Patented Nov. 26, 1929 1,737,140

UNITED STATES PATENT OFFICE

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PROCESS FOR THE RECOVERY OF TIN AND ITS ASSOCIATED METALS FROM ALLOYS, MECHANICAL MIXTURES, AND ORES

No Drawing. Application filed May 25, 1926, Serial No. 111,641, and in Germany July 5, 1924.

I have filed applications in Germany No. B. 114,764 VI/40 dated July 5, 1924 and in Czechoslovakia No. P. 3787—25 dated August 3, 1925.

The invention relates to a highly economical process for the recovery of tin and its associated metals from alloys and mechanical mixtures, such as tin dross, waste turnings, composition metals, etc., and consists substantially in dissolving the stanniferous metals or metal mixtures in hot hydrochloric acid, and at the same time adding salts which exert a catalytic action—so-called buffer solutions—to increase the dissociative action of the hydrochloric acid (which is employed on the counterflow system), and continuously precipitating the heavy-metal chlorides which are simultaneously formed.

A great variety of processes for recovering metallic tin and lead are already known. Apart from the well-known purely metallurgical processes, these processes consist in dissolving the starting materials in mineral acids, according to general analytical principles and without adopting any other special measures, the metals being deposited—mostly by electrolytic means—from the saturated solution, in a suitable manner according to the requirements of the case.

It is also known to add salts to the hydrochloric acid employed for acting on metals and minerals. Such salts comprise, for example, chlorates, chromates and nitrates, that is to say, salts which readily give off oxygen in the same way as nitric acid; and the sole reason for the addition of these salts is to increase the process of oxidation forming the object of the reactions. The addition of such salts is intended to impart to the hydrochloric acid the character of aqua regia.

In contrast to this, however, the salts added to the dissolving baths according to the invention are not oxidizing agents, and their addition is solely for the purpose of exerting a catalytic influence on the reaction.

To make the invention clear, it should be stated at the outset that the process constituting the invention is carried out under conditions involving reduction and not under conditions involving oxidation. My experience has shown that tin from ores is insoluble in concentrated HCl even in the presence of catalysts. In analytic chemistry it is well recognized that heated SnO_2 is not affected by acids, but according to the present invention, tin can also be recovered from ores by concentrating the tin, in the undissolved state, after leaching out the other metals, and then recovering the metallic tin from these residues by metallurgical treatment.

It has been found that all non-oxidizing salts, soluble in hydrochloric acid, such as chlorides, sulphates and phosphates, can be employed as buffer solutions, especially highly dissociated salts such as calcium chloride, sodium sulphate, magnesium chloride, cupric chloride and the like.

In comparison with the known processes, that according to the invention differs therefrom in that catalytic salts exclusively are used in conjunction, with pure hydrochloric acid unmixed with any other acids. In combination with the simultaneously employed counterflow system, consisting in the continuous renewal of the spent hydrochloric acid and the uninterrupted removal of the other metals which contaminate the metal to be recovered, these salts enable the process to be carried out in the perfectly economical manner which has often been attempted before, but always without success.

The added salts manifest themselves as decided catalysts, since they do not take any direct part in the process of solution. In this respect they differ in a very substantial manner from the oxidizing salts added to the hydrochloric acid in the known processes already referred to.

The process according to the invention is preferably carried out in such a way that, after the separation of the elementary copper and antimony and the removal of the lead chloride, the hydrochloric solution of stannous chloride, continuously enriched with fresh hydrochloric acid is allowed to act repeatedly on fresh metal, on the counterflow system, until practically saturated. By this means, 25 parts of tin can be dissolved, in addition to lead, copper, etc., in 100 parts of hydrochloric acid a result which could not

be anticipated and has never before been attained.

The tin is recovered from the hydrochloric solution of stannous chloride by neutralizing the solution with lime or chalk, separating by filtration the resulting solution of calcium chloride from the insoluble part, and drying such residue, from which the tin is then recovered by any convenient known method. The calcium chloride resulting from the neutralization with lime or chalk can be used again as catalyzer for dissolving a fresh batch of material.

