Jan. 11, 1972 F. D. GIBSON, JR., ET AL 3,634,216

ELECTRODEPOSITION OF LEAD DIOXIDE

Original Filed June 16, 1965

FIG. 1.

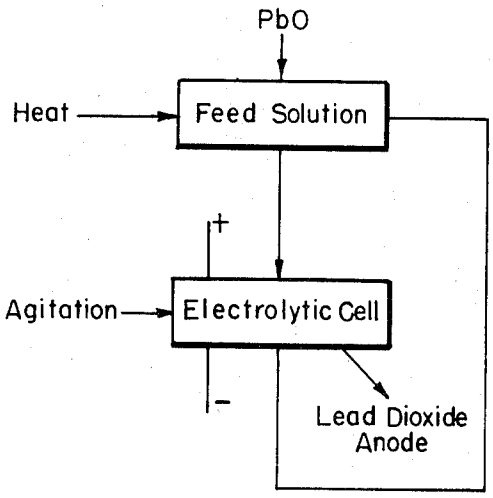


FIG. 2.

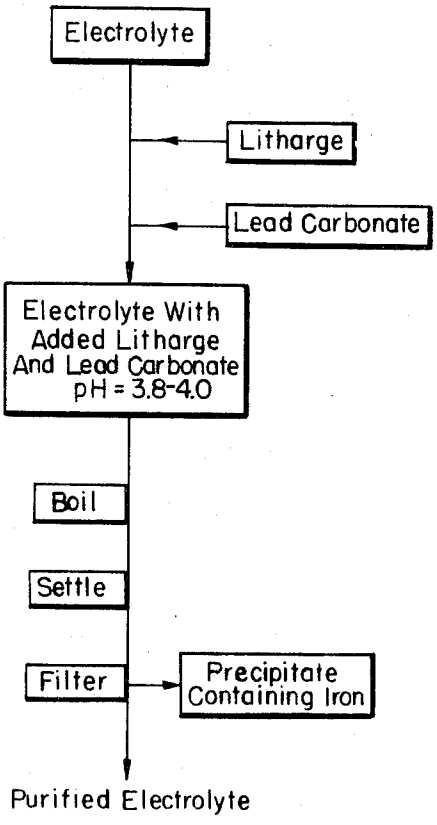
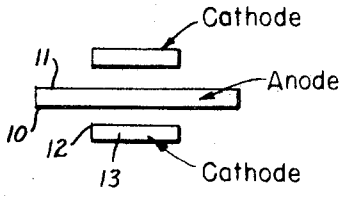


FIG. 3.



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ELECTRODEPOSITION OF LEAD DIOXIDE

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Division of application Ser. No. 520,341, Jan. 13, 1966, now Patent No. 3,463,707, which is a continuation-in-part of application Ser. No. 474,179, July 22, 1965, which in turn is a continuation of application Ser. No. 464,292, June 16, 1965. Divided and this application June 17, 1969, Ser. No. 834,010

The portion of the term of the patent subsequent to Aug. 26, 1986, has been disclaimed

Int. Cl. B01k 3/00

U.S. Cl. 204—83 5 Claims

ABSTRACT OF THE DISCLOSURE

Processes for manufacture of lead dioxide involving first plating onto a substrate a thin layer and, discontinuously, a thick layer and removing the thick layer while retaining the thin layer onto which a thick layer may again repeatedly be plated. The electrolyte contains lead nitrate and nitric acid having a concentration of about 5 to about 20 grams of free acid per liter and treating the electrolyte to reduce its iron content to below .02 gram per liter calculated as free iron.

This application is a division of our copending application Ser. No. 520,341, filed Jan. 13, 1966, now U.S. Pat. No. 3,463,707, which is a continuation-in-part of our copending U.S. application Ser. No. 474,179, filed July 22, 1965, and now abandoned, which latter application, in turn, is a continuation of our U.S. application Ser. No. 464,292, filed June 16, 1965, and now abandoned.

BACKGROUND OF THE INVENTION

Lead dioxide, also known as anhydrous plumbic acid, lead peroxide and lead superoxide, is a very useful material. When provided in the form of a pure, finely divided particulate solid, it is useful as an oxidizer in explosives and in incendiary devices, as a curing agent in the manufacture of polysulfide rubber and also in the manufacture of dyestuffs and intermediates.

