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Horn

[11] **3,907,653**

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[54] **PROCESS FOR RECOVERING TIN SALTS FROM A HALOGEN TIN PLATE SLUDGE**

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[52] **U.S. Cl.** ..... **204/94;** 204/54 R; 204/180 P

[51] **Int. Cl.²** **C25B 1/24;** C25D 3/30; C25B 7/00

[58] **Field of Search** ..... 204/54 R, 94, 180 P

[56] **References Cited**

UNITED STATES PATENTS

2,372,032	3/1945	Swalheim	204/54 R
2,402,185	6/1946	Schweikher	204/54.R
2,512,719	6/1950	Hull	204/54 R
2,758,075	8/1956	Swalheim	204/54 R
3,284,350	11/1966	Williamson	204/54 R
3,390,064	6/1968	Baltakmens et al.	204/94
3,623,962	11/1971	Beale	204/54 R
3,723,273	3/1973	Wilson	204/180 P
3,787,304	1/1974	Chlanda et al.	204/94
3,795,595	3/1974	Wilson	204/94

Primary Examiner—T. Tung

Attorney, Agent, or Firm—Stanley J. Price, Jr.

[57] **ABSTRACT**

The sludge of a halogen tin plating bath includes both sodium fluostannate and iron ferrocyanide. The sodium fluostannate is dissolved in water and separated from the iron ferrocyanide by filtration. The sodium fluostannate is thereafter reacted with sodium hydroxide to form tin hydroxide and sodium fluoride. The tin hydroxide is thereafter converted to metallic tin by a suitable electrolytic process. The described process includes reacting the tin hydroxide with sodium hydroxide and steam to form sodium stannate which is converted to metallic tin and sodium hyroxide in an electrolytic cell utilizing insoluble anodes. A multi compartment electrodialytic cell having a plurality of insoluble anodes and a soluble tin anode is utilized to split the sodium fluoride salt and transfer the sodium ion to the cathode compartment and the fluoride ion to the anode compartment. Sodium hydroxide is generated in the cathode compartment and hydrofluoric acid is generated in the insoluble anode compartment. The hydrofluoric acid from the insoluble anode compartment is introduced into an anode compartment containing the soluble tin anode. A solution containing a fluostannite complex is recovered from the soluble anode compartment and is recirculated to the plating bath. Where a sodium fluostannite is desired, a portion of the sodium fluoride is introduced into the soluble tin anode compartment. The sodium hydroxide generated in the cathode compartments may be used in the process for reaction with the sodium fluostannate solution and form the tin hydroxide. The iron ferrocyanide is reacted with a portion of the sodium hydroxide generated in the process to obtain sodium ferrocyanide which may also be utilized in the plating bath. With this process the reactants are generated in the process so that the process does not require other compounds.

