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METHOD OF ELECTROPLATING LEAD DIOXIDE

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The present invention relates to a novel method for electroplating lead dioxide and to a novel bath therefor; and, more particularly, the invention relates to a method for electroplating lead dioxide anodically from a lead nitrate bath whereby a markedly improved deposit of lead dioxide is obtained.

The deposition of lead dioxide anodically is known. Anodic electroplating of lead dioxide has been accomplished using three different systems: (1) an alkaline bath containing lead tartrate; (2) an acid bath containing lead perchlorate; and (3) an acid bath containing lead nitrate. The use of lead nitrate baths is generally preferred because of ease of preparation, safety in use, low cost and uniformity in plating results. The lead nitrate electroplating bath comprises a solution of lead nitrate in water to which may be added copper nitrate to prevent deposition of lead at the cathode. In order to reduce graininess of the lead dioxide deposit, it has been suggested to include in the plating bath such materials as gelatin and glue. The inclusion of these materials does reduce graininess; however, relatively massive lead dioxide deposits still have a very low fracturing strength, and, when broken, reveal many fine cracks radiating from the center to the outside surface. In addition, under certain conditions, when plating lead dioxide from baths containing gelatin, anodic gassing occurs resulting in the formation of small pockets and a general irregularity in the lead dioxide surface.

It is the principal object of the present invention to provide a method for anodically electroplating lead dioxide which results in markedly improved deposits of lead dioxide.

Another object of the present invention is to provide a novel method for anodically electroplating lead dioxide from a lead nitrate bath whereby the above-mentioned limitations of prior procedures based on the lead nitrate bath are eliminated and whereby a hard, dense, fine-grained lead dioxide deposit is obtained.

A further object of the present invention is to provide a novel lead nitrate-containing bath for anodically electroplating lead dioxide providing improved, hard, dense, fine-grained lead dioxide deposits.

Other objects will become apparent from a consideration of the following specification and the claims.

The present invention comprises, in the anodic electroplating of lead dioxide from an aqueous acid lead nitrate bath, the improvement which comprises carrying out the electrodeposition in an aqueous acid lead nitrate bath containing a non-ionic surface active agent soluble therein.

It has been found that the inclusion of a non-ionic surface active agent, particularly an alkyl aryl polyether alcohol, in an acid lead nitrate bath for electroplating anodically lead dioxide, markedly improves the character of the lead dioxide deposit. The resulting deposits are free from cracks, are hard and dense and possess a fine, grained structure, as compared to the deposits resulting from baths containing no non-ionic surface active agent or containing other agents, such as gelatin and glue. In addition, the inclusion of the non-ionic surface active agent readily permits the deposition of lead dioxide having the above-mentioned improved properties in massive layers, that is layers of at least 1/16" thick and upwards of 1 inch thick or more.

The bath employed in accordance with the present invention will comprise an acid, aqueous solution of lead nitrate. In preparing the bath, lead nitrate itself may be added, or the lead nitrate may be formed in situ in the bath, as by mixing lead oxide (PbO) with aqueous nitric acid. In connection with this latter embodiment, slow addition of the lead oxide in finely-divided form, to the aqueous nitric acid, with stirring, is advantageous.

The concentration of lead nitrate in the bath, at least at the start of the deposition operation, may vary widely. In this connection, the concentration of the lead nitrate in the bath may range from as low as about 50 grams per liter to as high as the maximum solubility thereof in the bath at operating temperature, which may be as high as about 700 grams per liter. In general, it is desirable, in order to produce a lead dioxide deposit of optimum homogeneity, strength and surface characteristics, to maintain high concentrations of lead nitrate in the vicinity of the anode. Accordingly concentrations above the lower end of the range, such as at least about 250 grams per liter and especially at least about 300 grams per liter, are preferred. In order to facilitate handling of the bath during shutdown periods and during continuous replenishing procedures discussed more in detail hereinafter, when the bath may be at or near room temperature, it is also preferable that the concentration of the lead nitrate not be substantially in excess of its solubility at these lower temperatures, which may run as high as about 400 grams per liter. In the preferred practice of the invention, the concentration of the lead nitrate will not exceed about 350 grams per liter.

