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ANTIMONY PLATING BATH

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4 Claims. (Cl. 204—45)

This invention relates to improvements in the electrodeposition of antimony and more particularly to an improved bath and process 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 poorly adherent and extremely brittle, but also have exhibited a poor surface quality and have been difficult to buff or polish.

We have now discovered that the aforementioned difficulties can be avoided and improved electrodeposits of antimony obtained from aqueous baths containing sulfonated hydroxy aromatic compounds. Preferred sulfonated hydroxy aromatic compounds contain, in addition to a sulfonate radical and hydroxy grouping on the aromatic nucleus, at least one additional substituted grouping which is capable of complexing dissolved metals to form five or six membered ring systems. Typical of the type of 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, B-resorcylic 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. Similarly, sodium, potassium, ammonium, amine, or antimony salts of the various compounds may be used.

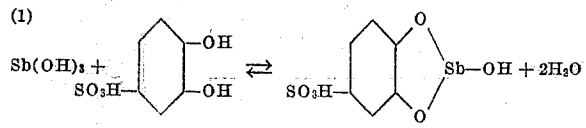
In general, additives of the present invention form various complex organo-metallic salts which regulate the availability of metallic ions in solution. The actual chemical and electrochemical reactions occurring during plating using the additives of the present invention are not clearly understood at 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

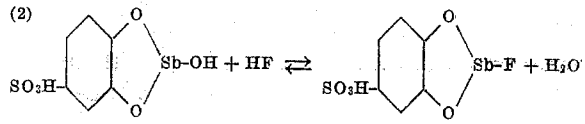
hydroxide which, in an acid solution, is indicated as follows:

(1)

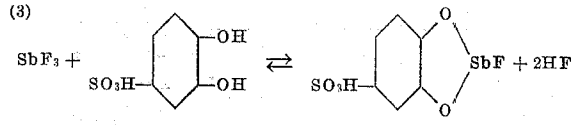


The following reactions indicate the ensuing formation of monosulfonated antimony-catechol complex:

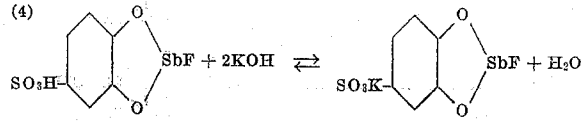
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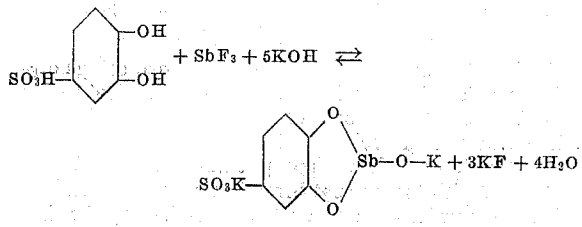
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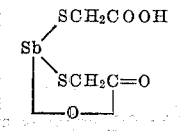
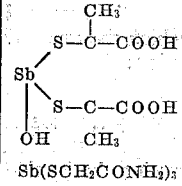
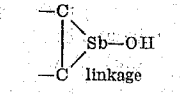
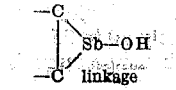
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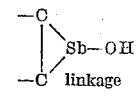
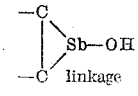
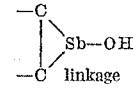
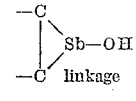
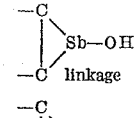
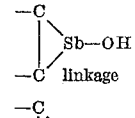
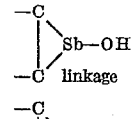
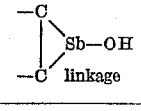


In an alkaline bath a similar series of equilibrium reactions occur as summarized in the following equation:



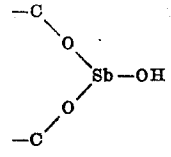
It will be understood, of course, that analogous antimony complexes can be formed using other additives of the present invention. The following table summarizes by compound and corresponding formula some of the antimony complexes formed in accordance with the present invention.

Compound	Formula
Antimony Catechol	$C_6H_4O_2SbOH$
Antimony Pyrogallol	$C_6H_3O_3SbOH$
Antimonyl Thioglycollic Acid	
Antimonyl Thiolactic Acid	
Antimonyl Thioglycollamide	$Sb(SCH_2CONH_2)_3$
Ethylene Glycol	
Propylene Glycol	

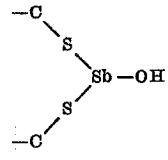
Compound	Formula
Trimethylene Glycol	
Glycerine	
Erythritol	
Pentaerythritol	
Sorbitol	
Mannitol	
Arabitol	
Dulcitol	

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 following is an example of a particular antimony bath of the present invention as used in an acid medium in which the quantities are expressed in grams per liter of solution:

Example I

Antimony fluoride	220
Sulfonated catechol	237
Potassium hydroxide	300

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

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

Example II

Antimony fluoride	220.
Crude sulfonated catechol mixture	405 (137 grams catechol).
Potassium hydroxide	420.

This bath generally may be operated at a pH of 12 or greater over a range of temperatures and at a current density within the range from about 10 to 30 amperes per square foot although at present it is preferred to operate the bath at a temperature of about 140° F. using approximately 12 amperes per square foot.

