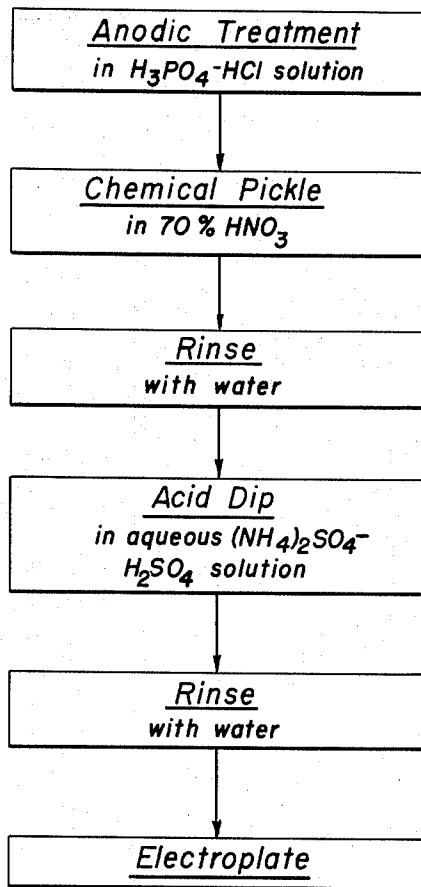


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J. G. BEACH ET AL  
ELECTROPLATING ON BERYLLIUM

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INVENTORS  
*John G. Beach*  
BY *Charles L. Faust*

*Roland A. Anderson*  
Atty.

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## ELECTROPLATING ON BERYLLIUM

John G. Beach and Charles L. Faust, Columbus, Ohio, assignors to the United States of America as represented by the United States Atomic Energy Commission

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7 Claims. (Cl. 204--32)

This invention relates to electroplating on a beryllium surface and in particular it pertains to a method for pretreatment of beryllium for electroplating.

Inasmuch as beryllium bodies tarnish in air readily, it would be desirable to form a protective electroplate. In the commercial preparation of most metals for electroplating the base metal surface must be chemically clean to obtain good adhesion.

Beryllium has displayed a resistance to electroplating when pretreated by methods commonly used in industrial electroplating practice. This has been attributed to incomplete activation of the beryllium surface. Inasmuch as a tight bond occurs only in a variegated manner over about one-third of the total surface, it is believed that certain crystal faces properly respond to usual pretreatment methods and that other crystal faces on different orientations remain impervious.

A method of electroplating of beryllium was developed by Morris Kolodney. In this process the beryllium body is etched as an anode in an aqueous solution containing phosphoric acid and hydrochloric acid, washed in water, immersed in a solution containing ammonium sulfate and sulfuric acid, washed in water, and electroplated with a metal. The process is described in report AECD-2845, entitled "Electroplating of Beryllium," published by United States Atomic Energy Commission, Oak Ridge, Tennessee. While Kolodney's method gives a satisfactorily adherent coating when the electrodeposit is thin (<1 mil), heavy electrodeposits (>2 mils); such as silver, could be peeled. Thus the degree of adherence left something to be desired. By virtue of this new treatment it is possible to produce a bond over a greater portion of the beryllium surface than was previously possible.

It is the primary object of this invention to provide an efficient method for preparing a beryllium surface for electroplating.

It is another object to provide a method of preparing a beryllium body with electroplated metal bonded thereto, regardless of the thickness of the electrodeposit.

Other objects and advantages of this invention will be readily apparent to those skilled in the art upon reading the following description.

The new method of pretreating beryllium has been discovered for obtaining greatly improved adherence of the electroplate. The entire electroplating process to be described includes a preliminary surface preparation, an intermediate pretreatment, including an anodic pickling and the novel chemical pickling, and finally an electroplating.

Generally, the adhesion, porosity, uniformity, and smoothness of electroplated metals are no better than the surfaces to which they are applied. Accordingly, the preparation of the beryllium surface is fundamental in determining the quality of the final product. The preliminary surface preparation includes degreasing and cleaning, which may be followed by chemically polishing with or without a later pickling. A water rinse is used after both the polishing and the pickling. Though most

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dirt can be removed chemically, greases and oils are best cleaned by organic solvents. However, residual dirt is removed by cathodic cleaning in a caustic solution. To reveal surface defects beryllium is chemically polished in a predominantly phosphoric acid solution which leaves a semi-passive film. Although this film is generally dissolved during subsequent operations, its removal in a dilute sulfuric acid solution at room temperature is preferred so as to more uniformly activate the beryllium surface.