The bath will be maintained on the acid side of neutrality. In general, the more acid the bath the better the operation thereof, and pH's as low as about 0.8 may be employed. At acidities appreciably greater than this acid fuming from the bath becomes excessive, especially at elevated operating temperatures. The exact acidity of any particular bath employed may depend upon the nature of the anode material onto which the lead dioxide is deposited. For example, with base materials that are not rapidly attacked at low pH's, such as tantalum, nickel, and the like, the pH of the bath may range between about 0.8 and about 2.8. However, with materials that are more readily attacked by acid, such as steel, it is preferred to maintain the pH at above about 2 to prevent excessive corrosion thereof. At pH's above about 3.5 there is a tendency for the formation of an electrical insulating film of lower lead oxides on the cathode. The bath initially made up and before operation has commenced may have a higher pH. Once operation has started, however, the pH drops to the desired level due to depletion of lead and release of nitric acid.

A small amount of copper nitrate may be included in the bath to prevent deposition of lead on the cathode. The amount of copper nitrate, $Cu(NO_3)_2.3H_2O$, may vary widely. The literature reports the addition of as much as about 30 grams per liter, although it has been found that, in the present bath, amounts as low as about 0.5 gram per liter provide significant results, and that amounts between about 0.75 and about 2 grams per liter are optimum.

In accordance with the present invention, there is included in the bath a non-ionic surface active agent. Since the bath is highly acid, the agent must be stable and soluble therein. In this connection, the alkyl aryl polyether alcohols, especially the alkyl phenoxy polyoxyethylene ethanols, have been found to be particularly

suitable. The solubility of such materials in the present bath has been found to be dependent upon the number of ethylene oxide units in the polyoxyethylene alcohol chain. In other words, the solubility increases and the cloud point rises as the length of the chain increases until compounds having at least about 30 ethylene oxide units in the chain are completely soluble even up to the boiling point of water. It has also been found that the solubility of the compounds having shorter chains, that is less ethylene oxide units, can be increased and their cloud point raised by the inclusion in the bath of an anionic surface-active agent, such as a sodium aryl sulfonate, like sodium tetrahydronaphthalene sulfonate. Hence, by such expedient, alkyl phenoxy polyoxyethylene ethanols having as low as about 4 ethylene oxide units may be used. The inclusion in the bath of an anionic surface-active agent also permits the attainment of higher cloud points with those non-ionic surface-active agents which may be soluble at room temperature (25° C.), but which cloud and precipitate from solution when the bath is heated to a higher temperature. The use of such a mixture of surface-active agents is not as effective in producing a fine-grained lead dioxide deposit with maximum strength as is the use of the non-ionic agent alone. Since the amount of anionic agent required depends upon the solubility of the non-ionic agent, which solubility in turn depends upon the number of ethylene oxide units in the polyoxyethylene ethanol chain, it will be seen that the greater the number of ethylene oxide units, up to a point, in the chain the more desirable the non-ionic agent. The preferred alkyl phenoxy polyoxyethylene ethanols are those containing at least about 24 ethylene oxide units in the chain. Compounds containing as many as 40 ethylene oxide units in the chain may be employed.

The amount of non-ionic surface active agent employed to realize the improved results referred to above, may be relatively small. The addition of as little as about 0.5 gram per liter will provide significant improvement, and the amount employed may range above this minimum to as high as about 10 grams per liter or even higher. However, between about 0.75 and about 2 grams per liter represents the optimum concentration, and little advantage is to be gained by employing larger amounts.

The amount of anionic-surface active agent employed will of course depend upon the particular non-ionic agent used and its solubility characteristics. No difficulty will be encountered, however, in determining the amount of anionic agent required in any particular situation since it is simply a case of adding the amount which solubilizes the non-ionic agent. As a general rule a weight ratio of anionic agent to non-ionic agent between about .25 and about 2 to 1, depending upon the solubility of the non-ionic agent, will suffice.

The preparation of the bath itself will present no problem to those familiar with the art, it being only necessary, in accordance with the broader aspects, to mix the main components in the desired proportions to provide an aqueous solution thereof. One procedure that has been found to be particularly suitable comprises adding finely-divided lead oxide (PbO) slowly to diluted nitric acid, with stirring, after which the non-ionic surface-active agent, and any copper nitrate employed, is added. If the initial lead nitrate solution is not at the concentration desired for operation, it may be diluted to the desired level before the non-ionic surface-active agent and copper nitrate are added. To insure solution of the components, the mixture may be heated with stirring. It is desirable to filter the resulting solution, as through sintered glass, to remove insoluble materials.

