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## LEAD-ANTIMONY ALLOY ELECTROPLATING BATH

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1

This invention relates to the electrodeposition of metals and more particularly to the electrodeposition of lead-antimony alloys from aqueous solutions.

The electrodeposition of lead-antimony alloys from aqueous solutions of certain of the metal salts has been described heretofore. For instance, it has been proposed to plate lead-antimony alloy from a fluoborate or fluosilicate plating bath (The Metal Industry, vol. 18, No. 6, pages 264 to 266, 1920) and from a tartrate bath containing phenol sulphonic acid (Korroziya i Borba s Nei 6: No. 2, pages 48 to 49, 1942), but the lead-antimony coatings obtained by such methods have been found to be inferior to the usual metal coatings such as zinc in preventing the corrosion of steel and similar metal bases.

It is therefore an object of this invention to provide means for forming a lead-antimony alloy coating having improved protective characteristics.

Another object of the invention is to provide a new plating bath for the electrodeposition of lead-antimony alloy.

Still another object of the invention is to provide means for improving the corrosion resistance of steel and other metals.

These and other objects and advantages are obtained in accordance with this invention by the provision of a novel plating bath in which the cations, lead and antimony, are associated with a combination of tartrate and fluoborate anions. It has now been found that a lead-antimony alloy coating can be electrodeposited from such a bath with protective characteristics greatly improved over those of a lead-antimony alloy coating electrodeposited from a bath containing only tartrate or only fluoborate anions. For instance, smooth, uniform, adherent lead-antimony alloy coatings substantially free of pin holes and the like may be electrodeposited on steel in accordance with this invention to provide steel-base articles having a corrosion resistance and other characteristics greatly superior to similar steel articles provided with the usual platings of zinc, or copper or the like.

The electroplating bath of this invention is employed in accordance with well-known plating practice. For instance, as is customary in the plating of lead from fluoborate solution, the bath should contain agents such as free fluoboric acid and free boric acid, or their equivalent, and a suitable addition agent such as glue, the fluoboric acid being present to increase the conductivity of the solution, the boric acid being present as

2

a stabilizer to prevent decomposition of the fluoborate and the glue or other addition agent being present to control among other things the grain size in the electrodeposited film. The effect of and necessity for the use of such agents or addition agents in an electroplating bath are well-known in the art.

The electroplating bath of this invention may be employed for electrodepositing lead-antimony alloys of practically any desired composition, for instance the antimony content may range from merely a trace in the coating up to a point where the alloy consists of a preponderance of antimony. Various means, well known in the art of plating alloys, may be employed to regulate the composition of the electrodeposited alloy. For instance, the ratio of lead to antimony in the plating is affected to a certain extent by changes in temperature and current density during the electrodeposition. Similarly the composition of the alloy plate may be regulated by the composition of the plating bath, that is, it may be stated in general that the percentage of antimony in the plate increases with an increased content of antimony in the plating bath. For this reason, the antimony content of the plating bath should be regulated such as to give the desired antimony content in the electrodeposited film.

The plating bath may be prepared in any suitable manner. In one preferred method, however, metallic antimony is dissolved in a mixture of nitric and hydrofluoric acids. Tartaric acid is then added to the solution and the mixture is heated until the reddish-brown fumes of oxides of nitrogen are no longer given off. It is important that substantially all the nitrate be removed in this operation since the presence of nitrate ion tends to cause the deposition of an uneven plate. The solution is then cooled and mixed with an aqueous solution of lead fluoborate containing free fluoboric and boric acids. The preparation of the bath is then completed by adding an addition agent such as glue.

Other oxidizing agents, for example hydrogen peroxide, may be used in place of the nitric acid in dissolving metallic antimony for addition to the plating bath, although nitric acid is preferred and good results can be obtained if the antimony is added to the bath in the form of antimony fluoride, antimony tartrate, or potassium antimonyl tartrate.

In order to further clarify the invention following is a detail description of the preparation and application of a plating bath illustrating an embodiment of the invention.

