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ANTIMONY PLATING PROCESS

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1 Claim. (Cl. 204—34)

This invention relates to a process for the deposition of metallic coatings on metal surfaces. More particularly, it relates to the electrodeposition of adherent and continuous coatings of antimony on steel, zinc alloy, or copper alloy metals.

It is an object of this invention to deposit antimony coatings on these metals by means of an intermediate layer of substantially pure iron on the metal. Another object is to deposit the coating of antimony on the metal by means of the intermediate layer of pure iron, without roughening the surface of the metal object previous to the coating, and thereby to produce a smooth coating. A further object is to apply an antimony coating on these metals continuously and completely over the object surface. A still further object is to provide a method of coating objects from weak antimony acid plating baths by means of an intermediate coating or layer of substantially pure iron.

With the exception of the method disclosed in copending application, Serial No. 604,593, insofar as is known, no entirely satisfactory method of coating antimony on steel has previously been found. While certain patents in the prior art allude to successful methods of coating antimony on steel directly, these methods require the utilization of strongly corrosive antimony fluoride acid solutions, and therefore are not completely satisfactory. Patent 2,683,114 is representative of the prior art in this respect. When these prior art methods are used to plate antimony directly on steel, the method calls for roughening the steel by sand blasting or etching processes.

Other prior art methods also disclose the more common method of antimony plating, in which a coating of another metal such as copper, zinc, or other nonferrous metal, is coated on the steel object prior to the antimony-plating operation.

In the process of this invention, the antimony plating may be carried out in a weak citric or other aliphatic hydroxy carboxylic acid bath on an unroughened and polished metal object because of the iron plating previously given to the surface of the object. The antimony plate produced by the method of this invention is strongly adherent and may be easily buffed to a high polish. In addition, the antimony plate is continuous, covering the exposed surface completely without leaving unplated spots.

Briefly, the process of this invention includes a new process step immediately prior to the antimony-plating steps. This new process step is an iron-plating operation on the surface of the object to be coated with antimony. The iron-plating operation is immediately followed with a rinse operation and the antimony-plating operation. An intermediate acid dip step may be used in some instances.

Various problems have been encountered in finding entirely satisfactory methods of plating antimony on steel. It has been found that the more commonly used conventional method, which is carried out by applying an intermediate coating of a material such as copper or zinc, is unsatisfactory because the intermediate coating materials

form alloys with antimony, by room-temperature diffusion. It has been found that these alloys are brittle and cause the plated coatings to peel.

This brittle alloy formation has also made antimony plating on zinc alloy metals or copper-base alloy metals unsatisfactory.

One of the other problems is the difficulty of obtaining a continuous coating over all the surface of a steel object. Objects on which a coating of antimony has been applied directly without the benefit of any prior surface treatment on the object other than conventional cleaning have been found to have many dispersed, randomly positioned, unplated spots on the surface. In the electroplating operation, it has been observed that those areas which will receive antimony plate will commence to plate in the very first few seconds after the current is turned on. However, those nonreceptive spots will be immediately apparent, and continued time in the plating operation will not cause any deposit on these spots.

From the observation of these problems, it is presently believed that the application of an adherent and continuous antimony plate on a steel object requires that the object have a chemically uniform surface. It is believed that the reason for nonreceptive spots in direct antimony-plating operations may be the existence at the nonreceptive spots of a greater over-voltage for the antimony than the over-voltage for the hydrogen in the plating bath. It is thought that in this invention, the provision of a previous coating of iron on the object reduces the over-voltage of the antimony at all points on the surface of the object, to a value less than the over-voltage for hydrogen in the plating bath, and the chemically uniform surface results in making possible the continuous antimony plating over all surfaces of the object.

In the operation of the method of this invention, the iron plating is carried out immediately prior to the antimony-plating operation with a rinse step, and possibly an acid-dip step, in between. Many iron plating baths may be used, and conventional techniques employed, in plating the iron on the object to be coated with antimony. It has been found that an iron-plating bath of the formate type will produce a uniform, dense, and continuous iron plate as required in the process of this invention.

A typical composition of an aqueous formate iron-plating bath, which has been successfully used, is as follows:

Ferrous sulfate ($FeSO_4 \cdot 7H_2O$)	g./l.	300
Ferrous chloride ($FeCl_2 \cdot 4H_2O$)	g./l.	42
Boric acid (H_3BO_3)	g./l.	30
Sodium formate ($NaCO_2H$)	g./l.	15
Ammonium sulfate [$(NH_4)_2SO_4$]	g./l.	15
Sodium lauryl sulfate	g./l.	1
Water, to make 1 liter.		
pH		4.0 to 4.2

The plating operations with the above-described bath are carried out preferably at a bath temperature of 140° F. However, sound deposits have been obtained in baths within the temperature range of 120° F. to 160° F.

It has been found that current densities of 30 to 40 amperes per square foot are preferable. However, the geometry of the object being plated, cathode racking procedures, anode placement, and agitation of the bath will dictate the best current density for a particular operation.

The anodes should be pure iron or an iron-carbon-alloy type, such as those known in the plating art as "Armco" or "Globe" iron.

Simple cathode bar agitation has been found satisfactory in the operation of the bath.

It is believed that other well-known iron-plating baths such as an iron sulfate chloride, an iron fluoborate, or

an iron chloride bath could be satisfactorily used in the process of this invention. However, the iron chloride bath would not be preferred because it is usually operated at a temperature of about 195° F. which makes plating operations difficult.