In the prior art, including U.S. Pat. No. 2,945,791, issued to Fred D. Gibson, Jr., the electrolytes proposed for deposition of lead dioxide have generally included lead nitrate, copper nitrate, nickel nitrate, and nitric acid. It may also be advantageous to include in the electrolyte small amounts of sodium fluoride and a surface-active agent as disclosed, for example, in the aforesaid Pat. No. 2,945,791. These various ingredients serve various purposes.

For instance, it has been considered important for the copper nitrate to be present to effect preferential plating of copper rather than lead on the cathodes of the cells in which the lead dioxide is being plated. While the copper does tend to build up deposits which would eventually short-circuit the cells unless they were periodically shut down to remove such deposits, such shut-downs, though expensive, are still less objectionable than the consequences of permitting lead to deposit on the cathodes.

The presence of the nickel nitrate has been considered an important factor in the attainment of desirable fineness in the crystalline structure of the lead dioxide deposit. Experience in the manufacture of high purity lead dioxide has shown that the above-described electrolytes should have an acid concentration of less than about 5 grams per liter. Although lead dioxide will, to be sure, plate out in the presence of higher concentrations of acid, the resultant deposit generally has been decidedly inferior in

quality. In actual practice, therefore, the acid concentration has been limited to about 2 to 3 grams acid per liter of electrolyte.

The continued research to produce improved lead dioxide on the one hand and to reduce the cost of its production on the other hand has led to the improved process of the present invention by which we have provided the surprising result of producing such improved powdered lead dioxide while at the same time making possible the use of an electrolyte having fewer ingredients than heretofore thought necessary. A further benefit is a reduction in operating costs, since the more expensive ingredients of the prior art electrolytes, i.e. copper nitrate and nickel nitrate, are not required in the process of the present invention.

Concerning the production of powdered lead dioxide, this material has heretofore been prepared commercially by a chemical process involving precipitation from an aqueous solution. A disadvantage of this process is the lack of uniformity of the product from batch to batch with respect to purity, reactivity, and color. This lack of uniformity has made it necessary to sample and analyze each drum of powdered lead dioxide, which is of course time-consuming and expensive. Frequently, the material is found, upon testing, to be entirely unuseable because of its failure to meet specifications. An electrochemical process is disclosed in Christensen Pat. No. 2,925,904 but this process does not produce as pure a product as is desired nor can it be operated continuously as is the case with the present invention.

In the electrolytic production of powdered lead dioxide according to prior technology, one of the problems encountered was that of plating a heavier coating of lead dioxide onto a suitable substrate, but with the lead dioxide coating purposely being poorly non-adherent, so that when the plating is completed, the coating can readily be removed from the substrate and thereafter ground to the desired particle size. The process of this invention, however, not only solves this problem but also makes possible the production of powdered lead dioxide which possesses consistently uniform physical and chemical properties and is, moreover, of a very high degree of purity. It is possible to exercise close control over the final particle size, as the lead dioxide which is stripped from the substrate material can be calibrated to any of a wide variety of particle sizes ranging from about 0.3 micron to about one-half inch.

With respect to production of powdered lead dioxide, the greatly improved and surprising results which are obtained by the method of this invention stem particularly from the use of an improved electrolyte. Broadly speaking, the electrolyte of this invention is one in which the acid concentration is maintained substantially above previously acceptable values in conjunction with limiting of the concentration of certain other constituents of the electrolyte to prescribed levels. Not only does the use of the improved electrolyte make possible a considerably improved anode, but also makes possible the production of such anodes at substantially lower cost than was possible heretofore. The improved electrolyte also makes possible the production of powdered lead dioxide of a high degree of purity and a high uniformity of physical characteristics. Also, it is now possible to continue the plating process for a much longer time than heretofore, so that a higher volume of production than with any prior art electrolytic process of production of powdered lead dioxide is now possible.

