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PROCESS FOR ELECTRODEPOSITION OF METAL

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This invention relates to anodes and more particularly to anodes which are electrochemically insoluble in electrolytes, especially in electrolytes in which lead is soluble.

There are numerous instances where it is desirable to employ insoluble anodes in electrolytic processes. Such anodes are used commercially in the electrolytic refining and plating industries and in numerous electrochemical processes in which electrolytic oxidation is performed. In many of these processes lead anodes have been used heretofore because lead is inexpensive, is easily obtained in the desired degree of purity, is readily formed into the shape most suitable for any particular process and has desirable mechanical properties. Lead oxide anodes have also been used in some instances. However, there are a number of electrolytic processes requiring insoluble anodes for which lead or lead oxide anodes are not suitable, usually because lead is soluble in the eletrolytes employed. Graphite anodes have been used extensively as insoluble anodes for some purposes, but they are relatively expensive and are subject to breakage because they are somewhat fragile. In addition, graphite anodes become oxidized by anodically released oxygen, which causes them to decompose and crumble, and, being somewhat porous, they tend to absorb the electrolytes in which they are immersed. Platinum anodes have also been used heretofore in certain instances where they are especially effective and their normally prohibitive cost is not a deterrent.

It has been suggested that sulphonic acids be employed in the electrolytic refining of mixtures containing some or all of the metals copper, tin and lead. Benzene disulphonic and phenol sulphonic acids have proved to be especially useful in such processes and one of the reasons why these acids are particularly satisfactory for this purpose is that copper, tin and lead are all soluble therein.

In Patent 2,111,575 there is described a process for refining copper-rich mixtures containing lead and/or tin by electrolyzing anodes thereof in sulphonic acid electrolytes. In this process, when anodes made of copper-rich mixtures containing both lead and tin are employed, pure copper is deposited at the cathodes of the electrolytic cells and lead and tin build up in the electrolyte. The lead and tin content of the bath must be reduced at intervals to insure the deposition of pure copper and this is accomplished by withdrawing a portion of the bath, removing the copper therefrom by cementation and electrolysis, and removing the lead and tin simultaneously by electrolysis. This process may be practiced to refine copper-bearing metals that include either one or both of lead and tin. For example, scrap brasses may contain no tin, while bronzes may be free from lead. These materials may be carried through the refining steps described in the same manner that is employed for materials containing both lead and tin, the only difference being that the products obtained would not include lead or tin, as the case may be.

In electrolytically removing the copper from that portion of the electrolyte which is withdrawn from the main body of the electrolyte and in electrolytically depositing lead and/or tin from the electrolyte after the removal of the copper, it is desirable to employ insoluble anodes. Heretofore it has been customary to use in processes of this nature anodes made of graphite or to use lead anodes enclosed in diaphragms. However, it is desirable to use for this purpose anodes which are inexpensive, may be readily formed into the desired shape and are mechanically strong. It is also desirable that the anodes be insoluble in sulphonic acid electrolytes, require no diaphragms and permit the electrolysis to proceed with a small electrical power consumption.

The object of the present invention is to provide effective, but inexpensive anodes, for use where insoluble anodes are required and especially to provide such anodes which are insoluble in electrolytes in which lead is soluble.

In accordance with the present invention, insoluble anodes are made of a lead-antimony alloy containing sufficient antimony to render the anodes substantially insoluble in electrolytes in which lead is electrochemically soluble. Such anodes are effective in most cases where insoluble anodes are required and they are especially useful for depositing out copper or lead and tin from one of the above described sulphonic acid electrolytes undergoing purification in the process disclosed in Patent 2,111,575. These anodes are relatively inexpensive, may be readily formed into any desired shape and size and are strong mechanically. They permit electrolytic operations, such as the depositing out of solder from sulphonic acid electrolytes, to proceed with the desired anode current densities without requiring the application of high voltages and they thus keep the power consumption low.

