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(54) **PROCESS FOR REDUCING AND RECLAIMING ELECTROLYTE CONTAINING TIN SALT.**

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Description

This invention relates to a process for the reduction regeneration of an electro-plating bath or a coloring electrolyte for aluminum and more particularly to a process for the regeneration of an electrolyte by reducing stannic ions in the electrolyte into stannous ions through the addition of metallic tin to the used or old electrolyte.

A tin salt aqueous solution containing stannous ions (Sn^{2+}) is generally used as an electrolyte containing tin ions. This aqueous solution containing stannous ions is very unstable since stannous ions are easily oxidized into stannic ions (Sn^{4+}) by oxygen in the air or oxygen generated during electrolysis.

As such stannic ions form in the electrolyte, the concentration of stannous ions in the electrolyte decreases and the current efficiency of electrolysis is reduced. Furthermore, it gives rise to the serious problem that the stannic ions become insoluble substances such as stannic acid, etc. which are likely to become colloids and therefore great difficulty is encountered in removing such insoluble substances by filtration. These insoluble substances attach onto the surface of the product and cause pitting thereon.

Therefore, in order to obtain good quality products, it is essential to control the concentration of stannic ions in the electrolyte.

With regard to preventing insoluble precipitates from forming, it is effective to add a chelating agent to the electrolyte to dissolve Sn^{4+}. In this case, however, Sn^{4+} is accumulated in the electrolyte, leading to an increase in the concentration of SN^{4+} and, as a result, electrolytic coloring or electro-plating tend to become difficult. Therefore, a tin salt aqueous solution in which the concentration of stannic ions has increased by oxidation has had to be abandoned.

The regeneration of the electrolyte by the reduction thereof has been effected. One of such regeneration methods is an electrolytic reduction method as described in Japanese Patent Publication No. 19856/1978. In accordance with this electrolytic reduction method, of stannous ions and stannic ions which are present in the electrolyte, the stannous ions are first reduced into metallic tin and thereafter the stannic ions are reduced into metallic tin. Therefore, although this method is excellent, a greatly long processing time is required and equipment and operation costs are increased.

Additionally, as the regeneration method of an electrolyte, a method of reducing stannic ions into stannous ions by adding those metals which are baser than tin has been carried out. According to this method, however, since the added metal is present in the electrolyte as a metal ion, it may exert bad influences on electrolytic processing. It is, therefore, necessary to remove such metal ions, but the removal operation of the metal ions is very complicated. Thus this method is not preferred from practical and economic standpoints.

FR—A1 334 413 discloses the regeneration of electrolytes containing stannic and stannous fluoborates, lead fluoborate and fluoboric acid by addition of metallic tin.

Object of the present invention is to provide a generally applicable method which removes the disadvantages in the prior art as described above and which permits the reduction of stannic ions in electrolytes in a short time and the formation of a regenerated electrolyte having a stable composition.

It has been found that this can be achieved by a process for regenerating an electrolyte containing tin salts by reducing stannic ions to stannous ions in the presence of metallic tin at an acidic pH which is characterised in that the electrolyte has a pH of from 0.5 to 4 and by adding metallic sponge-like tin to said electrolyte; and heating said electrolyte containing said added metallic tin at a temperature of from 80°C to the boiling temperature of said electrolyte.

In accordance with the process of this invention, the stannic ions in the electrolyte are regenerated into stannous ions. After the reaction is completed, the unreacted metallic tin is taken out of the electrolyte and, as necessary, additional processings such as adjustment in the concentrations of other components in the electrolyte, adjustment in pH, etc are applied. The thus regenerated electrolyte can be re-used.

When the above processings are continuously carried out, the electrolyte can be repeatedly used by recycling. Furthermore, in accordance with the process of this invention, the processings can be continuously carried out and the processing time can be greatly shortened. For example, in the method as described in Japanese Patent Publication No. 19856/1978, the time required for the reduction of the stannic ions is 6 hours or more whereas in the process of this invention it is 1 hour or less and usually sufficient to be about 30 minutes.

Additionally, equipment and operation costs can be lessened and the quality of the product obtained by using the regenerated electrolyte can be stabilized.

