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ELECTRODEPOSITION OF ANTIMONY

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The present invention relates generally to the electro-deposition of antimony upon conducting surfaces, more particularly to the electro-deposition of antimony upon the surfaces of metals, and most specifically to the electro-deposition of antimony upon the surfaces of objects composed of steel, copper, aluminum, zinc, lead, nickel, magnesium, and other metals commonly used in industry, and the alloys of such metals.

For modern electroplating purposes, the attainment in a coating of antimony upon a conducting surface, of the properties of ductility, malleability, and adherence to the conducting surface upon which such coating of antimony has been electrodeposited, is important.

Now I have found that it is possible to obtain, upon conducting surfaces, coatings of antimony which possess ductility, malleability, and adherence, for I have succeeded in producing upon surfaces of steel, copper, aluminum, zinc, lead, nicke, magnesium, and other metals commonly used in industry, and the alloys of such metals, coatings of antimony greater than 0.002" in thicknesses, which can be scratched with a knife blade or struck with a hammer or distorted by being bent through angles greater than 90° without peeling or flaking or cracking.

For modern electro-plating purposes, the attainment, in a coating of antimony upon a conducting surface, of the property of corrosion resistance, is of immense importance.

Now I have found that a bright cleavage surface of antimony can be left in a chemical laboratory with its customary fumes for several years without exhibiting any signs of tarnish, and that a bright cleavage surface of antimony can be left exposed to wind and rain during an entire autumn and winter without losing its luster completely. I have further found that antimony, ground to pass a 115 mesh sieve and placed in solutions 0.1 normal in sodium chloride, potassium chloride, ammonium chloride, hydrochloric acid, nitric acid, perchloric acid, sulphuric acid, or ammonium hydroxide, and containing additionally 1 percent of hydrogen peroxide (to provide an enhanced oxidizing environment), showed no appreciable change after four months of any one of such treatments, but that antimony, ground to pass a 115 mesh sieve and placed in solutions 0.1 normal in tartaric acid, oxalic acid, sodium carbonate, or sodium hydroxide, and containing additionally 1 percent of hydrogen peroxide (to provide an enhance oxidizing environment), was attacked rapidly, and that antimony, ground to pass a 115 mesh sieve and placed in a solution 0.1 normal in sodium fluoride, and containing additionally 1 percent of hydrogen peroxide (to provide an enhanced oxidizing environment), was completely converted to Sb_2O_4 in two weeks. It will be noted that the reagents wherein antimony passes into solution are precisely those reagents wherein antimony oxide is soluble.

For modern electro-plating purposes, the attainment, in a coating of antimony upon a conducting surface, and, in particular, in a coating of antimony upon a conducting surface of a substance electro-positive to antimony, of freedom from pores is of the greatest importance, if such coating of antimony is to be corrosion resistant, i. e., if such coating of antimony is to protect satisfactorily the underlying substance upon which it has been electro-deposited.

I have succeeded in producing coatings of antimony upon steel which have been exposed to wind and rain for six months without losing all of their lusters and which exhibit the property of non-corrodibility of the pure chemical element, as such, as above described. I have also subjected such coatings of antimony upon steel to the action of a salt spray bath conforming to the specifications of the test bath outlined in the A. S. T. M. Tentative Standard B-39T, and I have found that such coatings of antimony upon steel will stand up under this test for 120 hours and longer without exhibiting any visible signs of attack or tarnish. Furthermore, when to such coatings of antimony upon steel the ferroxyl test was applied, substantially no pores were revealed, for none of the familiar blue spots appeared after a ten-minute exposure to the test solution of potassium ferricyanide and sodium chloride.

For modern electro-plating purposes, the attainment, upon a conducting surface, of a coating of antimony which can be buffed with ease to a high luster is very desirable, both for reasons of aesthetics and for the furtherance of the impermeability of such coating of antimony. Now most of the coatings of antimony upon conducting surfaces that are described in the prior art are reported to be coarse-grained and difficult to buff.

I have succeeded in producing coatings of antimony upon steel, copper, aluminum, zinc, lead, nickel, magnesium, and other metals commonly used in industry, and the alloys of such metals, which not only are easy to buff to a high luster, but which also possess the property of "flowing" beneath the buffing wheel, thus furthering the impermeability of such coatings and masking out all normal surface irregularities of

the conducting surfaces upon which the coatings of antimony have been electro-deposited.

