

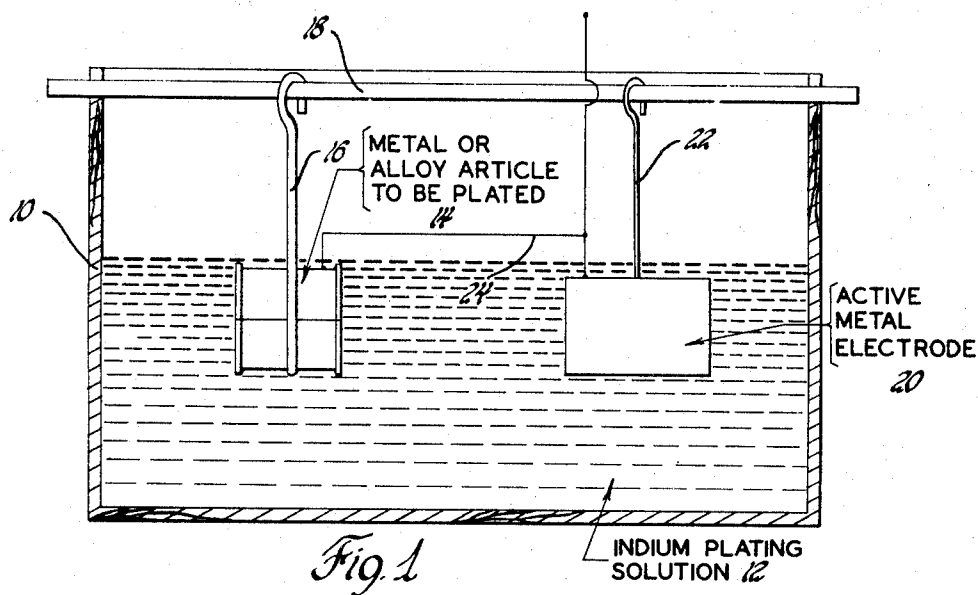
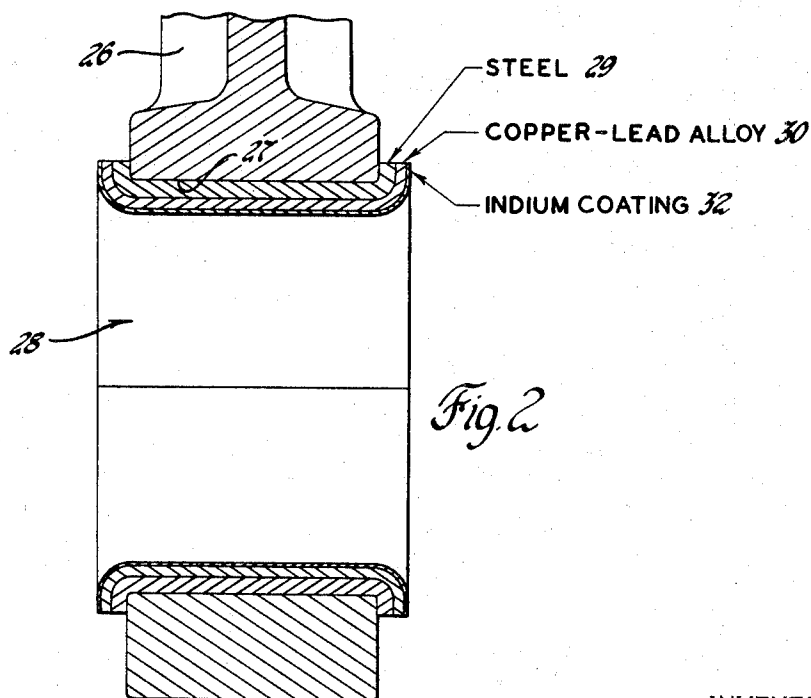
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J. L. GREENE

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METHOD OF INDIUM COATING METALLIC ARTICLES

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INVENTOR.
Joseph L. Greene
BY
Peter P. Kozak
ATTORNEY