14 Claims, 2 Drawing Figures

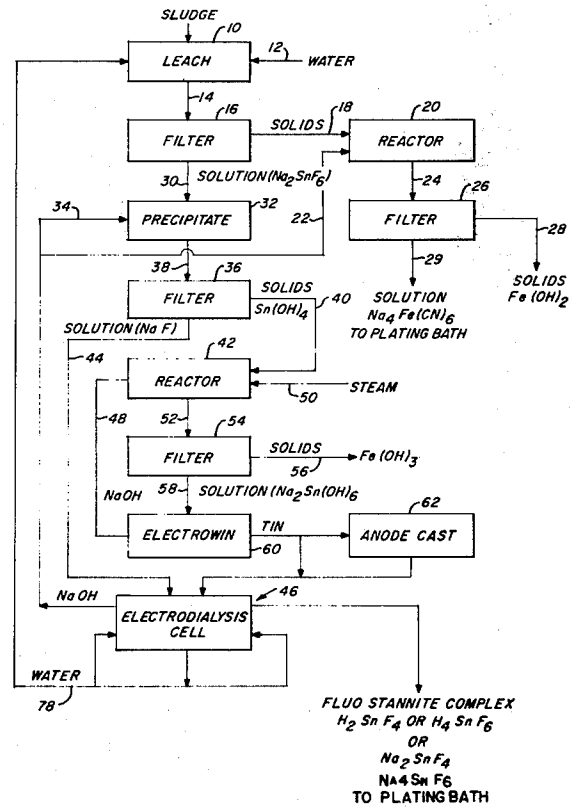


FIG. 1

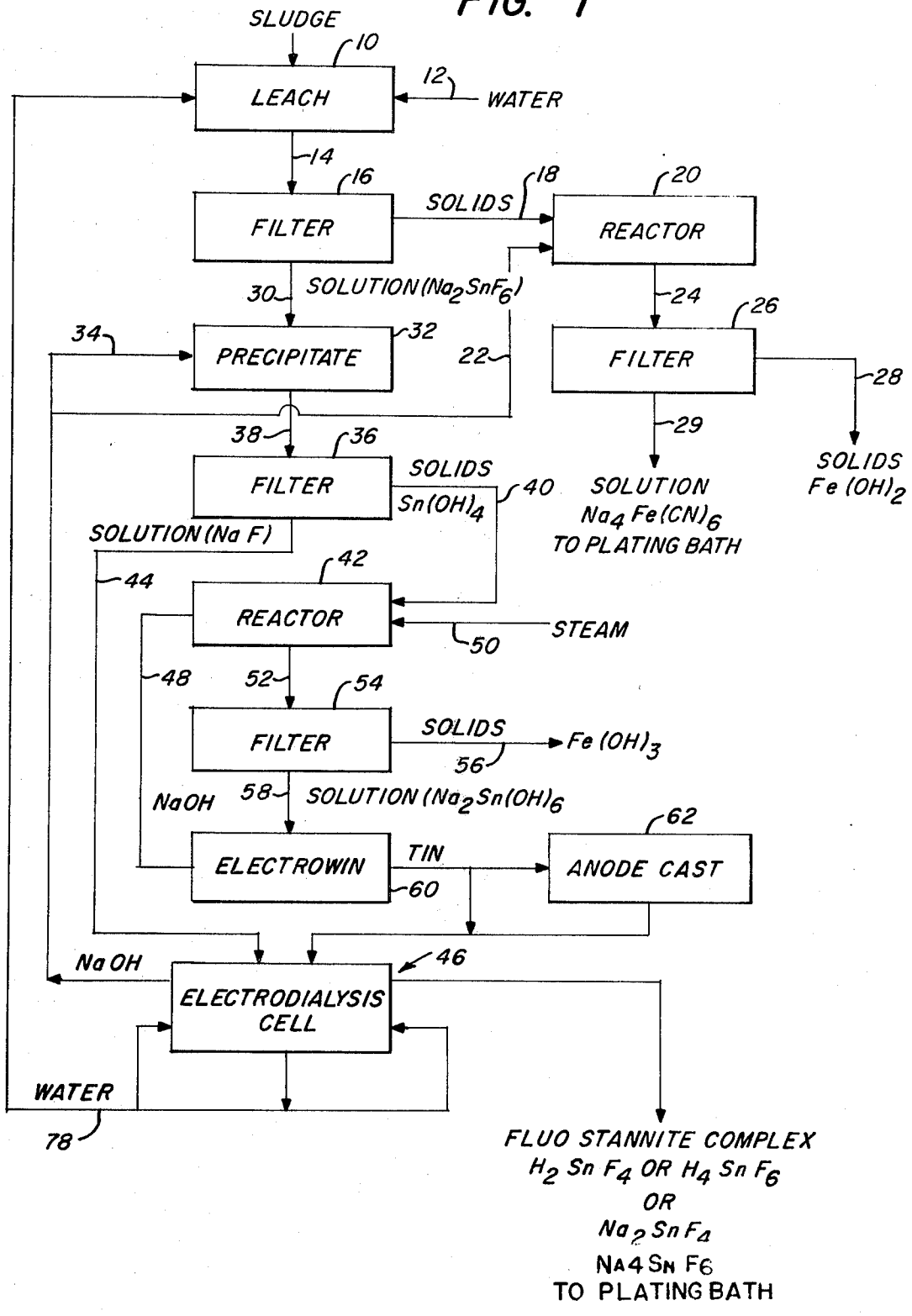
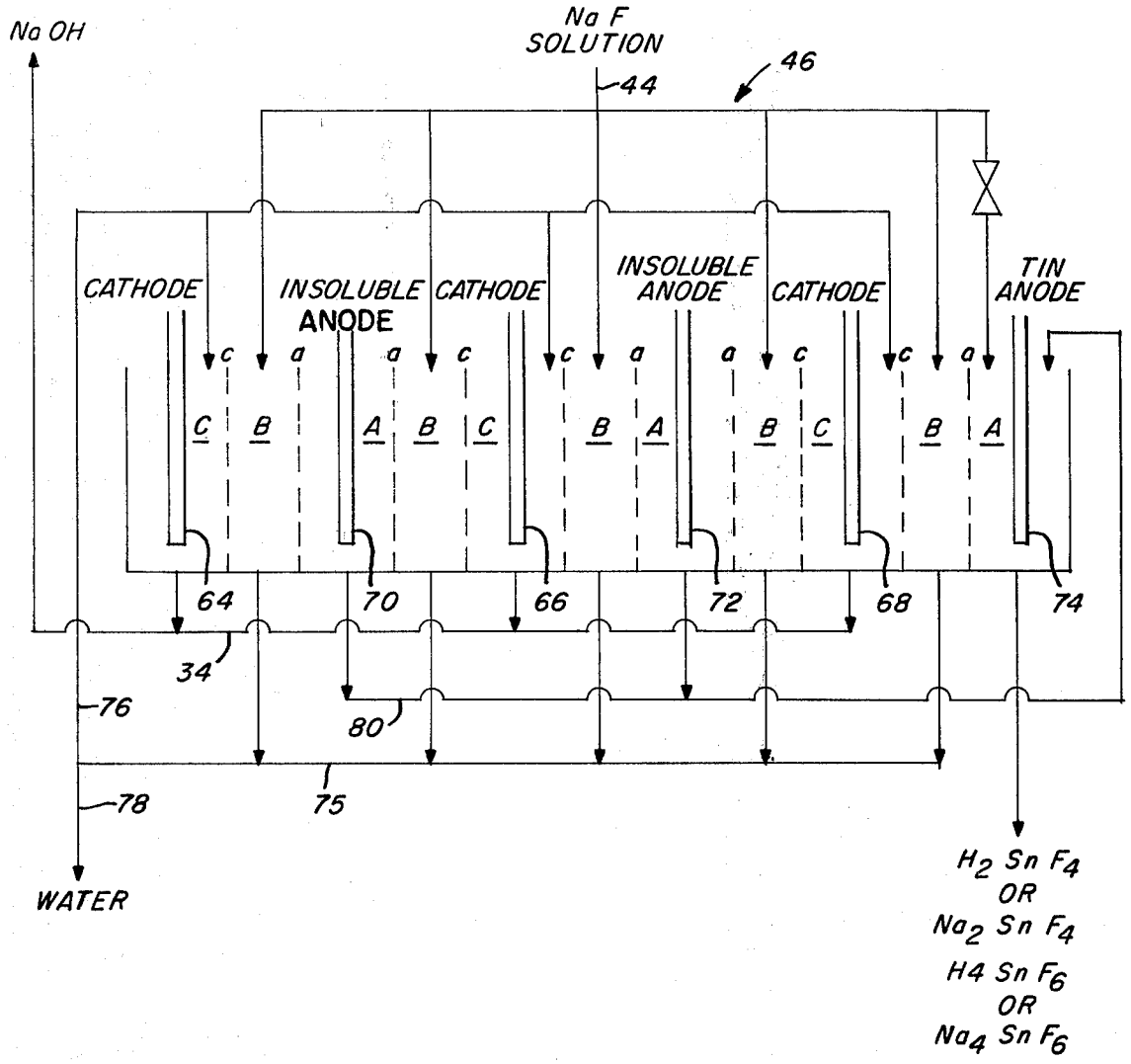

