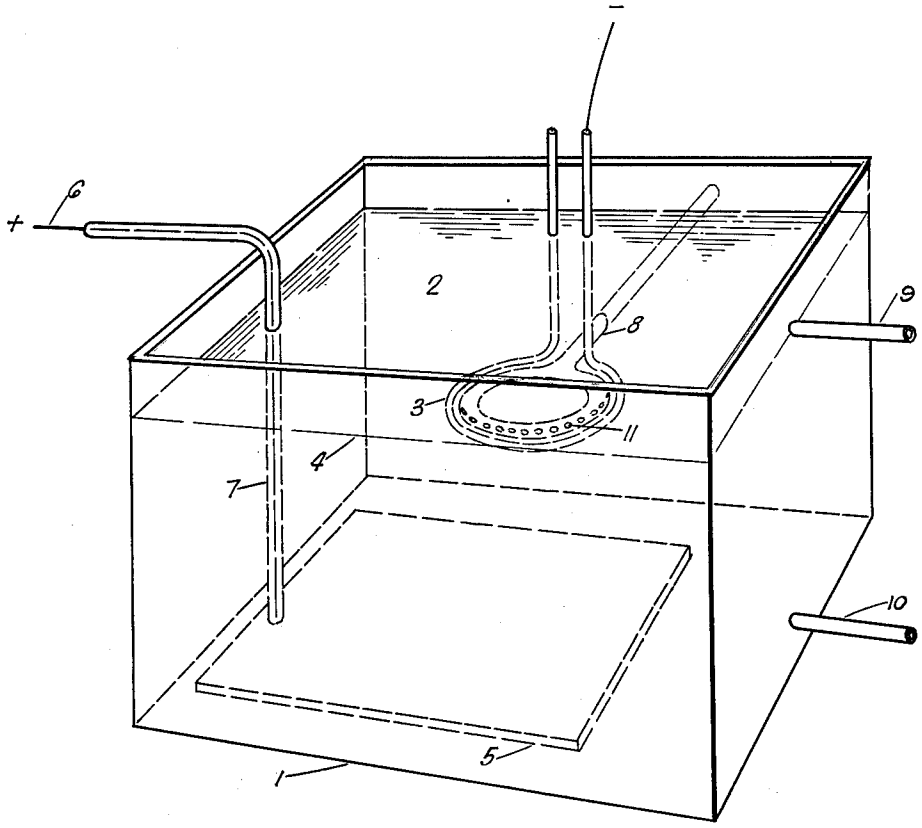
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ELECTROLYTIC PRODUCTION OF FLUOBORATES

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ELECTROLYTIC PRODUCTION OF FLUOBORATES

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This invention relates to the electrolytic production of metal salts of fluoboric acid and more particularly to the electrolytic production of lead and tin fluoborates.

Heretofore, it has been the practice, when preparing lead and tin fluoborates to suspend strips of lead or tin as anodes in a cell containing fluoboric acid. The cell cathodes were made of any suitably conducting material substantially resistant to the attack of the fluoboric acid. Upon passage of current through the cell, the metal of the anode passed into solution in the fluoboric acid electrolyte from which it continuously plated out onto the metal cathodes. In order to increase the amount of metal in solution and thus increase the concentration of the tin or lead fluoborate obtained, it was customary to surround the immersed portion of the cathode with porous cups or diaphragms generally made of porcelain, Alundum, asbestos, etc. To some extent, these porous cups prevented the plating of the tin or lead onto the cathodes since it was difficult for the metal ions to pass through the porous cups. Hence, more metal remained in solution.

This prcoess, however, is unsatisfactory where higher concentrations of the fluoborate are required, since only relatively dilute solutions of the tin or lead fluoborates can be prepared. When attempting to prepare solutions having concentrations of tin or lead, it was found that as the amount of metal in the acid increased the tendency for the metallic ions to leak through the diaphragm or porous cups also increased and a larger deposit of anodic metal on the cathode was obtained without any appreciable increase in the concentration of the lead or tin fluoborate formed. Also, it was found that the porous cups tended to deteriorate under the conditions of long operation at high current densities which are required for dissolving large amounts of metal in the acid. Thus increasingly larger quantities of metal ions were permitted to reach the cathode.