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METHOD OF INDIUM COATING METALLIC ARTICLES

Joseph L. Greene, Royal Oak, Mich., assignor to General Motors Corporation, Detroit, Mich., a corporation of Delaware

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ABSTRACT OF THE DISCLOSURE

A copper-base alloy bearing is immersed into an aqueous acidic bath consisting essentially of an indium salt; an acid; and sodium potassium tartrate, sodium tartrate, potassium tartrate, or sodium formate acting as buffer. The bath has a pH of about 0.5 to 3.0. The bearing is directly connected to an electrode immersed in said bath having a higher effective electrolytic oxidation potential than said bearing, such as zinc, which thereby forms a galvanic couple causing indium to deposit on the bearing.

The present invention relates generally to a method of coating metallic articles with indium. More particularly, the present invention relates to a method of depositing an indium coating on metallic articles by an immersion deposition technique, wherein a smooth, dense, lustrous, adherent, fine-grained, ductile coating of indium is deposited on the articles without the use of electrical energy supplied from an external source of electrical power.

Immersion deposition is a well-known, relatively simple and inexpensive plating process. This process does not require a source of external electrical power, as in the instance of electroplating, electrefining and other electrodeposition processes, since immersion deposition plating may be carried out using a simple battery-type galvanic action. In other words, deposition of metal is caused by the formation of a galvanic couple between two dissimilar metals having different electrolytic oxidation potentials which are immersed in an electrically contacting arrangement in an acidic aqueous bath containing ions of the metal to be plated. In operation, the metal ions in the bath are reduced and plate out on the less electrolytically active of the dissimilar metals while the more active metal dissolves in the bath.

However, immersion deposition techniques are subject to certain serious limitations and drawbacks. One difficulty heretofore experienced with this type of deposition has been the fact that the deposit formed is usually so thin that it is readily rubbed or worn off from the metallic undersurface, particularly where large objects are so plated. In addition, the deposit is frequently dull, rough and uneven, but conventional buffing and polishing techniques cannot be used due to the aforementioned lack of adherence of the deposit. Furthermore, the choice of base metals on which other types or metals may be deposited is relatively limited, since the active metal, the base metal, and the metal ions in the bath must all have suitable rela-

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tive electrolytic potentials to effect the desired deposition. To my knowledge, no satisfactory method has heretofore been devised for the immersion deposition of indium on metallic articles, and particularly, on copper base articles and alloys thereof, such as copper-lead alloys, which results in the deposit of a smooth, dense and strongly adherent indium coating on the article so plated.

Indium articles and articles which have been electroplated with an indium coating are widely used in many applications, such as bearing applications, due to the excellent corrosion- and wear-resistant properties of indium. For instance, electroplated indium coatings have heretofore been used to improve the wear- and corrosion-resistant properties of copper-lead alloys and cadmium-lead alloys which are commonly used in automobile connecting rod sleeve bearings. In this particular application, it has been found that an indium coating substantially minimizes bearing malfunction by preventing the lead constituent in the alloy from deteriorating due to attack by organic acids which develop in the automobile crankcase lubricants over a period of time. After an electroplated indium coating has been applied to such a bearing alloy, the indium usually is at least partially diffused into the copper-lead or cadmium-lead bearing alloy by a conventional heat treatment to obtain better bonding characteristics between the indium coating and the underlying bearing alloy.

However, the production costs involved in electroplating indium metal on various base metals are relatively high and, in the particular bearing application mentioned above, the costs are often so high as to be objectionable even when a mass production electroplating technique is employed. The high cost of electroplating or other electrodeposition processes which require the use of an external electrical power source stems from such factors as the labor costs and handling requirements involved in racking and unracking the parts to be plated both before and after the plating process, the cost of elaborate equipment necessary for electroplating and other electrodeposition processes, and the close supervision and control required to insure the proper functioning of the plating bath. Naturally, a method of depositing indium metal on other base metals or alloys that does not depend on an external source of electric current, such as an immersion deposition technique, could be expected to greatly reduce the abovementioned costs and handling requirements involved in providing an indium coating on a metallic article, such as a copper-lead alloy sleeve bearing.

