UNITED STATES PATENT OFFICE.

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ELECTROLYTIC REFINING OF TIN.

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To all whom it may concern:

Be it known that I, ELMER A. SPERRY, a citizen of the United States, residing at Brooklyn, in the county of Queens and State of New York, have invented new and useful Improvements in Electrolytic Refining of Tin, of which the following is a specification.

This invention relates to the refining of tin, such as slag tin, dross tin or other impure tins or alloys of tin, or tin bearing material.

I have discovered there are conditions under which an electric deposit of tin of great purity may be produced. Tin is a peculiar metal in that it alloys with a great many other metals and when so alloyed, even though the foreign metal may be present in minute quantity, the luster of the tin is destroyed, or so far reduced as to render it undesirable. In connection with the electrical production of tin of great purity I have discovered that at least two elements are essential: the first that the electrolyte used in the depositing bath should not only be suited to the conditions of the deposition, but the tin bearing material should itself have received a previous treatment with reference to its electrical depositing characteristic or the characteristics of the electrolytic deposition of its tin content, and it is to the satisfying of these conditions together with other collateral details that the present invention relates.

The first step in the present method or process is the treating or conditioning the tin bearing material; this may consist in eliminating some of the impurities which are found to prevent a deposit of high purity. Again I have found that some of the impurities upon or within the cathode tin are due to particles or bodies of slime emanating from the anode and being brought in contact with the cathode, and it is one of the objects of this invention to overcome this difficulty.

I find that there are a number of electrolytes that may be employed with advantage, some have advantage over others when handling anodes bearing certain impurities; among these may be cited the sulfates, ammonium-oxalate, ammonium-sulfid, the chlorids and fluorids, hydrochloric and hydrofluoric acids; all of these I assume have heretofore been known in the art. The novelty in the present invention rests in the combined steps of the process, which together produce the result or such a portion of such steps as produce the result, as is pointed out in the claims hereto annexed and forming a part hereof. I prefer an electrolyte in which copper is not soluble under the working conditions. I find that in most electrolytes the objectionable impurities, among which is lead, are segregated out from the other impurities which are left behind and together with the lead tend to deposit upon the cathode along with the tin; especially is this true at an elevated temperature which is preferable in increasing the electrical conductivity of the electrolytes and aiding in holding the cost of operation within commercial limits. From one standpoint it may be understood that this cost should be as low as possible, especially from the fact that the anode slimes and impurities in the raw tin or tin bearing material carry but comparatively small values. A particular difficulty with impure tin deposit at the cathode, and especially when the impurity is lead or associated with lead, consists in fact that such cathodes are spongy and porous and unfit for melting because of excessive amounts of dross, which is formed.

I first melt the anode tin, alloy, or tin bearing material and while still in the molten state and while considerably above the fusing point I prefer to treat it by a process known as poling; this is accomplished by plunging a log or logs of green wood into the molten mass whereupon the steam gradually generated from the water and salts in the sap of the wood agitates the metal and causes it together with the impurities to be subjected to the combined action of the gases and vapors and the air whereby some of the impurities become oxidized and eliminated. The dross is allowed to accumulate on the top of the metal, which consists in certain oxidation products of the lead and also some of the other objectionable impurities; this may be skimmed off and removed, leaving the tin bearing material sufficiently free or low in these impurities so that it may be employed to yield a cathode product of the desired purity when electrolyzed in a suitable electrolyte. During the poling operation or in lieu thereof I may employ a foreign substance as an oxidating agent, such for instance as a nitrating element. For instance I may employ saltpeter which is introduced very gradually into the molten mass to hasten the formation of the oxidation products. The use of the nitrating element only becomes necessary when the objectionable impurities are present in certain complex combinations, or in excessive amounts. It is while the tin

bearing material is at high temperature that in some instances I find it of advantage to add a sliming or non-soluble element, preferably a metallic element for the purpose hereinafter stated. The melt is now allowed to stand for some time, quiescent for the purpose of cooling, as one of the important features for best results is that the temperature should be correct when the anodes are cast. I have found that far better anodes are made from the tin bearing material, or alloys, that are cast "cool" than when poured hot. Anodes poured at a low temperature that is not far removed from its congealing point and especially at the predetermined temperature dissolve more smoothly and act far more uniformly, being freer from crystalline structure and irregularities and are also higher in electrical conductivity, all of which will be recognized as being important in this art. This casting melt may not be the same as the treating melt, but may be a separate melt and in different form of furnace and fixtures or it may be of advantage to treat the alloy at one point and to electrolyze it at a distant point. The anodes are now ready for the final step, namely, electro depositing; this is accomplished in the usual manner and in a general way—similar to copper deposition. In the case of tin great care is here necessary to prevent the anode slimes from reaching the cathodes, inasmuch as the amount of these slimes are considerably in excess of the amount present in the case of copper. Any of the well known methods may be employed for this process, as for instance, the use of a suitable diaphragm located between the electrodes or surrounding one of such electrodes. Furthermore, I prefer in most instances to circulate the electrolyte or anolyte to facilitate the removal of the impurities and slimes and to prevent them from accumulating in the immediate neighborhood of the anodes and thus cut down the electric conductivity of the bath. This circulation I may also utilize for maintenance of proper temperature and also for distributing such temperature throughout the cell or group of cells. For best results the temperature should be held with some electrolytes as high as 85 degrees centigrade; usually some degrees lower is a fair average found practical to maintain. In cases where the impurities are not found to produce "slimes" but tend to dissolve or disseminate throughout the electrolyte it is found an advantage to employ a coagulating material which is suitably added to the bath or to the molten tin bearing material or alloy as mentioned above. This naturally adds to bind or mass the impurities as they are released at the anode: to illustrate such metal copper may be mentioned—a small amount of which is dissolved and distributed throughout the melt.

