

[54] **METHOD OF PREVENTING SUPERSATURATION OF ELECTROLYTES WITH ARSENIC, ANTIMONY AND BISMUTH**

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[56] References Cited

UNITED STATES PATENTS

489,632 1/1893 Gruessner 204/108

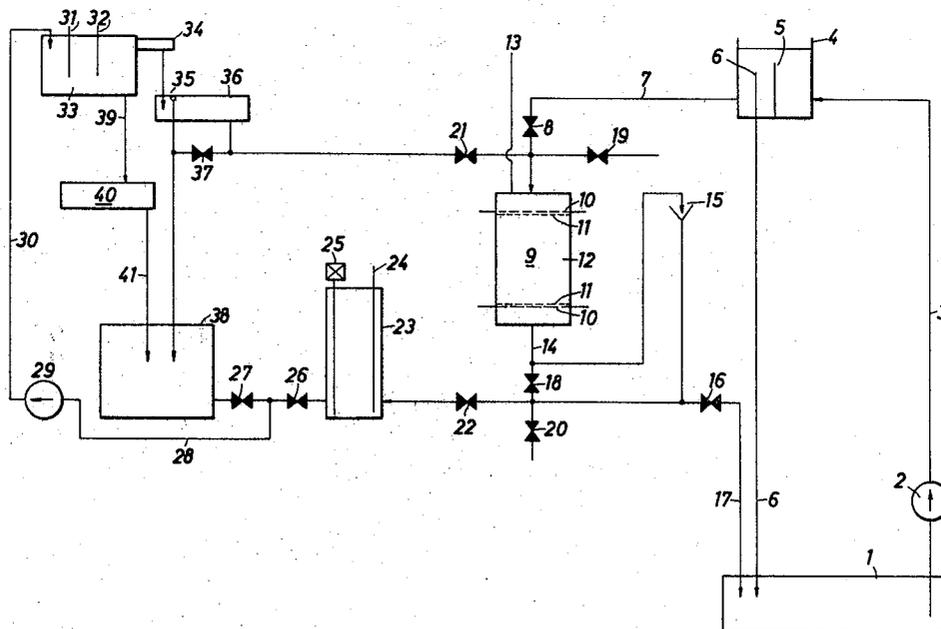
2,793,183	5/1957	Thurman	210/34
2,798,040	7/1957	Pye et al.	204/108
2,888,390	5/1959	Lapee	204/108
3,536,615	10/1970	Bunn	210/36
3,547,810	5/1968	Cooper	210/30
3,676,357	7/1972	Ciuti et al.	210/36
3,696,012	10/1972	Schulze	204/108
3,755,161	8/1973	Yokota et al.	210/36