Therefore, it is a principal object of the present invention to provide a relatively simple and economical process for depositing an indium coating on various base metals and alloys which does not require the use of an external source of electricity, thereby greatly minimizing the amount of handling and plating equipment required and the attendant costs involved in processes, such as electroplating.

It is another object of the present invention to provide a relatively simple and economical immersion deposition process and bath for depositing a smooth, lustrous, fine-

grained, adherent and ductile coating of indium on metallic articles which overcome the above-mentioned difficulties and limitations of conventional immersion deposition processes.

These and other objects are accomplished in accordance with the present invention by an immersion deposition technique wherein a relatively electrolytically active metal electrode, such as a strip of zinc, and a less electrolytically active dissimilar metal article, such as a copper base alloy article, are placed in an electrically contacting arrangement and immersed in an acidic, aqueous bath having a pH ranging between about 0.5 to 3.0 and containing a dissolved indium compound so that a galvanic couple is formed in the bath and the indium ions in the bath plate out on the article to provide a smooth, lustrous, fine-grained, adherent, ductile coating of indium thereon.

Other objects, features and advantages of the present invention will be apparent from the following detailed description of certain embodiments thereof taken in conjunction with the accompanying drawing, in which:

FIGURE 1 is a vertical sectional view of a typical immersion tank in which a relatively electrolytically active metal electrode and the less electrolytically active metal article to be plated are in an electrically contacting arrangement and immersed in the indium plating bath of the present invention; and

FIGURE 2 is a partial vertical sectional view of a typical automobile connecting rod arrangement in which the sleeve bearing part thereof is provided with a thin wear- and corrosion-resistant indium coating in accordance with the subject immersion deposition process of the present invention.

Referring to FIG. 1 of the drawing, a typical example of a simplified apparatus for carrying out the indium immersion deposition process of the present invention is illustrated. As shown in FIGURE 1, the tank 10 contains the indium plating solution or bath 12 and may be constructed of wood or other suitable electrically insulating material, or it may be a metal tank having a suitable electrically insulating liner therein. As will hereinafter be more fully explained in reference to certain specific examples and preferred embodiments of the present invention, the plating solution 12 is an acidic, aqueous solution containing a dissolved indium compound and a buffering compound.

The metal or alloy article 14 to be plated, such as a copper-lead alloy sleeve bearing, may be immersed in the plating solution 12 by suspending it from a hook 16 attached to a rod 18, which may be advantageously made of wood or other nonconducting material. Similarly, the electrolytically active metal electrode 20, such as a strip or bar of zinc, is likewise immersed in the plating solution 12 by suspending it on a hook 22 attached to the rod 18. The metallic article 14 may be electrically connected with the electrolytically active metal electrode 20 by any suitable means, such as by direct contact or by an electrical conductor, such as a copper wire 24.

In accordance with the subject immersion deposition process, an indium coating may be deposited on any metallic article using the apparatus described above provided that the metal surface being plated has a lower effective electrolytic oxidation potential than the electrolytic reduction potential of the indium ions in the bath, and further, provided that it is also lower than the electrolytic oxidation potential of the active metal electrode used for reducing the indium ions in the bath. Also, the metallic article to be plated and the metal electrode should not cause serious contamination of the bath when metal ions of the article or electrode go into solution in the bath. Of course, the active metal electrode must have a higher effective electrolytic oxidation potential than the electrolytic reduction potential of the indium ions in the bath so that a galvanic couple is formed in the bath to

effect the desired deposition of indium on the article. Hence, ions of the active metal electrode will go into solution more readily than ions of the metallic article being plated due to the differences in their electrolytic oxidation potentials. Thus, in operation, electrons will flow from the active metal electrode 20 through the conductor 24 to the metal article 14 being plated, thereby causing the indium ions in the bath to be reduced at the surface of the article which results in the desired deposition of indium on the article.