The temperature of the bath during operation may vary from room temperature to the boiling point. However, deposition is favored at elevated temperatures, and temperatures between about 60 and about 80° C. have been found to be particularly suitable.

During operation of the bath, an anode is immersed in the bath and connected to a suitable source of current. The anode is the material onto which the lead dioxide is to be deposited and may be selected from a wide range of conducting materials, including metals like steel, tantalum and nickel, and non-metals such as silicon. The specific preparation of an anode by electrodepositing lead dioxide onto tantalum and the resulting product forms the subject matter of copending application Serial No. 552,970, filed December 14, 1955 (now abandoned). The shape or form of the anode is immaterial according to the broader aspects of the invention, and the anode may be a sheet, cylinder, rod, or the like. In copending application Serial No. 552,968, filed December 14, 1955 (now Patent No. 2,872,405) are disclosed and claimed the deposition of lead dioxide on fine wires or screens or other foraminous metal bodies. The anode employed in the present process may also be in such form.

A cathode is also provided, and the cathode material may be selected from a wide variety of conducting materials, including lead itself, carbon, and the like. Preferably the cathode is a material non-reactive with the bath during shutdown, such as carbon.

Upon completion of the circuit lead dioxide begins to deposit at the anode, and the flow of current may be continued until the desired deposit has been built up. Anode curren density may vary, with densities as low as about 5 and as high as about 120 amperes per square foot having been found suitable. Normally, the anode current density will be between about 10 and about 30 amperes per square foot. Cathode current density is not critical, althought in preferred practice it is generally maintained higher than the anode current density by a factor of between about 2 and about 10 to 1.

Operation of the bath, of course, removes lead therefrom. Before the concentration of lead in the bath falls to the point where the bath no longer operates efficiently it will be necessary, for further deposition, to replenish the bath. The bath may be replenished periodically or continuously. In replenishing the bath more lead oxide (PbO) will be added. Some nitric acid is also lost from the bath during the operation so that it may be necessary to add further nitric acid as the bath is replenished in order to maintain the desired pH.

The bath may be periodically or continuously replenished by being flowed through another vessel containing a filter bed of, for example, glass wool. Finely-divided lead oxide (PbO) is added to the plating solution above the filter bed. The depleted plating solution gradually dissolves the lead oxide, passes through the filter bed and is then removed from the bottom of this vessel and back to the plating vessel. Nitric acid, when necessary, is also added to the replenishing vessel to maintain the bath at the desired pH.

The present invention will be more readily understood from a consideration of the following specific example which is given for the purpose of illustration only and is not intended to limit the scope of the invention in any way.

Example

269 ml. of 69.9% nitric acid (266.5 g. HNO_3) are added to 1000 ml. of distilled water. 472 g. of finely-divided lead oxide (PbO) are added slowly to the diluted nitric acid with stirring. After the addition of the lead oxide, the resulting solution is diluted to 2 liters. One and one half grams of copper nitrate, $Cu(NO_3)_2.3H_2O$, and 1.5 g. of nonyl phenoxy polyoxyethylene ethanol containing an average of 30 ethylene oxide units per molecule (Igepal CO–880) are added thereto. The resulting solution is heated to 75° C. with stirring. The solution is then allowed to cool and is filtered through sintered glass.

A nickel screen of 16 mesh having 0.012" wire and

having dimensions of 3 x 20" is immersed in the bath to a depth of 15". Graphite cathodes are also immersed in the bath. The bath is maintained at 70° C. The nickel screen anode and the graphite cathodes are connected to a suitable source of current and the circuit is completed. A lead dioxide plating ⅞" thick and 3½ x 15¾" in lateral dimensions and amounting to 6900 grams, by weight, is formed on the nickel screen. The deposit is hard, dense and finely-grained.

Considerable modification is possible in the selection of the various constituents making up the bath and in the amounts thereof as well as in the exact techniques followed in carrying out the method without departing from the scope of the invention.