The electrolyte for use in this invention is subject to no special limitations so long as it contains tin salts. In a fresh electrolyte, almost all of the tin ions are stannous ions and there are almost no stannic ions. As the electrolysis proceeds, the concentration of stannic ions increases whereas the concentration of stannous ions relatively decreases.

The process of this invention is applied to an electrolyte in which the concentration of stannic ions has increased to a certain extent, for example, the ratio of Sn^{4+}/Sn^{2+} has reached 1/2 or more. In general, the electrolyte contains a chelating agent in order to keep the stannous and stannic ions in the state that they are dissolved.

Hereinafter the process of this invention will be explained in greater detail:

First, the pH of the electrolyte is controlled to the acidic region of from 0.5 to 4 and preferably to the range of from 0.5 to 2. This control is not always required when the pH of the electrolyte is already in this region. Where the pH is too low, the reduction rate of stannic ions is somewhat reduced although metallic tin is promptly dissolved. On the other hand, where the pH exceeds 4, metallic tin is less dissolved and the reduction does not proceed promptly.

This control of the pH of the electrolyte is generally carried out by using acids. Those acids releasing the same anions as those existing in the electrolyte, such as sulfuric acid, hydrochloric acid, phosphoric acid, nitric acid, pyrophosphoric acid or various organic acids can be used singly or in admixtures comprising two or more thereof. In the process of this invention, sulfuric acid is most preferable.

Thereafter, metallic sponge-like tin is added to the electrolyte of which the pH has been controlled as mentioned above, and the resulting electrolyte is heated. The metallic sponge-like tin used has large specific surface areas.

Metallic sponge-like tin having such a high specific surface area can be produced as follows:

An acidic solution (e.g., an electro-plating solution or a coloring electrolyte for aluminium) containing stannous ions and/or stannic ions is used as an electrolyte and a direct current is passed through the electrolyte with electrically conductive material such as metal or carbon as anode and cathode whereby tin ions (Sn^{2+}, Sn^{4+}) are deposited as metallic tin on the cathode. The thus obtained metallic tin is in a sponge form, has a high specific surface area and can be easily separated from the cathode.

The amount of the metallic tin added to the electrolyte is not limited and can be suitably determined depending upon the concentration of stannic ions in the electrolyte, the required concentration of stannous ions, etc. In general, it should be about 1 to 10 times moles of the amount required entirely to reduce stannic ions in the electrolyte. Even if the metallic tin is excessively added, the unreacted metallic tin precipitates in the bottom of the reactor and can easily be separated. Therefore, it imposes no specific hindrance onto the electrolyte and the metallic tin so separated can be re-used as it is.

In the process of this invention, it is required to heat the electrolyte to which the metallic tin has been added at a temperature from 80°C to the boiling temperature of the electrolyte. If the electrolyte may be deteriorated in quality at high temperatures, the electrolyte to which the metallic sponge-like tin is added should be processed at the lower temperatures of the specified range.

With regard to the heating time, it is sufficient that the reduction reaction proceeds to the desired extent. While the heating time cannot be determined unconditionally since it varies depending upon the shape and amount of the metallic tin to be added and other various conditions, it is usually sufficient to be 1 hour or less.

The following examples are given to illustrate the invention in greater detail. In these examples, the concentration of stannic sulfate is shown as a concentration converted to $SnSO_4$.

Example 1

(1) Production of Metallic Sponge-Like Tin

A direct current was passed through an old or used coloring electrolyte for aluminum consisting of 9.0 grams/liter of stannous sulfate, 11.1 grams/liter of stannic sulfate, 70 grams/liter of citric acid and 20 grams/liter of sulfuric acid and having a pH of 1.5 with tin and stainless steel as anode and cathode respectively to deposit sponge-like metallic tin on the cathode.