Of course, it should be appreciated that there are several possible combinations of dissimilar metals and alloys which may be used as the active metal electrode and the metal article to be plated to provide the desired indium immersion deposition effect of the subject process. In other words, a variety of different active metal or alloy electrodes may be used in accordance with the subject process depending on their relative electrolytic oxidation potential with respect to that of the metal surface being plated and the electrolytic reduction potential of the indium ions in the plating bath. However, I prefer to use zinc as the active metal electrode for plating metallic articles made of copper, lead, cadmium, nickel, silver, aluminum, iron, steel and various alloys of these metals, such as copper-lead alloys.

Considerable variation in the make-up of the acidic aqueous indium plating solution or bath of the present invention is permissible. Indium sulfate, indium hydroxide, indium oxide, indium fluoroborate, or indium chloride may be employed as the source of indium ions in the bath, although indium sulfate is usually preferred, since it is the most convenient form of indium compound to use from the standpoint of cost and getting it into solution.

Sulfuric acid may be used in the aqueous bath to form an acid medium in which a galvanic couple may be formed between the two dissimilar metals to effect the desired plating reaction and to maintain indium ions in solution by preventing hydrolysis. However, other strong acids, such as hydrochloric acid and fluoroboric acid may also be used for these purposes, although sulfuric acid is normally preferred, due to its low cost, low volatility and ease of handling. Also, when zinc is employed as the active metal electrode in the subject immersion deposition process, the use of sulfuric acid substantially precludes side reactions which results in the formation of undesirable anions in the bath.

In addition, the subject acidic aqueous bath of the present invention should include a buffering agent or compound, such as sodium potassium tartrate, sodium tartrate, potassium tartrate or sodium formate, to reduce the effective hydrogen ion concentration of the bath. Preferably, a sufficient amount of a buffering compound should be employed to maintain the pH of the bath in a range of about 0.5 to about 3.0. Sodium potassium tartrate is a particularly suitable buffering compound for this purpose when a zinc electrode and sulfuric acid are employed in the subject process. I have found that the buffering compounds also exert a slight beneficial effect as grain refiners in the subject immersion deposition plating process. In the latter instance, it is believed that the buffering compound serves to provide a complexing reaction in the bath to retard the indium deposition rate to a degree which will provide a fine-grained deposit of indium on the article.

Satisfactory depositions of indium on various base metals and alloys have been obtained in accordance with the subject immersion deposition process using baths having a composition, per liter of water, of about 0.05 to about 0.25 mole of an indium compound, such as indium sulfate, indium oxide, indium fluoroborate, indium hydroxide or indium chloride, about 0.3 mole to about 2.0 moles of a strong acid, such as sulfuric acid, fluoroboric acid and hydrochloric acid, and about 0.2 mole to about

1.0 mole of a buffering compound, such as sodium potassium tartrate, sodium tartrate, potassium tartrate or sodium formate. However, when the subject immersion deposition process is used to provide an indium coating on a copper base article, such as a copper-lead alloy bearing, and zinc is used as the active metal electrode, the bath composition, per liter of water, preferably ranges from about 0.075 mole to about 0.20 mole of indium sulfate or indium hydroxide, about 1.0 mole to about 1.7 moles of sulfuric acid and about 0.3 mole to about 0.8 mole of sodium potassium tartrate or sodium formate.

To further illustrate the latter application of my invention, FIGURE 2 of the drawing shows the bearing portion of a typical steel automobile connecting rod which is used to connect a piston to an automobile crankshaft. The connecting rod shaft 26 has a cylindrical opening 27 in its lower portion in which a suitable bearing 28 embodying the present invention is snugly positioned. As shown in the drawing, the bearing 28 includes a semi-cylindrical backing member 29 made of a relatively hard and strong metal, such as steel, and a copper-lead alloy bearing facing 30 having a composition, by weight, of about 70% copper and 30% lead provided on the radially inner surface of the backing member 29.