The principal objects of the present invention are to prepare tin and lead fluoborates electrolytically in higher concentrations than are obtainable by methods described in the prior art and to eliminate the use of the diaphragms or porous cups heretofore found necessary.

We have discovered that by changing the cell design as described below and by controlling the current density of the cathode and the temperature of the electrolyte in the immediate vicinity of the cathode, concentrations of the fluoborates

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as high as 80% can be obtained without using the barriers or the porous cups of the prior art. When this concentration is compared with the approximately 40% fluoborate solutions obtained by the prior art methods of electrolytically producing tin and lead fluoborate, the improvement resulting from our process is immediately apparent.

We have found that if the electrolytic cell is so constructed and operated that the current density of the cathode is maintained above 200 amperes per square foot and the cathode current density is at least 5 times the current density of the anode, that mostly hydrogen is produced at the cathode with very little plating onto the cathode of the metal in solution. We have also noticed that this plating of metal onto the cathode can be further reduced by maintaining the electrolyte in the immediate vicinity of the cathode at a temperature below 100° F.

We have further discovered that by placing the cathode near the top of the cell and the anode near the bottom of the cell and passing a current through the cell for a sufficient length of time to obtain substantial quantities of anode metal in solution, the resulting fluoborate product in solution in the electrolyte is distributed in a concentration gradient throughout the cell, the concentration of fluoborate in the cell varying from the upper portion of the electrolyte down to the bottom of the cell with the more concentrated solutions of fluoborate near the bottom of the cell. Thus for tin, three separate strata were noted: about 75% tin fluoborate at the bottom, 61% tin fluoborate in the intermediate stratum and 3% tin fluoborate in the top stratum. When lead fluoborate was prepared, four separate strata were observed, the lowest containing about 80% lead fluoborate, the next containing about 64% lead fluoborate, the third containing about 58% lead fluoborate and the top stratum containing approximately 2% lead fluoborate. It was also observed that the concentration of the fluoboric acid was smallest in the upper portion of the cell. In the preparation of both tin and lead fluoborate, crystalline deposits of the respective salts were found on the bottom of the cell.

By constructing our cell in the above described manner, maintaining a relatively high current density on the cathode with respect to that of the anode, cooling the electrolyte immediately surrounding the cathode and withdrawing the fluoborate solutions from the lower portion of

the cell, we were able to obtain consistently high concentrations of both tin and lead fluoborate.

The attached drawing is a schematic sketch of an apparatus suitable for carrying out a continuous electrolytic process for the production of tin and lead fluoborates in accordance with our invention.

Referring more particularly to the drawing 1 designates a cell having an electrolyte 2 therein. A cathode 3, formed of a looped piece of copper tubing, is immersed in the electrolyte so that the relatively small loop lies in a substantially horizontal plane preferably ½ to 6 inches below the surface 4 of the electrolyte. In order to cool the electrolyte in the immediate vicinity of the cathode 3 a cooling fluid, for example, water, is circulated through the cathode. The anode 5 is disposed near the bottom or lower portion of the cell 1 in a plane lying 8 to 16 inches below that occupied by the cathode and is made of the metal, the fluoborate of which is being produced. The anode lead 6 is preferably surrounded by an insulating tube 7 to protect it from the acid electrolyte, the tube being made of a material such as glass which is relatively resistant to the attack of fluoboric acid. When operating the cell, fresh fluoboric acid is introduced through feed pipe 8 in the vicinity of the cathode 3 while concentrated solutions of the fluoborate formed together with any crystalline product are withdrawn through the lower conduit 10. An overflow conduit 9 is provided near the top of the cell where the most dilute solutions of metal fluoborates are present. This overflow conduit 9 is provided more for safety purposes since in operation it was found that generally evaporation from the surface of the electrolyte was sufficiently rapid to compensate for the fresh fluoboric acid added. It is apparent that a continuous process can be maintained by properly regulating the rate of flow of the incoming fluoboric acid and the rate of withdrawal of the products.

In the apparatus as illustrated the cathode and anode are shown as being substantially horizontal. This is to be preferred since the cathode can then be placed in a stratum containing dillute concentrations of metal fluoborates. Such placement tends to decrease still further the tendency of any metal dissolved in the fluoboric acid to plate out onto the cathode. Although this is the preferred arrangement, it is apparent that it is not absolutely necessary in practicing our invention that the cathode and anode be horizontally arranged since either or both, if desired, could be so mounted as to lie in substantially perpendicular planes. However, such arrangement would take little or no advantage of the stratification of the electrolyte.