The principal object of the present invention is to provide a technique for the electro-depositing of antimony upon conducting surfaces generally, more particularly upon the surfaces of metals, and most specifically upon the surfaces of objects composed of steel, copper, aluminum, zinc, lead, nickel, magnesium, and other metals commonly used in industry, and the alloys of such metals, producing ductile, malleable, and adherent coatings of antimony, resistant to abrasion, shock and distortion, non-corrodible per se, non-porous and hence corrosion resistant, and capable of yielding, upon buffing, surfaces of mirror-like finish.

Another object of the present invention is to provide a technique for the electro-depositing of antimony of the character described whereby coatings of antimony upon conducting surfaces suitable for use as bearing surfaces can be attained.

Another object of the present invention is to provide a technique for the electro-depositing of antimony of the character described whereby lamellar materials composed of bonded stratified layers of metallic electro-deposits bonded to metals and comprising layers of electro-deposited antimony can be attained.

All these and other objects of the present invention are attainable by the use of the novel technique for the electro-depositing of antimony upon conducting surfaces presently to be described, an appreciation of which can best be gained by consideration of the successive separate steps thereof, of which the first is the preparation of the electro-deposit-receiving surface.

It is a fact well known in the prior art of electro-plating generally, and, in particular, in the prior art of nickel-plating, that, in order to attain the optimum adherence, as well as the minimum porosity, in electro-deposits, the conducting surfaces upon which the coatings are to be electro-deposited should be as smooth as possible. Such smooth surfaces are also prerequisites in normal commercial plating whenever and wherever finished smooth and bright surfaces are desired, since it is generally not feasible to obtain such surfaces by buffing electro-deposits upon conducting surfaces not given smooth finishes prior to the receptions of the electro-deposits. Thus, for example, the normal procedure in modern electro-plating upon steel surfaces is to start with steel surfaces to which as high polishes as can be economically attained have been imparted.

Now I have found that, for the attainment of the best results in the electro-deposition of antimony, and, notably, for the production, upon conducting surfaces, of coatings of antimony that are remarkably ductile and malleable, a procedure substantially the antithesis of polishing is required, i. e., that the best results in the electro-deposition of antimony are attained when the conducting surface to receive the electro-deposit of antimony either already possesses, or has had imparted to it, a certain measure of roughness, or superficial irregularity. Such superficial irregularity can be imparted to the conducting surface to receive the electro-deposit of antimony either by mechanical means, such as sand blasting, frictional engagement with abrasive agents, or passage of the material through sand-blasted, or otherwise roughened roll, when feasible, or by chemical means, such as the etching of the conducting surface by substances corrosive of the material of the conducting surface. While such superficial irregularity as that produced by such mechanical or chemical roughening means is indispensable for the attainment of the best results in the electro-deposition of antimony upon conducting surfaces, the action of such mechanical or chemical roughening means need not, and should not, be unduly prolonged, since the more pronounced superficial irregularity effected by such prolonged treatments is not necessary, and it increases the difficulty of attaining, by buffing, surfaces of mirror-like finish, should they be desired.

Therefore, for the treatment of the conducting surfaces preliminary to the electro-depositing of the coatings of antimony, I follow the one or the other of the following procedures, depending upon whether mechanical or chemical roughening means are employed to impart to the conducting surfaces the requisite measures of superficial irregularity:

A. The smooth conducting surface is roughened by mechanical means, and then, if it is not clean, it is subjected to the customary cleaning techniques employed in the electro-plating industry, it is then rinsed in water, it is then subjected to the usual activating pickle to remove scale and to destroy passivity, and it is then given a final rinse in water, whereupon if no water breaks are observable upon the roughened conducting surface, the roughened conducting surface is then ready to receive the electro-deposit of antimony from the electro-depositing bath.