Example 1

1 kilogram of waste turnings is granulated, and in the case of a typical composition of 50% tin, 25% lead, 12% antimony, 10% copper, 1% zinc and 2% iron is suffused with 3000 grms. of concentrated hydrochloride acid, with the addition of 1500 grms. of water containing 500 grms. of calcined calcium chloride in solution. The whole is heated to boiling, and is maintained at that temperature for 4 hours, the acid being filtered off from the copper and antimony while hot, and left to cool, thus causing the lead chloride to separate out. This is removed by filtration, and the filtrate is allowed to act on a fresh charge of granulated material in the same way as before. The operation is repeated until the liquor ceases to act on a fresh charge, a condition usually attained after the fifth charge has been treated. The total duration of the reaction is about twelve hours. The original material is repeatedly subjected to the action of fresh acid, until completely decomposed. After the hot filtration from copper and antimony, the final solution is diluted to about 5 litres, to ensure the complete deposition of the lead, and the filtrate, now free from lead, is neutralized with lime or chalk, about 1 kilog. of chalk being used in the case of the above charge. Boiling effects the complete deposition of the tin, which is then pressed and dried, the residue being further treated, in known manner, to recover the tin in the metallic state.

Example 2

1 kilog. of composition dross, containing 35% of tin, 40% of lead, 10% of antimony, 3% of copper and 2% of zinc, is granulated and treated in the above described manner with 2 kilogs. of concentrated hydrochloric acid, 1 kilog. of water and 333 grms. of calcium chloride. In the case of this crude metal, the period of reaction must be prolonged but in other respects the treatment is the same as in Example 1.

Example 3

1 kilog. of ore, concentrated and roasted for the recovery of lead, is leached with 1–1⅜th kilogs. of boiling hydrochloride acid (of 20–22° Bé. strength), according to the lead content, and treated with 200 grms. of calcium chloride, dissolved in 100 litres of water, in order to obtain complete dissociation. After the first working period of about four hours the liquid is drawn off, and cooled in order to deposit the lead chloride. The almost lead-free acid is employed to act on a fresh charge of ore, whilst the ore which has already been leached once is acted upon by fresh acid. This process is repeated until all the lead has been extracted, which is usually the case after the fourth treatment. The spent acid still contains a little lead, copper and zinc, and is first diluted with water, to ensure complete deposition of the lead, after which it is filtered off and the copper and zinc are recovered in known manner.

What I claim is:—

1. The hereindescribed process of recovering tin and associated metals from alloys and mechanical mixtures which contain tin and which may or may not contain iron, consisting in treating such alloys and mixtures with a hot solution containing predetermined amounts of hydrochloric acid and of a non-oxidizing soluble salt of a strong acid.

2. The hereindescribed process of recovering tin and associated metals from alloys and mechanical mixtures which contain tin and which may or may not contain iron, consisting in subjecting such alloys and mixtures to counter-flow treatment with a hot solution containing predetermined amounts of hydrochloric acid and of a non-oxidizing soluble salt of a strong acid.

3. The hereindescribed process of recovering tin and associated metals from alloys and mechanical mixtures which contain tin and which may or may not contain iron, consisting in treating such alloys and mixtures with a hot solution containing predetermined amounts of hydrochloric acid and of a non-oxidizing soluble salt of a strong acid, and continuously precipitating heavy metal chlorides from the solution.

4. The hereindescribed process of recovering tin and associated metals from alloys and mechanical mixtures which contain tin and which may or may not contain iron, consisting in treating such alloys and mixtures with a hot solution containing predetermined amounts of hydrochloric acid and of a non-oxidizing soluble salt of a strong acid to form a solution of stannous chloride, continuously enriching the solution with fresh hydrochloric acid, and permitting the enriched solution to act repeatedly on fresh metal.

5. The hereindescribed process of recovering tin and associated metals from alloys and mechanical mixtures which contain tin and which may or may not contain iron, consisting in treating such alloys and mixtures with a hot solution containing predetermined

amounts of hydrochloric acid and of a non-oxidizing soluble salt of a mineral acid.

6. The hereindescribed process of recovering tin and associated metals from alloys and mechanical mixtures which contain tin and which may or may not contain iron, consisting in treating such alloys and mixtures with a hot solution containing predetermined amounts of hydrochloric acid and of a non-oxidizing soluble salt of a mineral acid, and continuously precipitating heavy metal chlorides from the solution.

7. The hereindescribed process of recovering tin and associated metals from alloys and mechanical mixtures which contain tin and which may or may not contain iron, consisting in treating such alloys and mixtures on the counter-flow system with a hot solution containing predetermined amounts of hydrochloric acid and of a non-oxidizing soluble salt of a mineral acid.

8. The hereindescribed process of recovering tin and associated metals from alloys and mechanical mixtures which contain tin and which may or may not contain iron, consisting in treating such alloys and mixtures on the counter-flow system with a hot solution containing predetermined amounts of hydrochloric acid and of a non-oxidizing soluble salt of a mineral acid, and continuously precipitating from the solution those metals which contaminate the tin.

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