An additional advantage of the invention resides in the ability to plate satisfactorily with lower concentrations of lead nitrate in the electrolyte. Thus, in using the prior are electrolyte described, for example, in Pat. No. 2,945,-

791, it is found that satisfactory plating of lead dioxide cannot occur with a lead nitrate concentration of less than about 150 grams per liter; whereas, when using the electrolyte of the present invention, we have found that the lead nitrate concentration can go as low as about 50 grams per liter and yet plate at a satisfactory rate.

In plating lead dioxide onto a substrate, it has previously been considered that the most suitable substrate material is graphite, as disclosed for example in the aforesaid Pat. No. 2,945,791. However, we have now discovered that other substrate materials may be used with the improved electrolyte of the invention, provided that the improvided that the substrate material is properly treated prior to the electrodeposition process. For example, we have found that lead dioxide may be plated satisfactorily on a substrate of titanium metal, and also tantalum, zirconium, hafnium, and columbium.

When plating lead dioxide onto a substrate for use as an anode in an electrochemical cell, the process of plating is designed to produced a very tightly-adherent coating of lead dioxide to the substrate material. On the other hand, where it is desired to produce powdered lead dioxide, it becomes an objective to plate a heavy coating of lead dioxide onto the substrate which can readily be stripped therefrom and then ground, and accordingly the process of the present invention provides also for the plating of a lead dioxide coating which will readily adhere during normal handling of the substrate in the plating process but which can readily be broken off the substrate so as to be ground, with the substrate being available for repeated replating with subsequent coatings of lead dioxide.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a process for the electrodeposition of lead dioxide from an aqueous solution containing lead nitrate, but not requiring either copper nitrate or nickel nitrate, onto a base substrate material such as carbon, titanium, tantalum, zirconium hafnium, and columbium, and their alloys.

Another object of the invention is to provide a process for the production of a lead dioxide coating on a suitable substrate material, which coating is far less likely than those of the prior art to be non-adherent, porous, or contain fissures.

It is a further object of the invention to provide a process for the manufacture of powdered lead dioxide of uniform physical characteristics and high purity.

It is another object of the invention to provide a process for the coating of a high purity lead dioxide onto a substrate.

It is a further object of the invention to provide a process for the preparation and control of the constituency of an electrolyte for use in the electrodeposition of lead dioxide.

It is another object of this invention to achieve the depositing of lead dioxide onto a prepared substrate using a specifically formulated lead nitrate electrolyte, the constituents of which are carefully controlled, and by employing a certain sequence of operating conditions.

BRIEF DESCRIPTION OF THE DRAWINGS

Describing the invention, reference will be made to the accompanying drawings in which:

FIG. 1 diagrammatically illustrates the processes of the present invention for the production of lead dioxide on a substrate material;

FIG. 2 is a flow diagram illustrating the process of the present invention for treatment of the electrolyte to remove iron therefrom;

FIG. 3 illustrates a preferred arrangement of the electrodes in a cell for the production of thick coatings of lead dioxide intended for the production, ultimately, of powdered lead dioxide.

DETAILED DESCRIPTION OF THE INVENTION

Electrolyte

Described briefly, the improved process of our invention makes possible the production of powdered lead dioxide, together with a lowering of the cost of its production, and accomplishes this, in part, by careful control of the amounts of several constituents appearing in the electrolyte, particularly iron and chlorides. Proper control of the amounts of these constituents makes possible the elimination of both copper and nickel nitrate from the electrolyte and also makes possible the elimination of a surface-active agent. A further important result of the process of this invention, one which significantly reduces the cost of lead dioxide plating, is the ability to operate the cells almost continuously. This is in sharp contrast to the prior art processes which required periodic cell shutdown, particularly to remove copper that plated on the cathodes.

More specifically, the electrolyte of this invention comprises an aqueous solution which comprises lead nitrate in the concentration of about 50 to about 200 grams per liter of anhydrous lead nitrate, nitric acid in the concentration of about 5 to about 20 g.p.l., and sodium fluoride in the concentration of about 0.5 g.p.l. During the electrodeposition process, it is periodically necessary to replenish the lead in the electrolyte. Accordingly, at the start of deposition, it is desirable to have the lead nitrate concentration near the 200 grams per liter value stated above. The lower level of 50 grams per liter mentioned above has been found to be a practical lower limit, below which the plating process proceeds only quite slowly. The electrolyte is treated to limit the concentration of iron, calculated as metallic iron, to a value in the range of 0 to about 0.02 g.p.l., and is also treated to remove chlorides. It should be understood that a concentration of 0.2 g.p.l. of iron does not constitute an upper limit for iron at which a substrate can satisfactorily be plated with lead dioxide but rather represents a control limit for production of lead dioxide coatings of consistently high quality. Thus, substrates have been plated in solutions having iron content of .05 to .10 g.p.l. of iron, but it has been found that the rejection rate is then at an unsatisfactorily high level Incidentally, the amount of iron present is determined through the use of sulfosalicylic acid with a pH of 2.0 (colorimetric).