SLUDGE
10
LEACH
12
WATER
14
16
FILTER
SOLIDS
18
20
REACTOR
30
SOLUTION (Na_2SnF_6)
24
26
34
PRECIPITATE
32
22
FILTER
28
29
38
36
FILTER
SOLIDS
$Sn(OH)_4$
40
SOLUTION
$Na_4Fe(CN)_6$
TO PLATING BATH
SOLIDS
$Fe(OH)_2$
SOLUTION (Na F)
44
42
REACTOR
STEAM
50
48
52
54
FILTER
SOLIDS
56
$Fe(OH)_3$
NaOH
58
SOLUTION ($Na_2Sn(OH)_6$
62
ELECTROWIN
TIN
60
ANODE CAST
NaOH
46
ELECTRODIALYSIS CELL
WATER
78
FLUO STANNITE COMPLEX
H_2SnF_4 OR H_4SnF_6
OR
Na_2SnF_4
Na_4SnF_6
TO PLATING BATH

FIG. 2


Na OH
Na F SOLUTION
44
46
CATHODE
INSOLUBLE ANODE
CATHODE
INSOLUBLE ANODE
CATHODE
TIN ANODE
c
a
C
B
A
64
70
66
72
68
74
34
76
80
75
78
WATER
$H_2 Sn F_4$
OR
$Na_2 Sn F_4$
$H4 Sn F_6$
OR
$Na_4 Sn F_6$

PROCESS FOR RECOVERING TIN SALTS FROM A HALOGEN TIN PLATE SLUDGE

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a process for recovering tin salts from a halogen tin plate sludge and more particularly to a process for recovering tin salts suitable for use in a tin plating bath from a halogen tin plate sludge.

2. Description of the Prior Art

In the continuous tin plating of strip steel a typical electro-tinning bath has the following composition:

Stannous Tin	4.5 oz./gal.
Fluoride	4.75 oz./gal.
Sodium Chloride	4.60 oz./gal.
Sodium Ferrocyanide	0.15 oz./gal.
Organic Brighteners	30 ml/gal.
pH	3.3
Mole Ratio	F:Sn = 6-7:1

The bath is prepared commercially from stannous chloride, sodium bifluoride and sodium fluoride. A reaction occurs between the stannous chloride and the sodium bifluoride to form a tin fluoride complex with a fluostannite ion. The reaction is set forth below in equations (1) and (2).