It has been found that anodes which are relatively insoluble in electrolytes in which lead is soluble may be formed of lead-antimony alloys containing as little as 12 per cent antimony. However, if such anodes are employed in electrolytes in which lead is soluble they gradually lose lead and never reach the degree of insolubility exhibited by anodes with higher antimony contents. Such anodes are, therefore, undesirable where insoluble anodes are required.

As the antimony content of the alloys increases the solubility of the lead decreases and at antimony contents of above 20 per cent the anodes are substantially insoluble. Hence, the anodes

embodying the invention should never contain less than about 20 per cent of antimony. Where insoluble anodes are required, the anodes should be made of a lead-antimony alloy containing enough antimony to completely inhibit the solution of the lead contained therein. Such alloys should contain at least about 35 per cent of antimony and an alloy that will be especially valuable for all around use may be made of about 50 per cen lead and 50 per cent antimony.

Of course, the antimony content of the alloys may be varied in accordance with the uses to which the anodes are to be put and the antimony may run as high as almost 100 per cent of the total content of the alloys. However, anodes made of lead-antimony alloys containing more than 50 per cent of antimony tend to be more brittle and less suitable mechanically than those containing less antimony and such alloys containing from about 35 per cent to about 50 per cent of antimony are best suited for most purposes.

The fact that anodes consisting of almost pure antimony may be used as insoluble anodes suggests that pure antimony might be used with equal success for the purposes of this invention. However, it has been found that when pure antimony anodes are employed the voltage required to maintain a given anode current density is excessive and the anodes are characteristically different from those made of lead-antimony alloys even though the lead content of the latter may be only 5 per cent or less.

Apparently, there is a point somewhere between the compositions of 95 per cent antimony and 100 per cent antimony where the voltage characteristics of the anodes change suddenly because lead-antimony anodes containing 95 per cent of antimony have substantially the same voltage characteristics as those containing much less antimony. This would suggest that substantially pure antimony anodes might be used where oxidation reactions at high anode potentials are desired, for example, in the electrolytic oxidation of sugars or alcohols to acids. However, pure antimony anodes are not suitable where it is desirable to maintain specified anode current densities at low voltages.

The characteristics of a number of lead-antimony and pure antimony anodes of the same dimensions, when employed under similar conditions and with like cathodes in a substantially pure benzene disulphonic acid electrolyte containing about 240 grams per liter of free acid, are outlined in the following table:

Per cent Sb	Wt. anode dissolved, gm. loss/-amp. hr.	Hours run	Volts to maintain 15 amps./sq. ft. at anode
12	1.38	First 71	2.5
	.70	Next 55	2.8
22	.03	First 240	3.0
	.0015	Next 19	2.8
35	.0005	19	3.0
50	Negl.	First 19	3.0
	.0005	Next 183¼	3.0
85	0	20	3.5
95	0	98	3.5
100	0	194	30.0

From this table it is evident that anodes containing only 12 per cent of antimony are not entirely insoluble but that the solubility of such anodes is very slight. Anodes containing as much as 22 per cent of antimony are substantially insoluble for practical purposes, while those containing 35 per cent or more of antimony may be considered as totally insoluble.

It will be noted that with the anodes containing both lead and antimony, even though the lead content may be only about 5 per cent, the voltage required to maintain an anode current density of 15 amperes per square foot is only 2.5 to 3.5 volts, whereas with pure antimony anodes 30 volts are required to maintain this anode current density. Consequently, it is obvious that antimony acts in a manner entirely different from that of the lead-antimony alloys and that the addition of only a small amount of lead changes the characteristics of the anodes materially.

While the alloys described hereinabove are referred to as pure lead-antimony alloys, it is obvious that the invention relates to such alloys which contain minute amounts of other materials as impurities as well as to alloys containing minor quantities of other metals that do not alter materially the characteristic properties of the lead-antimony alloys in question which render them especially suitable for use as insoluble anodes.

What is claimed is:

1. The process for the electrodeposition of metal of the group consisting of copper, tin and lead, which comprises electrolyzing an electrolytic bath consisting solely of an aqueous solution of an aromatic sulphonic acid and dissolved metal of said group with an insoluble anode made of an alloy consisting of lead and antimony in which the amount of antimony present is at least about 20% of the total composition but is insufficient to materially increase the operating voltage over that required with such an anode containing about 20% of antimony.