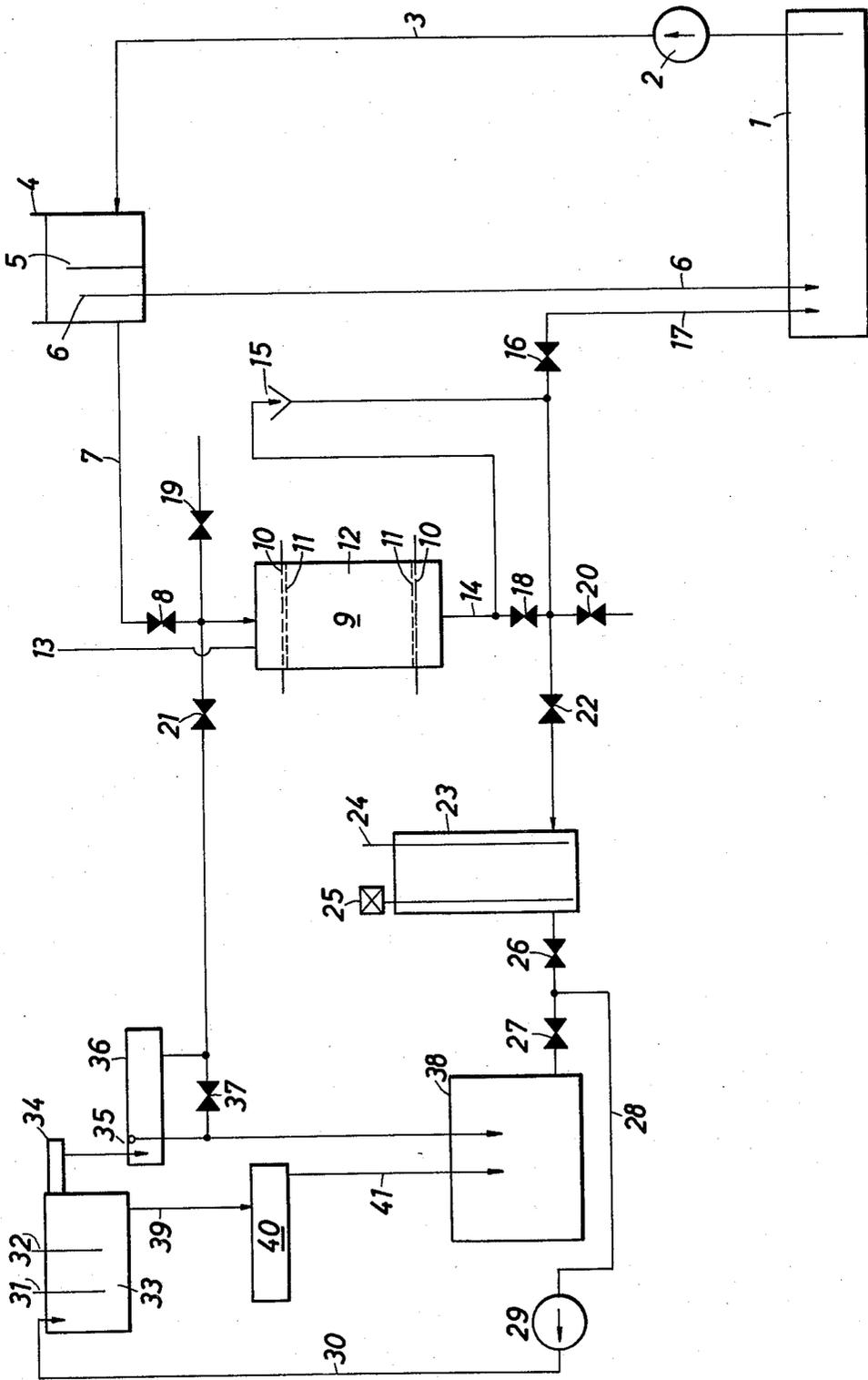
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[57] ABSTRACT

A method of preventing supersaturation of electrolytes with arsenic, antimony and bismuth in which the electrolyte solutions are contacted with stannic acid and the stannic acid is regenerated with electrolytically produced sulfuric acid having a higher concentration than the sulfuric acid in the electrolyte. The regeneration of the stannic acid chemisorbent is carried out in the same adsorber as the adsorption and using floating adsorbent particles in a bath.

4 Claims, 1 Drawing Figure





METHOD OF PREVENTING SUPERSATURATION OF ELECTROLYTES WITH ARSENIC, ANTIMONY AND BISMUTH

FIELD OF THE INVENTION

The present invention relates to a method of preventing supersaturation of electrolytes with arsenic, antimony and bismuth and represents an improvement over the system described and claimed in my commonly assigned U.S. Pat. No. 3,696,012.

BACKGROUND OF THE INVENTION

In the aforementioned patent, I describe a process for preventing excessive accumulation of arsenic, antimony and bismuth in electrolytes used in the electrolytic refining of non-ferrous metals, especially copper, the process involving the adsorption of the impurities upon a chemisorbent in the form of a low-soluble metal-oxide hydrate, namely stannic acid, stable in the presence of sulfuric acid.

In the patent I point out that, in the electrolytic refining of non-ferrous metals, especially copper, solubilization of the anode containing the impure metal gives rise to accumulation in the solution of electrolytes of one or more impurities from GROUP V (A) of the PERIODIC TABLE, namely arsenic, antimony and bismuth. These impurities create various difficulties.

