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PROCESS FOR ELECTROLYTIC DEPOSIT OF TIN

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This invention relates to a process of electrolytically depositing tin from solution. The process may be used for the recovery of tin from solutions used in leaching tin either from tin cans or recovering tin from solutions used for leaching tin from other sources. It also may be used as a part of the process of electrolytically refining tin where tin is employed, for example, as the anode of a cell.

Heretofore, in the electrolytic deposit of tin from solution considerable difficulty has been experienced in securing a good smooth fine-grained deposit of tin on the cathode of the cell. In order to secure an adherent fine-grained, uniform deposit of tin on the cathode, it has been usually found necessary to operate on relatively expensive solutions.

The present invention has for its general object to provide a process for depositing tin from solution which will result in an adherent, fine-grained, uniform deposit of tin on the cathode of the cell from an inexpensive solution which may be easily controlled.

The present invention embodies a number of discoveries with respect to the process of depositing tin in electrolytic cells, these discoveries residing mainly in the oxidation versus reduction condition of the tin ion in solution, the effect of glue on the deposit, as well as the concentration and effects of other ingredients present.

I have discovered that the oxidation versus reduction condition of the tin ion present in an acid solution has a controlling influence on the character of the tin deposit which will be formed. For example, if one seeks to deposit tin electrolytically from a hydrochloric acid solution of tin, the following phenomena will be observed:

Starting, first, with an acid solution containing the tin in the stannous condition and electrolytically depositing the tin on the cathode of the cell, the first deposit formed will consist very largely of needles and fern-like growths upon the cathode, and this form of deposit, which is quite unsatisfactory in the process, will continue until approximately one-half to two-thirds of the tin remaining in solution has reached the stannic condition. At this period in the process, there is a rather abrupt change and the deposit of tin from the solution proceeds generally with the formation of smaller shorter crystals which produce a finer-grained deposit. In accordance with the process of the present invention, therefore, to obtain electrolytically a good, smooth, dense and fine-grained deposit of tin, it is desirable to maintain at all times in the process the tin of the solution of the cell at least two-thirds in the stannic form.

The process of the present invention is useful in the depositing of tin from solutions containing not only tin but also iron. When electrolyzing tin from a solution containing iron, it is found that the iron in the solution remains nearly completely in the ferrous condition until the tin of the solution has nearly all been oxidized to the stannic condition, after which time the iron in solution starts to be converted to the ferric condition. For the operation of the process of the present invention, it is found of considerable value to maintain the iron in solution in substantially the ferrous condition. A solution containing iron in the ferric form attacks very rapidly any iron present, and since it is desirable to form a portion at least of the apparatus with iron, a solution containing the ferric ion is to be avoided.

Another important feature of the present invention consists in the discovery that by the addition of a small part of glue to the solution electrolyzed marked improvements may be effected in the character of the deposit of tin secured. By the addition of a small part of glue, the deposit becomes smoother and more consolidated.

The present invention, together with various further objects and advantages thereof, will best be understood from a description of a preferred form or example of depositing tin in accordance with the present invention. I have, therefore, hereinafter described a preferred form or example of the process of depositing tin embodying the present invention.

The invention may take two forms: one, wherein the invention is applied to recovering tin from a solution used for leaching tin from various sources, and the other being where the process is applied for the purpose of electrolytically refining tin. In the first case, the solution, for example, from a process of leaching the tin plate from used tin cans, is fed continuously into an electrolytic cell, wherein the solution is maintained under vigorous mechanical agitation. Vigorous mechanical agitation is maintained so as to bring the solution entering the cell which may contain a high content of stannous ion quickly to a solution containing most of the tin in the stannic condition through rapid and immediate admixture with the bulk of the solution in the cell. There is thereby avoided the formation of an undesirable form of deposit of the tin. A further advantage of vigorous mechanical agitation is that it lowers the cell voltage. The solu-

tion fed to the cell may contain the tin mainly in the stannous condition.

Within the electrolytic cell the solution is subjected to electrolytic action to deposit the tin of the solution upon the cathode of the cell. For example, I have used in such a process a graphite anode and a sheet steel tin-plated cathode. The solution within the electrolytic cell is preferably kept near a temperature of 70° F. An increase of temperature above this figure has the effect of increasing the current density in the cell, but the higher temperatures have the disadvantages of increasing the rate at which the solution will dissolve tin and iron from the cell equipment. Temperatures within the range of 60 to 100° F. are satisfactory in operation, but I prefer to employ a temperature of around 70° F. for the electrolytic operation. The lower temperatures have been found to give a smoother deposit of tin.

