United States Patent Office

2,823,176

Patented Feb. 11, 1958

2,823,176

ANTIMONY PLATING BATH AND PROCESS

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No Drawing. Application November 30, 1953
Serial No. 395,292

8 Claims. (Cl. 204—45)

This invention relates to improvements in the electrodeposition of antimony and more particularly to an improved electrolyte for the deposition of smooth adherent coatings of antimony.

In many instances electrodeposits of antimony produced by prior antimony plating solutions and processes have not only been coarse-grained, poorly adherent and extremely brittle but also have had a poor surface quality which has necessitated extensive buffing and/or polishing.

We have now discovered that an improved electrodeposit of antimony is obtained from electrolytes utilizing a combination of certain addition agents. The first type of addition agents of the present invention comprises sulfonated hydroxy aromatic compounds and preferably those which, in addition to a sulfonate radical and hydroxy grouping, have at least one additional substituted grouping which is capable of complexing dissolved metals to form five or six membered ring structures. Typical of the type of organic addition agents contemplated in the present invention are the compounds obtained by sulfonating substituted phenols, catechol, derivatives of catechol such as 3-5 dihydroxy toluene (orcinol), isomers of catechol such as resorcinol; trihydroxy phenols such as pyrogallol, phloroglucinol; hydroxy aromatic carboxylic acids such as salicylic acid or B-resorcyclic acid; hydroxy aromatic aldehydes such as salicylaldehyde; 8-hydroxy quinoline; and naphthols such as 1-3 or 1-8 dihydroxy naphthalene.

In certain applications, it is advantageous to employ, in addition to, or in lieu of the above-mentioned additives, certain unsulfonated compounds including polyhydric alcohols such as glycerol, ethylene glycol, propylene glycol, mannitol, sorbitol, dulcitol, erythritol, or pentaerythritol; unsulfonated sugars such as dextrose, levulose or sucrose; as well as unsulfonated sugar acids such as gluconic, mucic, and saccharic acids. It will be understood, of course, that the present invention contemplates the use of the above addition agents as well as mixtures thereof. Moreover, sodium, potassium, ammonium, amine, or antimony salts of the various compounds also may be used.

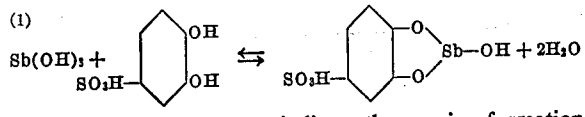
In general, additives of the present invention form various complex organo-metallic salts which regulate the availabilty of metallic ions in solution. The actual chemical and electrochemical reactions occurring during plating using the additives of the present invention are not clearly understood at present. However, the following discussion, indicating sulfonated catechol as an additive, is set forth to aid in understanding the invention.

Sulfonated catechols may be used effectively in either acid or alkaline antimony plating baths. It will be understood, of course, that in the sulfonation of catechol, mono, di and tri sulfonic acids are obtained, the amounts of each depending upon the technique of sulfonation. Hence,

in the following reactions, although a mono-sulfonic acid is illustrated, similar reactions occur using di-sulfonic acid, tri-sulfonic acid or a mixture of these acids.

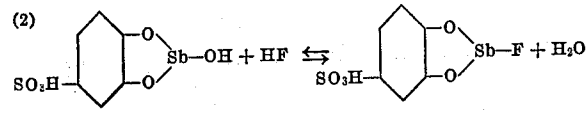
The effectiveness of the sulfonated catechol is thought to depend primarily on the complexing of antimonious hydroxide which, in an acid solution, is indicated as follows:

(1)

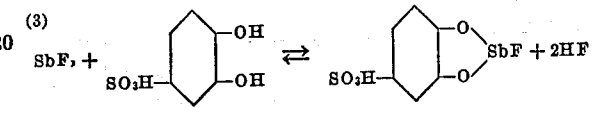


The following reactions indicate the ensuing formation of mono-sulfonated antimony-catechol complex:

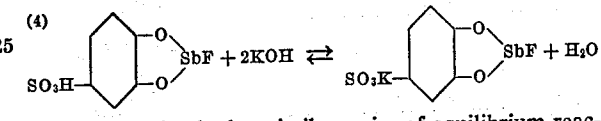
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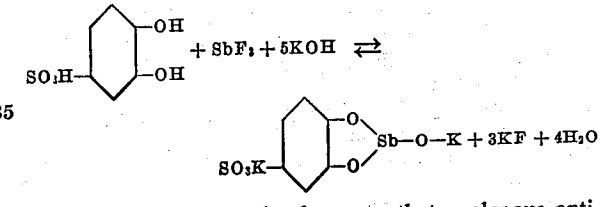
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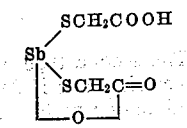
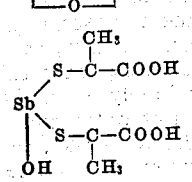
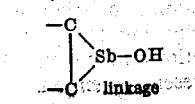
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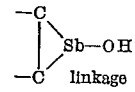
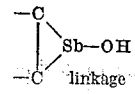
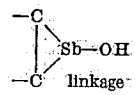
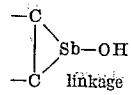
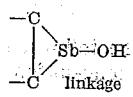
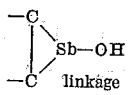
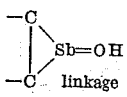
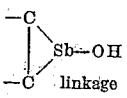
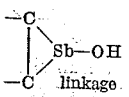


In an alkaline bath a similar series of equilibrium reactions occur as summarized in the following equation:



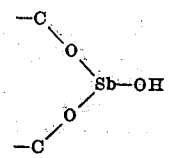
It will be understood, of course, that analogous antimony complexes can be formed using other additives of the present invention. The following table summarizes by compound and corresponding formula some of the antimony complexes formed in accordance with the present invention.

Compound	Formula
Antimony Catechol	$C_6H_4O_3SbOH$
Antimony Pyrogallol	$C_6H_4O_3SbOH$
Antimonyl Thioglycollic Acid	
Antimonyl Thiolactic Acid	
Antimonyl Thioglycollamide	$Sb(SCH_2CONH_2)_3$
Ethylene Glycol	 linkage

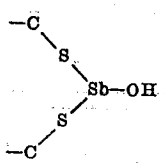
Compound	Formula
Propylene Glycol	
Trimethylene Glycol	
Glycerine	
Erythritol	
Penta Erythritol	
Sorbitol	
Mannitol	
Arabitol	
Dulcitol	

Similar antimony complexes may be formed using polyhydroxy aldehydes and ketones, polyhydric alcohols of the cyclohexane type such as quercitol and inositol, as well as various sugar acids.

In general, organic antimony complexes formed in accordance with the present invention may be characterized as organic esters and/or thioesters having the following structure:



or as



The second type of additive, which may be used alone in certain cases if desired, but is preferably employed in combination with one or more of the aforementioned organic additives, comprises certain inorganic cations other than antimony, as, for example, zirconium, magnesium, nickel, copper, cobalt and strontium ions. Such cations preferably are provided by the addition to the plating solution of water-soluble salts of the desired metals such as sulfates, nitrates, acetates or chlorides although satisfactory results also are obtained by employing salts which are relatively or substantially insoluble in water, sufficient dissolution being obtained in the plating solution. The following tabulation sets forth a number of inorganic cations which may be employed in the practice of the present invention.