Then, in accordance with the present invention, the radially inner surface of the bearing facing 30 is provided with a thin, adherent, wear- and corrosion-resistant coating of indium metal 32 by the subject immersion deposition process to protect the lead constituent of the alloy facing from attack by organic acids which develop in automobile crankcase lubricants over a period of time. It should be appreciated that the thickness of the indium coating 32 is greatly exaggerated in the drawing for the purpose of illustration, since an indium coating having a thickness ranging between about 0.0001 inch to about 0.010 inch is suitable for this purpose. The immersion deposited indium coating 32 having such a thickness may be readily applied to the copper-lead alloy bearing facing 30 using a zinc electrode and an apparatus similar to that shown in FIGURE 1 of the drawing.

However, the copper-lead alloy bearing facing preferably is first vapor degreased and then subjected to a slight pickling treatment prior to being placed in the bath. The vapor-degreasing step may be conveniently accomplished by any suitable means, such as suspending the bearing in a suitable vapor chamber containing vapors from a boiling solvent, such as perchloroethylene or trichloroethylene. In accordance with conventional vapor-degreasing techniques, the vapors condense on the copper-lead alloy bearing facing 30 and then run off to the liquid reservoir below in the vapor chamber, carrying with them the grease, oils and loosely adherent surface contaminants on the copper-lead bearing facing. After about five minutes of such treatment, the bearing may be removed from the vapor chamber and the remaining solvent on the facing surface evaporated, leaving only tightly adherent contaminants.

The acid pickling technique serves to remove these residual surface contaminants from the copper-lead alloy bearing facing and also provides an active metal surface which will readily accept the indium coating 32 which is subsequently deposited by the subject immersion deposition process of the present invention. A conventional pickling treatment using warm dilute nitric acid bath may be suitably employed to treat the copper-lead alloy bearing facing 30 of the bearing 28 for the above-mentioned purposes. The pickling treatment preferably is allowed to continue only until the bearing facing appears to be clean and bright, and then the bearing is removed from the pickling bath, rinsed in cold water, and immediately placed into the indium plating solution in the immersion tank along with the zinc electrode in an electrically contacting arrangement as illustrated in FIGURE 1 of the drawing.

As previously mentioned, the composition of the indium plating solution or bath may vary considerably in accordance with the present invention. For instance, the bearing 28, which was vapor degreased and pickled in the above-mentioned manner, and a zinc bar were immersed in a bath having a composition of 40 grams indium hydroxide, 100 milliliters of sulfuric acid, 100 grams of sodium potassium tartrate and one liter of water at a bath temperature of 140° F. After ten minutes, the bearing 28 was removed from the bath and an indium coating was deposited on the copper-lead alloy bearing facing 30 to a thickness of about 0.0001 inch. This indium coating was smooth, lustrous, fine-grained, ductile and strongly adherent to the copper-lead alloy bearing facing. As with electroplated indium coatings, the adherence of the coating may be improved by subsequently partially diffusing the indium into the copper-lead alloy facing by a heat treatment at a temperature of about 340° F. for about 30 minutes.

The zinc consumption under the process conditions described above was relatively small, and the efficiency of the bath was about 70% based on the weight of indium deposited to the weight of zinc consumed. Thus, the bar of zinc may be used repeatedly in plating other articles by the subject indium immersion deposition process. Also, it was found that the bath could be used continuously without addition of more indium hydroxide until about 5 grams of indium remained per liter of solution. These, of course, are important economic and handling advantages of the subject immersion deposition process over processes, such as electroplating, which requires close supervision and control of the bath composition during the plating process.

A further handling advantage of the subject process is that the spent bath may be revitalized at any time by the addition of sulfuric acid and indium hydroxide or indium sulfate to form approximately the same original bath concentration of acid and indium ions in the bath. Of course, the pH of the bath should be maintained in the range of 0.5 to 3.0 to effect the desired deposition of indium. It was also determined that the accumulation of zinc salts, such as zinc sulfate, in the bath up to the point of saturation (about 83 grams per liter) had no perceptible effect on the quality of the indium deposit in the above-described process and lead to only slight reduction in the deposition rate of indium on the copper-lead alloy surface. This rate dropped from about .0001 inch in ten minutes to about .0001 inch in fifteen minutes at saturation with zinc sulfate at 140° F. and an indium concentration of 28 grams per liter of solution.