The amount of glue maintained in the solution does not appear to be highly critical. I have found entirely satisfactory results to be obtained with five parts of glue per million, and have increased the concentration of glue up to and including 1,000 parts per million. If too much glue is used, some of it may separate as a gelatinous precipitate. Such a precipitate has not been observed at glue concentrations of 100 parts per million or less.

The over-all electrolytic reaction taking place in the cell is the conversion of stannous to stannic ions, with the deposit of tin in accordance with the following typical equation:

$$2SnCl_2 \rightarrow Sn + SnCl_4$$

Stannous chloride — Tin — Stannic chloride

In the preferred form of the process, the solution within the electrolytic cell is maintained at nearly the point of completion of the above reaction; that is to say, the solution is preferably maintained only slightly short of the point where all of the tin present is in the stannic form. However, satisfactory deposits may be obtained whenever at least two-thirds of the tin present in the solution is in the stannic form. The solution entering the cell may as a rule contain the tin, principally in the stannous condition, and the solution within the cell is maintained principally in the stannic condition by proper rapid mechanical agitation of the entering solution with the solution of the cell. In normal operation there is withdrawn from the cell solution corresponding substantially in amount to that of the entering solution. If the solution within the cell itself is permitted to contain more than about one-third of its tin in the stannous form, it has been found substantially impossible to avoid the formation by the tin being deposited of undesirable fern-like or needle growths.

The quantity of tin within the solution is of relatively minor consequence. I prefer to employ, for example, a solution containing about 0.12 molal parts of stannic chloride per liter, although I have operated satisfactorily with solutions containing as low as 0.006 molal parts of stannic chloride, and as high as 0.24 molal parts of stannic chloride. Increase of the concentration of stannic chloride present decreases the net rate at which tin is deposited from solution for a given cathode current density. For example, at a cathode current density of 20 amperes per square foot, using a 0.06 molal solution with respect to stannic chloride, I have deposited 0.0022 gram per square inch per minute of tin, whereas, using a solution 0.24 molal with respect to stannic chloride under similar conditions, deposited only 0.0004 gram per square inch of tin. The disadvantage of using a lower concentration of stannic chloride than about 0.06 molal and more preferably 0.12 molal is that the maximum permissible cathode current density is thereby decreased. The cell may gas or produce loose deposits if high current densities are used with too low a concentration of stannic chloride present. I prefer that the solution should also contain excess acid. As a rule, hydrochloric acid about 1.9 molal in strength has been used. Different acid concentrations may be used, and I have varied the hydrochloric acid concentration from ½ to 4 molal. The higher the concentration of acid, the higher the current density for a given voltage on the cell. On the other hand, increasing the acid concentration decreases the rate of deposit with a given current density.

I have found that the current density usable in the process may vary widely, and if the remaining conditions of the process are adhered to the current density is not a particularly critical factor. I have used current densities, for example, of between 2.2 and 46 amperes per square foot. In general, as long as hydrogen is not evolved, an increase of cathode current density will result in an increase of cathode current efficiency. Hence, it is usually desirable to operate with a cathode current density as high as possible without causing the cell to evolve hydrogen. Except at low concentration of $SnCl_4$, such as .006 molal, an important controlling factor of the process appears to be the actual voltage applied across the cell. Above about 1.7 to 1.8 volts I have found that a cell having a graphite anode, a tin cathode spaced one inch from the anode and having the electrolyte rapidly circulated commences to gas and the resulting deposit ceases to remain in the smooth fine-grained, tightly adhering condition desired. The cell operating voltage is preferably kept below about 1.7 and at some suitable value higher than the no-current voltage of the cell, which is about one volt, and any desired current density consistent with these voltages and other factors of the process may be used satisfactorily. As high a current density should be used as is possible without the evolution of hydrogen. The higher the current density, the greater the cathode current efficiency. At extremely low concentrations of stannic chloride in solution, such as 0.006 molal, voltages below 1.1 have been used. These are employed in treating clean-up solutions.

The solution preferably contains ferrous chloride, but not ferric chloride. I prefer to maintain the concentration of ferrous chloride in the electrolytic cell at about 0.27 molal. However, I have varied the ferrous chloride concentration from about 0.03 molal to about 0.54 molal. With the lower concentrations of ferrous chloride the current density in the cell is lower for a given voltage than at the higher concentrations of ferrous chloride. For example, using a cell voltage of 1.7 volts, the current density was 8 amperes per square foot when electrolyzing a solution 0.031 molal in ferrous chloride, whereas a current density of 48 amperes per square foot at the same cell potential was obtained using a solution of 0.54 molal with respect to ferrous chloride.

