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PROCESS FOR PREVENTING SUPERSATURATION OF ELECTROLYTES WITH ARSENIC, ANTIMONY AND BISMUTH

Reinhold Schulze, Hamburg, Germany, assignor to Norddeutsche Affinerie, Hamburg, Germany

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9 Claims

ABSTRACT OF THE DISCLOSURE

A process for preventing excessive accumulation of arsenic, antimony and bismuth in electrolytes used in the electrolytic refining of nonferrous metals, especially copper. The process involves adsorbing these impurities upon a chemical adsorbent in the form of a low-solubility metal-oxide hydrate (especially stannic acid) stable in the presence of sulfuric acid.

(1) FIELD OF THE INVENTION

My present invention relates to a process for preventing the accumulation of excesses of arsenic, antimony and bismuth, in electrolytes and, more particularly, for preventing the supersaturation of electrolytes used in the electrolytic refining of copper with arsenic, antimony or bismuth and combinations thereof.

(2) BACKGROUND OF THE INVENTION

In the electrolytic refining of nonferrous metals, especially copper, solubilization of the anode containing the impure metals, give rise to accumulation in the solution or electrolyte of one or more impurities from Group V-A of the Periodic Table. These impurities, namely arsenic, antimony and bismuth, 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 formed contain undesirable impurities including the Group V-A elements, namely arsenic, antimony and bismuth, as well as 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 of the deposition of anode slime upon the cathode surfaces and the incorporation, entrapment or inclusion of such precipitated impurities in the growing cathode. To an extent, moreover, the impurities may be incorporated in the cathode in solution in the electrolyte which may in part be trapped within the cathode, i.e. in capillary cracks of the cathode, in interstices or openings such as the spaces between the metal of the cathode and the supporting loops, etc. Finally, saturation of the electrolyte with antimony and bismuth eventually give rise to the formation of precipitates which can be incorporated mechanically in the growing cathode.

It has, therefore, been a problem long recognized in the art that excessive concentrations of antimony, arsenic and bismuth in electrolytes for the electrodeposition of nonferrous metals may increase the contamination of the end product and cause difficulty in processing of the electrolyte. It is known, for example, that solutions (electrolytes) become saturated with the aforementioned impurities and form slimes or precipitates earlier when arsenic is present, since arsenic leads to the formation of so-called floating slimes. Precipitation will also occur rapidly if the solution is saturated with calcium sulfate. Moreover, the solubility of salts of the impurities is known to decrease

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with decreasing temperature and the electrolyte often cools as it is drawn from the electrorefining tank for prosecution. There is, consequently, a deposition of precipitate in the drains and conduits of the tanks, the deposits being extremely hard and difficult to remove. In fact, they have stone-like character and may have thicknesses in excess of some centimeters and can include, for example, 2% by weight bismuth, 18% by weight arsenic and 48% by weight antimony. In practice, replacement of the pipes, fittings and conduits is required at regular intervals at considerable cost.

It is also obvious that the dangers which arise with the presence of increasing quantities of antimony and bismuth in the electrolytic refining of copper themselves increase with the increasing amounts in which these elements may be introduced from the anodes into the electrolytic solution. On the one 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 and, consequently, the entire metallurgical procedure. On the other hand, there is the fact that low concentrations of these impurities in the electrolyte permit the electrolytic refining process itself to proceed efficiently. Finally, it is not a practical solution to increase the purity of the anodes since economic and technological considerations on 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 of copper containing large proportions of antimony and bismuth, i.e. high-antimony and high-bismuth copper. In these procedures, the electrolyte is processed to keep the antimony and bismuth concentration below the saturation level. If the amounts of these impurities are low, it is merely necessary to use the procedures which are employed to recover nickel from a copper-anode electrode. In this procedure, high-nickel electrolyte is discarded and low-nickel electrolyte is supplied to the electrorefining tank. The low-nickel electrolytic solution is supplied at a well defined rate with respect to the quantity of electrolyte discarded, the ratio being described as the discarding ratio and is, for example, about 1% per day.

When a concentration of 0.25 g./liter of antimony and 0.035 g./liter bismuth is considered tolerable in the electrolyte and ten metric tons of anode copper are processed every day with 100 m.³ of the electrolyte solution, the maximum concentration in the anode of antimony will be 0.0025% and 0.00035% for bismuth provided that all of the antimony and bismuth are dissolved. Hence anodes with more than 0.0025% antimony and more than 0.00035% bismuth can only be processed without changing the cathode analysis and without deposition of hard substances on the bath walls and in the pipe lines when a corresponding amount in excess of 1% of the electrolytic solution is discarded per day. However, the economic limits of the process are soon reached when the impurity level of the anodes is higher because of the high cost of processing the discarded solution or in supplying the corresponding quantity of fresh electrolyte.

(3) OBJECTS OF THE INVENTION

It is, therefore, the principal object of the present invention to provide an improved process for controlling the buildup of antimony and bismuth (also arsenic) in an electrolyte for the processing of nonferrous metals, generally copper.