Depending on the nature of the deposit and upon the process conditions, in the electrorefining of copper by electrodeposition upon a cathode of copper from a solution and the solubilization of impure copper from an anode, the cathodes produced contain undesirable impurities including the GROUP V (A) elements, namely arsenic, antimony and bismuth together with lead, nickel, selenium and other impurities. The presence of these impurities in the cathode, where they contaminate the end product of the electrolytic refining process, arises because the electrolyte solubilizes these elements from the anode slime and carries these components of the anode slime to the cathode surfaces, the impurities being trapped in the growing cathode. To an extent, moreover, the impurities may be incorporated in the cathode from solution or electrolyte which is mechanically received, e.g. in capillary cracks in the electrode, in interstices or openings such as the space between the metal of the cathode and the supporting loops, etc. Finally, saturation of the electrolyte with antimony and bismuth eventually gives rise to the formation of precipitates which can be incorporated mechanically in the growing cathode.

It has, therefore, long been a problem recognized in the art, that excessive concentrations of antimony, arsenic and bismuth in electrolytes for the electrodeposition of nonferrous metals may cause contamination of the end product and difficulties in the regeneration or processing of the electrolytes.

It is known, for example, that solutions such as the aforementioned electrolytes become saturated with the afore-described impurities and form slimes or precipitate earlier when arsenic is present, since arsenic leads to the formation of so-called floating slimes. Precipitation will also occur rapidly after the solution is saturated with calcium sulfate. Moreover, the solubility of salts of the impurities is known to decrease with decreasing temperature and the electrolyte often cools as it is drawn from an electrorefining tank for processing.

It is consequently deposited as a precipitate in the drains and conduits of the tanks, the deposits being extremely hard and difficult to remove. In fact, they have a stone-like character and may have thicknesses in excess of some centimeters. The deposits may include, for example, 2 percent by weight bismuth, 18 percent by weight arsenic and 48 percent by weight antimony. In practice, replacement of the drains, pipes, fittings and conduits is required periodically at considerable cost.

It is also obvious that the dangers which arise with increase in the proportions of antimony and bismuth in the electrolytic refining of copper, themselves increase with increasing transfer of these elements from the anode into the electrolyte. On the other hand, there is the tendency to produce anodes which avoid these impurities, thereby increasing the cost of the raw materials of the electrolytic refining process. There is also the fact that low concentrations of the impurity elements in the electrolyte permit the electrolytic refining process to proceed more efficiently. It is not a practical solution to increase the purity of the anodes since economical and technological considerations in the pyrometallurgical level have been found to limit such purity.

As a result, the art has determined that various measures should be found for the electrorefining copper containing large proportions of antimony and bismuth, i.e. high-antimony and high-bismuth copper. In these processes, the electrolyte is processed to keep the antimony and bismuth levels below saturation. If the amounts of the impurities are low, it is merely necessary to use the processes which have been employed to recover nickel from a copper-containing electrolyte. In this process, high nickel electrolyte is discarded and low nickel electrolyte is supplied to the refining tank, the low nickel electrolyte being fed at a well-defined rate with respect to the quantity of electrolyte discarded, this "discarding ratio" being for example about 1 percent per day. This solution to the problem of antimony and bismuth concentration in an electrolyte is, of course, wasteful.

OBJECTS OF THE INVENTION

It is the principal object of the present invention to provide a process for preventing saturation of an electrolyte with arsenic, antimony and bismuth which extends the principles set forth in the aforementioned patent and improves thereon.

Another object of the invention is to provide an improved process for controlling the buildup of antimony, bismuth and arsenic in an electrolyte for the processing of non-ferrous metals, especially copper.

Another object of this invention resides in the provision of a process for preventing supersaturation of copper-electrowinning electrolytes with members of GROUP V (A) of the PERIODIC TABLE.

Still another object of the invention is to provide an improved method of operating a system for the electrorefining of copper from anodes containing antimony, bismuth and arsenic in amounts exceeding the acceptable limits of these elements in the cathode.

Another object of the invention is to provide an economical method of removing members of the GROUP V (A) series of elements of the PERIODICAL TABLE from acid electrolytes as obtained in the electrolytic refining of copper.