The fresh acid should preferably be so introduced into the cell as to have a substantially horizontal inflow, the acid entering the cell in the vicinity of the cathode. Obviously this may be done in many ways. In the drawing one method is shown wherein the inlet 8 for the fresh fluoboric acid extends to a point near the cathode and terminates in a ring having a plurality of horizontally arranged small openings 11 through which the entering fluoboric acid flows. By such a construction the fresh acid is brought into the immediate vicinity of the cathode in such manner as to least disturb the stratification of the solution. The introduction of the fresh acid in the immediate vicinity of the cathode increases the conductivity of the solution at this point as well as further reducing the amount of metal ions present. This results in a further reduction of any tendency of metal ions to plate out onto the cathode.

The anode, as illustrated, lies directly under the cathode. This arrangement has certain advantages in that any tree or moss formation of metal appearing on the cooled cathode can be scraped off, whereupon it falls onto the horizontaly disposed anode and again enters the electric circuit so as to be passed again into solution. It is apparent, however, that the anode does not necessarily have to be directly below the cathode in order to operate the cell in accordance with our invention. The anode should preferably be spaced at least 8 inches from the cathode so as to take maximum advantage of the stratification appearing in the electrolyte and further to prevent the treeing of metal across the gap between the anode and the cathode with consequent shorting of the cell.

The following examples of non-continuous electrolytic operations to produce tin and lead fluoborates will help further to illustrate our invention.

Example 1

A cell was used having substantially the same construction as that shown in the drawing with the exception that there was no inlet pipe 8 and no outlet pipe 9. The cell consisted of an 8 liter battery jar into which was poured about 8 liters of 42% fluoboric acid which contained about 3% of boric acid. The anode consisted of a 4'' x 8'' tin plate placed near the bottom of the cell in a manner similar to the anode 8 illustrated in the drawing. The lead to the anode was protected by a glass tube sealed near the bottom so the electrolyte could not attack the anode lead. The cathode was formed of ⅛ inch diameter copper tubing bent into a 4 inch diameter circle which was placed approximately one inch below the surface of the electrolyte. The battery jar was water-cooled by immersing in a water bath so that the temperature of the electrolyte was kept at about 35° C. Water at about 20° C. was circulated through the cathode.

The cell was operated for about 40 hours. At the start the current was approximately 11 amperes, the current flow gradually decreasing to about 5 amperes at the end of the period of operation. No treeing of the tin between the anode and cathode was noted throughout the operation. At the end of the 40 hours, samples of the electrolyte taken from near the bottom, about the middle, and near the top of the cell were analyzed. The respective concentrations of tin fluoborate in these samples were 75.5%, 61% and 3%.

Example 2

Lead fluoborate was prepared in a cell similar to that used in Example 1. In place of the tin anode, a lead anode formed of a 4'' x 8'' piece of lead plate was employed. The conditions of operation were substantially the same as those given in Example 1, the main difference being that the cell was operated at a current of about 8 amperes for about 41 hours. At the end of this period, four samples were taken from four different levels in the electrolyte. Analysis of these four samples revealed a concentration of 70% lead fluoborate near the bottom of the cell, 64% lead fluoborate in the sample taken from the next highest portion of electrolyte, 58% lead

fluoborate in the sample taken from the next highest layer and 2% lead fluoborate in the sample taken from near the surface.

In order to better illustrate our invention, a schematic sketch of a cell and two specific examples of the preparation of fluoborates have been given. The invention, however, should not be limited to these specific illustrations since it is apparent that there may be considerable variation with respect to the structural features of the cell employed and the conditions of cell operation without departing from our invention. It is preferred that the cell be so constructed and operated that the current density of the cathode is at least above 200 amperes per square foot and the temperature of the electrolyte in the immediate vicinity of the cathode is below 100° F. We also find that in order to obtain the best results the anode should be disposed near the bottom of the cell while the cathode is disposed near the upper portion of the cell electrolyte, the anode and cathode preferably being in horizontal planes. It is apparent, however, that electrolytic processes may be employed in which all of these conditions are met and yet in which there is a large variation of structure and operating conditions.

