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METHOD FOR REFINING ANTIMONY BY ELECTROLYSIS OF ACID ELECTROLYTES

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This invention relates to a method for refining antimony by electrolysis of acid electrolytes.

A crude antimony, which is adapted for electrolytical purposes, may contain lead, tin, iron, nickel, zinc, copper, bismuth, silver and gold besides other more rare impurities. Of greater practical importance is the fact, that greater amounts of lead for example 5% and tin for example 8% and more may be present in the crude antimony without disturbing the electrolysis. Arsenic however has to be removed from the crude antimony by remelting it with alkali.

According to the invention the refining of crude antimony is carried through by electrolyzing electrolytes containing antimony tri-fluoride, in which a considerable excess of free sulphuric acid and small amounts of free hydrofluoric acid are maintained. When using such electrolytes the deposition of disturbing basic antimony salts upon the anode is avoided.

It has already been proposed to use electrolytes containing antimony trifluoride for the electrolytical refining of crude antimony. A very detailed description of this method is to be found in the "Transactions of the American Electrochemical Society, vol. 28, 1915, page 325." There however it is stated, that the electrolyte should be absolutely free from sulfuric acid. It is further stated that lead present in the anodes goes over into the cathodes. The antimony electrolytically deposited upon the cathodes contained for example 0.35% Pb and was therefore of inferior quality.

According to the present invention the above described difficulties are avoided, when using an electrolyte containing a considerable excess of free sulfuric acid for example 60–600 gr. H_2SO_4 per liter and a small amount of free hydrofluoric acid for example 20 gr. HF per liter. With such a strongly acid solution a clogging of the anode by precipitated basic antimony sulfate is avoided and by the great excess of sulfuric acid the solubility of the lead in the electrolyte is so much reduced, that it cannot enter the cathode. An electrolyte containing the antimony trifluoride in a strong sulfuric acid solution is well adapted for the electrolysis of even very impure antimony with best results. The pure metal obtained contains 99.8% Sb. Difficulties at the anodes do not occur and the electrolyte is comparatively cheap, as it allows to operate with a minimum of hydrofluoric acid.

For the preparation of the electrolyte pulverized crude antimony is boiled with concentrated sulfuric acid in kettles of cast iron, until the development of sulfur dioxide stops. For example 100 kg. antimony are boiled with 250 kg. sulfuric acid 60° Bé. The pasty mass obtained contains much free sulfuric acid and hydrofluoric acid is added, whereby the antimony is at once dissolved, as antimony trifluoride. Only a small excess of free hydrofluoric acid is necessary; the obtained solution contains for example 200 gr. Sb per liter and is diluted with water and if necessary cleared in order to obtain an electrolyte ready for use. Instead of using raw antimony also other materials containing antimony may be employed, so far as solutions of trivalent antimony may be obtained from them.

If the electrolyte should contain less free sulfuric acid than 60 gr. per liter, more acid is added. An upper limit for the content of free sulfuric acid is not given, as electrolytes containing 300 and even 600 gr. H_2SO_4 per liter may be used with satisfactory results.

The electrolysis is carried through in vessels with lead lining. It is not necessary to heat the electrolyte; heating would only lead to losses of hydrofluoric acid. The anodes are cast plates of crude antimony with copper ears for suspending them. The cathodes are for example copper plates, from which the pure antimony deposited may be easily removed. In some cases one may replace the foregoing acids by other ingredients, but I have found such substitutions not to be as satisfactory. For example, one may replace the free sulphuric acid by alkali-bisulphate and the free hydrofluoric acid by a mixture of alkali-fluoride and free sulphuric acid.

The waste electrolytes may be easily worked up for their content of free hydrofluoric acid. For this purpose the metals precipitable from

acid solution are removed by known methods and by concentration of the obtained liquid the free and bound hydrofluoric acid is driven off and thus recovered. The residue containing sulfuric acid and certain metal sulfates is worked up by other known methods.

I claim:

1. A process for refining crude antimony which comprises preparing an electrolyte containing antimony trifluoride, a considerable excess of a substance containing the radical HSO_4 and a small excess of HF, introducing thereinto an anode soluble at least in part in said electrolyte and containing impurity substantially insoluble therein, said electrolyte being of a character such as to prevent said anode from becoming passive, and electrolyzing the solution to deposit antimony without the deposition of the impurity therewith.

2. A process for refining crude antimony which comprises preparing an electrolyte with antimony trifluoride containing a considerable excess of free sulfuric acid and a small excess of free hydrofluoric acid, introducing thereinto an anode soluble in said electrolyte containing impurities such as lead, said electrolyte being of a character such as to prevent said anode from becoming passive, and electrolyzing the electrolyte to deposit antimony substantially without the deposition of the lead therewith.

3. A process for refining crude antimony which comprises preparing an electrolyte with antimony trifluoride containing a considerable excess of free sulfuric acid and a small excess of free hydrofluoric acid introducing thereinto an antimony anode soluble in said electrolyte and containing impurities such as lead insoluble therein, said electrolyte being of the character such as to prevent said anode from becoming passive, and electrolyzing the electrolyte to deposit antimony substantially without the deposition of the lead therewith.

4. A process of refining crude antimony which comprises preparing an electrolyte with antimony trifluoride containing at least 60 grams free sulfuric acid per liter and a small amount of free hydrofluoric acid, introducing thereinto an antimony anode soluble in said electrolyte and containing impurities such as lead insoluble therein, said electrolyte being of a character such as to prevent said anode from becoming passive, and electrolyzing the electrolyte to deposit antimony substantially without the deposition of the impurities therewith.

5. A process of refining crude antimony which comprises preparing an electrolyte with antimony trifluoride containing about 100 grams free sulfuric acid per liter and about 20 grams free hydrofluoric acid per liter, introducing thereinto an antimony anode soluble in said electrolyte and containing impurities such as lead insoluble therein, said electrolyte being of a character such as to prevent said anode from becoming passive, and electrolyzing the electrolyte to deposit antimony substantially without the deposition of the lead therewith.

In testimony whereof I affix my signature.

HEINRICH ROSCHER.