SUMMARY OF THE INVENTION

These objects are attained, in accordance with the present invention, by a modification of the aforescribed system which enables recovery of the impurities without introducing other impurities into the process. Essentially, the invention is carried out by regenerating the chemisorbent in the same adsorber or adsorbers as the adsorption step is carried out originally. The adsorbent floats, in accordance with the invention, and the adsorption and regeneration steps are carried out with floating adsorbent particles, the sulfuric acid required to regenerate the chemisorbent being circulated and regenerated, in turn, in an electrolytic unit which is included in the sulfuric acid recirculation path. As a result of the electrolytic regeneration of the sulfuric acid, the amount of sulfuric acid required to regenerate the adsorbent is reduced (owing to the low solubility of the impurities) and the impurities themselves are recovered in a high concentration in elemental form.

The process of the present invention thus comprises removing from electrolyte solutions, especially solutions used in the electrolytic-copper process, the impurities arsenic, antimony and bismuth substantially continuously with their introduction into the electrolyte with a large-surface chemisorbent which may float in the electrolyte (preferably the chemisorbent is or includes stannic acid) and regenerating the stannic acid with sulfuric acid of a higher concentration than the sulfuric acid in the spent electrolyte.

The regeneration is carried out with agents which remain in the adsorbers or acid cycles and need not be separately treated and under such conditions that the adsorption apparatus may be relatively small.

It is an important aspect of the present invention that the adsorbent is floated upon the solutions with which it is to be contacted, i.e. the electrolyte to be treated by the adsorbent and the acid used to treat the adsorbent, while both adsorption and regeneration are carried out with the floating adsorbent particles. This affords the advantage that liquids can be passed at a higher velocity from above through the adsorber or adsorbers because the floating particles provide virtually no resistance to such floating. Each of the liquids which is passed through the adsorber can be substantially completely removed therefrom without significant rinsing so that there is virtually no mixing of the different solutions. This is particularly important because the electrolyte carrying the impurities and the regenerating sulfuric acid are passed through the adsorber or adsorbers alternately to deposit impurities upon the adsorber and strip the impurities therefrom in successive half-cycles. Air can be blown through the adsorbent, according to the present invention, although substantially no air is retained after a change of liquids. Where stationary porous substances are used, on the contrary, the retention of air in pockets or by surface adhesion reduces the effective surface area and the capacity. In addition, retained air in these latter systems obstructs the passages through the porous body and thus the flow of liquid through the system.

According to another feature of the invention, the chemisorbent is provided in a layer which is coated onto a floating support together with layer-forming or film-forming materials. The supports are preferably particles of a foamed synthetic resin, especially polystyrene or polyurethane and the film-forming material is

preferably a substance having a high wear resistance, high capacity (for the reaction and adsorbent) and a high degree of activity, when combined with the reactant, so that the layer possesses a high reaction rate. It goes without saying that the film-forming substance must also have high chemical stability and adhesivity or bond strength, being able to bond even the peptizable chemisorbents. These requirements are met by the use of film-forming binders which have heretofore been employed as paints or coatings for preventing access of a corrosive environment to a protected surface. It is indeed surprising that the high reactivity layer, which is used in accordance with the present invention, may make use of compositions which have hitherto found their principal utility in preventing chemical or physical-chemical activity.

The coating, preferably, comprises a solution or suspension of the chemisorbent in a mixture of binders, at least one of which acts as a flocculating agent for the reactant. The solution or suspension containing the mixture is used to coat the supports and, after drying, forms a tough, firmly adherent and swellable film which contains the reactant (i.e. the chemisorbent).

Best results have been obtained with a binder system consisting of a mixture of binders including a water-insoluble component or a component which swells only slightly in the presence of water and which imparts toughness and adhesive strength to the mixture. Another component which is soluble or swellable in water and which, when combined with the water-soluble component, is substantially insoluble in water so as to be retained in the coating after drying and renders the coating sufficiently permeable to access solutions to allow access of the reactant in the coating to the solution to be treated thereby or used to treat the reactant.