Metal Constituent	Source of Metal	Solubility
Al	$Al_2(SO_4)_3.9H_2O$	Soluble.
Ba	BaF_2	Slight.
Be	Beryllium Stearate	Very Slight.
Cd	$Cd(SO_3)_2$	Do.
Co	$CoSO_4.7H_2O$	Slight.
Cr	CrO_3	Soluble.
Fe	$FeSO_4.7H_2O$	Slight.
Mg	$MgSO_4.7H_2O$	Do.
Mn	$MnSO_4.7H_2O$	Do.
Mo	$H_2MoO_4.H_2O$	Do.
Ni	$NiSO_4.6H_2O$	Do.
Si	$Si(SO_4)_2$	Do.
Ta	TaK_2F_7	Do.
Th	$Th(NO_3)_4.4H_2O$	Soluble.
Ti	TiO_2	Very Slight.
Va	$VaSO_4.7H_2O$	Soluble.
Zr	ZrF_4	Do.
Sr	$SrSO_4$	Do.

The following are examples of antimony baths in accordance with the present invention as used in acid media in which the quantities expressed are per liter of water:

Example I

125 g. antimony fluoride
135 cc. sulfonated catechol (81.0 g. catechol)
175 g. potassium hydroxide
10 g. aluminum sulfate

pH	1–4.0.
Current density	15–25 A. S. F.
Temperature	115–125° F.
Anodes	Bagged antimony.
Agitation	Cathode rod.

Example II

220 g. antimony fluoride
241 cc. sulfonated catechol (144.5 g. catechol)
50 g. magnesium sulfate heptahydrate
300 g. potassium hydroxide

pH	3.0–4.5.
Current density	15–25 A. S. F.
Temperature	120° F.
Anodes	Bagged antimony.
Agitation	Cathode rod.

Example III

220 g. antimony fluoride
241 cc. sulfonated catechol (144.5 g. catechol)
325 g. potassium hydroxide
50 g. zirconium fluoride

pH	4.0.
Current density	20 A. S. F.
Temperature	130° F.
Anodes	Bagged antimony.
Agitation	Cathode rod.

Example IV

220 g. antimony fluoride
235 cc. sulfonated catechol (141.0 g. catechol)
300 g. potassium hydroxide
25 g. nickel catechol sulfonate

pH	4.0.
Current density	15.0–25 A. S. F.
Temperature	115–130° F.
Anodes	Bagged antimony.
Agitation	Cathode rod.

Example V

220 antimony fluoride
235 cc. sulfonated catechol (141.0 g. catechol)
300 g. potassium hydroxide
35 g. cobalt catechol sulfonate

pH	4.0.
Current density	20 A. S. F.
Temperature	125° F.
Anodes	Bagged antimony.
Agitation	Cathode rod.

The above baths may be operated satisfactorily within a pH range from about 1 to 5, the upper pH limit generally being that at which precipitation of antimony occurs. It is preferred to operate the bath using a current density within the range of from 10 to 25 amperes per square foot. The preferred bath temperature is 120° F. although the baths generally may be operated at a temperature within the range from room temperature, i. e., 70° F. to 75° F., to about 165° F.

In many instances it is preferred to employ a metallic salt of an organic additive such for example, as nickel catechol sulfonate or cobalt catechol sulfonate. Such a salt provides additional organic additive in solution while supplying the desired inorganic cation without introducing undesired foreign ions into the bath.

Acid baths of the present invention as illustrated by the foregoing examples generally may contain from about 20 to 300 grams per liter of dissolved antimony, 150 grams per liter being preferred and about 20 to 300 grams per liter of total organic additive. Using antimony fluoride, 110 to 265 grams per liter produce superior results, 220 grams per liter being preferred. The amount of potassium hydroxide to be employed is determined by the amount of free acid present in the organic additive, the concentration of antimony, and, of course, the pH desired. The quantity of a particular metal salt (source of the cationic additive) to be used generally may vary from a small but effective amount, i. e. a few milligrams of metal per liter, to an upper limit determined by the solubility of the salt in the plating solution.

Illustrative of an alkaline bath embodying the invention is the following in which the quantities expressed are per liter of water:

Example VI

90 g. antimony fluoride
150 g. potassium hydroxide
95 cc. catechol sulfonate (57 g. catechol)
10 g. aluminum sulfate

pH	12.0.
Current density	15–24 A. S. F.
Temperature	120° F.
Anodes	Bagged antimony.
Agitation	Cathode rod.