B. The smooth conducting surface, if it is not clean, is subjected to the customary cleaning techniques employed in the electro-plating industry, it is then rinsed in water, it is then subjected to an etching by substances corrosive of the material of the conducting surface, it is then rinsed in water, it is then subjected to the usual activating pickle to remove scale and smut and to destroy passivity, and it is then given a final rinse in water, whereupon, if no water breaks are observable upon the etched conducting surface, the etched conducting surface is then ready to receive the electro-deposit of antimony from the electro-depositing bath. The substances corrosive of the material of the conducting surface which are used necessarily depend upon the character of the material of the conducting surface. Thus, for example, for a mild steel surface, I find that subjection of the mild steel surface to the corrosive action of a solution of nitric acid of moderate concentration is suitable, while for a copper surface, I find that subjection of the copper surface to anodic electrolytic action in a solution of phosphoric acid is suitable, and I find that, for an aluminum surface, subjection of the aluminum surface to the corrosive action of a solution of hydrochloric acid of moderate concentration is suitable. These specific chemical means for imparting to surfaces of mild steel, copper, and aluminum superficial irregularity are illustrative: other substances corrosive of mild steel, copper, and aluminum may be employed, if desired, while substances corrosive of other metals commonly used in industry are employed for the purpose of imparting the desired superficial irregularities to their surfaces.

I have found that baths comprising antimony trifluoride and a monovalent base will yield upon roughened or etched conducting surfaces coatings of antimony that fulfill the stated objects of the present invention, and that baths comprising antimony trifluoride and a fluoride of a mono-

valent base yield superior results, because, in all probability, the antimony ion concentrations in such baths are low owing to the formations of complex compounds by and between the antimony trifluoride and the fluorides of the monovalent bases, while baths comprising antimony trifluoride and the fluoride of a monovalent base, in aqueous solution having a hydroxide ion concentration somewhat less than that necessary to produce precipitation, yield still better results. Specifically, I have found that baths comprising antimony trifluoride, and ammonium fluoride, and ammonium hydroxide, in aqueous solution having a hydroxide ion concentration somewhat less than that necessary to produce precipitation, yield electro-deposits of antimony possessing the most desirable characteristics of ductility, malleability, and adherence to the conducting surfaces upon which such electro-deposits of antimony have been electro-deposited.

I have found that the following baths will yield upon roughened or etched conducting surfaces coatings of antimony that fulfill the stated objects of the present invention:

	Grams per liter
A. Antimony trifluoride	248
Sodium hydroxide	7
B. Antimony trifluoride	248
Ammonium hydroxide	53
C. Antimony trifluoride	248
Sodium fluoride	12
D. Antimony trifluoride	248
Ammonium fluoride	200
E. Antimony trifluoride	248
Sodium fluoride	12
Sodium hydroxide	40
F. Antimony trifluoride	248
Ammonium fluoride	200
Ammonium hydroxide	105

In the last mentioned example, the point of precipitation of antimony from the solution at room temperature is about 6.6, while the pH of the solution is about 5.8, or approximately one pH unit below the point of precipitation.

Upon immersion of the roughened or etched conducting surfaces in these electro-depositing baths, two modes of electro-deposition are, in some instances, possible, viz: (*a*) an immersion deposit, and (*b*) the electro-deposits resulting from the direct use of a current of electricity, with the electro-deposit-receiving surfaces forming the cathodes in the electro-depositing baths.

In producing electro-deposits of antimony by the direct use of a current of electricity, I prefer to proceed as follows: after I have imparted to the conducting surface the suitable measure of superficial irregularity and have otherwise prepared it to receive the electro-deposit of antimony, I then immerse it in one of the baths previously described, making it the cathode and using antimony or inert anodes, with a cathodic current density of 15 to 35 amperes per square foot, at room temperature, until an electro-deposit of antimony about 0.0015'' in thickness has been produced upon the conducting surface, which operation requires from an hour to a half hour when the cathodic current densities specified above are used. When antimony anodes are employed, anodic surface sufficiently great to avoid polarization effects must be provided. At low antimony ion constituent concentrations, low cathodic current densities must be employed in order to avoid the appearance of the phenomenon known as "treeing": with larger antimony ion constituent concentrations, larger cathodic current densities can be employed without the occurrence of "treeing" at the corners of the cathode. I have found that, with the use of baths comprising antimony trifluoride, a fluoride of a monovalent base, and the corresponding monovalent base, in aqueous solution having a hydroxide ion somewhat less than that necessary to produce precipitation, not only is "treeing" obviated, but the grain size is decreased and the "throwing power" of the bath is increased. If further decrease in grain size and further increase in "throwing power" of the bath are desired, the following "addition agents," viz, copper fluoride (CuF_2), mercuric fluoride (HgF_2), and telluric fluoride (TeF_4), may be employed in concentrations of approximately 1 to 3 grams of copper, mercury, and tellurium content per liter of bath. Some of the baths described above, to which such "addition agents" have been added, will yield bright electro-deposits of antimony.