A plating bath suitable for the electrodeposition of a lead-antimony alloy containing about 8% to 10% antimony is prepared by first dissolving about 200 grams, i. e. about 200 parts by weight, of antimony in about 500 cubic centimeters, i. e. about 650 parts by weight of an aqueous solution containing 24% of hydrofluoric acid, i. e. 150 parts by weight, and 35% of nitric acid i. e. about 230 parts by weight. About 400 grams of tartaric acid, i. e. about 400 parts by weight, in about 200 cubic centimeters or parts by weight of water are then added and the mixture is heated until the reddish-brown fumes of oxides of nitrogen are no longer given off and the solution is then cooled.

About 4882 cubic centimeters, or about 6800 parts by weight, of an aqueous solution acidified with about 5% boric acid and containing about 660 grams per liter of lead fluoborate and 35 grams per liter of free fluoboric acid is diluted with water to a total volume of about 22.7 liters, i. e. to a total of about 24,600 parts by weight, and the diluted solution and the solution of antimony prepared as described above are then mixed. The resulting mixture thus contains about 200 parts by weight antimony, about 340 parts by weight boric acid, about 3200 parts by weight lead fluoborate, about 400 parts by weight tartaric acid, and about 170 parts by weight fluoboric acid, or stated in terms of anions and cations, the mixture contains about 200 parts by weight antimony cations, about 1700 parts by weight lead cations, about 1600 parts by weight fluoborate anions, and about 300 parts by weight tartrate anions. The preparation of the bath is then completed by the addition of about 51 grams of animal glue, i. e. about 50 parts by weight dispersed in about 700 cubic centimeters or parts by weight of hot water.

Such a bath may be employed to electroplate properly cleaned steel articles, for instance steel shot shell heads and other ammunition components. For example, steel shot shell heads, after the usual electrolytic and other cleaning operations, are treated in a solution containing one mol of zinc chloride and one mol of ammonium chloride per liter of water at room temperature for about five minutes. The heads are then washed and placed in the electroplating bath prepared as described above.

The electroplating is carried out in the usual type of plating barrel. Lead anodes, or anodes of lead-antimony alloy containing about 8% antimony, are employed with a current density of about 15 amperes per square foot for a period of about 20 minutes at a temperature of about 80° to 85° Fahrenheit. By coating the shot-shell heads under such conditions, a coating of an alloy of lead containing about 8% to 10% antimony is obtained, about 0.00025 inch to 0.0005 inch thick. Immediately after the plating process is finished the shot-shell heads are washed and then dried and polished, preferably by tumbling in any suitable vessel with clean sawdust.

When such shot shell heads have gone through the assemblying operation necessary to form a loaded round of ammunition and are subjected to a spray of 20% sodium chloride solution at a temperature of 95° F., in accordance with the standard A. S. T. M. Salt Spray Test Specification No. B-117-41T, it is found that the heads will remain in the spray for as long as from 6 to 24 and more hours without corroding. In comparison, steel shot shell heads coated with copper or zinc about 0.0005 inch thick, after the assemblying operation show signs of corrosion products after only about 1.5 to 6 hours in the salt spray.

Although the plating of steel is described in the above specific embodiment it should be understood that the plating bath of this invention may be employed to electrodeposit lead-antimony alloys on other ferrous metals and non-ferrous metals, for instance copper or brass.

Although, as described above, the plating bath of this invention contains free fluoboric acid and boric acid, or their equivalent, and an addition agent such as glue, and may contain antimony fluoride and the like, the essential and identifying characteristics of the bath are that it contains lead and antimony cations associated with broth tartrate and fluoborate anions. The exact association, structure and inter-relation of the cations and anions of the bath are unknown and likewise the theory of operation of the bath is not completely understood. It has been found, however, that if the bath contains lead, antimony, fluoborate and tartrate and the practice, well known in the electroplating art, of adding other suitable agents and addition agents to the bath is followed, an electrodeposited film of lead-antimony alloy may be obtained superior to that obtained from either a tartrate or a fluoborate bath.

This invention accordingly provides a novel electroplating bath suitable for electrodepositing a film of lead-antimony alloy having improved protective characteristics, provides means for improving the corrosion resistance of steel and other metals, and thus opens a wide field for the application of such alloys.