(1) $SnCl_2 + 2NaF.HF \rightarrow Na_2SnF_4 + 2HCl$ or

(2) $SnCl_2 + 2NaF.HF + 2NaF \rightarrow Na_4SnF_6 + 2HCl$

The fluostannite ion so formed has been referred to by the formulas SnF_4^{-2} and SnF_6^{-4}. The literature confirms that the success of the above enumerated electrotinning bath is due to the formation of the fluoride complex.

The following United States patents describe the tin plating process.

2,402,185	2,407,579
2,457,152	2,461,507
2,512,719	2,585,902
2,736,692	2,758,075

The fluoride complex is stable and does not precipitate the basic tin salts when the pH of the bath is within the range of 2.5 to 4.0. Further, it is desirable to maintain the fluoride to tin mole ratio in the bath at between about 6 and 7 to 1.

During the tin plating of the strip steel the strip moves very rapidly through the bath and air is introduced into the bath by the rapid movement of the sheet steel and agitation from other sources. The air introduced into the bath oxidizes a portion of the tin fluoride complex. The oxidized tin is in the form of a stable anionic complex and has the formulation Na_2SnF_6. The oxidized tin compound does not have any adverse effects on the bath but, because of its low solubility, precipitates and settles to the bottom of the bath in a crystalline mass. Also, sodium ferrocyanide is added to the bath and the sodium ferrocyanide reacts with the iron drawn in with the rapidly moving strip to form an iron ferrocyanide compound.

The oxidation process results in a loss of tin and fluoride compounds and increases the pH of the bath due to the formation of sodium hydroxide. The loss of tin due to oxidation does not change the fluoride to tin mole ratio of the bath. The increases in pH, however, require the addition of sodium bifluoride (NaF.HF) to

maintain the ph at the desired level of between 2.5 and 4.0. The reactions that take place in the bath are set forth in equations (3), (4) and (5).

(3) $Na_4SnF_6 + \frac{1}{2} O_2 + H O \rightarrow Na_2SnF_6 + 2NaOH$

(4) $Na_2SnF_4 + 2NaF + \frac{1}{2} O_2 + H_2O \rightarrow Na_2SnF_6 + 2NaOH$

(5) $NaOH + NaF.HF \rightarrow 2\ NaF$

The precipitate which is also referred to as a sludge is periodically removed from the bath. In the past the precipitate or sludge has been subjected to smelting to recover the tin values or units therein. Smelting to recover the tin values results in a total loss of the fluoride values or units and the fluoride is a source of pollution during the recovery of the tin by smelting. Further, the tin in the bath must be replaced by a tin compound which is more expensive than the tin recovered by smelting. Attempts to reduce the oxidized tin compound back to the fluostannite from a water solution have not been successful because the voltage required for reduction is not achievable in an aqueous solution. As set forth below other proposed methods for recovering the tin or the fluoride tin compounds are disclosed in U.S. Pat. Nos. 3,284,350 and 2,372,032.

U.S. Pat. No. 3,284,350 uses lime to precipitate the tin and results in a large mass of precipitate that must be smelted to recover the tin. As above discussed, the fluoride units are lost with this process.

U.S. Pat. No. 2,372,032 reduces the fluostannate compound. The compound must, however, be isolated from the other precipitated material and all of the water must be removed so that the dry salt is reacted with molten tin at high temperatures. This process is expensive because of the large amount of water that must be removed and the process is not practical from a commercial aspect.

There is a need for a relatively simple process that will recover both the tin units and the fluoride units from the bath and preferably in the same form that they are utilized in the plating bath, i.e. as an anionic fluostannite complex.

SUMMARY OF THE INVENTION

The invention relates to a process for recovering a tin salt from the sludge of a halogen tin plating bath and includes the steps of obtaining a sludge that contains sodium fluostannate. The sodium fluostannate is reacted with a basic solution to form tin hydroxide and an electrolyte solution containing fluoride ions. The tin hydroxide is then converted to metallic tin that may be utilized as a soluble anode in an electrodialytic cell. At least a portion of the electrolyte solution containing the fluoride ions is converted to hydrofluoric acid. The hydrofluoric acid is introduced into the electrodialytic cell anode compartment containing the soluble anode and by means of passing a current through the electrodialytic cell is converted to a solution containing a fluostannite complex salt that is suitable for use in the plating bath.