The water-insoluble synthetic resin material, which may be used in alkaline and acid solutions, may be any of those hitherto employed as latex paint vehicles. Preferably, the water-insoluble components is an acrylic ester in the form of the homopolymer or of polymers with vinyl ester, styrene, vinyl esters, vinyl chlorides or vinylidene chlorides. The soluble or swellable component of the binders, which is locked into the film so as to be insoluble but as to contribute to the permeability, is preferably a flocculating agent of the polyacrylate, polyacrylic ester, polyacrylamide, acrylic acid copolymer or polyethylene imine type. The mixing ratio between the water-insoluble synthetic resin component and the water-soluble or water-swellable synthetic resin components (which is rendered insoluble in the film) may vary within wide limits and depends only upon the ultimate properties desired in the film. For films of higher hardness or greater toughness and lower permeability, the water-insoluble binder component may be increased in proportion whereas, for greater permeability, the proportion of water-soluble and water-swellable binder components (insoluble in the film) will be present in greater proportion. The water-soluble synthetic resin generally should make up 0.1 to 5 percent by weight, preferably 1 percent by weight, of the binder components, based upon the amount of water-insoluble resins, while the remainder may also consist of 10 to 1,000 percent by weight, preferably 200 percent by weight of water-swellable resins based on the amount of water-insoluble synthetic resin. The resulting coating has been found to have a satisfactory permeability and air resistance. It is thus desirable to use water-soluble

and water-swellaable synthetic resin materials in combination.

The activity of the coating may be increased by the addition of soluble or insoluble substances to the solution or suspension forming the coating. These substances can be removed by solubilization and/or decomposition, e.g. into a gas, once the coating has been formed upon the support to leave pores in the coating to promote the reaction. The substance which may be used to form the pores includes substances which meet the aforementioned solubility requirements, e.g. simple organic compounds such as sugar, urea and the like, simple organic or inorganic salts, especially sodium and potassium salts such as chlorides, sulfates, acetates and oxylates, substances which have thermal decomposition temperatures within the stability range of the coating and produce gas upon heating such as the hydrogen carbonates and carbonates (especially of the alkali metals and the alkaline-earth metals), chalk and dolomite or sulfites. The hydrogen carbonates and carbonates yield carbon dioxide upon heating while the sulfates generate sulfur dioxide. Mixtures of these pore-forming substances may be used and the upper limit as to the proportion of the pore-forming materials is established only by the mechanical stability of the film, i.e. the maximum proportion of the pore-forming material should be such that the film does not lose its cohesion. It is preferred to use about 5 percent by weight of the soluble or low-solubility substances from this group and 50 percent by weight of insoluble substances based on the total content of the dry binder.

With systems of the type described it has been found that viscosity control is important to provide a film-forming or smooth-coating homogenous deposit and that it may be necessary to add viscosity modifiers such as monomeric or polymeric amines and amino alcohols to eliminate the film-forming or homogenous character of the coating composition. These materials, which also serve as plasticizers, may be used in amounts up to 1,000 percent by weight based upon the water-insoluble synthetic resin component.

DESCRIPTION OF THE DRAWING

The above and other objects, features and advantages of the present invention will become more readily apparent from the following description, reference being made to the sole FIGURE of the drawing which shows a system for carrying out the present invention.

SPECIFIC DESCRIPTION

A pump 2 withdraws enriched solution from a collecting box 1 through a conduit 3 and supplies the solution into a box 4 provided with an overflow weir 5. A conduit 6 connected to the upper portion of the box 4 continuously returns a major part of the solution back into the collecting box 1. In spite of the long pipeline 3, fresh solution from the box 1 will always be available at a suitable temperature in the overflow box 4 if the solution is recycled through 6 at a sufficiently high rate.

Solution is supplied to an adsorber 9 through a conduit 7 and a valve 8. The floating active mass 12 is disposed between flange-connected sieve plates 10.

Filter cloths 11 having a suitable mesh size may also be used as retaining means, if desired. The air from the adsorber 12 can escape through a venting conduit 13. To ensure that the adsorber 12 remains always filled with solution, the adsorptively treated solution is re-

turned into the collecting box 1 through a conduit 14, which constitutes a siphon, a draining funnel 15, a valve 16, and a conduit 17.

When the adsorption has been terminated, the valve 8 is closed and a valve 18 is opened so that the solution is drained from the adsorber. Rinsing water is supplied through a valve 19 into the collecting box 1 or can be separately withdrawn through 14, 15, and a valve 20. The rinsing water will be drained when 19 is closed and 18 is opened.