The intermediate pretreatment follows the preliminary surface preparation and includes the steps of an anodic pickle, a chemical pickle, a water rinse, and an acid dip. The anodic pickle is an etch treatment in an aqueous solution comprising a polybasic oxygen-containing acid and a monobasic oxygen-free acid while passing an electric current therethrough. The chemical pickle is also an etch treatment in a nitric acid solution, e. g., 70% nitric acid, with the etching time depending upon the nitric acid concentration. After these etch treatments the beryllium is rinsed in water and is ready for electroplating. In the event that the metal to be electroplated from highly alkaline solutions is either silver or tin, it is necessary in addition to the foregoing steps to subject the beryllium to an additional step of etching in an aqueous acidic solution including ammonium sulfate and sulfuric acid. This is followed by a water rinse.

*Example*

The preferred conditions including the specific solutions for the process of this invention have been found to be as follows:

The cathodic cleaning used in the preliminary surface preparation employs a caustic solution of 50 to 100 g./liter NaOH or KOH at room temperature through which a current is passed at a current density of 25 to 75 amp./ft.<sup>2</sup>. Following this the surface defects are removed by a chemical polish. This polish is obtained by immersion in a solution of 5% (by weight) H<sub>2</sub>SO<sub>4</sub>, 75% (by weight) H<sub>3</sub>PO<sub>4</sub>, 5% (by weight) CrO<sub>3</sub>, and the balance water, at approximately 120° F. By this immersion one mil of surface metal is removed in twenty minutes. Thereafter the beryllium is pickled from one-quarter to one-half minute in 10% (by volume) of concentrated sulfuric acid at 80°±10° F., whereby any surface film remaining after the preceding chemical polish is removed.

In the intermediate pretreatment the anodic pickle follows the preceding sulfuric acid pickle and is essentially an etch treatment for two minutes in an aqueous solution including 10% (by volume) of 85% H<sub>3</sub>PO<sub>4</sub>, 2% (by volume) of 38% HCl, and the balance water using a current density of 100±50 amp./ft.<sup>2</sup> at a temperature of 80° F. Subsequently the beryllium is subjected to a chemical pickle which is an etch treatment in 70% HNO<sub>3</sub> for approximately two minutes at a temperature of 80°±10° F. After these etch treatments the beryllium is rinsed in water and is ready for electroplating, except when the electrolytes are highly alkaline.

Various metals have been plated to beryllium including aluminum, chromium, copper, iron, manganese, nickel, silver, tin, and zinc. Thick electroplates obtained were firmly bonded to the beryllium surface and could not be peeled therefrom.

When electroplating from alkaline baths, the beryllium body after the anodic and chemical pickles and water rinse is immersed in an aqueous solution at 80°±10° F. and containing 100 g./liter of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and sufficient H<sub>2</sub>SO<sub>4</sub> to provide a pH of 2. After an immersion for one-half to one minute, the body is removed and rinsed with water.

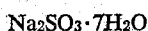
Other metals may be applied either directly or indirectly or over another metal that can be electroplated

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directly. Direct plating requires that the bath be chemically unreactive with beryllium. Most of the plating baths used are commercial-type baths, as shown below, for manganese and tin.

Iron is electroplated directly on beryllium using a bath consisting of 300 g./liter of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , 42 g./liter of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ , 35 g./liter of  $\text{H}_3\text{BO}_3$ , 15 g./liter of  $\text{NaCOOH}$ , and 1 g./liter of Duponol ME (fatty alcohol sulfate emulsifying and dispersing agent used in electroplating), and having a pH of 4.0 at a temperature of 140° F. A current density of 40 amp./ft.<sup>2</sup> is used. This bath is also suitable for plating over a preceding zinc coating.

Manganese is electroplated directly on beryllium from the bath consisting of 40 g./liter of  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ , 135 g./liter of  $(\text{NH}_4)_2\text{SO}_4$ , at least 0.5 g./liter of



to give a pH of 7.5 at a temperature of 100° F. A current density of 40 amp./ft.<sup>2</sup> is used.

Tin is plated directly on beryllium from a bath consisting of 150 g./liter of  $\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$ , 15 g./liter of  $\text{NaOH}$ , and 22.5 g./liter of  $\text{NaC}_2\text{H}_3\text{O}_2$ , at a temperature of 150° F. A current density of 25 amp./ft.<sup>2</sup> is used.

Silver is electroplated directly on beryllium using a strike bath at 80° ± 10° F. as for plating silver on copper, said bath consisting of 4.5 g./liter of  $\text{AgCN}$ , and 70.0 g./liter of  $\text{MaCN}$  for five minutes. A current density of 7.5 amp./ft.<sup>2</sup> is used. Thicker silver deposits are built up in a silverplating bath at 120° F. consisting of 75 g./liter of  $\text{AgCN}$ , 112 g./liter of  $\text{KCN}$ , and 22.5 g./liter of  $\text{K}_2\text{CO}_3$ , and  $\text{KOH}$  to give a pH of 13.0. When a current density of 25 amp./ft.<sup>2</sup> is used, one mil is deposited per 15 minutes.