The process may be applied to the electrolytic refining of tin in various manners. For example, if it is desired to electrolytically refine tin, the anode of the cell may be composed of the tin which it is desired to refine and the same

conditions with respect to the solution within the cell maintained as before given, except that it may be desirable to maintain more of the tin in the stannous condition than was indicated in the preceding discussion. Cathode current efficiency increases as the concentration of stannous ion with respect to the concentration of stannic ion is increased. In a process such as the electrolytic refining of tin in which rapid solution of tin by the cell solution is not necessarily desirable, it may be advantageous to increase the relative concentration of stannous ion, since such an increase results in an improvement of cathode current efficiency. For this reason, it may be desirable to operate the cell with as high a relative concentration of stannous ion as is possible and at the same time obtain a tin deposit of satisfactory character. The control of the relative oxidation conditions between the stannous and stannic ions present may be effected by varying the area of the tin of the anodes, or if the solution rate of the tin of the anodes is insufficient the solution may be circulated from the cell over the tin to be refined and returned to the cell.

In any case, in the electrolytic deposition of tin, according to the process of this invention, the major important factors to preserve are:

(1) That the tin present in the solution should be at least two-thirds in the stannic condition;

(2) That a small portion of suitable addition agent, such as glue, be present;

(3) That the solution be acid;

(4) That the current density be limited so that hydrogen is not evolved in the cell.

While the particular form of the process herein described is well adapted to carry out the objects of the invention, it is to be understood that various modifications and changes may be made, all without departing from the scope of the invention as defined in the appended claims.

I claim:

1. A process for producing tin, which comprises subjecting a solution to electrolysis for the deposit of tin, said solution comprising an hydrochloric acid solution of tin and iron the oxidation condition of the solution during the electrolytic action being at all times maintained at a point corresponding to nearly 100% of the tin present being in the stannic condition but not beyond such oxidation condition as to retain the iron present in the ferrous state.

2. A process for producing tin, which comprises subjecting to electrolytic action an hydrochloric acid solution of tin, such solution being between 0.006 and 0.24 molal with respect to tin, from 0.03 to 0.54 molal with respect to iron, and having throughout the electrolytic action an oxidation condition corresponding to between one-half and all of the tin present in the stannic form whereby the iron is present substantially entirely in the ferrous form.

3. A process for producing tin, which comprises subjecting to electrolytic action an hydrochloric acid solution of tin, such solution being between 0.006 to 0.24 molal with respect to tin, from 0.03 to 0.54 molal with respect to iron, and having throughout the electrolytic action an oxidation condition corresponding to between one-half and all of the tin present in the stannic form whereby the iron is present substantially entirely in the ferrous form, the voltage applied to the electrolytic action being below about 1.7.

4. A process for producing tin, which comprises subjecting a solution to electrolysis for the deposit of tin, said solution comprising an hydrochloric acid solution of tin and iron, the oxidation condition of the solution throughout the electrolytic action during the electrolytic action being maintained at a point corresponding to nearly 100% of the tin being present in the stannic condition but not beyond such oxidation condition as to retain the iron present in the ferrous state, the solution undergoing electrolytic action containing a small quantity of glue.

5. A process for producing tin, which comprises subjecting to electrolytic action an hydrochloric acid solution of tin, such solution being between 0.006 and 0.24 molal with respect to tin, from 0.03 to 0.54 molal with respect to iron, and having an oxidation condition throughout the electrolytic action corresponding to between one-half and all of the tin present in the stannic form whereby the iron is present substantially entirely in the ferrous form, the solution undergoing electrolytic action containing a small quantity of glue.

6. A process for producing tin, which comprises subjecting to electrolytic action an hydrochloric acid solution of tin, such solution being between 0.006 and 0.24 molal with respect to tin, from 0.03 to 0.54 molal with respect to iron, and having an oxidation condition throughout the electrolytic action corresponding to between one-half and all of the tin present in the stannic form whereby the iron is present substantially entirely in the ferrous form, the voltage applied to the electrolytic action being below about 1.7, the solution undergoing electrolytic action containing a small quantity of glue.

7. A process of electrolytically producing tin, which comprises subjecting to electrolytic action a supply of hydrochloric acid solution of tin, such solution containing iron and having an oxidation condition throughout the electrolytic action corresponding to between one-half and all of the tin present being in the stannic form whereby the iron is present in the ferrous form, continuously feeding to the supply of solution undergoing electrolytic action a fresh supply of solution containing tin mainly in the stannous condition, subjecting the supply of solution and the feed solution to vigorous agitation, and continuously withdrawing solution from the cell.

8. A process for producing tin, which comprises subjecting a solution to electrolysis for the deposit of tin, said solution comprising a hydrochloric acid solution of tin and iron, from 0.03 to 0.54 molal with respect to iron, the oxidation condition of the solution during the electrolytic action being at all times maintained at a point corresponding to between one-half and all of the tin present being in the stannic form but not beyond such oxidation condition so as to retain the iron present in the ferrous state.

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