Another object of this invention resides in the provision of a process for preventing supersaturation of electrolytes, in the electrowinning of copper, with members of the Group V-A series of the Periodic Table.

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 Periodic Table from an acid electrolyte, e.g. of the type provided in the electrowinning of copper.

(4) SUMMARY OF THE INVENTION

These objects and others which will become apparent hereinafter attained, in accordance with the present invention, which is based upon the surprising discovery that there exists a class of inorganic compounds, namely the metal-oxide hydrates of low solubility and high stability in sulfuric acid, which preferentially adsorb antimony, bismuth and arsenic, i.e. the Group V-A, from aqueous electrolytes of the character described.

Accordingly, the process of the present invention comprises continuously contacting at least a portion of the electrolyte used for the electrorefining of a nonferrous metal, e.g. electrorefining of copper, with a chemical adsorbent of the class described to maintain the concentration of antimony and bismuth below at a level considered detrimental to operation of the electrolytic process and, therefore, below that at which supersaturation may occur in the electrolyte.

Chemical adsorbents which can be used to advantage in the present process include a low-solubility metal-oxide hydrate having large effective surface area and high stability in sulfuric acid and include manganese oxide hydrate (pyrolusite) and stannic acid ($\text{SnO}_2 \cdot x\text{H}_2\text{O}$).

The use of stannic acid has proved to be particularly desirable. Stannic acid has a particular high stability in a solution of sulfuric acid and, for this reason, may be used in much smaller quantities than other metal oxide hydrates. Furthermore, stannic acid can be regenerated much more easily and much more completely.

The chemical adsorbent is preferably pelletized or granular and may be simply charged into the electrolytic solution and may be removed by filtering or decantation. Alternatively, the chemical adsorbent may be held in porous bags which are suspended directly in the electrolyte. It has proved to be particularly desirable to contact the electrolytic solution with the chemical adsorbent in a separate adsorber which is included in the electrolyte cycle. The adsorber may consist of a drum which contains the adsorbent and is covered at both ends by a filter cloth and designed so that the liquor enters the drum at one end and purified liquid leaves the drum at another end.

In all these cases, the stannic acid is desirably used in granular or pelletized form. In this case the adsorber may consist of an adsorption tower in which the chemical adsorbent is used as in the known ion-exchange columns.

Because the chemical adsorbent, particularly stannic acid, need not remove all antimony and bismuth from the electrolytic solution but it is sufficient to keep the contents of these impurities below the saturation level, the process can be carried out in a particularly desirable embodiment in which only part of the electrolytic solution which flows through the cells is contacted with the chemical adsorbent and, when purified, is combined with the main flow of the solution.

The technical literature contains descriptions of processes of producing stannic acid by a treatment of metallic tin, its alloys and compounds with acids and oxidizing agents or directly with oxidizing acids.

It has now been found that the use of stannic acid in the process according to the invention affords the additional advantage that such stannic acid need not be pure. It has surprisingly been found that it is even possible to use a stannic acid which contains certain amounts of those impurities which are to be removed by the process

according to the invention from the electrolytic liquors used in refining non-ferrous metals. Hence, stannic acid may be used which has been formed by a reaction of acids, particularly dilute hydrochloric acid, with calcium stannate formed as a result of the refining of lead with caustic soda (Harris process). This stannic acid is particularly inexpensive because the calcium stannate obtained as a result of the refining of lead by the Harris process is a particularly inexpensive source of tin and may be easily reacted in stoichiometric amounts with dilute acids and at room temperature to produce stannic acid in stoichiometric quantities. Hydrochloric acid is preferable for this purpose because of its low cost. Washing and filtering result in a product which may be used directly and which may have, e.g., the composition stated in Table 1.

When the stannic acid is no longer sufficiently effective because it has been highly charged with impurities from the electrolytic liquor, the stannic acid can be regenerated by a treatment with acid and the regenerated stannic acid may be reused in the process according to the invention. The stannic acid may be desirably regenerated by a treatment with nitric acid, hydrochloric acid or sulfuric acid in a concentration which is higher than the acid concentration in the liquor used for the electrolysis of copper. The stannic acid may be particularly effectively regenerated by being re-converted into calcium stannate, from which stannic acid is recovered by the above-described treatment with acid. The stannic acid may be reconverted into calcium stannate by a direct treatment with milk of lime. In a particularly desirable process of regenerating stannic acid, the same is recycled to a Harris process of refining lead to form calcium stannate, from which new stannic acid is recovered.

(5) 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 in which the sole figure is a flow diagram illustrating various phases of the present invention.

(6) SPECIFIC DESCRIPTION

In the drawing, I show diagrammatically at 10 a tank for the electrowinning of copper using a sulfuric acid electrolyte and having a cathode and an anode as represented at 11 and 12. The anode may be relatively impure and can contain concentrations of antimony and bismuth above those which are tolerable in the cathode. In accordance with the usual practice, electrolyte may be removed by a duct 13 and a pump 14 and passed via a distribution valve 15 through the electrolyte reprocess cycle which is diagrammatically represented at 16. Depleted ingredients of the electrolyte may be replenished at this point and nickel removed, the electrolyte thereafter returning at 17 to the refining tank 10.