The tin hydroxide is reacted with sodium hydroxide to obtain sodium stannate which is then converted to metallic tin. The sodium fluoride recovered from the reaction of sodium fluostannate with sodium hydroxide is introduced into the center compartment of an electrodialytic cell having insoluble anodes. The sodium fluoride is split and a solution containing hydrofluoric acid is generated in the electrodialytic cell anode compartment and is introduced into the anode compart-

ment containing the soluble tin anode. Where desired, a portion of the sodium fluoride solution may be introduced into the anode compartment containing the soluble tin anode to form a sodium fluostannite solution suitable for use in the tin plating bath.

It will be apparent with the above process that the constituents required to form a solution of sodium fluostannite from the sludge, convert the sodium fluostannite to metallic tin and thereafter form the fluostannite complex salt in the electrodialytic cell are generated in the process so that it is not necessary to add constituents to the process for recovering the fluostannite complex salt from the fluostannate in the sludge.

With the above process the tin values and the fluoride values are recovered from the oxidized precipitate and they are recovered in the same stable form as they are utilized in the plating bath. The recovered fluostannite complex reduces substantially the requirements for stannous chloride and sodium bifluoride in the bath. Also, the process can be operated at the site where the tin plating takes place and at a substantially reasonable cost because the recovered products are maintained in solution form.

Accordingly, the principal object of this invention is to provide a process for recovering both the tin and fluoride units from the oxidized halogen tin plate precipitate obtained from a halogen tin plate bath.

Another object of this invention is to provide a process for recovering from an oxidized precipitate of a halogen tin plating bath tin and fluoride units in a stable form capable of being utilized in a halogen tin plating bath.

These and other objects and advantages of this invention will be more completely disclosed and described in the following specification, the accompanying drawings and the appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** is a schematic flow diagram for the recovery of tin and fluoride units from the precipitate of a halogen tin plating bath.

FIG. **2** is a diagrammatic representation of the electrodialysis unit illustrated in FIG. **1.**

DESCRIPTION OF THE PREFERRED EMBODIMENT

Referring to the drawings and particularly FIG. **1,** the sludge or precipitate from halogen tin plate bath is introduced into a leach tank **10** where the sludge is admixed with water which enters through conduit **12.** The water introduced into the leach tank **10** is preferably at an elevated temperature as, for example, about 140°F. The leach tank **10** may include a suitable mixing device to admix the sludge with water and form a slurry. The slurry is then conveyed through conduit **14** to a filter **16.** The solids which are iron ferrocyanides are withdrawn from the filter **16** on a suitable conveyor device **18** and introduced into a reactor **20.** The reactor is a suitable tank containing an agitating device for admixing the iron ferrocyanide with sodium hydroxide introduced through conduit **22.** The sodium hydroxide reacts with the iron ferrocyanide to form sodium ferrocyanide in accordance with the following equation.

$$(6)\ Fe_4(Fe(CN)_6)_3 + 12\ NaOH \rightarrow 3\ Na_4Fe(CN)_6 + 4Fe(OH)_3$$

The slurry from reactor **20** is introduced through conduit **24** onto a filter **26** where the solids, i.e. $Fe(OH)_3$ are removed by a conveying device **28.** The filtrate withdrawn through conduit **29** from filter **26** is a solution of sodium ferrocyanide that is circulated to the plating bath for use therein.

The filtrate from the filter **16** is a clarified sodium fluostannate solution which is introduced through conduit **30** into a suitable tank **32** where it is reacted with sodium hydroxide introduced into tank **32** through conduit **34.** The reaction in accordance with the following equation precipitates the tin as tin hydroxide.

$$(7)\ Na_2SnF_6 + 4\ NaOH \rightarrow Sn(OH)_4\ (ppt) + 6\ NaF$$

The reactants from tank **32** are conveyed to a filter **36** through conduit **38** and the solids containing the tin hydroxide are removed by a suitable conveying device **40** and introduced into a reaction tank **42.** The filtrate which is a solution of sodium fluoride is removed from filter **36** through conduit **44** and conveyed by conduit **44** to an electrodialysis unit generally designated by the numeral **46** where it is introduced into compartments of the electrodialysis cell as later explained.

The tin hydroxide introduced into the reactor **42** is reduced to metallic tin by any conventional method and preferably electrolytically since electrolytic reduction removes any impurities present, such as iron or the like. The iron is present with the sodium fluostannate as a fluoferrate ion. In reactor **42** the stannic hydroxide is preferably reacted with additional sodium hydroxide introduced through conduit **48** to form sodium stannate in the presence of steam introduced through conduit **50** according to the following equation:

$$(8)\ Sn(OH)_4 + 2NaOH \rightarrow Na_2Sn(OH)_6$$

The reactants from vessel **42** are conveyed through conduit **52** to filter **54** where the solids, $Fe(OH)_3$, are removed through conduit **56** and the filtrate is withdrawn from the filter **54** through conduit **58.** The filtrate is sodium stannate. The sodium stannate solution is introduced into a conventional electrolytic cell **60** that utilizes insoluble anodes. The sodium stannate reacts electrolytically according to the following equation to provide metallic tin, sodium hydroxide, oxygen and water.

