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ELECTRODEPOSITION OF TIN AND ITS ALLOYS

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15 Claims. (Cl. 204—54)

This invention relates to the electrodeposition of metals and more particularly to the electroplating, electrorefining, electrowinning and electroforming of tin and tin alloys, such as solder and terne.

One object of the present invention is to provide a novel and improved process and electrolyte for the production of a smooth, dense, fine, adherent deposit of the above metals and alloys, which is free from objectionable impurities.

Another object is to provide a cheap, dependable, efficient and commercially practical process and electrolyte for electrodepositing a plate or coating of superior quality.

Another object is to provide an efficient, dependable and economical process for the commercial production of tin plate.

Another object is to provide a novel and improved process for the electrorefining, electroplating, electrowinning or electroforming of tin, and tin-lead alloys.

Various other objects and advantages will be apparent as the nature of the invention is more fully disclosed.

Although the novel features which are believed to be characteristic of this invention are more particularly pointed out in the claims appended hereto, the invention itself may be better understood by referring to the following description in which a specific embodiment thereof has been set forth for purposes of illustration.

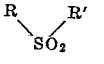
The present process is an improvement on that disclosed in my prior Patent No. 1,487,124, dated Mar. 18, 1924, which utilizes the aromatic sulphonic acids of benzene, phenol and cresol, together with a protective agent, such as sulfuric acid, to precipitate lead as an electrolyte for the electrodeposition of tin. When used in conjunction with cresylic acid and glue as addition agents, according to Pat. No. 1,397,222 to F. C. Mather, dated Nov. 15, 1921, the process functions very satisfactorily for certain refining operations. However, organic addition agents, particularly cresylic acid and like materials, contain impurities of a tarry nature. The latter not only contaminate the bath, but are, to a certain extent, mechanically occluded or co-deposited with the metal at the cathode. While this action may be unobjectionable from a refining standpoint where the cathode is eventually melted, the presence of such material is highly objectionable in a plating operation producing thin tin coatings for protective or decorative purposes. Moreover, the usual addition agents formerly used are depleted rapidly during the electrolysis, thus requiring constant renewal, if the optimum concentration of addition agent is to be maintained and the best deposit produced at all times. I have found that, if a compound of the class hereinafter disclosed is present as a component of the electrolyte, smooth, dense, fine crystalline deposits substantially free from objectionable organic impurities can be continuously produced.

The present invention is also applicable to electrorefining, electroforming or electrowinning operations and provides a deposit which adheres to the cathode and may subsequently be stripped therefrom and/or melted down for the recovery of the metal.

In the electrodeposition of tin, the metal is cast into anodes which are used in a suitable electrolyte for plating or depositing onto a cathode. If tin only is to be deposited, the electrolyte is operated under conditions to prevent deposition of other metals. The bath may, for example, contain a protective agent such as sulphuric acid to precipitate any lead which may be present and prevent the same from depositing at the cathode. If lead and tin are to be co-deposited as an alloy such an agent is, of course, omitted.

The present invention provides an ingredient which, when incorporated in the electrolyte, causes the deposit to have the characteristics above mentioned. This ingredient is herein referred to for convenience as an addition agent, although it is not consumed to the extent of the usual addition agent, but is substantially permanent in its effect, being in this respect similar to a catalyst. The term "addition agent" is accordingly not to be construed as descriptive of the operation or action of the ingredient.

More specifically, I have found that certain sulphonyl compounds (sulphones) of the type



where R and R′ represent aromatic radicals of the benzene or naphthalene series, each having as substituents one or more hydroxy groups, are suited for the above purpose. I prefer a sulphone of phenol having the formula

$$(C_6H_5OH)_2SO_2$$

Other soluble aromatic sulphones may also be used, such as the sulphones of cresol, resorcinol, and naphthol, or, in general, those forming soluble salts of the metal or metals to be deposited.

The above mentioned substances may be used in various electrolytes. For the deposition of tin or tin-lead alloys the electrolyte may comprise

the mono- and poly-sulphonic acids of benzene, phenol and cresol and the related chloro and nitro sulphonic acids, fluosilicic acid or fluoboric acid. The above acids are readily obtainable at low cost and have the property of readily dissolving tin or tin and lead from the anodes.

The disulphonic acids are particularly suitable because they form extremely soluble salts of tin and lead. I prefer benzene disulphonic acid.

A satisfactory electrolyte may have the following composition:

	Grams per liter
Benzene meta disulphonic acid	200–400
Sulphone of phenol	5– 25
Tin, or tin and lead	20– 80

Other suitable acids may, of course, be substituted in place of benzene disulphonic acid.

For refining purposes, a temperature range of from 40 to 80 degrees C. may be used with a current density of from 10 to 100 amperes per sq. foot. The cell voltage at a current density of 15 amperes per sq. foot and an electrode spacing of 1¼ inches may vary from 0.10 volt to 0.30 volt, depending upon the age and purity of the anode. For plating thin deposits, higher voltages and current densities may be employed.

Other addition agents, such as glue, may be used if desired, but are not essential and if used at all the quantity should be small. The sulphone is the essential ingredient in promoting the formation of a smooth, dense, firm, adherent deposit, substantially free from organic impurities. The comparatively high acid content and elevated temperature range is favorable to good deposition and reduces the electrical energy required.

In all cases for the deposition of pure tin, a precipitating agent such as sulphuric acid is added to remove the lead as in my prior Patent No. 1,487,124. The other metals which may be present as impurities are either insoluble and go into the slimes, or are not deposited until after the tin has been removed.