In accordance with one aspect of this invention, valve 15 branches at 18 a portion of the recirculating electrolyte through a drum-type adsorber 19 in which a mass 20 of stannic acid adsorber pellets is held between a pair of filter cloths 21 and 22. In the adsorber, a preferential removal of antimony and bismuth is effected, the electrolyte being returned at 23 to the refining tank 10.

Alternatively or in addition, porous bags 24 of electrolyte permeable cloth (filter cloth) containing the stannic acid adsorbent in granular form may be suspended at 25 in the electrolyte within the refining tank.

Alternatively, or in addition, a valve 26 may be provided to branch all or part of the electrolyte to be processed into adsorption column 27 in which the electrolyte passes downwardly through the stannic acid adsorbent therein. The electrolyte may then be returned at 28 to the tank 10. Finally, a portion or all of the electrolyte may be passed through a filter 30 to recover the depleted adsorbent when the latter is deposited directly in the electrolyte of refining tank 10 as represented at 31. The

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electrolyte can then be returned at 32 to the normal re-process cycle represented at 16.

The depleted adsorbent is delivered at 33 from the bags 24, at 34 from the drum 19, at 35 from the filter 30 and at 36 from the column 27 to a regenerating stage 37 at which lime may be added to form calcium stannate which, in turn, is delivered at 38 to the stannic acid production stage 50. Alternatively, the depleted stannic acid is delivered at 39, 40, 41 and 42 to the lead-refining stage 43 in which the Harris process is practiced. The addition of caustic soda in the Harris process is represented at 44.

The calcium stannate derived at 45 from the lead-refining stage and the calcium stannate from the lime precipitator 37 are delivered to the stannic acid regenerator 50 to which a dilute mineral acid is supplied at 46 to produce stannic acid in stoichiometric quantities as described before. Alternatively, the depleted adsorbent is delivered at 51, 52, 53 and 54 directly to the stannic acid regenerator 50, to which a mineral acid is supplied at 46. The regenerated stannic acid is delivered to the column 27 as represented at 47, is introduced into the bath directly as shown at 31, is placed in the bags 24 as indicated at 48 and is supplied to the adsorbent drum 19 as shown at 49.

(7) SPECIFIC EXAMPLES

Example I

100 grams stannic acid recovered from calcium stannate that had been formed in a Harris process—this stannic acid is designated A in Table 1—were charged in a state of fine division into 100 liters of a warm electrolytic liquor at a temperature of 60° C., which was shaken for a short time, whereafter the stannic acid was filtered off immediately. The temperature was maintained constant during these steps. The residue retained by the filter 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 suction used in the filtration step.

TABLE 1

Substance.....	Percent of—		Grams of—		
	A	B	A	B	B-A
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, percent.....			-1.4	-31.8	-20	

The test 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 conven-

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tional liquors used in the electrolysis of copper and that the electrolytic liquors need not be cooled for this purpose.

Example II

5 Anode copper containing 0.1% antimony and 0.015% bismuth was processed at a rate of 100 metric tons per day. The electrolyte was constantly treated with stannic acid 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 no deposits on the pipe walls of the electrolyte conduit system were observed.

I claim:

1. In a process for the electrolytic refining or electro-winning of a nonferrous metal with a sulphuric acid electrolyte for the electrolytic refining of copper, the improvement which comprises the step of contacting at least a portion of said electrolyte with a chemical adsorbent constituted as a metal-oxide hydrate selected from the group which consists of pyrolusite and stannic acid and adapted to remove from said electrolyte at least one element selected from the group which consists of arsenic, antimony and bismuth, thereby preventing accumulations of excesses of said elements in said electrolyte.

2. The improvement defined in claim 1 wherein said electrolyte is circulated through an electrolyte-replenishment cycle including an adsorbent containing said metal-oxide hydrate.

3. The improvement defined in claim 1 wherein said electrolyte is recirculated, further comprising the step of passing only a portion of the electrolyte through an adsorbent containing said metal-oxide hydrate and thereafter recombining said portion of said electrolyte with the recirculating flow thereof.

4. The improvement defined in claim 1 wherein said metal-oxide hydrate is used in the form of particles.

5. The improvement defined in claim 1 wherein said metal-oxide hydrate is stannic acid, further comprising the step of forming said stannic acid by treating calcium stannate with a mineral acid.

6. The improvement defined in claim 5 wherein the stannic acid following adsorption is regenerated by treatment with sulfuric acid of a concentration in excess of the concentration of the acid in the electrolyte.

7. The improvement defined in claim 5 wherein the stannic acid following adsorption is regenerated by treatment with a mineral acid.

8. The improvement defined in claim 5 wherein said calcium stannate is derived from the refining of lead with caustic soda.

9. The improvement defined in claim 8 wherein the stannic acid subsequent to adsorption, is recycled to the lead-refining to produce the calcium stannate.

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