The electrolyte of the present invention is thus substantially different from what has heretofore been used in the plating of lead dioxide. As previously stated, it has been customary to employ an aqueous solution of lead nitrate, with added ingredients comprising nitric acid, copper nitrate, nickel nitrate, sodium fluoride, and a surface active agent. Moreover, it has been found in the past that the concentration of nitric acid must be kept below about 5 grams per liter since otherwise it was impossible to plate a continuous coating of lead dioxide onto the substrate. Now, however, control of the amounts of the constituents of the electrolyte, particularly the iron, in conjunction with the employment of a significantly higher concentration of nitric acid, i.e. about 5 to about 20 grams per liter, makes possible the elimination of the copper nitrate and also the nickel nitrate, thereby reducing the cost of manufacture of plating of lead dioxide and also producing a higher degree of purity of lead dioxide.

Of course, it is possible to have small amounts of copper nitrate in the electrolyte without detriment. Thus, where the appended claims refer to the "substantial absence" of any material, e.g. copper nitrate, it should be understood that the amount of copper nitrate which might in normal practice be introduced as an impurity in one or more of the raw materials, can readily be tolerated. A further advantage of the invention is that the process can now be operated without frequent shutdowns, as will later be explained, thereby substantially reducing production costs.

For the most part, iron, chlorides and organics are introduced into the electrolyte from the substrate material. Thus, iron frequently appears in trace or larger amounts throughout the body of the substrate, and various organics may also be present on the surface thereof. Iron is also introduced as a result of the periodic addition of litharge to the electrolyte, since minute quantities of iron are frequently present in the litharge. Chlorides and organics are also introduced with the water which is used in the preparation of the electrolyte, even when treated water is used.

With respect to the elimination of the copper nitrate from the electrolyte, this becomes possible indirectly as a result of the close control of the amount of iron in the electrolyte. Thus, we have found that when the amount of iron is carefully restricted and a higher amount of acid, i.e. from about 5 to 20 grams per liter of nitric acid, is used in the electrolyte, the copper nitrate whose principal effect has been to effect preferential plating of copper rather than lead on the cathodes becomes unnecessary. Previously, a high acid concentration in the electrolyte was found to be undesirable since it was found that a plating of inferior quality was produced, and the concentration of nitric acid was accordingly limited to about 2 to 3 grams per liter.

Nickel nitrate has heretofore been added to the electrolyte because of its function as a crystalline modifier having the effect of producing a finer grain of the lead dioxide plating. It has been found, however, that entirely satisfactory results are obtained by using the electrolyte of the present invention which contains no nickel nitrate. If it is desired to use nickel nitrate, nevertheless, in order to produce an especially fine grain of lead dioxide coating, then nickel nitrate may be added with a concentration of about 10 grams per liter.

During the course of the electrodeposition process, it is necessary to replenish the lead in the electrolyte and also to maintain the electrolyte at the proper pH. This is accomplished by feeding the effluent from the cell to a feed tank and thereafter adding lead dioxide as required to maintain an acid concentration of approximately 5 to 20 grams per liter and a lead nitrate concentration of approximately 200 grams per liter. A continuous circuit is provided so that the replenished electrolyte is continuously fed to the cell. The electrolyte is heated in the feed tank to maintain an electrolyte temperature in the cell in the range of about 73 to about 92° C.

Reference may be made to FIG. 1 which illustrates diagrammatically the process of the present invention and particularly discloses the addition of litharge to the feed solution. As shown, the feed solution is heated to the prescribed temperature and then allowed to flow to the electrolytic cell where constant agitation is maintained.