The above described electrolyte has been found to continuously produce a deposit which is substantially free from objectionable organic impurities, and will operate without adjustment over considerably longer periods of time than has heretofore been possible. The process is suited to any use in which tin is to be deposited, such as refining, winning, forming, plating, etc. and is also applicable to the deposition of tin-lead alloys such as solder or terne. Of course, for the latter purpose the presence of sulphuric acid in the electrolyte would be avoided, otherwise the lead would be precipitated out and deposition thereof would be prevented.

While certain specific embodiments of the invention have been set forth for purposes of illustration, it is to be understood that the invention may be applied to various uses and that changes and modifications may be made therein as will be apparent to a person skilled in the art. The invention is only to be limited in accordance with the following claims.

What is claimed is:

1. An electrolyte for the deposition of a substance selected from the group consisting of tin, and tin-lead alloys, which comprises an acid solution of said substance and a sulphone of a substance selected from the group consisting of phenol, cresol, resorcinol and naphthol.

2. An electrolyte for the deposition of a substance selected from the group consisting of tin, and tin-lead alloys, which comprises an acid solution of said substance and a sulphone of phenol.

3. An electrolyte for the deposition of a substance selected from the group consisting of tin and tin-lead alloys which comprises said substance in solution in an acid selected from the group consisting of the mono and poly sulphonic acids of benzene, phenol and cresol, and the related chloro and nitro sulphonic acids, and a sulphone of a substance selected from the class consisting of phenol, cresol, resorcinol and naphthol.

4. An electrolyte for the deposition of a substance selected from the group consisting of tin, and tin-lead alloys, which comprises said substance in solution in benzene disulphonic acid and a sulphone of phenol.

5. An electrolyte for the deposition of a substance selected from the group consisting of tin and tin-lead alloys, which comprises the following ingredients in about the following proportions:

	Grams per liter
Benzene disulphonic acid	200 to 400
Sulphone of phenol	5 to 25
Tin or tin plus lead	20 to 80

6. The method of refining metallic materials containing a substance selected from the group consisting of tin, and tin-lead alloys, which comprises making such material into an anode and electrolyzing the same in an electrolyte comprising an acid solution of said substance, and a sulphone of a substance selected from the group consisting of phenol, cresol, resorcinol and naphthol.

7. The method of refining metallic materials containing a substance selected from the group consisting of tin, and tin-lead alloys, which comprises making such material into an anode and electrolyzing the same in an electrolyte comprising an acid solution of said substance and a sulphone of phenol.

8. The method of refining metallic materials containing a substance selected from the group consisting of tin, and tin-lead alloys, which comprises making such material into an anode and electrolyzing the same in an electrolyte comprising an acid selected from the group consisting of the mono and poly sulphonic acids of benzene, phenol and cresol, and the related chloro and nitro sulphonic acids, and a sulphone of a substance selected from the group consisting of phenol, cresol, resorcinol and naphthol.

9. The method of refining metallic materials containing a substance selected from the group consisting of tin, and tin-lead alloys, which comprises making such material into an anode and electrolyzing the same in an electrolyte comprising benzene disulphonic acid and a sulphone of phenol.

10. The method of refining metallic materials containing a substance selected from the group consisting of tin, and tin-lead alloys, which comprises making such material into an anode and electrolyzing the same in an electrolyte comprising the following ingredients in about the following proportion:

	Grams per liter
Benzene disulphonic acid	200 to 400
Sulphone of phenol	5 to 25
Tin or tin plus lead	20 to 80

11. The method of electrodepositing a substance selected from the group consisting of tin and tin-

lead alloys from an acid electrolyte containing said substance in solution, which comprises electrolyzing the same in the presence of a sulphone represented by the formula



where R and R′ each represents an aromatic radical selected from the group consisting of the benzene and the naphthalene radicals, each aromatic radical having as substituent at least one hydroxy group.

12. An electrolyte for the deposition of a substance selected from the group consisting of tin, and tin-lead alloys, which comprises an acid solution of said substance and a sulphone represented by the formula



where R and R′ each represents an aromatic radical selected from the group consisting of the benzene and the naphthalene radicals, each aromatic radical having as substituent at least one hydroxy group.

13. An electrolyte for the deposition of a substance selected from the group consisting of tin, and tin-lead alloys, which comprises said substance in solution in an acid selected from the group consisting of the mono and poly sulphonic acids of benzene, phenol and cresol, and the related chloro and nitro sulphonic acids, and a sulphone represented by the formula



where R and R′ each represents an aromatic radical selected from the group consisting of the benzene and the naphthalene radicals, each aromatic radical having as substituent at least one hydroxy group.

14. The method of refining metallic materials containing a substance selected from the group consisting of tin, and tin-lead alloys, which comprises making such material into an anode and electrolyzing the same in an electrolyte comprising an acid solution of said substance and a sulphone represented by the formula



where R and R′ each represents an aromatic radical selected from the group consisting of the benzene and the naphthalene radicals, each aromatic radical having as substituent at least one hydroxy group.

15. The method of refining metallic materials containing a substance selected from the group consisting of tin, and tin-lead alloys, which comprises making such material into an anode and electrolyzing the same in an electrolyte comprising an acid selected from the group consisting of the mono and poly sulphonic acids of benzene, phenol and cresol, and the related chloro and nitro sulphonic acids, and a sulphone represented by the formula



where R and R′ each represents an aromatic radical selected from the group consisting of the benzene and the naphthalene radicals, each aromatic radical having as substituent at least one hydroxy group.

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