The refined tin produced by this method is of a high degree of purity; the total impurity should be well under .01%; it is farther characterized by a high degree of brightness and a remarkable freedom from tarnishing on exposure to damp atmosphere; the durability and tenacity with which it retains its silvery luster is one of its marked characteristics.

The impurities accumulate in the electrolyte and are eliminated by periodical withdrawal of portions and treatment thereof or withdrawal and replacing with pure and fresh electrolyte. The treatment in this case may be illustrated in the use of stannous chlorid as electrolyte. Here the electrolyte withdrawn is treated with quick lime or milk of lime or a suitable alkali and the tin precipitated as tin oxyhydrate, which is utilized as raw tin oxid, is smelted or is "roasted" and separated or concentrated to eliminate the impurities. The tin may then either be smelted or utilized as fixed oxid; the impurities in whole or part are left behind in the precipitating process. That portion thrown down with the precipitate is eliminated in the roasting or concentrating or separating process.

Having pointed out the essential features of my process or method of refining tin, I may state that the process should in no way be limited to the exact details of the method described in reference to any particular step or the exact order of steps which are simply given as illustrating one method of carrying my process into effect. It should also be mentioned that my process may be varied in some of its parts to suit the special alloy or peculiarities of raw tin or alloy to be refined; thus suiting itself to the characteristics of the impurity carried. In these cases, some of the steps may be altered or omitted entirely and the invention extends to such use as set forth in the claims forming a part hereof.

I claim,

1. The method of refining tin which consists in dissolving a tin bearing material in a suitable electrolyte passing an electric current through an electrolytic diaphragm within the electrolyte, and depositing tin at the cathode.

2. The method of refining tin which consists in electrolytically dissolving tin bearing material at the anode in the suitable electrolyte and depositing tin at the cathode, and suitably isolating the cathode from contact with the residues of such solution.

3. The method of refining tin which consists in dissolving a tin bearing material in a suitable electrolyte passing an electric current through an electrolytic diaphragm within the electrolyte depositing tin at the cathode and circulating the electrolyte.

4. The method of refining tin which consists in dissolving a tin bearing material in a

suitable compound electrolyte passing an electric current through an electrolytic diaphragm within the electrolyte depositing tin at the cathode and circulating the anolyte.

5. The method of refining tin which consists in melting the raw alloy, bringing the molten material to a high temperature, thus changing its electro depositing characteristics and electro depositing the mass so treated in a suitable electrolyte.

6. The method of refining tin which consists in bringing the material while in the molten state to a high temperature, thus bringing about a condition which will yield a predetermined characteristic in the electrolytic deposit of the tin content and electrolyzing the resulting mass in a suitable electrolyte and depositing tin therefrom.

7. The method of refining tin which consists in bringing the material while in the molten state to a high temperature, thus bringing about a condition which will yield a predetermined characteristic in the electrolytic deposit of the tin content and electrolyzing the resulting mass and depositing tin therefrom in the presence of a halogen acid.

8. The method of refining tin which consists in melting the raw alloy, bringing the molten material to a high temperature, thus changing its electro depositing characteristic and electro depositing the mass so treated in a suitable electrolyte, at an elevated temperature.

9. The method of refining tin, which consists in melting the alloy or tin bearing material, treating the molten material to improve its slime coagulating qualities and electro depositing the resulting mass in a suitable electrolyte.

10. The method of refining tin, which consists in melting the alloy or tin bearing material, treating the molten material to improve its slime coagulating qualities and also to a high temperature to change its electro depositing characteristic and electro depositing the resulting mass in a suitable electrolyte.

11. The method of refining tin, which consists in melting the raw alloy, treating the molten material by process known as "poling" to change its electro depositing characteristic and electro depositing the mass so treated in a suitable electrolyte.

12. The method of refining tin which consists in melting the raw alloy, treating the molten material with a chemical re-agent to oxidize same and thus change its electro depositing characteristic and electro depositing the mass so treated in a suitable electrolyte.

13. The method of refining tin, which consists of melting the raw alloy, bringing the molten material to a high temperature, thus changing its electro depositing characteristics, cooling the mass, pouring into molds, and electro depositing the mass thus obtained in a suitable electrolyte.

14. The method of refining tin, which consists of melting the raw alloy, bringing the molten material to a high temperature, thus changing its electro depositing characteristics, cooling the mass to a predetermined point, pouring into molds, and electro depositing the mass thus obtained in a suitable electrolyte.

15. The method of refining tin, which consists in suitably preparing anodes of tin bearing material, dissolving same in a suitable electrolyte, passing electric current through an electrolytic diaphragm within the electrolyte, depositing tin at the cathode, circulating the electrolyte, withdrawing a portion of such electrolyte and treating same to eliminate impurities.

16. The method of refining tin, which consists in suitably preparing anodes of tin bearing material, dissolving same in a suitable electrolyte, passing electric current through an electrolytic diaphragm within the electrolyte, depositing tin at the cathode, circulating the electrolyte, withdrawing a portion of such electrolyte and treating same to eliminate both the tin content and impurities and returning the tin to the process.

17. The method of refining tin, which consists in melting the raw tin or alloy, suitably treating the molten mass at an elevated temperature to improve its slime-coagulating qualities, allowing the mass to cool to a predetermined point, then casting into anodes; electrolyzing the anodes in a diaphragm cell, heating and agitating the electrolyte in such cell, withdrawing portions of such electrolyte, precipitating the tin bearing materials from such portions, treating the precipitate by suitably concentrating it to eliminate impurities and returning the heated precipitate to the process.

In testimony whereof I have hereunto set my hand in presence of two subscribing witnesses.

ELMER A. SPERRY.

Witnesses:
A. M. STURR,
S. S. TAYLOR.