in excess of that stoichiometrically equivalent to the stannous tin by an amount of from 30–80 g./l., sodium fluoride in the amount of from 30–80 g./l., an organic addition agent, and approximately 1 g./l. of sodium bifluoride for each gram per liter of tin in excess of 10 g./l., wherein the ratio of said excess sulfate radical to sodium fluoride is approximately 1:1.

2. An aqueous electrolytic tinplating bath which comprises stannous sulfate in the amount of from 9–30 g./l., sulfate radical, introduced as sulfuric acid, in excess of that stoichiometrically equivalent to the stannous tin by an amount of from 40–55 g./l., sodium fluoride in an amount of from 40–55 g./l., an organic grain refining agent and approximately 1 g./l. of sodium bifluoride for each gram per liter of tin in excess of 10 g./l., wherein the ratio of said excess sulfate radical to sodium fluoride is approximately 1:1.

3. The method of tinplating a metal workpiece which comprises electrolyzing said workpiece in an aqueous solution containing stannous sulfate in an amount of from 9–55 g./l., sulfate radical, introduced as sulfuric acid, in excess of that stoichiometrically equivalent to the stannous tin in an amount of from 30–80 g./l., sodium fluoride in an amount of from 30–80 g./l., an organic grain refining agent in an amount of from 0.25–3.0 g./l., and approximately 1 g./l. of sodium bifluoride for each gram per liter of tin in excess of 10 g./l., wherein the ratio of said sulfate radical to sodium fluoride is such that the pH is maintained between 2.9 and 3.5.

4. The method of tinplating a metal workpiece which comprises electrolyzing said workpiece in an aqueous solution containing stannous sulfate in an amount of from 9–55 g./l., sulfate radical, introduced as sulfuric acid, in excess of that stoichiometrically equivalent to the stannous tin by an amount of from 30–80 g./l., sodium fluoride in an amount of from 30–80 g./l., an organic grain refining agent in an amount of from 0.25–3.0 g./l. and approximately 1 g./l. of sodium bifluoride for each gram per liter of tin in excess of 10 g./l., wherein the ratio of said excess sulfate radical to sodium fluoride is approximately 1:1.

5. An aqueous electrolytic tinplating bath which comprises stannous sulfate in an amount of from 9–55 g./l., sulfate radical, introduced as sulfuric acid, in excess of that stoichiometrically equivalent to the stannous tin by an amount of from 30–80 g./l., sodium fluoride in an amount of from 30–80 g./l., a polyalkylene oxide compound having a molecular weight over 400 in an amount of from 0.25–3.0 g./l., and approximately 1 g./l. of sodium bifluoride for each gram per liter of tin in excess of 10 g./l., wherein the ratio of said excess sulfate radical to sodium fluoride is approximately 1:1.

6. An aqueous electrolytic tinplating bath which comprises stannous sulfate in an amount of from 9–55 g./l., sulfate radical, introduced as sulfuric acid, in excess of that stoichiometrically equivalent to the stannous tin by an amount of from 30–80 g./l., sodium fluoride in an amount of from 30–80 g./l., a polyethylene oxide having a molecular weight over 400 in an amount of from 0.25–3.0 g./l., and approximately 1 g./l. of sodium bifluoride for each gram per liter of tin in excess of 10 g./l., wherein the ratio of said excess sulfate radical to sodium fluoride is approximately 1:1.

7. An aqueous electrolytic tinplating bath which comprises stannous sulfate in an amount of from 9–55 g./l., sulfate radical, introduced as sulfuric acid, in excess of that stoichiometrically equivalent to the stannous tin by an amount of from 30–80 g./l., sodium fluoride in an amount of from 30–80 g./l., a quaternary ammonium compound grain refining agent in an amount of from 0.25–3.0 g./l., and approximately 1 g./l. of sodium bifluoride for each gram per liter of tin in excess of 10 g./l., wherein the ratio of said excess sulfate radical to sodium fluoride is approximately 1:1.

8. An aqueous electrolytic tinplating bath which comprises stannous sulfate in an amount of from 9–55 g./l., sulfate radical, introduced as sulfuric acid, in excess of that stoichiometrically equivalent to the stannous tin by an amount of from 30–80 g./l., sodium fluoride in an amount of from 30–80 g./l., decyl triethyl ammonium p-toluene sulfonate in an amount of from 0.25–3.0 g./l., and approximately 1 g./l. of sodium bifluoride for each gram per liter of tin in excess of 10 g./l., wherein the ratio of said excess sulfate radical to sodium fluoride is approximately 1:1.