Alkaline plating solutions embodying the present invention may be operated at various pH values although it is preferred to employ a pH of 10 or higher, the upper practical limit or pH being that at which undesirable precipitates form. The amounts of the alkaline bath ingredients can, of course, be varied, the organic additive content varying from about 20 to 300 grams per liter. The maximum antimony content is generally dictated by the solubility of the antimony compound in the bath, the amount increasing with an increase in pH. To employ a maximum amount of antimony, it is essential that the molar ratio of antimony to the organic additive be at least 1:1. The amount of potassium hydroxide depends on the pH regulation necessary. As in the case of acid baths, the quantity of inorganic ions utilized may vary from a very small amount, such as a few milligrams of metal per liter up to the limit of solubility of the source of the cations in the plating solution.

Various antimony salts, in addition to antimony fluoride, such as antimony oxide, antimony sulfonate, antimony pentafluoride, antimony pentoxide, potassium meta antimonite, butyl amine antimonyl tartrate, urea antimonyl tartrate, aniline antimonyl tartrate, benzyl amine antimonyl tartrate, phenyl hydrazine antimonyl tartrate, ammonium antimonyl citrate, potassium antimonyl glycollate, potassium antimonyl citrate, sodium antimonyl citrate, antimony potassium tartrate, antimony sodium tartrate, and antimony tartrate also may be employed.

Similarly, instead of the sodium hydroxide or potassium hydroxide indicated in the examples, the pH may be regulated using ammonia, or organic amines, such as butyl amine, trimethylamine or ethanolamine.

In the electrodeposition of antimony, as in other plating processes, proper preparation of the surface to be coated is essential. In depositing antimony on copper, for example, we have found that it is desirable to electrolytically etch the surface to be coated for about one to five minutes at a current density of approximately 5 amperes per square foot in a 63% by volume solution of phosphoric acid. In depositing antimony on steel it is generally advantageous to etch the steel in nitric acid, preferably diluted 1:3.

As an example of the preparation of a plating bath embodying the invention, 890 grams of catechol were added slowly to 1568 grams of C. P. sulfuric acid while maintaining the temperature of the reaction mass within the range from 85° C. to 95° C. for two hours after the last catechol was added. The resultant catechol sulfonic acid contained approximately .62 gram of catechol per cubic centimeter of crude sulfonation mass. To complete preparation of the bath, 241 cc. of the sulfonation mass was then added to an antimony fluoride solution containing about 165 grams per liter of antimony, and 50 grams per liter of aluminum sulfate, the pH being adjusted to about 5 using sodium hydroxide.

It is to be understood that, although the invention has been described with specific reference to particular embodiments thereof, it is not to be so limited since changes and alterations therein may be made which are within the full intended scope of this invention as defined by the appended claims.

What is claimed is:

1. An electroplating bath comprising approximately 20 to 300 grams per liter of solution of antimony, a metallic cation in addition to antimony in a small amount effective to provide a smooth, adherent, non-brittle antimony plate up to the maximum amount soluble in the plating bath, and a complexing agent capable of complexing dissolved antimony to form a five-membered ring, wherein said ring-forming complexing agent is sulfonated catechol present in approximately 20 to 300 grams per liter of solution.

2. An electroplating bath as in claim 1 in which the metallic cation other than antimony is aluminum.

3. An electroplating bath as in claim 1 in which the metallic cation other than antimony is zirconium.

4. An electroplating bath as in claim 1 in which the metallic cation other than antimony is magnesium.

5. An electroplating bath as in claim 1 in which the metallic cation other than antimony is nickel.

6. An electroplating bath as in claim 1 in which the metallic cation other than antimony is copper.

7. An electroplating process which comprises passing electric current from an anode to a cathode through the bath of claim 1.

8. An electroplating bath as in claim 1 in which the antimony is present in the form of antimony fluoride.

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