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INDIUM ELECTROPLATING

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This invention relates to the electrodeposition of indium and to electroplating baths useful in connection therewith.

Several processes have heretofore been proposed for the electrolytic deposition of indium, but so far as we are aware, these processes are troublesome to operate because they require frequent adjustment of the chemicals in the solutions to keep them up to strength. Some of those using acid electrolytes with soluble anodes also tend to hydrolyze, producing decomposition products, and, after running for varying periods of time, the electrolytes must be reworked and purified or replaced by fresh solutions. These requirements increase the cost of operating these processes.

The principal object of our invention accordingly is to provide a simple, efficient process which shall avoid some of the difficulties mentioned.

Another object of the invention is to provide a process of this kind capable of producing good, fine-grained, smooth deposits on the bearing surfaces of bearings and other objects to be electroplated with indium.

The invention accordingly comprises the novel processes and steps of processes, specific embodiments of which are described hereinafter by way of example and in accordance with which we now prefer to practice the invention; and the indium-containing electrolytic baths which may be employed therewith.

We have found in accordance with our invention that indium may be electrodeposited from solution on objects such as bearing surfaces, and various other surfaces capable of receiving electrodeposits by preparing an electrolyte containing an indium salt of perchloric acid and also a quantity of said peracid in uncombined or free form, which is stable under the conditions of operation chosen, and passing a current through electrodes in the electrolyte to deposit indium on the cathode which may consist of the bearing or other object to be plated.

In accordance with our invention, the electrolyte preferably consists of an aqueous solution of indium perchlorate, $In(ClO_4)_3$, and free perchloric acid, $HClO_4$. In operating our process, an electrolyte is prepared consisting of perchloric acid and indium perchlorate as mentioned. A pure indium metal anode is employed as one electrode and the article to be indium plated is placed in the tank as a cathode. Upon passing electric current, the indium is continually dissolved from the indium anode and plated on the

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cathode. The electrolyte may be easily prepared as described below and, after it has been placed in service, the indium content and acid content are readily maintained within proper limits during electrolysis. This is preferably done by a simple operation, namely, the acid or pH value of the solution is automatically recorded by well-known means for such purpose and if the pH value falls outside of the desired range, the necessary adjustment is made to restore it. We have found a good working pH range to be from about 0.5 pH to about 1.5 pH, when operating at room-temperature-(about 70° F.). Upon maintaining such pH, the indium content readily adjusts itself.

We have found that good, fine-grained, smooth deposits over a wide range of conditions may be obtained. For example, deposits of this character have been plated out from the following preferred ranges using indium perchlorate and perchloric acid: A current density from about 10 to about 55 amperes per square foot, a voltage from about 0.6 to about 2.5, a temperature from about 75° F. to about 130° F., indium content of electrolyte from about 20 grams to about 60 grams per liter, and uncombined perchloric acid from about 1 gram to about 75 grams per liter.

One of the advantages which we have found in the operation of the process involving the use of our electrolytic baths mentioned is that they show little tendency to hydrolyze in operation which is one of the disadvantages of some prior processes. Our electrolyte is especially well adapted to the use of soluble anodes when compared to other processes.

Furthermore, although we may employ an inert anode, we prefer to employ an anode of substantially pure indium; that is, containing about 99.8% or more of indium. Thus, in using such pure indium anode, as the indium is removed from the bath and deposited on the cathode by electrolysis, it is continually replaced by the indium from the anode so that the indium content of the bath remains within the desired limits automatically. Since substantially no hydrolysis occurs, substantially no change will occur in the plating bath as long as the current characteristics remain the same. If for any reason these should change substantially and corresponding change occurred in the acid value of the bath, this would be indicated by the pH machine and corrected accordingly as mentioned. Such changes in the conditions, however, are not apt to occur and, accordingly, once the process starts, it continues with little or no attention thereafter.