The subject indium immersion deposition process may be suitably carried out at room temperature (about 70° F.) but, in most applications, it preferably is carried out at a bath temperature ranging from about 120° F. to about 150° F. to reduce plating cycle time. The actual temperature of the bath which is used for carrying out the subject process in most applications will, of course, depend on the particular bath composition, the composition of the metal being plated and the results desired. Moreover, the thickness of the indium deposit on the metal being plated will similarly depend upon the bath composition, the metal composition, the temperature of the bath and the amount of exposure time of the metal in the bath. Smooth, adherent indium coatings have been deposited on various metals, such as aluminum, iron, steel, nickel, cadmium base metals and alloys of these metals, by the subject immersion process up to about 0.01 inch in thickness. An immersion time ranging between about ten minutes to about thirty minutes is suitable for most applications utilizing the subject process to effect the desired deposition of indium metal on the metal article being plated.

Other specific examples of bath compositions and process variables which have been utilized in accordance with the present invention to provide a smooth, adherent im-

mersion coating of indium on various base metals are shown in Table I:

bearing without the aid of an external source of electric power, said method comprising the steps of vapor de-

TABLE I

	I	II	III	IV	V	VI	VII	VIII
A Bath Composition:								
Indium sulfate, grams.....	40	50	65	-----	35	-----	-----	14
Indium hydroxide, grams.....	-----	-----	-----	-----	-----	34	-----	-----
Indium fluoroborate, grams.....	-----	-----	-----	-----	-----	-----	38	-----
Indium chloride, grams.....	-----	-----	-----	20	-----	-----	-----	-----
Sulfuric acid, ml.....	95	50	100	-----	70	-----	-----	75
Fluoroboric acid, ml.....	-----	-----	-----	-----	-----	70	-----	-----
Hydrochloric acid, ml.....	-----	-----	-----	40	-----	70	-----	-----
Sodium tartrate, grams.....	-----	-----	-----	-----	-----	85	-----	-----
Sodium potassium tartrate, grams.....	184	-----	-----	-----	-----	-----	-----	160
Potassium tartrate, grams.....	-----	-----	162	-----	150	100	-----	-----
Sodium formate, grams.....	-----	25	-----	50	-----	-----	20	-----
Water, liter.....	1	1	1	1	1	1	1	1
B Bath Temperature, ° F.....	140	125	70	100	140	120	70	120
C Immersion Time, mins.....	10	15	20	10	10	15	10	10
D Active Metal Electrode.....	(1)	(1)	(1)	(1)	(1)	(1)	(1)	(1)
E Composition of Metal Being Plated.....	(2)	(2)	(2)	(4)	(3)	(6)	(4)	(7)
F Indium Coating Thickness, inch.....	.001	.0007	0.001	.0003	.0008	.0007	.0006	.0005

¹ Zinc.

² Cu-Pb alloy (70% Cu, 30% Pb).

³ Copper.

⁴ Aluminum.

⁵ Cd-Pb alloy (95% Cd, 5% Pb).

⁶ Nickel.

⁷ Iron.

While I have described my invention in terms of certain preferred embodiments and specific examples thereof, it is not intended to be limited thereby, except as defined by the claims that follow.

