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ALKALINE ANTIMONY PLATING

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This invention relates to alkaline antimony plating and more specifically to an alkaline antimony plating solution and process involving the use of antimony compounds of the antimonyl type together with hydroxycarboxylic acids and sufficient alkaline material to produce the desired high pH.

While alkaline antimony tartrate plating solutions have been mentioned in the literature, they have left something to be desired in stability and practical plating results and have not found commercial use to any substantial extent so far as I am aware. Antimonyl compounds are fairly soluble but are known to be unstable in that precipitation is likely to occur when the temperature is elevated. Alkaline antimony plating is suitable for application to zinc base die castings where acid solutions are not successful and basket type anode containers composed of steel can be used in an alkaline solution whereas steel would be attacked by an acid solution. It is therefore clear that the art is in need of an improved plating process making use of an alkaline antimony solution.

It is an object of the present invention to provide a stable alkaline antimony plating solution capable of producing smooth, continuous and strongly adherent antimony deposits. A further object is to provide such a solution which remains stable at elevated temperatures, at least as high as 160° F. and preferably as high as 210° F. A further object is to provide a solution in which an antimony anode will corrode smoothly and efficiently. A still further object is to provide a solution which will be continuously stable for a long period of time and free from precipitation due to minor pH changes.

The foregoing and other objects, as will be pointed out, can be attained by the use of solutions which will now be described. The batch ingredients may be:

(1) An antimony compound of the antimonyl type, based upon a hydroxy carboxylic acid such as tartaric acid or gluconic acid,

(2) A hydroxycarboxylic acid, or an alkali metal or amine salt of a hydroxy carboxylic acid,

(3) An alkaline material of the class consisting of alkalies such as alkali metal hydroxides and carbonates, and amine bases such as alkyl and alkanol amines and alkyl and alkanol ammonium hydroxides. Such solutions contain in equilibrium, (*a*) trivalent antimonyl complex ions, such as antimonyl tartrate,

$$((SbO)C_4H_4O_6)^{--}$$

antimonite ions $(SbO_2)^-$, and the ions of the alkali (e. g. sodium) and the organic acid employed. The concentration of the trivalent antimony ions is at all times small, the complex ion acting as a reservoir of antimony. When the stabilizer such as triethanolamine or tetraethanol ammonium hydroxide is used as suggested hereinafter, there will be present also an antimony amino complex the structure of which is not known with certainty but which is believed to be analogous to the metal ammonium complexes such as the cuprammonium complex.

Compounds of the antimonyl type which preferably are utilized according to the invention are sodium antimonyl tartrate and sodium antimonyl gluconate. The corresponding potassium compounds can be used almost as satsifactorily but are somewhat less effective when used in the same concentration and substantially more expensive. It has been found that aqueous solutions of these compounds, although not satisfactory for antimony plating when used alone, become so when used in connection with an excess of hydroxycarboxylic acid radical over and above that present in the antimonyl complex and at a suitable pH. In other words, in addition to such compounds as sodium antimonyl tartrate and sodium antimonyl gluconate, it is necessary to employ therewith compounds such as sodium tartrate and sodium gluconate and sufficient alkali such as caustic soda or amine base, such as an alkyl amine or an alkanol amine or an alkyl ammonium hydroxide or an alkanol ammonium hydroxide, to adjust the pH to a value within the range from 8.5 to 13.0.

The amount of antimonyl complex suitably is such that the concentration of antimony element (Sb) is from 20 to 90 grams per liter. The concentration of hydroxy carboxylic acid radical (combined in the antimonyl complex and outside such complex) must be within such limits that the ratio of gram equivalent weights of alphahydroxyl to the gram atomic weights of Sb is from 4:1 to 8:1. Stated another way, t he number of hydroxyl groups in alpha position, considered as ultimate groups, made up of one atom of hydrogen and one atom of oxygen, must be from 4 to 8 times the number of antimony atoms. This is more than the number of alpha hydroxyl groups which can be contained in the antimonyl complex and defines the concentration of alpha hydroxy acid radical not contained in the antimonyl complex. The concentration of caustic soda, triethanol amine, triethanol ammonium hydroxide or the like is that which is required to produce a pH from 8.5 to 13.0.

In the case of gluconic acid there is one alpha hydroxyl for each formula weight while in the case of tartaric acid there are two. Thus, in the case where gluconic acid is the basis, the number of formula weights in grams is the number of gram equivalents of alpha hydroxyl. In the case of tartaric acid, the number of formula weights in grams is one-half the number of gram equivalents of alpha hydroxyl, there being two alpha hydroxyl groups in tartaric acid.