9. An aqueous electrolytic tinplating bath which comprises stannous sulfate in an amount of from 9–55 g./l., sulfate radical, introduced as sulfuric acid, in excess of that stoichiometrically equivalent to the stannous tin by an amount of from 30–80 g./l., sodium fluoride in an amount of from 30–80 g./l., decamethylene bis-(hexyl diethyl ammonium toluene sulfonate) in an amount of from 0.25–3.0 g./l., and approximately 1 g./l. of sodium bifluoride for each gram per liter of tin in excess of 10 g./l., wherein the ratio of said excess sulfate radical to sodium fluoride is approximately 1:1.

10. An aqueous electrolytic tinplating bath which comprises stannous tin in an amount of from 5–30 g./l., sodium and fluorine ions calculated as sodium fluoride in an amount of from 30–80 g./l., sulfate radical, in excess of that stoichiometrically equivalent to the tin by an amount of from 30–80 g./l., total sodium in an amount of from 16–55 g./l., total fluorine in an amount of from 14–55 g./l., and an organic grain refining agent, wherein the ratio of said excess sulfate radical to said calculated sodium fluoride is approximately 1 to 1.

11. The method of tinplating a metal workpiece which comprises electrolyzing said workpiece in an aqueous solution containing stannous tin in an amount of from 5–30 g./l., sodium and fluorine ions calculated as sodium fluoride in an amount of from 30–80 g./l., sulfate radical in excess of that stoichiometrically equivalent to the tin by an amount of from 30–80 g./l., total sodium in an amount of from 16–55 g./l., total fluorine in an amount of from 14–55 g./l., and an organic grain refining agent wherein the ratio of said excess sulfate radical to said calculated sodium fluoride is approximately 1 to 1.

12. The method of tinplating a metal workpiece which comprises electrolyzing said workpiece in an aqueous solution made up from stannous sulfate in an amount of from 9–55 g./l., sulfate radical in excess of that stoichiometrically equivalent to the tin in stannous sulfate by an amount of from 30–80 g./l., sodium fluoride in an amount of from 30–80 g./l., an organic grain refining agent in an amount of from 0.25–3.0 g./l. and approximately 1.0 g./l. of sodium bifluoride for each gram per liter of tin

in excess of 10 g./l. wherein the ratio of said excess sulfate radical to sodium fluoride is approximately 1 to 1.

13. The method of tinplating a metal workpiece which comprises electrolyzing said workpiece in an aqueous solution containing stannous tin in an amount of from 5–30 g./l., sulfate radical in excess of that stoichiometrically equivalent to the stannous tin by an amount of from 30–80 g./l., sodium and fluorine calculated as sodium fluoride in an amount of from 30–80 g./l., total sodium in an amount of from 16–55 g./l., total fluorine in an amount of from 16–55 g./l., an organic grain refining agent in an amount of from 0.25–3.0 g./l. and sodium and fluorine calculated as sodium bifluoride in an amount equal to 1 g./l for each gram per liter of stannous tin in excess of 10 g./l., wherein the ratio of said excess sulfate radical to sodium fluoride is approximately 1:1.

14. The method which comprises electrolyzing a metal workpiece in an aqueous electrolytic tinplating bath containing stannous tin in the amount of from 5–30 g./l., sulfate radical in excess of that stoichiometrically equivalent to the stannous tin by the amount of from 30–80 g./l., sodium fluoride in the amount of from 30–80 g./l., an organic addition agent, and approximately 1 g./l. of sodium bifluoride for each gram per liter of tin in excess of 10 g./l., wherein the ratio of said excess sulfate radical to sodium fluoride is approximately 1 to 1, and containing iron, silica and stannic tin, and controlling said bath by maintaining sodium and fluorine ions in the bath in amounts necessary to combine stoichiometrically with said iron as Na_2FeF_4, said silica as Na_2SiF_6 and said stannic tin as Na_2SnF_6.