I claim:

1. A method of providing an immersion deposited indium coating on a metallic article without the aid of an external source of electrical current, which article is comprised principally of a material which has a lower electrolytic oxidation potential than said indium, which method comprises the steps of immersing said article in a buffered, acidic, aqueous, indium plating bath having a pH ranging between about 0.5 to about 3.0, said bath consisting essentially of, per liter of water, between about 0.05 mole to about 0.25 mole of at least one dissolved indium compound selected from the group consisting of indium sulfate, indium hydroxide, indium oxide, indium fluoroborate and indium chloride, between about 0.2 mole to about 1.0 mole of at least one buffering compound selected from the group consisting of sodium potassium tartrate, sodium tartrate, potassium tartrate and sodium formate, and between about 0.3 mole to about 2.0 moles of at least one acid selected from the group consisting of sulfuric acid, fluoroboric acid and hydrochloric acid, directly electrically connecting said article to a metal electrode having a higher effective electrolytic oxidation potential than said article, and said indium, and contacting said electrode with said bath to form a galvanic couple in said bath which causes said indium coating to be deposited on said article.

2. A method of providing an indium coating on a copper base article without the aid of an external source of electrical current, said method comprising the steps of immersing said copper base article in a buffered, acidic, aqueous, indium plating bath having a pH ranging between about 0.5 to about 3.0, said bath consisting essentially of, per liter of water, between about 0.075 mole to about 0.20 mole of indium sulfate, about 1.0 to 1.7 moles of sulfuric acid and about 0.3 mole to about 0.8 mole of sodium potassium tartrate, maintaining the temperature of said bath between about 120° F. to 150° F., directly electrically connecting said article to a zinc electrode, immersing said electrode in said bath to form a galvanic couple in said bath, which causes said indium coating to be deposited on said article, and subsequently removing said article from said bath after said coating has been deposited to a thickness between about 0.0001 inch to about 0.01 inch.

3. A method of providing a smooth, dense, fine-grained, adherent indium coating on a copper-lead alloy

greasing said article to remove loosely adherent impurities from the bearing surface of said copper-lead alloy bearing, pickling said article to remove tightly adherent impurities from said copper-lead alloy bearing surface, immersing said copper-lead alloy bearing in a buffered, acidic, aqueous, indium plating bath, said bath consisting essentially of, per liter of water, between about .075 mole to 0.20 mole of at least one indium compound selected from the group consisting of indium sulfate and indium hydroxide, between about 1.0 mole to 1.7 moles of sulfuric acid, and between about .3 mole to .8 mole of at least one buffering compound selected from the group consisting of sodium potassium tartrate and sodium formate, directly electrically connecting said copper-lead alloy bearing with a zinc electrode, immersing said zinc electrode in said bath to form a galvanic couple in said bath which results in said indium coating being deposited on said bearing surface, maintaining said bath at a temperature ranging between about 120° F. and 150° F., maintaining said copper-lead alloy bearing and said zinc electrode in said bath between about 10 to about 30 minutes, and subsequently removing said electrode and said copper-lead bearing from said bath after said indium coating has been formed on said bearing surface.

4. A method for increasing the corrosion and wear resistant properties of copper-based alloy bearings by depositing an indium coating on said bearing without the aid of an external source of electrical current, said method comprising the steps of immersing said bearing in a buffered, acidic, aqueous, indium plating bath having a pH ranging between about 0.5 to about 3.0, said bath consisting essentially of per liter of water between about 0.05 to about 0.25 mole of at least one dissolved indium compound selected from the group consisting of indium sulfate, indium hydroxide, indium oxide, indium fluoroborate, and indium chloride, between about 0.2 mole to about 1.0 mole of at least one buffering compound selected from the group consisting of sodium potassium tartrate, sodium tartrate, potassium tartrate and sodium formate, and between about 0.3 mole to about 2.0 moles of at least one acid selected from the group consisting of sulfuric acid, fluoroboric acid and hydrochloric acid, directly electrically connecting said bearing to a metal electrode having a higher effective electrolytic oxidation potential than said bearing and said indium and contacting said electrode with said bath to form a galvanic couple for a time sufficient to deposit about 0.0001 inch to about 0.01 inch of indium on said bearing.

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10 JOHN H. MACK, *Primary Examiner*.

HOWARD S. WILLIAMS, *Examiner*.

G. KAPLAN, *Assistant Examiner*.