At repeated intervals, samples of the electrolyte are tested to determine the amount of iron and chlorides present. Whenever either of these constituents is found to exist in an amount exceeding predetermined limits, a portion of the electrolyte is withdrawn from the continuous circuitry described and transferred to a treatment tank.

With respect to the upper limit of iron which can be present in the electrolyte, numerous experiments have demonstrated that the quality of the lead dioxide plate will start to deteriorate when the iron content exceeds .02 gram per liter, at least at the start of the electrodeposition process. It has been found that the amount of iron can be permitted to go somewhat above this limit once the plating process is started.

With respect to chlorides and organics, treatment is undertaken to remove these from the electrolyte whenever inspection of the anode plated lead dioxide shows the slighest evidence of the presence of these materials.

As previously stated, one of the outstanding attributes of the present invention resides in the ability to have the process operate without requiring periodic shut-downs to remove copper from the cathodes. In the prior art systems, where copper nitrate is added to the electrolyte to effect preferential plating, the cathode eventually becomes fully covered by copper, and it is periodically necessary to remove the copper plating since otherwise the cathodes will short to the anode. One way in which the copper has been removed in the past is to shut down the cell periodically and then to recirculate the electrolyte through the cell until the copper has been dissolved. Such a procedure has the distinct disadvantage that the cell must be out of operation throughout the rather considerable time taken to dissolve the copper. An alternative means used in the prior art processes is to add acid to the electrolyte in the amount required to dissolve the copper, then to add litharge in the amount to neutralize a portion of the excess acid, but this procedure has the disadvantage that the lead concentration gradually increases so that, as the process is continuually repeated, the lead concentration eventually reaches saturation. To prevent this, it is necessary to add water and copper nitrate, but this means that the quuantity of electrolyte in the system is continuously being increased, which necessarily results in increased costs of operation.

By means of the present invention, on the other hand, both of the expedients employed by the prior art become unnecessary since preferential plating is not employed. Excessive build-up of lead on the cathodes does not occur with the electrolyte of the present invention. Because of this, there is no need to shut down the cell for this purpose.

An additional advantage resulting from control of the amount of iron present in the electrolyte is the better utilization of the sodium fluoride which generally constitutes one ingredient of the electrolyte. Sodium fluoride is usually added to provide a greater anode efficiency in the plating process. When iron is present to any substantial extent in the electrolyte, much of the sodium fluoride becomes unavailable for its intended use because the iron combines with the sodium fluoride to produce iron fluoride Fe_2F_6. Reducing the iron content to less than .02 gram per liter makes considerably more of the sodium fluoride available for its intended use. In addition, it has been found that the reduction of iron below the maximum level specified results in considerably less criticality in the amount of sodium fluoride which must be present in the electrolyte to obtain the desired anode efficiency. Incidentally, although fluoride is usually employed in the form of sodium fluoride, other forms of soluble fluoride may instead be used.

PRODUCTION OF POWDERED LEAD DIOXIDE

In the production of powdered lead dioxide, it is, of course, desired that the lead dioxide plated onto the substrate be readily removable therefrom. To accomplish this, the substrate, which may be either titanium, tantalum, zirconium, hafnium or columbium, is first abraded as with a wire brush. This thoroughly cleans the surface of the substrate, but does not produce the rough and jagged surface which is provided by sand blasting, as is done when the substrate is to be plated for use as an anode. Following this surface treatment, a thin coating of lead dioxide is plated onto the substrate, and this is followed by removal of the substrate from the cell and washing. The anode is then re-inserted in the cell and plating is started again.

The removal of the substrate from the cell, even though briefly, provides a definite discontinuity between the initial, thin plating of lead dioxide and the subsequent heavier plating. This facilitates the easy stripping of the heavy plating from the anode without disturbing the tightly-adhering initial coating. If this were not done, it would be difficult to strip the lead dioxide from the anode substrate, as a tight bond is formed between the substrate and the initial layer of lead dioxide. Of course, after the first usage of the anode, the treatment just described need not be repeated since the initial thin coating is re-

tained indefinitely, and the same substrate may be re-plated over and over again repeatedly.