15. The method which comprises electrolyzing a metal workpiece in an aqueous electrolytic tinplating bath containing stannous tin in the amount of from 5–30 g./l., sulfate radical in excess of that stoichiometrically equivalent to the stannous tin by the amount of from 30–80 g./l., sodium fluoride in the amount of from 30–80 g./l., an organic addition agent, and approximately 1 g./l. of sodium bifluoride for each gram per liter of tin in excess of 10 g./l., wherein the ratio of said excess sulfate radical to sodium fluoride is approximately 1 to 1, and containing iron, silica and stannic tin, and controlling said bath by maintaining sodium and fluorine ions in the bath in amounts necessary to combine stoichiometrically with said iron as Na_2FeF_4, said silica as Na_2SiF_6 and said stannic tin as Na_2SnF_6 and sufficient to maintain said ratio at approximately 1 to 1.

16. The method which comprises electrolyzing a metal workpiece in an aqueous electrolytic tinplating bath containing stannous tin in the amount of from 10–16 g./l., sulfate radical in excess of that stoichiometrically equivalent to the stannous tin by the amount of from 40–50 g./l., sodium fluoride in the amount of from 40–50 g./l., an organic addition agent, and approximately 1 g./l. of sodium bifluoride for each gram per liter of tin in excess of 10 g./l., wherein the ratio of said excess sulfate radical to sodium fluoride is approximately 1 to 1, and containing iron, silica and stannic tin, and controlling said bath by maintaining sodium and fluorine ions in the bath in amounts necessary to combine stoichiometrically with said iron as Na_2FeF_4, said silica as Na_2SiF_6 and said stannic tin as Na_2SnF_6 and sufficient to maintain said ratio at approximately 1 to 1.

17. The method which comprises electrolyzing a metal workpiece in an aqueous electrolytic tinplating bath containing stannous tin in the amount of from 10–20 g./l., sulfate radical in excess of that stoichiometrically equivalent to the stannous tin by the amount of from 35–60 g./l., sodium fluoride in the amount of from 35–60 g./l., an organic addition agent, and approximately 1 g./l. of sodium bifluoride for each gram per liter of tin in excess of 10 g./l., wherein the ratio of said excess sulfate radical to sodium fluoride is approximately 1 to 1, and containing iron, silica and stannic tin, and controlling said bath by maintaining sodium and fluorine ions in the bath in amounts necessary to combine stoichiometrically with said iron as Na_2FeF_4, said silica as Na_2SiF_6 and said stannic tin as Na_2SnF_6 and sufficient to maintain said ratio at approximately 1 to 1.

18. An aqueous electrolytic tinplating bath which comprises stannous tin in the amount of from 5–30 g./l., sodium fluoride in the amount of from 30–80 g./l., sulfate radical in excess of that stoichiometrically equivalent to the tin by the amount of from 30–80 g./l., approximately 1.0 g./l. of sodium bifluoride for each gram per liter of tin in excess of 10 g./l., and an organic grain refining agent, wherein the ratio of said excess sulfate radical to sodium fluoride is approximately 1 to 1, said bath also containing iron, silica and stannic tin, and amounts of sodium and fluorine, in adition to that contained in said fluorides, necessary to combine stoichiometrically with said iron as Na_2FeF_4, said silica as Na_2SiF_6 and said stannic tin as Na_2SnF_6.

19. The method which comprises electrolyzing a metal workpiece in an aqueous electrolytic tinplating bath containing stannous tin in the amount of from 5–30 g./l., sulfate radical in excess of that stoichiometrically equivalent to the stannous tin by the amount of from 30–80 g./l., sodium and fluorine ions calculated as sodium fluoride in the amount of from 30–80 g./l., an organic addition agent, and approximately 1 g./l. of sodium bifluoride for each gram per liter of tin in excess of 10 g./l., and wherein the ratio of said excess sulfate radical to said calculated sodium fluoride is approximately 1 to 1, said bath containing iron, silica and stannic tin, and controlling the bath by maintaining sodium and fluorine ions in the bath in amounts necessary to combine stoichiometrically with said iron as Na_2FeF_4, said silica as Na_2SiF_6 and said stannic tin as Na_2SnF_6 and sufficient to maintain said ratio at approximately 1 to 1.

References Cited in the file of this patent

UNITED STATES PATENTS

2,402,185 Schweikher ---------- June 18, 1946

OTHER REFERENCES

Discher: Journal Electrochemical Society, vol. 102 (November 1955), page 617.