2. The process for the electrodeposition of metal of the group consisting of copper, tin and lead, which comprises electrolyzing an electrolytic bath consisting solely of an aqueous solution of an aromatic sulphonic acid and dissolved metal of said group with an insoluble anode made of an alloy consisting of from about 20% to slightly less than 100% of antimony and the balance lead, the amount of antimony in the anode being insufficient to materially increase the operating voltage over that required with such an anode containing less than 95% of antimony.

3. The process for the electrodeposition of metal of the group consisting of copper, tin and lead, which comprises electrolyzing an electrolytic bath consisting solely of an aqueous solution of an aromatic sulphonic acid and dissolved metal of said group with an insoluble anode made of an alloy consisting of lead and antimony and containing at least 35% but not substantially more than about 95% of antimony.

4. The process for the electrodeposition of metal of the group consisting of copper, tin and lead, which comprises electrolyzing an electrolytic bath consisting solely of an aqueous solution of an aromatic sulphonic acid and dissolved metal of said group with an insoluble anode made of an alloy consisting of lead and antimony and containing at least 50% but not substantially more than about 95% of antimony.

5. The process for the electrodeposition of metal of the group consisting of copper, tin and lead, which comprises electrolyzing an electrolytic bath consisting solely of an aqueous solution of an aromatic sulphonic acid and dissolved metal of said group with an insoluble anode made of an alloy consisting of lead and antimony and

containing from about 20% to about 95% of antimony.

6. The process for the electrodeposition of metal of the group consisting of copper, tin and lead, which comprises electrolyzing an electrolytic bath consisting solely of an aqueous solution of benzene disulphonic acid and dissolved metal of said group with an insoluble anode made of an alloy consisting of from about 35% to about 50% of antimony and the balance lead.

7. The process for the electrodeposition of metal of the group consisting of copper, tin and lead, which comprises electrolyzing an electrolytic bath consisting solely of an aqueous solution of phenol sulphonic acid and dissolved metal of said group with an insoluble anode made of an alloy consisting of from about 35% to about 50% of antimony and the balance lead.

8. The process for the electrodeposition of metal of the group consisting of copper, tin and lead, which comprises electrolyzing an electrolytic bath consisting solely of an aqueous solution of benzene disulphonic acid and dissolved metal of said group with an insoluble anode made of an alloy consisting of lead and antimony in substantially equal proportions.

9. The process for the electrodeposition of metal of the group consisting of copper, tin and lead, which comprises electrolyzing an electrolytic bath consisting solely of an aqueous solution of phenol sulphonic acid and dissolved metal of said group with an insoluble anode made of an alloy consisting of lead and antimony in substantially equal proportions.

10. The process for refining copper-rich metallic mixtures containing metal of the group consisting of lead and tin, which comprises electrolyzing an electrolytic bath consisting solely of an aqueous solution of an aromatic sulphonic acid having such a metallic mixture dissolved therein with an insoluble anode made of an alloy consisting of from about 20% to slightly less than 100% of antimony and the balance lead, the amount of antimony in the anode being insufficient to materially increase the operating voltage over that required with such an anode containing less than 95% of antimony.

11. The process for refining copper-rich metallic mixtures containing metal of the group consisting of lead and tin, which comprises electrolyzing an electrolytic bath consisting soley of an aqeuous solution of benzene disulphonic acid having such a metallic mixture dissolved therein with an insoluble anode made of an alloy consisting of from 35% to 50% of antimony and the balance lead.

12. The process for refining copper-rich metallic mixtures containing metal of the group consisting of lead and tin, which comprises electrolyzing an electrolytic bath consisting solely of an aqueous solution of phenol sulphonic acid having such a metallic mixture dissolved therein with an insoluble anode made of an alloy consisting of from 35% to 50% of antimony and the balance lead.

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