Patented May 27, 1941 2,243,165

UNITED STATES PATENT OFFICE

2,243,165

RECOVERY OF TIN

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No Drawing. Application March 8, 1940, Serial No. 323,034

11 Claims. (Cl. 204—121)

This invention relates to the recovery of tin, particularly by the utilization of electrolytic methods, and includes novel types of electrolytic baths for the recovery of tin.

In the prior art a great many attempts have been made in various directions to recover tin from tin scrap and other alloys containing the metal tin, because of the very wide use of tin for industrial and commercial purposes. These prior art methods are of various types including both electrolytic and non-electrolytic methods, although the electrolytic methods have proved most feasible, and have gone into wide use. In the use of electrolytic methods difficulties are encountered, particularly in the recovery of tin from tin scrap, especially where such tin scrap involves tin plate utilized in food containers or for analogous purposes, which tin scrap includes for the most part decorated, varnished or lacquered tin or tin plate. While electrolytic methods have been applied to the recovery of tin from such tin scrap, the prior art methods have necessitated initial treating operations to free the metal from the decorated coatings in order to avoid interference of such coatings with the electrolytic methods usually carried out under alkaline conditions. Unless initially removed in the prior art methods, the coating materials were attacked by the alkali in the electrolytic bath and interfered with the maintenance of preferred conditions in the electrolytic cell. But initial washing or alkaline treatment of the scrap prior to electrolytic treatment require additional steps in the operation, and are undesirable and uneconomical. They have nevertheless been widely used because no methods have heretofore been known which enable the recovery of tin to be carried out without such initial treatment, if any economy of operation and efficiency of process is to be approached. In addition, a number of the prior art methods attempt to recover the tin under conditions where the tin is converted into a salt or component of an electrolytic bath, which is subjected to electroplating of the tin upon a desired article or surface. The solutions thus obtained, however, are not economically used directly for electroplating methods, and attempts to recover the tin in the form of an electrolyte directly applicable for electroplating has interfered with more economical methods for recovery of the tin from tin scrap and other tin plate and tin alloys.

Among the objects of the present invention is included the recovery of tin from tin plate, tin scrap and tin alloys by simple and economical methods.

Other objects include electrolytic baths enabling such processes to be carried out.

Still further objects and advantages will appear from the more detailed description set forth below, it being understood that this more detailed description is given by way of illustration and explanation only and not by way of limitation, since various changes therein may be made by those skilled in the art without departing from the scope and spirit of the present invention.

In accordance with the present invention, tin is recovered from metals containing it, including tin scrap, tin plate and tin alloys, particularly with lead, copper and antimony in an alkaline electrolytic bath containing additions and adjuvants which enable the electrolytic treatment to be carried out directly applied to the material serving as the source of tin used as anode, without requiring any initial washing or alkaline treatment, or other preparation of the tin scrap or other source of tin prior to the electrolytic treatment. Pre-treatment or preparation of the metal for recovery of the tin is thus eliminated. No attempt is made in the electrolytic step of recovering the tin as a plating or as a substantially pure metal, nor is the tin produced in the form of an electrolyte suitable for use in electroplating operations. The treatment in accordance with the present invention is carried out under electrical conditions that a deposit is obtained on any desired cathode, such as iron or tin plated iron, in the form of a mud containing substantial amounts of tin, both in the free state and as oxide. The mud thus obtained is subjected to any desired treatment for recovery of the tin values therefrom. For example, the mud is desirably compressed into briquettes and heated to a temperature sufficient to melt the tin therein, which molten metal drains from the mud briquette and is collected. Tin oxide in the mud is recovered by reduction as by heating with charcoal or other reducing agents under such conditions that the tin produced is melted and drained from the mass. Under proper working conditions the tin thus recovered is obtained substantially free from other metals, and particularly from copper, antimony and lead so frequently used for alloying purposes with tin.

It has been found that certain specific metal compounds should be present for the most efficacious recovery of the tin in the electrolytic step referred to. The metals employed for this

purpose are cobalt and aluminum. The cobalt is desirably in the form of oxide, or hydrated oxide, and preferably in the cobaltous rather than the cobaltic state, while the aluminum, because of the use of the alkaline bath, is in the form of aluminate. While either of these metals can be used alone, the most feasible process is that in which both cobalt and aluminum are present in the electrolyte, by which means the tin is recovered substantially free from contaminating metals of the character noted. The cobalt may be added as oxide directly to the alkaline bath, or the addition of any soluble cobalt salt will result in the precipitation of oxide, or hydrated oxide, or hydroxide by the alkali present. The aluminate may be added as such, or more desirably is formed directly in the electrolyte from any soluble aluminum salt, or from any compound which will form aluminate in reaction with the alkali.

Other adjuvants include substances which desirably affect the electrolytic treatment being carried out, and particularly such substances as dextrine and starch, which substances materially improve the operation.

The path employed is, therefore, an aqueous bath containing free caustic soda, the metallic compounds, cobalt oxide and aluminate, and the adjuvants, dextrine and starch. While the proportions of those ingredients may vary, for the production of the best type of metal and economy in operation, the amount of free alkali should be from 7 to 10% free caustic soda in the solution, while the cobalt, aluminum, dextrine and starch additions should desirably be about 1½%, and these additions should desirably be in a definite ratio of 4 parts of cobalt oxide to 2 parts of aluminate, 2 parts of dextrine and 1 part of starch. In giving these proportions, it should be understood that the specific values indicated give pronounced results; but variation from those proportions can be made, although the efficacy of the process is affected to some extent.