We have found that indium does not dissolve readily in perchloric acid and, accordingly, we find it preferable to use one or the other of the following procedures for preparing the electrolyte. The electrolyte of indium and free perchloric acid may be formed by placing a substantially pure indium anode in a tank containing a solution of perchloric acid and with a very small cathode, the current being passed until a suitable indium content as perchlorate in the acid is obtained. Alternatively, the electrolyte may be made by dissolving cupric oxide, CuO, or other metallic oxide below indium in the electromotive series, in an aqueous perchloric acid solution and then cementing out the copper with substantially pure indium chips, leaving a solution of indium perchlorate. This procedure takes less time than the electrolytic method of preparing the electrolyte, although the electrolytic method is commerically simpler and more practical. Another method which may be employed is to dissolve substantially pure indium hydroxide, $In(OH)_3$, or even indium oxide, In_2O_3, (if these materials are available) in a strong aqueous perchloric acid solution and then diluting to the desired value. The desired indium content and acid content of the electrolyte may be readily obtained by any of the methods mentioned.

We have found that the plating bath, as indicated, has excellent "throwing" power and we have plated indium from such electrolyte on various metals and alloys, some of which are mentioned below.

The process, as stated, may be used for plating bearings, as well as for other objects with more complicated contours. Of course, various shaped anodes may be used depending upon the size and shape of the object being plated.

Although the current efficiency in the plating of small amounts of metal is not vitally important, as, for example, in the plating of lead-bearing surfaces on lead-silver-steel bearings, tests show that with high acid concentrations, say 60 grams per liter and above, the current efficiency is low, namely, about 20 to 25%, whereas, at low free acid concentrations, say 5 grams per liter down to 1 gram per liter, for example but without limitation, the efficiencies were close to 100%.

The plating may best be done in a glass tank if the work is small, whereas for larger work, a tank made of steel or composition painted with an acid-resisting paint which may be a plastic dissolved in a hydrocarbon vehicle, giving an acid-resistant coating which withstands temperatures of 180° F. wet and 550° F. dry. Tanks made of ceramics, acid-resisting bricks or rubber-lined tanks may be used also.

In operating our process, we have found that very smooth deposits can be obtained without any addition agents. However, even more desirable finer deposits are obtainable by the addition of small amounts of glue or other similarly acting addition agent.

The following are examples of our invention as we now prefer to practice it. It is to be understood that these examples are illustrative and that the invention is not to be restricted thereto except as indicated in the appended claims.

Example 1

Fifty-five grams of cupric oxide (CuO) was dissolved in a solution containing 160 grams per liter of perchloric acid ($HClO_4$), 100%. The dissolving of the CuO was speeded up by heating; however, the solution was not heated to the boiling point.

As soon as the CuO was all in solution, a calculated quantity of pure indium was submerged in the $Cu(ClO_4)_2$ solution and $In(ClO_4)_3$ was formed by cementing out the copper. Upon completion of the reaction, when no trace of copper remained in the solution, the cement copper was filtered off, leaving a water-white solution of indium perchlorate.

This solution, prepared as above, was placed in a glass tank and a pure indium metal slab suspended as an anode. The following metals, employed as cathodes, were plated in this solution: Copper, brass, aluminum, silver, lead, steel and cadmium, of which copper, silver, lead and cadmium are well-known components of bearings.

The same conditions were maintained in each case and these were as follows: Current density, 30 amperes per square foot of cathode surface; temperature, 78 to 80° F.; voltage, 1.15 volts.

The plating time was 30 minutes for each metal and fine-grained smooth deposits were made in each case. The time of plating can, of course, be increased or decreased, depending on the thickness of deposit desired and the current density can also be varied as previously mentioned.

Example 2

In this example, the electrolyte was made up as mentioned above and all other conditions recited in Example 1 were observed, except 200 milligrams of glue per liter of electrolyte were added and a somewhat higher voltage occurred. During the run the voltage rose to 1.3 volts. The deposits with the glue were noted to be even finer grained and smoother than without the glue.

Example 3

Instead of preparing the electrolyte by means of solution of cupric oxide in perchloric acid, the electrolyte was prepared by electrochemical solution of indium as follows:

A liter of aqueous solution of perchloric acid containing 140 grams per liter of $HClO_4$ was electrolyzed by submerging 7.5 square inches of a substantially pure indium anode containing at least 99.8% indium and a stainless steel sheet having an area of 1.5 square inches as cathode. A current density of 20 amperes per square foot of anode area was used and the electrolyte consisting of $In(ClO_4)_3$ in water with some free acid built up to 30 grams per liter of $In(ClO_4)_3$ after operating for about 50 hours.