$$(9)\ Na_2Sn(OH)_6 \rightarrow Sn + 2NaOH + O_2 + H_2O$$

The metallic tin is either melted or stripped from the cathodes and cast into anodes in a suitable casting device **62** or preferably a cathode material resistant to anodic attack by fluorides, for example, platinum, carbon or platinum coated tantalum or tin itself, is used for the substrate on which the tin is coated. With this arrangement the cathodes are removed when the desired thickness of tin is obtained and used as anodes for the dissolution step in the electrodialytic unit **46.** When the tin is dissolved from the cathodes the cathodes are returned to the electrolytic bath to acquire more tin thereon. The sodium hydroxide recovered from the electrolytic bath is introduced through conduit **48** to the reactor **42** previously described.

The sodium fluoride solution recovered from the stannic hydroxide precipitation in reactor **42** and filtered in filter **36** is conveyed into the electrodialytic cell **46** or a diaphragm cell of the salt splitting type. The electrodialytic cell **46** is of multiple cell design as illustrated diagrammatically in FIG. **2** and includes a plurality of cells that have a cathode compartment C, anode compartment A and center compartment B between the anode compartment A and the cathode compartment C. The respective compartments are separated from each other by cation and anion semi-permeable

membranes illustrated in dotted lines and indicated by the letters *a* and *c*.

As illustrated in FIG. **2**, the multiple cell unit includes cathodes **64, 66** and **68** and insoluble anodes **70** and **72** and a soluble tin anode **74**. The metallic tin recovered electrolytically in the electrolytic cell **60** is introduced in the form of an anode into the anode compartment containing the soluble anode **74**. The insoluble anodes **70** and **72** are separated from the soluble anode **74** so that the resulting fluostannite complex is not oxidized by the oxygen generated at the insoluble anodes. The ratio of insoluble to soluble anodes is such that the fluostannite complex is produced wherein a mole ratio of fluoride to tin is maintained at at least 4:1 and preferably 6:1, thereby maintaining the tin in a stable anionic complex.

In the electrodialytic cell **46** sodium hydroxide is recovered from the cathode compartment C and conveyed through conduit **34** to the reactor **32** where it is utilized to precipitate stannic hydroxide. The water recovered from the intermediate compartment B is introduced into conduit **75** and a portion is conveyed through conduit **76** to the cathode compartment C and the remainder is conveyed through conduit **78** to dilute the sludge and dissolve the soluble Na_2SnF_6. The hydrofluoric acid solution generated in the insoluble anode compartments containing insoluble anodes **70** and **72** is conveyed through conduit **80** and introduced into the anode compartment containing the soluble tin anode **74**. Where desired, other electrolytes, such as sodium fluoride solution or the plating solution, may also be introduced into the anode compartment. The presence of the sodium fluoride solution in the soluble anode compartment results in the generation of a sodium fluostannite complex. The fluostannite complex solution is removed from the soluble anode compartment through conduit **82** and introduced directly into the plating bath. The product formed in the anode compartment and removed therefrom is dependent on the operating conditions of the plating bath, the ratio of insoluble and soluble anodes and the electrolyte and may be so controlled to conform with the requirements of the plating bath. It should be understood that electrolyte solutions other than those described and illustrated in the examples may be utilized in the anode, cathode and intermediate compartments. Also, electrolyte solutions other than those previously enumerated may be introduced in the cathode and intermediate compartments and other compounds formed in the respective compartments during the electrodialysis process and it is not intended to limit the invention to the specific electrolytes enumerated.

The following examples are illustrative of the above described process.

EXAMPLE 1

Three hundred grams of waste halogen tin plate sludge were diluted to a volume of 1,250 mls. with water to form a slurry and mixed for four hours at a temperature of about 140°F. The slurry was permitted to settle and thereafter filtered. 1,150 mls. of filtrate were obtained that had an analysis as follows: 37.5 gms./1 tin; 38.2 gms/1 fluoride; the fluoride to tin mole ratio was 6.28:1. This solution had a pH of 4.5. 375 mls. of 4N NaOH were added to the solution to neutralize the solution and increase the pH to 8.2, yielding 1525 mls. of a slurry of stannic hydroxide precipitate. The slurry was filtered and yielded 1100 mls. of clear sodium fluoride solution. This solution contained 60.5 gms/1 of sodium fluoride. The tin hydroxide solids were reacted with additional sodium hydroxide to produce sodium stannate according to equation (8). This required an additional 240 mls. of 4N NaOH which was mixed with the tin hydroxide precipitate and reacted at 240°F. The solution was diluted to one liter and contained 43 gms/1 tin and 9 gms/1 free sodium hydroxide. This solution is an optimum solution for the electrowinning of tin by means of an electrolytic cell as previously described.