The pH may be adjusted by means of an alkali metal hydroxide or carbonate or alkyl amine or alkyl ammonium hydroxide without utilizing any alkylol amine base, but for greatest stability, at least part of the alkaline material used for pH elevation should be an alkylol amine base, suitably an alkanol amine or alkanol ammonium hydroxide having from 2 to 8 carbon atoms. It is essential in these solutions to use the alkylol amine or the alkylol ammonium hydroxide rather than the alkyl amine or alkyl ammonium hydroxide in order to obtain the special stabilizing effect beyond that due merely to higher pH. When operating at the lower end of the pH range of 8.5 to 13.0, it is more important to have the benefit of the alkylol amine or alkylol ammonium hydroxide. The quantity of alkanol amine thus employed may vary from an effective amount to the entire amount of alkaline

material needed for pH adjustment, suitably from one gram per liter to 150 grams per liter.

The following specific examples will serve to illustrate the invention:

Example No.	1	2	3	4	5	6	7	8	9	10
$SbCl_3$, g./l.	80	80	80	80					80	80
Sb_2O_3, g./l.					52	52	52	52		
Tartaric Acid, g./l.	168	168	168	112	112	112	168	168		
Gluconic Acid, g./l.			25		15	35	15	50	275	100
Triethanolamine, cc./l.		100								
Tetraethanolammonium hydroxide g./l.										50
Pb^{++}, g./l.	.05									
Glue, g./l.	2.0									
NaOH or amine base to a pH of	13.5	8.5	8.5	13.5	13.2	13.2	13.2	9.0	8.5	11.0
Temperature, ° F.	140	140	140	140	140	140	140	140		
Cathode Current Density, ASF	20	20	20	20	20					

Having thus described the invention, what is claimed is:

1. An alkaline antimony electroplating solution comprising, in addition to water, antimonyl complex material selected from the class consisting of sodium antimonyl tartrate, sodium antimonyl gluconate and mixtures thereof, the sodium salt of a hydroxy acid of the class consisting of tartaric acid and gluconic acid, and sodium hydroxide, the concentration of antimony (Sb) being from 20 to 90 grams per liter, and the ratio of gram equivalent weights of alpha hydroxyl to the gram atomic weights of antimony being from 4:1 to 8:1, and the concentration of sodium hydroxide being sufficient to produce a pH value from 8.5 to 13.0.

2. A process comprising electrolyzing the solution of claim 1 at a cathode current density from 5 to 40 amperes per square foot.

3. An alkaline antimony electroplating solution comprising, in addition to water, sodium antimony tartrate, the sodium salt of tartaric acid and sodium hydroxide, the concentration of antimony (Sb) being from 20 to 90 grams per liter, the ratio of gram equivalent weights of alpha hydroxyl to the gram atomic weights of antimony (Sb) being from 4:1 to 8:1, and the concentration of sodium hydroxide being sufficient to produce a pH value from 8.5 to 13.0.

4. A process comprising electrolyzing the solution of claim 3 at a cathode current density from 5 to 40 amperes per square foot.

5. An alkaline antimony electroplating solution comprising, in addition to water, sodium antimony gluconate, the sodium salt of gluconic acid, and sodium hydroxide, the concentration of antimony (Sb) being from 20 to 90 grams per liter, the ratio of gram equivalent weights of alpha hydroxyl to the gram atomic weights of antimony (Sb) being from 4:1 to 8:1, and the concentration of sodium hydroxide being sufficient to produce a pH value from 8:5 to 13.0.

6. A process comprising electrolyzing the solution of claim 5 at a cathode current density from 5 to 40 amperes per square foot.

7. An alkaline antimony electroplating solution comprising, in addition to water, an antimonyl complex of a polyhydroxy acid, the concentration of said complex being such that the antimony content thereof is from 20 to 90 grams per liter, there being an excess of said polyhydroxy acid over the theoretical amount contained in said complex and the ratio of gram equivalent weights of alpha hydroxyl to the gram atomic weights of antimony being from 4.1 to 8:1 and there being present sufficient alkaline material of the class consisting of alkali metal hydroxides and carbonates, ammonium hydroxide, alkyl amines and alkyl ammonium hydroxides to produce a pH in the range from 8.5 to 13.0.

8. A process comprising electrolyzing the solution of claim 7 at a cathode current density from 5 to 40 amperes per square foot between a cathode and an antimony anode.

9. An electroplating solution according to claim 7 wherein the said alkaline material is replaced to the extent of from one gram per liter to 100% by an amine base of the class consisting of alkanol amines and alkanol ammonium hydroxides having from 2 to 8 carbon atoms.

10. An electroplating solution according to claim 1 wherein the sodium hydroxide is replaced by an amine base to the extent of at least one gram per liter and not more than 150 grams per liter of such amine base, the latter being selected from the class consisting of alkanol amines and alkanol ammonium hydroxides having from 2 to 8 carbon atoms.

11. An electroplating solution according to claim 3 wherein the sodium hydroxide is replaced by an amine base to the extent of at least one gram per liter but not more than 150 grams per liter of such amine base, the latter being selected from the class consisting of alkanol amines and alkanol ammonium hydroxides having from 2 to 8 carbon atoms.

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