I claim:

1. In the anodic electrodeposition of lead dioxide from an acid aqueous solution of lead nitrate the improvement comprising conducting the electrodeposition with at least about 0.5 gram per liter of an alkylaryloxy polyoxyethylene ethanol having from 4 to 40 ethylene oxide units dissolved in said solution.

2. The method of claim 1 wherein said alkylaryloxy polyoxyethylene ethanol is an alkyl phenoxy polyoxyethylene ethanol.

3. The method of claim 2 wherein said alkyl phenoxy polyoxyethylene ethanol contains at least about 24 ethylene oxide units.

4. In the anodic electrodeposition of led dioxide from an acid aqueous solution of lead nitrate the improvement comprising conducting the electrodeposition with at least about 0.5 gram per liter of an alkylaryloxy polyoxyethylene ethanol having from 4 to 40 ethylene oxide units dissolved in said solution and with said solution at a pH between about 0.8 and about 3.5.

5. The method of claim 4 wherein said alkylaryloxy polyoxyethylene ethanol is an alkyl phenoxy polyoxyethylene ethanol.

6. The method of claim 5 wherein said alkyl phenoxy polyoxyethylene ethanol contains at least about 24 ethylene oxide units.

7. In the anodic electrodeposition of lead dioxide from an acid aqueous solution of lead nitrate the improvement comprising conducting the electrodeposition at a temperature above room temperature and below the boiling point of the solution and with at least about 0.5 gram per liter of an alkylaryloxy polyoxyethylene ethanol having from 4 to 40 ethylene oxide units dissolved in said solution.

8. The method of claim 7 wherein the temperature is between about 60 and about 80° C., and wherein the alkylaryloxy polyoxyethylene ethanol is an alkyl phenoxy polyoxyethylene ethanol.

9. The method of claim 8 wherein said alkyl phenoxy polyoxyethylene ethanol contains at least 24 carbon atoms.

10. In the anodic electrodeposition of lead dioxide from an acid aqueous solution of lead nitrate the improvement comprising conducting the electrodeposition at a temperature above room temperature and below the boiling point of the solution, with at least about 0.5 gram per liter of an alkylaryloxy polyoxyethylene ethanol having from 4 to 40 ethylene oxide units dissolved in said solution and with said solution at a pH between about 0.8 and about 3.5.

11. The method of claim 10 wherein the temperature is between about 60 and about 80° C., and wherein said alkylaryloxy polyoxyethylene ethanol is an alkyl phenoxy polyethylene ethanol containing at least 24 ethylene oxide units.

12. In the anodic electrodeposition of lead dioxide from an acid aqueous solution of lead nitrate the improvement comprising conducting the electrodeposition with at least about 0.5 gram per liter of an alkylaryloxy polyoxyethylene ethanol having from 4 to 40 ethylene oxide units dissolved in said solution through the agency of an anionic surface-active agent.

13. The method of claim 12 wherein the alkylaryloxy polyoxyethylene ethanol is an alkyl phenoxy polyoxyethylene ethanol containing between about 4 and about 30 ethylene oxide units and wherein the anionic surface-active agent is a sodium aryl sulfonate.

14. The method of claim 1 wherein the alkylaryloxy polyoxyethylene ethanol is present in an amount between about 0.75 and about 2 grams per liter.

15. A bath for the anodic electrodeposition of lead dioxide comprising an acid aqueous solution of lead nitrate containing at least about 0.5 gram per liter of an alkylaryloxy polyoxyethylene ethanol having from 4 to 40 ethylene oxide units dissolved therein.

16. The bath of claim 15 wherein the alkylaryloxy polyoxyethylene ethanol is an alkyl phenoxy polyoxyethylene ethanol, and wherein the pH of the bath is between about 0.8 and about 3.5.

17. The bath of claim 15 wherein the alkylaryloxy polyoxyethylene ethanol is dissolved therein through the agency of an anionic surface-active agent.

18. The method of claim 1 wherein said alkylaryloxy polyoxyethylene ethanol is nonyl phenoxy polyoxyethylene ethanol.

19. The method of claim 13 wherein said alkyl phenoxy polyoxyethylene ethanol is nonyl phenoxy polyoxyethylene ethanol.

20. The bath of claim 15 wherein the alkylaryloxy polyoxyethylene ethanol is nonyl phenoxy polyoxyethylene ethanol.

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