An anode of cast tin having a surface area of 0.1 square feet recovered by means of the conversion to metallic tin by the electrolytic cell above described was positioned in the anode compartment of a three compartment electrodialytic cell of the salt splitting type. The anode compartment was separated from the center compartment by an anionic semi-permeable membrane manufactured by the Ionac Chemical Company and designated "MA-3475". A liter of hydrofluoric acid solution containing 25 gms/1 HF was introduced into the anode compartment to simulate the hydrofluoric acid solution produced in the insoluble anode compartments of a multi cell unit as previously described.

A liter of sodium fluoride solution obtained during the precipitation of the tin hydroxide containing 60.5 gms/1 NaF was introduced into the center compartment of the electrodialytic cell that was separated from the cathode compartment by a cation semi-permeable membrane manufactured by the Ionac Chemical Company and designated "MC-3470".

The cathode compartment contained a stainless steel cathode of 0.1 square feet of surface area. A liter of sodium hydroxide solution containing 8.48 gms/1 of sodium hydroxide was circulated in the cathode compartment. Current was impressed across the cell at 4.2 v. and 4 a., which yielded a current density of 40 asf.

The results of the electrodialysis are listed below in Table 1. The resultant solution in the anode compartment contained 58.65 gms/1 tin and 43.90 gms/1 fluoride to yield 0.497 moles of H_2SnF_4 plus a slight excess of HF. The table clearly illustrates the moles of fluoride transferred from the center compartment to the anode compartment to yield the H_2SnF_4 and the transfer of sodium from the center compartment to the cathode compartment to increase the moles of sodium hydroxide in the cathode compartment.

TABLE 1

Time Hours	Moles Sn Anode Compartment	Moles F Transferred	Moles Na^+ Transferred	Sn at Anode	NaOH at Cathode	Loss Of F	Moles Ratio F:Sn	Efficiency
1	0.0745	0.143	0.146	8.79	14.32	2.72	19.6	100

TABLE 1—Continued

Time Hours	Moles Sn Anode Compartment	Moles F Transferred	Moles Na^+ Transferred	Sn at Anode	NaOH at Cathode	Loss Of F	Moles Ratio F:Sn	Efficiency
2	0.147	0.286	0.292	17.42	20.17	5.43	10.8	99
3	0.220	0.430	0.437	26.02	25.94	8.15	7.9	99
4	0.292	0.574	0.584	34.50	31.82	10.90	6.47	97.9
5	0.360	0.715	0.717	42.48	37.18	13.58	5.64	96.7
6	0.428	0.858	0.864	50.44	43.04	16.30	5.08	95.74
7	0.497	0.994	1.00	58.65	48.52	18.88	4.65	95.3

EXAMPLE 2

A similar procedure was followed to obtain the metallic tin and the sodium fluoride solution as enumerated in Example 2. An electrodialysis cell similar to that used in Example 2 was set up as follows.

In the anode compartment one liter of hydrofluoric acid having a concentration of 25.2 gms/1 HF and a tin anode of 0.1 square feet cross-sectional area was separated from the center compartment, utilizing a neutral or nonionic membrane manufactured by the Union Carbide Corporation and designated "Visking".

Through the center compartment a liter of sodium fluoride solution containing 60 gms/1 of sodium fluoride was circulated and separated from the cathode compartment by the same cationic membrane used in the previous example. Through the cathode compartment a liter of solution containing 26.72 gms/1 of sodium hydroxide was circulated and current of 4.9 v. and 5 a. or 50 asf was impressed across the cell for a period of 6 hours. The results of the electrodialysis are set forth below.

TABLE 2

Time Hours	Anode Tin	Anode Fluoride	Cathode NaOH	Center Compartment Sn	Center Compartment NaF	Mole Ratio F:Sn	Efficiency
0	0.0	25.20	26.72	0.0	60.0		
1	11.00	27.45	34.12	0.0	52.24	15.48	100
2	21.89	30.96	41.50	0.0	44.47	8.78	99.5
3	32.78	34.44	48.82	0.0	36.77	6.53	99.0
4	43.64	37.91	56.13	0.02	29.08	5.38	99.2
5	54.44	41.35	63.38	0.38	21.49	4.74	98.71
6	65.26	44.78	70.58	1.02	14.22	4.2	98.92

The results enumerated in Table 2 clearly illustrate the increase in sodium hydroxide in the cathode compartment and the increase of the tin fluoride complex in the anode compartment.

According to the provisions of the patent statutes, the principle, preferred construction and mode of operation of the invention have been explained and what is now considered to represent its best embodiment has been illustrated and described. However, I desire to have it understood that, within the scope of the appended claims, the invention may be practiced otherwise than is illustrated and described.