The temperature of the electrolyte during the treatment may be room temperature, or higher temperatures may be employed as, for example, hot solutions may be used, such as at temperatures of 60 to 80° C. The current density employed is that ordinarily used in the recovery of tin from tin scrap, both low and high current densities being available. For example, 70 amperes per square meter may desirably be used.

In illustrating the method of the present invention, tin scrap decorated or undecorated may be used as anode, and subjected to electrolysis in an aqueous electrolytic bath containing 7 to 10% free caustic soda, and 1½% of cobalt oxide, aluminate, dextrine and starch in the preferred ratio of 4:2:2:1 as indicated above, using the usual cathode such as iron or iron plate. Upon electrolysis a cathode mud is produced containing tin and tin oxide, substantially free from contaminating metals. The mud is removed from the electrode and refined in any desired way to recover the tin values. Thus the mud scraped from the electrode may be compressed into briquettes, and the latter placed directly over a grate using a wood fire. The free tin present melts and drips through the grate to a collecting plate. The tin oxide falls through the grate and mixes with the hot ashes and charcoal, which serves to reduce the oxide of tin. The reduction operation is desirably carried out in the absence of air, as by covering the fire.

The electrolytic bath used gives pronounced effects, and it is believed that the cobalt present prevents contamination of the cathode mud by copper, that the aluminum present prevents contamination of the mud by iron, while the dextrine and starch respectively prevent contamination by antimony and lead. Regardless of any theoretical considerations, however, utilization of electrolytic baths of the character set forth enables the results described to be obtained. Desirably, therefore, the electrolytic bath utilized contains all of the ingredients specified. The concentration of caustic should be maintained substantially within the limits indicated, and additions of caustic may be made from time to time to maintain the desired concentration.

Having thus set forth my invention, I claim:

1. In the process of electrolytic detinning decorated or undecorated tin, tin scrap, or tin alloys with copper, antimony and lead without any initial washing treatment, the step of treating said tin product as anode in an aqueous electrolytic bath containing free caustic alkali and a small quantity of cobalt oxide under current conditions depositing a cathode mud containing tin and tin oxide.

2. In the process of electrolytic detinning decorated or undecorated tin, tin scrap, or tin alloys with copper, antimony and lead without any initial washing treatment, the step of treating said tin product as anode in an aqueous electrolytic bath containing free caustic alkali and a small quantity of cobalt oxide and an alkali metal aluminate under current conditions depositing a cathode mud containing tin and tin oxide.

3. In the process of electrolytic detinning decorated or undecorated tin, tin scrap, or tin alloys with copper, antimony and lead without any initial washing treatment, the step of treating said tin product as anode in an aqueous electrolytic bath containing free caustic alkali and a small quantity of an alkali metal aluminate under current conditions depositing a cathode mud containing tin and tin oxide.

4. In the process of electrolytic detinning decorated or undecorated tin, tin scrap, or tin alloys with copper, antimony and lead without any initial washing treatment, the step of treating said tin product as anode in an aqueous electrolytic bath containing free caustic alkali and a small quantity of cobalt oxide, an alkali metal aluminate, dextrine and starch under current conditions depositing a cathode mud containing tin and tin oxide.

5. In the process of electrolytic detinning of decorated or undecorated tin, tin scrap, or tin alloys with copper, antimony and lead without any initial washing treatment, the step of treating said tin product as anode in an aqueous electrolytic bath containing free caustic alkali in an amount of from 7 to 10% and about 1½% collectively of a cobalt oxide, an alkali metal aluminate, dextrine and starch under current conditions depositing a cathode mud containing tin and tin oxide.

6. In the recovery of tin by electrolytic detinning of decorated or undecorated tin, tin scrap, or tin alloys with copper, lead and antimony without any initial washing treatment of the metal under conditions producing a cathode mud containing tin and tin oxide, an aqueous electrolytic bath of free caustic alkali, and a small amount of a cobalt oxide.

7. In the recovery of tin by electrolytic detinning of decorated or undecorated tin, tin scrap, or tin alloys with copper, lead and antimony without any initial washing treatment of the metal under conditions producing a cathode mud containing tin and tin oxide, an aqueous electrolytic bath of free caustic alkali, a small amount of a cobalt oxide, and an alkali metal aluminate.

8. In the recovery of tin by electrolytic detinning of decorated or undecorated tin, tin scrap, or tin alloys with copper, lead and antimony without any initial washing treatment of the metal under conditions producing a cathode mud containing tin and tin oxide, an aqueous electrolytic bath of free caustic alkali, and a small amount of an alkali metal aluminate.

9. In the recovery of tin by electrolytic detinning of decorated or undecorated tin, tin scrap, or tin alloys with copper, lead and antimony without any initial washing treatment of the metal under conditions producing a cathode mud containing tin and tin oxide, an aqueous electrolytic bath of free caustic alkali, and a small amount of a cobalt oxide, an alkali metal aluminate, dextrine and starch.

10. In the recovery of tin by electrolytic detinning of decorated or undecorated tin, tin scrap, or tin alloys with copper, lead and antimony without any initial washing treatment of the metal under conditions producing a cathode mud containing tin and tin oxide, an aqueous electrolytic bath containing free caustic alkali in an amount of from 7 to 10% and 1½% collectively of a cobalt oxide, an alkali metal aluminate, dextrine and starch.

11. In the recovery of tin by electrolytic detinning of decorated or undecorated tin, tin scrap, or tin alloys with copper, lead and antimony without any initial washing treatment of the metal under conditions producing a cathode mud containing tin and tin oxide, an aqueous electrolytic bath containing free caustic alkali in an amount of from 7 to 10% and 1½% collectively of a cobalt oxide, an alkali metal aluminate, dextrine and starch, in the ratio of 4:2:2:1.

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