Valves 21 are opened to initiate the regeneration of the adsorber mass 12. Sulfuric acid now flows into the adsorber and through 14, 15 and a valve 22 into a drain container 23. A heater 24 heats the acid to the desired temperature. Under control of a float switch 25, a pump 29 discharges the acid through a valve 26 and conduits 28 and 30 into the electrolytic cell 33, which is provided with insoluble anodes 31 and with cathodes 32. Only one anode and one cathode are shown.

It may be desirable, for instance, to use anodes of lead and cathodes of copper. The shape of the cathodes is not critical. They may consist of plates, rods, tubes, perforated plates or the like. Where plates are used, however, it will be recommended to immerse only narrow webs into the solution for a supply of current so that the gas-laden, floating mud which has been formed at the cathode can be carried without obstruction together with the draining acid through an outlet 34 onto a filter 36. All conventional units may be used as filters because the mud can be filtered well. Any acid which is supplied in excess is not filtered but is conducted over an overflow 35 into a reservoir 38.

When the regeneration has been terminated, 21 is closed and the valve 18 and a valve 37 are opened so that the float switch 25 ensures that the acid can be completely drained from the adsorber and collected in the reservoir 38 even if there is no sufficiently large difference between the levels of the adsorber and drain container. When the float switch 25 is disconnected and the valve 27 is opened, the electrolysis of the acid can be continued in a separate cycle. Bottom sludge in the electrolytic cell 33 is fed through a bottom pipe 39 onto a filter 40. The acid which is carried along flows through a conduit 41 into the tank 38. In this way, the electrolyte solution can be purified only in an operation which is interrupted for the regeneration of the adsorbent mass. This is no disadvantage in many cases because during the time for which the adsorption is interrupted the collecting box 1, owing to its high capacity, can be filled to such an extent and the purity of the electrolyte solution contained in said box can be adjusted so that the time required to regenerate the chemisorbent is bridged. Alternatively, a second adsorber may be provided and the two adsorbers can operate in alternation so that the adsorption need not be interrupted.

SPECIFIC EXAMPLES

EXAMPLE 1

0.2 kilogram of a flocculating agent consisting of polyacrylamide are dissolved in 20 kilograms of a low-viscosity dispersion (25 percent) of an acrylate copolymer which is conventional as a paint vehicle. 20 kilograms diethanolamine are added to the viscous, filament-forming solution to render it spreadable. This mixture and 40 kilograms of a high-viscosity dispersion of an acrylic ester copolymer conventional as a paint

vehicle, 50 kilograms calcium stannate, 1 kilogram sodium hydrogen carbonate and 10 kilograms prefoamed Styropor P 455 (polystyrene) beads are intimately blended until a uniform sticky coating has been formed on each Styropor particle. The material is dried in loosened layers at temperatures up to about 100°C. The process can be considerably accelerated even at a low temperature by a circulation of air, the use of a vacuum, and tumbling. It will be highly desirable to tumble and at the same time to supply warm air through the tumbling mechanism.

Together with or without the supports on which the material is dried and which consist of paper, sheet metal, perforated sheet metal, or the like, the material is coarsely crushed and is activated by being reacted with hot hydrochloric acid of about 1 percent concentration. The disintegration into the individual particles will be accelerated by kneading, stirring or other mechanical agitation. Because the material is bouyant, it should be immersed into the hydrochloric acid by a perforated plate or the like. It will be desirable to perform the activation in a closed rotary drum, which is provided with suitable internal fixtures to break the flow.

coated particles in the working media, any desired insoluble substances, preferably barite or lead sulfate, may be admixed in the required amount to the mixtures.

EXAMPLE 4

100 grams stannic acid on polystyrene beads treated as above to contain calcium stannate and reformed into stannic acid as described in the aforementioned patent — this stannic acid is designated A in Table 1 — were charged into 100 liters of a warm copper-refining electrolytic liquor at a temperature of 60°C, the electrolyte being drawn off from the adsorber in which the stannic acid/foamed polystyrene floated. The temperature was maintained constant during these steps. The residue retained in the adsorber is designated B in Table 1. The duration of the entire process was only ¼ hour. The conditions and results of the experiment are stated in Tables 1 and 2. The moisture values are not characteristic because they will obviously depend on the degree of elimination of electrolyte. The stannic acid was regenerated by circulating sulfuric acid downwardly through the floating particles.