The coatings of antimony so produced, when dried, can be buffed to mirror-like finishes. Owing to the fact that a coating of antimony, in buffing, flows upon the surface upon which it has been electro-deposited, a mirror-like surface is produced quite regardless of the superficial irregularity of the conducting surface upon which the coating of antimony has been electro-deposited. This result is of immense importance in the electro-deposition of corrosion resistant and decorative metallic coatings upon steel. Heretofore, it has been necessary to subject steel surfaces to polishing operations of such magnitude as to constitute items of cost greater than the costs of the subsequent electro-depositing and the final finishing of the corrosion resistant and decorative metallic coatings, but by the use of the present invention, the initial costs of the preparation of steel surfaces to receive the corrosion resistant and decorative metallic coatings may be reduced to a minor item.

I have also found that coatings of antimony constitute excellent substrata for electro-depositions of other metallic coatings.

Since the foregoing description and outline of the general character and modes of operation of the present invention comprise preferred embodiments of the present invention, it is to be understood that wide departures from the given procedures and the means employed in such procedures are comprised by the present invention. Thus, for example, the several baths hereinbefore set forth are not to be limited in compositions to the precise compositions given, which are illustrative rather than definitive. Nor, in the preparation of such baths, am I to be limited to the precise ingredients set forth, for it is a well known fact that antimony trifluoride forms with fluorides of monovalent bases double salts; and since certain of the baths hereinbefore set forth can, most conveniently, be prepared by the use of such double salts, and since these baths, so prepared by the use of such double salts, are in no respect different from these baths prepared by the use of antimony trifluoride and fluorides of monovalent bases, obviously such baths are comprised by the present invention.

Having described my invention, I claim:

1. In a process for electroplating antimony, the step which comprises electrodepositing antimony from an aqueous solution comprising essentially antimony trifluoride and an ammonium fluoride, the pH of the solution being less than about 6

and below the precipitation point of antimony oxide from the solution.

2. In a process for electroplating antimony, the step which comprises electrodepositing antimony from an aqueous solution comprising essentially antimony trifluoride, a fluoride of a monovalent base, and a monovalent base, the pH of the solution being less than about 6 and below the precipitation point of antimony oxide from the solution.

3. A bath for electroplating antimony, said bath comprising essentially the products of aqueous solution of antimony trifluoride, ammonium fluoride and ammonium hydroxide, the pH of the solution being less than about 6 and below the precipitation point of antimony oxide from the solution.

4. In a process for electroplating a ductile and malleable bonded electrodeposit of antimony, the step which comprises electrodepositing antimony from an aqueous solution comprising essentially antimony trifluoride and a fluoride of a monovalent base, the pH of the solution being less than about 6 and below the precipitation point of antimony oxide from the solution, upon a conductive cathode having a surface of superficial irregularity.

5. The process of claim 4 in which the fluoride of a monovalent base is an ammonium fluoride.

6. The process of claim 4 in which the superficial irregularity of the cathode surface is produced by etching said surface with a solution of nitric acid in moderate concentration.

7. In a process for electroplating a ductile and malleable bonded electrodeposit of antimony on an electrode, the step which comprises electrodepositing antimony from an aqueous solution comprising essentially the products of aqueous solution of antimony trifluoride, ammonium fluoride and ammonium hydroxide, the pH of the solution being less than about 6 and below the precipitation point of antimony oxide from the solution, upon a conductive cathode having a surface of superficial irregularity.

8. In a process for electroplating antimony, the step which comprises electrodepositing antimony from an aqueous solution comprising antimony trifluoride, a fluoride of a monovalent base and a material selected from the group consisting of cupric fluoride, mercuric fluoride and telluric fluoride for reducing grain size and increasing throwing power.

9. As an article of manufacture, a conductive corrodible base having a surface of superficial irregularity and adhering to said surface a ductile, malleable corrosion-resistant coating of fine-grained electrodeposited metallic antimony, substantially devoid of pores, which coating, when in a thickness of about 0.0015'' and subjected to a salt spray bath conforming to the specifications of the test bath outlined in A. S. T. M. Tentative Standard B–39T, will stand up under this test for a period of 120 hours.

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