In producing coated lead dioxide by electrodeposition, it is desirable that the anode current density not be allowed to exceed about 60 to 70 amperes per square foot. If the current density is permitted to go above this range, there is substantial "treeing" of the lead dioxide at the anode which may eventually result in a short circuit between the anode and cathode. To prevent the current density from reaching an excessive value locally, precautions are taken to prevent the respective edges of the anode and cathode from being immediately adjacent to each other. Thus, the anodes and cathodes may be positioned relative to each other in a manner shown in FIG. 3. In FIG. 3, the anode and cathode both have a generally rectangular cross section, but the anode is wider than the cathode as shown, and the two are so positioned relative to each other as to prevent edge **10** of anode **11**, for example, from being immediately adjacent a corresponding edge **12** of cathode **13**.

Although a maximum anode current density value has been stated above, it should be understood that this value does not represent an absolute upper limit but instead represents a value above which "treeing" occurs at a rapid rate. When steps are taken to remove the treed plating periodically, so as to prevent short circuits, then current densities above 60 to 70 amperes per square foot can be used with a proportionate reduction in plating time to achieve a given thickness of plating.

Plating is generally carried on until about a ¼" thickness of lead dioxide plating is achieved. With an anode current density of about 65 amperes per square foot, about 24 hours are required to obtain a plating of this thickness. A practical upper limit for the plating time is that which produces a plating of such thickness that the plating comes into contact with the cathode.

After the plated anode is removed from the cell, the plating is removed mechanically, and this may readily be accomplished in any of numerous ways since the discontinuity between the thin intial plating and the subsequent heavier plating greatly facilitates the removal of the outer layer of lead dioxide. One very convenient way in which to remove the lead dioxide is simply to flex the plate as this quickly fractures the coating which then breaks off in large pieces.

The lead dioxide is then washed with de-mineralized water to prevent the formation of lead sulphate precipitates and to remove all traces of lead nitrate. The lead dioxide is then crushed and then finally ground to the desired particle size. The following example illustrates our process for the production of powdered lead dioxide:

EXAMPLE

A sheet of substrate, formed of titanium, tantalum, zirconium, hafnium or columbium is first abraded, as by a wire brush. Immediately preceding electrodeposition, the substrate is soaked in de-mineralized water and is thereafter immediately transferred to the electrolyte.

An aqueous electrolyte is prepared containing the following compounds in the concentrations shown for each:

	Grams per liter
$Pb(NO_3)_2$	200
NaF	0.5
HNO_3	5–20

The electrolyte is tested to determine the amount of iron present. Provided that such test shows that iron is present in an amount greater than .02 gram per liter, the following procedure is used: Litharge is added in an amount to drop the free acid content from its then-existing value to the range of about .5 to about 1.0 gram per liter. After this, lead carbonate is added to raise the pH to the region of about 3.8 to about 4.0. After this, the solution is boiled and subsequently allowed to set one hour at a temperature not less than 80° C. throughout which time the pH is not allowed to drop below 3.8. During this time, the iron precipitates out of solution and is readily removed by filtration. It is important that the pH be maintained between the prescribed limits during the setting time since, if the pH is allowed to go above about 4.0, lead will also precipitate out of solution; whereas, if the pH is allowed to go substantially below 3.8, the iron will go back into solution. After this, acid is added to raise the acid content to the normal value of 5 to 20 grams per liter before starting to plate the graphite anodes.

In the foregoing treatment, it is possible to use lead carbonate from the beginning rather than to add first litharge and subsequently lead carbonate, but this has the disadvantage of being more costly because of the higher cost of lead carbonate as compared to litharge. It is also possible, as another alternative, to use litharge throughout rather than to use litharge first and subsequently lead carbonate, but the disadvantage of this alternative is the greater difficulty in controlling the pH of the solution as it reaches the desired range of about 3.0 to about 4.0.

Reference may be made to the flow diagram of FIG. 2 which illustrates the foregoing process for the removal of iron from the electrolyte.

The electrolyte is poured into a cell and heating and agitation of the solution is started. On reaching a temperature of 85° C., the substrate and graphite cathode are installed and arranged substantially as illustrated in FIG. 3, and electrodeposition is started. Electrical connection is made directly to the substrate above the solution level before immersion in the electrolyte. Immediately after immersion, the current is turned on to avoid any battery action.