Table 1

Substance	A (%)	B (%)	A (grams)	B (grams)	B-A (grams)
Amount	—	—	100	133.5	33.5
Moisture	55.9	31.9	55.9	42.6	-13.3
Sn	27.4	20.5	27.4	27.4	0
As	0.31	5.0	0.31	6.69	6.38
Sb	1.0	11.7	1.0	15.6	14.6
Bi	0.009	0.85	0.009	1.14	1.13
Cu	0.03	0.46	0.03	0.62	0.59
Ni	—	0.08	—	0.107	0.107
Se	0.11	0.114	0.11	0.152	0.042
Fe	0.05	0.04	0.05	0.054	0.004
Ca	0.02	0.04	0.02	0.054	0.034

Table 2

	Cu	Ni	As	Sb	Bi	H ₂ SO ₄
Initial liquor, grams per liter	39.7	20.5	7.2	0.48	0.05	165
Final liquor, grams per liter	39.7	20.5	7.1	0.33	0.04	165
Difference, grams per liter	—	—	-0.1	-0.15	-0.01	—
Difference, %	—	—	-1.4	-31.3	-20	—

The end of the reaction is indicated by a change in color from gray to yellow. When washed with water, the mass is ready for use and will resist even 60 percent sulfuric acid at 70°C.

EXAMPLE 2

The same mixture is prepared as in Example 1. In this case, 0.2 kilogram flocculating agent consisting of polyacrylamide are added as an aqueous solution of 1 percent concentration. 2 kilograms polyethyleneimine are added to thicken the mixture.

EXAMPLE 3

The same mixture is prepared as in Example 1. In this case, 1 kilogram sodium hydrogen carbonate as a pore-forming agent is replaced by a mixture of 0.5 kilogram sodium hydrogen carbonate, 10 kilograms chalk and 2.5 kilograms common salt.

When it is desired to reduce the buoyance of the

The data show clearly that the treatment with stannic acid results within a short reaction time in a removal mainly of antimony and bismuth, as well as of small amounts of calcium, selenium, arsenic, etc. from conventional liquors used in the electrolysis of copper and that the electrolytic liquors need not be cooled for this purpose.

EXAMPLE 5

Anode copper containing 0.1 percent antimony and 0.015 percent bismuth was processed at a rate of 100 metric tons per day. The electrolyte was constantly treated with floating stannic acid particles (as described) in a separate adsorber plant and was then returned into the electrolytic cycle. 1.1 metric tons of tin in the form of stannic acid was used in this process, by which the concentration of impurities in the electrolyte was held at 0.1 gram antimony per liter and 0.035 gram bismuth per liter. In this process, no floating slime and not deposits on the pipe walls of the electrolyte conduit

system were observed. The regenerating acid was recirculated H₂SO₄.

I claim:

1. A process for preventing supersaturation of an electrolyte with an impurity selected from the group which consists of arsenic, antimony and bismuth which comprise the steps of:

- a. treating said electrolyte with floating particles of a chemisorbent adapted to take up said impurity in an adsorber;
- b. draining said electrolyte from said adsorber;
- c. circulating a regenerating solution through said adsorber and into contact with said floating particles to strip said impurity therefrom; and
- d. electrolytically regenerating said solution along the circulating path thereof; wherein said chemisorbent is stannic acid, said electrolyte is a sulfuric acid electrolyte for the electrolytically refining of copper and said regenerating solution is sulfuric acid more concentrated than said electrolyte.

2. The process defined in claim 1 wherein said parti-

cles are formed by coating said chemisorbent in a film-forming binder system onto foam synthetic resin particles.

3. The process defined in claim 2 wherein said particles consist of a resin selected from the group which consists of polystyrene and polyurethane and said binder system comprises a water-insoluble binder component selected from the group which consists of polymers of acrylic acid, homopolymers and copolymers of acrylic esters with vinyl esters, styrene, vinyl ethers, vinyl chloride and vinylidene chloride, a further binder component serving as a flocculating agent for said chemisorbent and selected from the group which consists of polyacrylates, polyacrylic esters, acrylic esters copolymers, polyacrylamides and poly-ethylene imines.

4. The process defined in claim 3 wherein said system further includes at least one component removable upon formation of the film, said process further comprising the step of removing said removable component to render said film permeable.

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