I claim:

1. A process for recovering a tin salt suitable for use in a tin plating bath from the sludge of a halogen tin plating bath comprising,

obtaining a sludge from a halogen tin plating bath that contains sodium fluostannate,

reacting the sodium fluostannate with a basic solution and forming tin hydroxide and an electrolyte solution containing fluoride ions,

converting the tin hydroxide to metallic tin,

positioning the metallic tin as a soluble anode in an electrodialytic cell,

introducing said electrolyte solution containing fluoride ions into the electrodialytic cell anode compartment containing the soluble metallic tin anode,

passing a current through the electrodialytic cell and generating a solution containing a fluostannite complex ion in the anode compartment containing the metallic tin soluble anode, and

recovering a solution containing the fluostannite complex ion suitable for use in a tin plating bath.

2. A process for recovering a tin salt as set forth in claim 1 which includes,

reacting the sodium fluostannate with sodium hydroxide and forming tin hydroxide and a sodium fluoride solution.

3. A process for recovering a tin salt as set forth in claim 2 which includes,

introducing the sodium fluoride solution into the intermediate compartment of an electrodialytic cell,

passing a current through the electrodialytic cell and generating an electrolyte solution containing hydrofluoric acid in the anode compartment of the electrodialytic cell having an insoluble anode.

4. A process for recovering a tin salt as set forth in claim 1 which includes,

generating a sodium hydroxide solution in the cathode compartment of the electrodialytic cell.

5. A process for recovering a tin salt as set forth in claim 4 which includes,

recovering a sodium hydroxide solution from the cathode compartment of the electrodialytic cell,

reacting the sodium fluostannate with sodium hydroxide in the sodium hydroxide solution recovered from the cathode compartment of the electrodialytic cell.

6. A process for recovering a tin salt as set forth in claim 1 in which,

the sludge contains sodium fluostannate and iron ferrocyanide,

dissolving the sodium fluostannate in water to form a sodium fluostannate solution,

separating the iron ferrocyanide from the sodium fluostannate solution, and

reacting the iron ferrocyanide with sodium hydroxide to recover a sodium ferrocyanide solution.

7. A process for recovering a tin salt as set forth in claim 1 which includes,

reacting a tin hydroxide with sodium hydroxide and recovering sodium stannate.

8. A process for recovering a tin salt as set forth in claim 7 which includes,

converting the sodium stannate electrolytically to metallic tin and sodium hydroxide.

9. A process for recovering a tin salt as set forth in claim 1 which includes,

introducing an electrolyte containing sodium ions into the electrodialytic cell anode compartment containing the soluble metallic tin anode,

generating a solution containing a sodium fluostannite compound in the anode compartment suitable for use in a tin plating bath.

10. A process for recovering a tin salt as set forth in claim 1 which includes,

a multi compartment electrodialytic cell with a plurality of anode compartments separated from adjacent cathode compartments by an intermediate compartment,

at least one of said anode compartments containing a metallic tin soluble anode and the other anode compartments containing insoluble anodes,

introducing said electrolyte containing fluoride ions into the intermediate compartments between cathode compartments and anode compartments containing insoluble anodes and generating an electrolyte solution containing hydrofluoric acid,

introducing said electrolyte solution containing said hydrofluoric acid into said anode compartment containing said metallic tin soluble anode,

generating a solution containing said fluostannite complex ion in the anode compartment containing the metallic tin soluble anode.

11. A process for recovering a tin salt as set forth in claim 10 which includes,

reacting the sodium fluostannate with sodium hydroxide and forming tin hydroxide and a sodium fluoride solution,

introducing said sodium fluoride solution into said intermediate compartments between cathode compartments and anode compartments containing insoluble anodes.

12. A process for recovering a solution containing a fluostannite complex ion from a solution containing a fluostannate complex ion comprising,

reacting the solution containing a fluostannate complex ion with a basic solution and forming a tin hydroxide,

converting the tin hydroxide to metallic tin,

utilizing the metallic tin as a soluble anode in an electrodialytic cell,

introducing an electrolyte containing fluoride ions into the electrodialytic cell containing the soluble metallic tin anode,

passing a current through the electrodialytic cell and generating a solution containing a fluostannite complex ion.

13. A process for recovering a solution containing a fluostannite complex ion from a material containing sodium fluostannate as set forth in claim 12 in which,

said fluostannite complex ion is contained in a compound selected from the group consisting of H_3SnF_6, H_2SnF_4 or Na_2SnF_4 or Na_4SnF_6 or mixtures thereof.

14. A process for recovering a tin salt as set forth in claim 1 which includes,

converting at least a portion of the electrolyte solution containing fluoride ions into hydrofluoric acid,

introducing said electrolyte solution containing said hydrofluoric acid into the electrodialytic cell anode compartment containing the soluble metallic tin anode.

* * * * *