The iron formate-type plating bath described above is preferred because the following process requirements are met: (1) ease of operation, (2) reproducibility of thick, sound, pit-free plating, (3) the iron deposits are stable when heated to annealing temperatures, and (4) the bath does not chemically attack the object being electroplated.

At a current density of between 30 and 40 amperes per square foot, 4×6-inch flat, steel panels may be satisfactorily plated in a period of between 5 and 10 minutes. The time for plating will be dependent on the current density, bath temperature, and shape of the object.

After the object is plated with iron, the object is rinsed and immediately plated with antimony from a weak citric or other aliphatic hydroxy carboxylic acid bath directly on the previously applied iron plate. It may be desirable to perform an acid-dipping operation followed by a rinse between the iron-plating operation and the antimony-plating operation. This intermediate acid dip will insure the removal of precipitated iron salts from the surface of the object which would prevent antimony plating.

A typical citric acid antimony-plating bath is composed and operated as follows:

Composition:	
Potassium citrate ($K_3C_6H_5O_7.H_2O$) ____g./l__	145
Citric acid ($H_3C_6H_5O_7$) ____g./l__	185
Antimony oxide (Sb_2O_3) ____g./l__	60
Water, to make 1 liter.	
pH ____	3.5 to 3.7
Operating conditions:	
Temperature ____° F__	120
Anodes ____	Antimony
Cathode current density ____amp./sq. ft__	30

An example of a typical complete antimony-plating operation on 4×6-inch flat, steel panels, in which the iron-plating step of this invention is combined is as follows:

(1) First the object to be coated is cleaned in a conventional alkaline cleaner solution.

(2) The object is rinsed in water.

(3) The object is immersed or dipped in an acid bath to remove oxide, smut, and other surface impurities. Either sulfuric or hydrochloric acid may be used.

(4) The object is rinsed in water.

(5) The object is connected as the cathode in an aqueous iron-plating bath having the following constituents: ferrous sulfate 300 g./l., ferrous chloride 42 g./l., boric acid 30 g./l., sodium formate 15 g./l., ammonium sulfate 15 g./l., sodium lauryl sulfate 1 g./l., and the balance water. The object is immersed in the plating bath for about 5 minutes with the bath at a temperature of about 140° F. Armco iron anodes are provided. The plating operation is carried out at current density of about 30 amperes per square foot.

(6) The object is rinsed in water.

(7) The object is dipped in an acid bath.

(8) The object is rinsed in water.

(9) The object is electroplated in a citric acid bath of the composition and operating conditions previously described.

One of the advantages to be found in the process of this invention is that a continuous over-all plating of antimony may be produced on an object by means of one of the above-described weak antimony acid plating baths. In the prior art methods of coating antimony on steel by means of strongly corrosive antimony fluoride acid baths, the corrosive nature of the plating bath is a decided disadvantage. The use of such highly corrosive acids makes necessary the provision of expensive ventilating and handling equipment. This invention, by making possible the use of the weak aliphatic hydroxy carboxylic acids, eliminates these problems.

In these prior art methods of plating antimony directly on steel by strong antimony fluoride acid solutions, there is also the disadvantage that these acid solutions attack the object to be plated during the early stages of the plating operation before the object is covered with antimony plate, and, therefore, there is a loss of metal from the object and contamination of the plating bath.

In other prior art methods of coating antimony on steel by means of intermediate coatings such as copper and zinc, it has been found that intermediate coatings of these materials form alloys with antimony by room-temperature diffusion, and that these alloys are brittle and cause the plated coatings to peel. The intermediate coating of iron provided in this invention has been found to remain ductile, and brittle alloys with antimony are not formed. Coatings by the method of this invention have been formed to an angle of 180 degrees after being stored for six months, and the coatings have been found to be pliable with no tendency to peel.

When the iron-plating step of this invention is applied in antimony plating on zinc alloys or copper-base metal alloys, the formation of a brittle alloy between the zinc or copper is prevented. Therefore, by the process of this invention, satisfactory antimony platings can be made on these metals.

It has been found that electropolishing will also condition the surface of the steel to accept antimony plating. However, the electropolishing operation removes metal but the iron preplating process does not. Of course, in a process which removes metal, there is the disadvantage of bath contamination caused by the metal which is successively removed from the succeeding objects. In addition, when the contamination builds up in the electropolishing bath, the iron salts will often be carried into the antimony-plating bath in a normal successive dipping cycle.

It will be understood, of course, that while the forms of the invention herein shown and described constitute preferred embodiments of the invention, it is not intended herein to illustrate all of the possible equivalent forms or ramifications of the invention. It will also be understood that the words used are words of description rather than of limitation and that various changes may be substituted without departing from the spirit or scope of the invention herein disclosed.

What is claimed is:

The process of electrodepositing a continuous spot-free antimony coating on steel from a weak acid solution comprising: cleaning said steel in an alkaline cleaner solution; then rinsing said steel; then treating said steel in an acid dip; then subjecting said steel to a second rinsing; then plating said steel in an aqueous iron plating bath at a temperature of about 140° F., consisting of ferrous sulfate 300 g./l., ferrous chloride 42 g./l., boric acid 30 g./l., sodium formate 15 g./l., ammonium sulfate 15 g./l., sodium lauryl sulfate 1 g./l., and the balance water, said bath having a pH of from about 4.0 to 4.2; then subjecting said steel to a third rinsing; and then electroplating antimony on said steel in a weak citric acid plating bath comprising potassium citrate 145 g./l., citric acid 185 g./l., antimony oxide 50 g./l., and the balance water, said bath having a pH of from about 3.5 to 3.7.

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