Thereafter, the solution was placed in a glass tank and with a pure indium metal slab as anode, plating was carried out in the same way as described in Example 1 above.

That the electrolyte has excellent throwing power was illustrated in these tests by the fact that the side of the objects away from the anodes were also plated with indium and it was estimated that the thickness of the deposit on the reverse side was about half that of the side facing the anode.

Although not restricted to such use, our above-described invention is well suited as above stated for the plating of bearing surfaces. One of the well-known bearings in general use today is a steel ring coated with silver followed by a thin plating of lead over the silver. A bearing so prepared may then be plated with a thin coat of indium over the lead, applied in accordance with our above-described invention. Other bearings such as copper-lead bearings may be similarly treated. Among other uses also contemplated by

us for our invention is the coating of silver or other tarnishable metals capable of being plated by indium to prevent such tarnishing. In all of these practical methods, a particular advantage of our plating process is that the solution has excellent throwing power and so is capable of delivering a fine uniform coating on articles having irregular contours.

It is possible that the indium electroplating bath may become contaminated from an outside source or otherwise, with metallic material which can be precipitated out of the solution by circulating it through shot indium.

What we claim is:

1. A process for electrodepositing indium which comprises, preparing an aqueous solution of indium perchlorate of about 20 to about 60 grams per liter and free perchloric acid of about 1 to about 75 grams per liter, passing a current through electrodes in said electrolyte, the anode consisting of substantially pure indium, and depositing a fine-grained smooth deposit on the cathode.

2. A process for electrodepositing indium, which comprises electrolyzing an aqueous solution of perchloric acid with a substantially pure indium anode until an electrolyte consisting of indium perchlorate in water with some free acid is formed, the content of indium perchlorate being of about 20 to about 60 grams per liter and the content of free perchloric acid being of about 1 to about 75 grams per liter, and then using a substantially pure indium metal slab as anode and a bearing as cathode in said electrolyte, depositing a smooth fine-grained bearing surface of indium on said bearing.

3. A process for electrodepositing indium which comprises, dissolving cupric oxide in perchloric acid, adding sufficient substantially pure indium to the solution to remove the copper therefrom by cementation, to produce an electrolyte containing indium perchlorate and free perchloric acid, adjusting the indium content thereof to about 20 to about 60 grams per liter and free perchloric acid content to about 1 to about 75 grams per liter, employing a substantially pure indium metal as anode and a bearing as cathode in said electrolyte, and electrodepositing indium on the bearing surface of said bearing, adjusting the current density to about 10 to about 55 amperes per square foot, voltage to about 0.6 to about 2.5, and the temperature of electrolyte to about 75° F. to about 130° F.

4. An indium electroplating bath consisting essentially of an aqueous solution of indium perchlorate in the approximate proportion of 20 to 60 grams per liter and free perchloric acid in the approximate proportion of 1 to 75 grams per liter.

5. A process for electrodepositing indium which comprises, taking an aqueous solution of indium perchlorate and free perchloric acid containing about 20 to about 60 grams per liter of indium perchlorate and about 1 to about 75 grams per liter of free perchloric acid, employing a substantially pure indium metal as anode and a bearing as cathode in said electrolyte, and electrodepositing indium on the bearing surface of said bearing, adjusting the current density to about 10 to about 55 amperes per square foot, voltage to about 0.6 to about 2.5, and the temperature of electrolyte to about 75° F. to about 130° F.

6. A process for electrodepositing indium which comprises, electrolyzing an aqueous solution of perchloric acid with electrodes including a substantially pure indium anode until an electrolyte consisting of indium perchlorate in water with some free acid is formed, adjusting the indium content thereof to about 20 to about 60 grams per liter and free perchloric acid content to about 1 to about 75 grams per liter, employing a substantially pure indium metal as anode and a bearing as cathode in said electrolyte, and electrodepositing indium on the bearing surface of said bearing, adjusting the current density to about 10 to about 55 amperes per square foot, voltage to about 0.6 to about 2.5, and the temperature of electrolyte to about 75° F. to about 130° F.

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