It is to be understood that the embodiments of the invention described herein are only illustrative and that many changes may be made therein without departing from the spirit and scope of the invention as set forth in the following claims.

Having thus described the invention, what is claimed and desired to secure by Letters Patent is:

1. The process of making an electroplating bath suitable for the electrodeposition of lead-antimony alloy, which comprises dissolving antimony in a mixture of concentrated nitric and hydrofluoric acids, adding tartaric acid, heating said solution until the oxides of nitrogen are no longer given off, and thereafter mixing said solution of antimony with a lead fluoborate plating bath composed of an aqueous solution of lead fluoborate, fluoboric acid, and boric acid.

2. In a process for forming an electroplating bath for the electrodeposition of lead-antimony alloy, the steps of incorporating antimony into said bath which comprise dissolving about 200 parts by weight antimony in an aqueous mixture of about 150 parts by weight hydrofluoric acid and about 230 parts by weight nitric acid, adding about 400 parts by weight tartaric acid thereto and heating the solution until the appearance of reddish-brown fumes ceases, forming a mixture of this solution with an aqueous solution containing ingredients in the proportion of about 340 parts by weight boric acid, about 3200 parts by weight lead fluoborate, and about 170 parts by weight fluoboric acid, and adding thereto about 50 parts by weight animal glue dispersed in hot water.

3. In a process for forming an electroplating bath for the electrodeposition of lead-antimony alloy, the steps of incorporating antimony into said bath which comprise dissolving about 200 parts by weight antimony in an aqueous mixture of about 150 parts by weight hydrofluoric acid

and about 230 parts by weight nitric acid, adding about 400 parts by weight tartaric acid thereto and heating the solution until reddish-brown fumes of oxides of nitrogen are no longer given off, and thereafter mixing the so-formed solution of antimony with a solution of lead fluoborate containing free boric acid and free fluoboric acid.

4. A bath suitable for the electrodeposition of a lead alloy containing about 8 to 10% antimony having as its functioning ingredients in an aqueous medium antimony, lead, fluoborate anions, and tartrate anions, said ingredients being substantially in the relative proportions of about 200 parts by weight antimony cations, about 1700 parts by weight lead cations, about 1600 parts by weight fluoborate anions, and about 300 parts by weight tartrate anions.

5. In the process for forming an electroplating bath for the electrodeposition of lead-antimony alloy, the steps of incorporating antimony into said bath which comprise dissolving about 200 parts by weight antimony in about 650 parts by weight of an aqueous mixture containing about 150 parts by weight of hydrofluoric acid and about 230 parts by weight of nitric acid, adding about 400 parts by weight tartaric acid dispersed in 200 parts by weight water thereto and heating the solution until the reddish-brown fumes of oxides of nitrogen are no longer given off, forming a mixture of this solution with about 24,600 parts by weight of an aqueous solution containing about 340 parts by weight boric acid, about 3200 parts by weight lead fluoborate, and about 170 parts by weight fluoboric acid, and adding thereto about 50 parts by weight animal glue dispersed in about 700 parts by weight water.



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## REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

| Number | Name | Date |
|---|---|---|
| 792,307 | Betts | June 13, 1905 |
| 952,704 | Boessneck | Mar. 22, 1910 |
| 1,780,944 | Roscher | Nov. 11, 1930 |

FOREIGN PATENTS

| Number | Country | Date |
|---|---|---|
| 629,071 | Germany | Apr. 22, 1936 |
| 130,302 | Great Britain | July 29, 1919 |

OTHER REFERENCES

Knox, Metal Industry, vol. 18, No. 6 (June 1920), pp. 264–266.

Mellor, Treatise on Inorganic and Theoretical Chemistry, vol. IX, (1929), pp. 381, 463.

Korroziya i Borba s Nei 6, No. 2, (1942), pp. 48–49.

Chemical Abstracts, vol. 37 (1943), p. 1336.

Transactions American Electrochemical Society, vol. 28 (1915), pp. 325–338.