Having thus described our invention, we claim:

1. In a method for electrolytically producing a fluoborate of the group consisting of lead fluoborate and tin fluoborate the improvement comprising providing fluoborate acid as an electrolyte in a cell having a cathode and an anode at least a portion of the active surface of said anode being formed of the metal the fluoborate salt of which is being produced, passing an electric current through said cell while maintaining the relative current densities of the cathode and anode such that the current density of the cathode is at least 5 times that of the anode and maintaining the temperature of the electrolyte in the immediate vicinity of said cathode below 100° F. and below the temperature of the main body of the electrolyte in said cell.

2. In a method for electrolytically producing a fluoborate of the group consisting of lead fluoborate and tin fluoborate the improvement comprising providing fluoboric acid as an electrolyte to a cell having a cathode and an anode at least a portion of the active surface of said anode being formed of the metal the fluoborate salt of which is being produced, cooling the electrolyte in the immediate vicinity of said cathode to below 100° F. and to a temperature below that of the temperature of the main body of electrolyte in said cell and maintaining the current density of said cathode above 200 amperes per square foot while passing an electric current through said cell.

3. In an electrolytic cell for the production of metal fluoborates a hollow horizontally disposed cathode adapted to have a cooling fluid circulated therethrough said cathode having an inlet and an outlet for said cooling fluid, a horizontally disposed anode lying in a plane below said cathode said plane being spaced not less than 8 inches from the active face of said cathode, said anode having at least a portion of its active surface formed of a metal of the group consisting of lead and tin and the active surface area of said cathode being less than 20% of the active surface area of said anode.

4. In a method of electrolytically producing a fluoborate of the group consisting of lead fluoborate and tin fluoborate, the improvement comprising providing fluoboric acid as an electrolyte in a cell and maintaining a stratification of electrolyte in said cell during operation whereby the stratum containing the highest concentration of metal fluoborate is in the lower portion of said cell while the stratum having the lowest concentration of metal fluoborate is in the upper portion of said cell, said stratification being maintained by horizontally disposed anode and cathode active surfaces, the cathode active surface being positioned above the anode active surface which is formed, at least in part, of the metal the fluoborate salt of which is being produced, maintaining the cathode active surface at a temperature below that of the main body of the electrolyte and at least below 100° F. and passing an electric current between said active surfaces while maintaining the current density of said active cathode surface above 200 amperes per square foot.

5. In a method for electrolytically producing a fluoborate of the group consisting of lead fluoborate and tin fluoborate, the improvement comprising providing fluoboric acid as an electrolyte in a cell and maintaining a stratification of electrolyte in said cell during operation whereby the stratum containing the highest concentration of metal fluoborate is in the lower portion of said cell and the stratum having the lowest concentration of metal fluoborate is in the upper portion of said cell, said stratification being maintained by horizontally disposed anode and cathode active surfaces, the cathode active surface being positioned 8 to 16 inches above the anode active surface which is formed, at least in part, of the metal the fluoborate salt of which is being produced, maintaining the cathode active surface at a temperature below that of the main body of the electrolyte and at least below 100° F. and passing an electric current between said active surfaces while maintaining the current density of said active cathode surface above 200 amperes per square foot.

6. The process of claim 4 in which said metal fluoborate is tin fluoborate and said active anode surface is tin.

7. The process of claim 4 in which said metal fluoborate is lead fluoborate and said active anode surface is lead.

8. In a continuous process for electrolytically producing a fluoborate of the group consisting of lead fluoborate and tin fluoborate, the improvement comprising providing fluoboric acid as an electrolyte in a cell and maintaining a stratification of electrolyte in said cell during operation whereby the stratum containing the highest concentration of metal fluoborate is in the lower portion of said cell and the stratum having the lowest concentration of metal fluoborate is in the upper portion of said cell, said stratification being maintained by horizontally disposed anode and cathode active surfaces, the cathode active surface being positioned at least 8 inches above the anode active surface which has an active surface which is formed of the metal the salt of which is being produced, feeding fluoboric acid into the immediate vicinity of said cathode active surface while maintaining the cathode active surface at a temperature below that of the main body of the electrolyte and at least below 100° F., passing an electric current between said active surfaces while maintaining the relative current densities of the cathode active surface and anode active surface such that the current density of the cath-

ode active surface is at least five times that of the anode active surface and removing cell liquor from the lower stratum.

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