(2) Regeneration by Reducing

To an old or used coloring electrolyte for aluminum consisting of 4.0 grams/liter of stannous sulfate, 15.1 grams/liter of stannic sulfate, 30 grams/liter of tartaric acid, 30 grams/liter of nickel sulfate and 20 grams/liter of ammonium sulfate and having a pH of 7.5 was added 40 grams/liter of sulfuric acid to adjust the pH to 0.9. Thereafter, 18 grams/liter of the sponge-like metallic tin as obtained in (1) was added to the above electrolyte and the resulting mixture was heated for 20 minutes at 100°C. After heating, the obtained electrolyte contained 21.2 grams/liter of stannous sulfate and 0.7 gram/liter of stannic sulfate.

Example 2

To an old or used neutral tin electro-plating solution consisting of 41 grams/liter of stannous sulfate, 89 grams/liter of stannic sulfate, 150 grams/liter of ammonium citrate and 100 grams/liter of ammonium sulfate and having a pH of 6.5 was added 60 grams/liter of sulfuric acid to adjust the pH to 0.7. Thereafter, 148 grams/liter of the sponge-like metallic tin as obtained in Example 1 was added to the plating solution and the resulting mixture was heated at 96°C for 40 minutes. After heating, the obtained plating solution contained 222 grams/liter of stannous sulfate and 8 grams/liter of stannic sulfate.

Example 3

To an old or used lustrous tin-cobalt electroplating solution consisting of 10 grams/liter of stannous sulfate, 10 grams/liter of stannic sulfate, 50 grams/liter of cobalt sulfate and 200 grams/liter of sodium pyrophosphate was added 60 grams/liter of sulfuric acid. Thereafter, 10.7 grams/liter of the sponge-like metallic tin as obtained in Example 1 was added to the plating solution and the resulting mixture was heated at 100°C for 10 minutes. After heating, the obtained plating solution contained 21 grams/liter of stannous sulfate and 4 grams/liter of stannic sulfate.

Example 4

To an old or used coloring electrolyte for aluminum consisting of 9.0 grams/liter of stannous sulfate, 11 grams/liter of stannic sulfate, 70 grams/liter of citric acid and 20 grams/liter of sulfuric acid and having a pH of 1.5 was added

21.4 grams/liter of the sponge-like metallic tin as obtained in Example 1. The resulting mixture was heated at 98°C for 10 minutes. After heating, the obtained electrolyte contained 30 grams/liter of stannous sulfate and 4 grams/liter of stannic sulfate.

Example 5

The procedure of Example 4 was repeated except that 100 mesh powdery tin reagent on the market was used in place of the sponge-like metallic tin. After heating, the obtained electrolyte contained 11.5 grams/liter of stannous sulfate and 9 grams/liter of stannic sulfate.

Commercial Utilization

The process of this invention is greatly useful for the regeneration of an electroplating bath or a coloring electrolyte for aluminum containing tin salts.

Claim

A process for regenerating an electrolyte containing tin salts by reducing stannic ions to stannous ions in the presence of metallic tin at an acidic pH, characterised in that the electrolyte has a pH of from 0.5 to 4 and by adding metallic sponge-like tin to said electrolyte; and heating said electrolyte containing said added metallic tin at a temperature of from 80°C to the boiling temperature of said electrolyte.

Revendication

Procédé de régénération d'un électrolyte contenant des sels d'étain en réduisant les ions stanniques en ions stanneux en présence d'étain métallique à un pH acide, caractérisé en ce que l'électrolyte a un pH allant de 0,5 à 4, en ce qu'on ajoute de l'étain métallique spongieux dans ledit électrolyte et en ce qu'on chauffe ledit électrolyte contenant l'étain métallique ajouté à une température allant de 80°C jusqu'au point d'ébullition dudit électrolyte.

Patentanspruch

Verfahren zur Regenierung eines Zinnsalze enthaltenden Elektrolyten durch Reduktion von Zinn-IV-Ionen zu Zinn-II-Ionen, in Anwesenheit von metallischem Zinn, bei einem sauren pH-Wert, dadurch gekennzeichnet, daß der Elektrolyt eine pH-Wert von 0,5 bis 4 hat, und daß schwammartiges metallisches Zinn zu dem Elektrolyten zugesetzt wird; und der Elektrolyt, der das zugesetzte metallische Zinn enthält, bei einer Temperatur von 80°C bis zur Siedetemperatur des Elektrolyten, erwärmt wird.