The following are examples of other antimony plating baths and preferred operating conditions in accordance with the present invention.

Example III

Antimony fluoride	220 g./l.
Glycerol C. P	92 cc.
Ammonium hydroxide	To regulate pH to 2.0.
Current density	25 a. s. f.
Temperature	140° F.

Example IV

Antimony fluoride	220 g./l.
Sorbitol	160 g./l.
Ammonium hydroxide	To regulate pH to 2.0.
Current density	20 a. s. f.
Temperature	140° F.

Example V

Antimony fluoride	220 g./l.
Mannitol	124 g./l.
Ammonium hydroxide	To regulate pH to 2.0.
Current density	30 a. s. f.
Temperature	140° F.

Example VI

Antimony fluoride	220 g./l.
Dextrose	75 g./l.
Ammonium hydroxide	To regulate pH to 2.0.
Current density	25 a. s. f.
Temperature	135° F.

Example VII

Antimony fluoride	220 g./l.
Sucrose	75 g./l.
Ammonium hydroxide	Regulate pH to 2.0.
Current density	20 a. s. f.
Temperature	135° F.

Example VIII

Antimony fluoride	220 g./l.
Levulose	180 g./l.
Ammonium hydroxide	Regulate to 2.0 pH.
Current density	20 a. s. f.
Temperature	135° F.

Example IX

Antimony fluoride	220 g./l.
Mucic acid	20 g./l.
Ammonium hydroxide	To regulate pH to 2.0.
Current density	20 a. s. f.
Temperature	125° F.

Example X

Antimony fluoride	220 g./l.
Gluconic acid	10 g./l.
Ammonium hydroxide	To regulate pH to 3.0.
Current density	20 a. s. f.
Temperature	120° F.

Example XI

Antimony fluoride	220 g./l.
Catechol sulfonic acid mixture	125 cc. (75 g./l. catechol).
Sorbitol	75 g./l.
Sodium hydroxide	To regulate pH to 3.5.
Current density	20 a. s. f.
Temperature	130° F.

Example XII

Antimony fluoride	220 g./l.
Catechol sulfonic acid mixture	190 cc. (114 g./l. catechol).
Gluconic acid	50 g./l.
Sodium hydroxide	To regulate pH to 4.0.
Current density	20 a. s. f.
Temperature	130° F.

Example XIII

Antimony fluoride	220 g./l.
Catechol sulfonic acid mixture	200 cc. (120 g./l. as catechol).
Levulose	45 g./l.
Potassium hydroxide	To regulate pH to 4.0.
Current density	20 a. s. f.
Temperature	125° F.

Example XIV

Antimony fluoride	220 g./l.
Catechol sulfonic acid mixture	200 cc. (120 g./l. as catechol).
Dextrose	45 g./l.
Potassium hydroxide	To regulate pH to 3.5.
Current density	20 a. s. f.
Temperature	125° F.

Example XV

Antimony fluoride	220 g./l.
Sulfonated catechol	71 g./l. (as catechol).
Gluconic acid	107 g./l.
Sodium hydroxide	To regulate pH to 4.0.
Current density	24 a. s. f.
Temperature	120° F.

Example XVI

Antimony fluoride	220 g./l.
Sulfonated catechol	120 g./l. (as catechol).
Mucic acid	30 g./l.
Sodium hydroxide	To regulate pH to 4.0.
Current density	24 a. s. f.
Temperature	120° F.

It will be understood, of course, that the above examples are illustrative only and that suitable pH adjustments can be made to permit operation in an alkaline medium. Moreover, the particular antimony salts employed, as well as the particular addition agents, may be varied. Although the quantities of bath ingredients can be varied, we have found that in most instances it is desirable to employ one or more compounds of antimony in a sufficient amount to provide from about 20 to 165 grams of metallic antimony per liter of solution and an additive of the present invention in an amount generally within the range of about 20 to 300 grams per liter of solution.

Although the above examples illustrate bath compositions using antimony fluoride, it will be understood, of course, that various antimony salts may be employed such as antimony oxide, antimony sulfonate, antimony pentafluoride, antimony pentoxide, potassium meta antomonite, 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 tartrate and antimony sodium tartrate.

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 we have found that it is desirable to electrolytically etch the surface to be coated from one to five minutes at about 5 amperes per square foot in a 63% by volume solution of phosphoric acid at room temperature. 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 1500 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-sulfuric acid mixture contained approximately .60 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 150 grams per liter of metallic ion, the pH adjusted to about 5 using sodium hydroxide, and the resultant mixture heated to 150° F. and treated with activated carbon (3 g./l.) for 2 hours and filtered.

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 electrolytic bath consisting essentially of approximately 20–165 grams per liter of solution of metallic antimony and a complexing agent capable of complexing dissolved antimony to form a five-membered ring, wherein the ring-forming complexing agent is sulfonated catechol present in a concentration of about 20–300 grams per liter of solution.

2. The method of electroplating antimony which comprises passing electric current from an anode to a cathode through the bath of claim 1.

3. An electrolytic bath as in claim 1 in which the antimony is present in the form of antimony fluoride.

4. The method of electroplating antimony which comprises passing electric current from an anode to a cathode through the bath of claim 3.

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