Circulation of the electrolyte is started at the same instant electrodeposition is initiated and is continuous thereafter. Litharge (PbO) is added to the electrolyte as it leaves the cell in a sufficient quantity to maintain the nitric acid (HNO_3) concentration in the range of 5–20 grams per liter. Agitation of the electrolyte is continuous throughout the plating time.

Operating conditions for above example

Electrolyte:	Grams per liter
Lead nitrate	200
Sodium fluoride	0.5
Nitric acid	5–20

Anode: 1/16 x 8 x 30" titanium, tantalum, zirconium, hafnium or columbium, with surfaces abraded by wire brush. Immersed in solution 26" giving available plating area of approximately 416 sq. in.

Cathode: A cathode measuring 1/16 x 5 x 30" is disposed at each side of the anode.

Spacing: 2½" between cathode surface and anode surface.

Temperature: 73° C.–92° C.

Current Density: 65 amperes per sq. ft.

Plating Time: About 24 hours or until a coating of about ¼" thickness is obtained on all surfaces of the anode.

For the first use of the substrate, a thin film of lead dioxide is plated onto its surface by plating the anode in the electrolyte and allowing plating to proceed for only a few minutes. The anode is then removed from the electrolyte, washed in de-mineralized water, and then re-inserted into the electrolyte, after which plating occurs as set forth above. The initial thin film of lead dioxide is retained on the anode after the heavier coating is removed so that it is not necessary to plate a thin film onto the anode again during subsequent re-plating.

Upon removal of the anode from the cell, the lead dioxide coating is mechanically removed as by flexure of the substrate, which causes the lead dioxide coating to fracture and break off. The lead dioxide is then washed with de-mineralized water and broken with a jaw crusher into pieces not exceeding ¼" in any dimension.

Following this, the crushed lead dioxide is broken up in a hammer mill to a particle size not exceeding 3.5 microns. Thereafter, the particles of lead dioxide are fed to a fluid energy-type mill, which further reduces the particle size the desired amount, to a low of about .3 micron.

What we claim is:

1. In a method for electrolytically producing powdered lead dioxide by depositing lead dioxide on a substrate in an electrolyte which includes lead nitrate and free nitric acid, the improvement which comprises:

commencing the electrodeposition with electrolyte having an iron concentration therein of no more than about .02 grams per liter, calculated as free iron;

introducing iron into the electrolyte as an impurity during the operation of the celll;

before the iron content in the electrolyte reaches a concentration of 0.1 gram per liter, removing from the cell a portion of the electrolyte, treating the removed electrolyte for reducing the iron concentration to a level below about .02 gram per liter, calculated as free iron, and returning the treated electrolyte to the cell;

maintaining free nitric acid and lead nitrate in the electrolyte at concentrations in the ranges of about 5 to about 20 grams per liter and about 50 grams per liter to about saturation, respectively, and operating the electrodeposition discontinuously with an interruption therein after a thin layer of lead dioxide has been coated on the substrate, whereby said thin coating tightly adheres to the substrate and is retained thereon whereas the subsequently deposited lead dioxide can readily be removed from the substrate allowing the substrate with its thin coating to be thereafter used repeatedly for plating and subsequent removal of lead dioxide platings.

2. The method of claim 1 in which the substrate is selected from the group consisting of titanium, tantalum, zirconium, hafnium, or columbium.

3. The method of claim 1 in which the surface of the substrate is abraded by a wire brush prior to its initial insertion in the electrolyte.

4. The method of claim 1 in which said interruption of the electrodeposition is effected by removing the thinly-plated substrate from the electrolyte, washing the plated substrate, and re-insertion of the substrate into the electrolyte followed by a continuation of the plating.

5. The method of claim 1 in which the current density of the anode during the electrodeposition process is not permitted to exceed about 70 amperes per square foot.

References Cited

UNITED STATES PATENTS

1,574,055	2/1926	Pedersen	204—49
2,945,791	7/1960	Gibson	204—57
3,023,149	2/1962	Zeman	204—12
3,463,707	8/1969	Gibson et al.	204—57

TA-HSUNG TUNG, Primary Examiner

U.S. Cl. X.R.

204—10, 57, 96