Copper is electroplated directly on beryllium in a cyanide bath at 120° F. consisting of 30 g./liter of  $\text{NaCN}$ , 22.5 g./liter of  $\text{CuCN}$ , 15 g./liter of  $\text{Na}_2\text{CO}_3$  and 0.5 g./liter of  $\text{Na}_2\text{S}_2\text{O}_3$ . It contained sufficient tartaric acid to give a pH of 9.0. A current density of 25 amp./ft.<sup>2</sup> is used. Chromium can be plated over copper from a usual chromic acid bath.

Nickel is electroplated on beryllium directly. The bath used is at 90° F., consists of 143 g./liter of  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ , 75 g./liter of  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ , 15 g./liter of  $\text{H}_3\text{BO}_3$ , 15 g./liter of  $\text{NH}_4\text{Cl}$ , and 20 cc./liter of XXXD (a sulfated alcohol type of wetting agent made by Harshaw Chemical Company). It has a pH of 5.5 ± 0.1. A current density of 15 amp./ft.<sup>2</sup> is used. Thicker deposits may be obtained in the following bath: 300 g./liter of  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ , 50 g./liter of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ , 35 g./liter of  $\text{H}_3\text{BO}_3$ , 15 g./liter of  $\text{NaCOOH}$ , and 20 cc./liter of XXXD having a pH 4 and temperature of 140° F. When a current density of 40 amp./ft.<sup>2</sup> is used, a thickness of one mil per 30 minutes can be obtained.

Other variations in the improved methods of this invention will be apparent to those skilled in the art and may be made without departing from the spirit and scope of the invention as indicated by the appended claims.

What is claimed is:

1. In a method of electroplating a beryllium body including the steps of passing an electric current through the

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beryllium body as an anode in an aqueous solution of phosphoric acid and hydrochloric acid, rinsing the beryllium body with water, and electroplating a metal on a surface of the body, the improvement comprising immersing the beryllium body in 70% nitric acid for two minutes at a temperature from 70° to 90° F. after said anodic treatment and before the water rinse.

2. In a method of electroplating a beryllium body including the steps of passing an electric current through the beryllium body as an anode in an aqueous solution of 10% (by volume) of 85%  $\text{H}_3\text{PO}_4$ , 2% (by volume) of 38%  $\text{HCl}$ , and the balance water, using a current density of 100 to 200 amp./ft.<sup>2</sup> at 80° F., rinsing the body with water, and electroplating a metal on a surface of the body, the improvement comprising immersing the body in 70% nitric acid solution for two minutes at a temperature of 80° ± 10° F. after said anodic treatment and before the water rinse.

3. The method of claim 2 in which the metal electroplated is iron.

4. The method of claim 2 in which the metal electroplated is copper.

5. The method of claim 2 in which the metal electroplated is nickel.

6. In a method of electroplating a beryllium body including the steps of passing an electric current through the body as an anode in an aqueous solution of 10% (by volume) of 85%  $\text{H}_3\text{PO}_4$ , 2% (by volume) of 38%  $\text{HCl}$ , and the balance water using a current density of 100 to 200 amp./ft.<sup>2</sup> at 80° F., rinsing the body a first time with water, immersing the body in an aqueous solution containing 100 g./liter of  $(\text{NH}_4)_2\text{SO}_4$  and sufficient  $\text{H}_2\text{SO}_4$  to provide a pH of 2.0 and at a temperature of 80° ± 10° F. for 0.5 to 1.0 minute, rinsing the body a second time with water, and electroplating with tin from an alkaline solution on a surface of the body, the improvement comprising the step of immersing the body in 70% nitric acid solution for two minutes at a temperature of 80° ± 10° F. after the anodic treatment and before the first water rinse.

7. In a method of electroplating a beryllium body including the steps of passing an electric current through the body as an anode in an aqueous solution of 10% (by volume) of 85%  $\text{H}_3\text{PO}_4$ , 2% (by volume) of 38%  $\text{HCl}$ , and the balance water using a current density of 100 to 200 amp./ft.<sup>2</sup> at 80° F., rinsing the body a first time with water, immersing the body in an aqueous solution containing 100 g./liter of  $(\text{NH}_4)_2\text{SO}_4$  and sufficient  $\text{H}_2\text{SO}_4$  to provide a pH of 2.0 and at a temperature of 80° ± 10° F. for 0.5 to 1.0 minute, rinsing the body a second time with water, and electroplating with silver from an alkaline solution on a surface of the body, the improvement comprising the step of immersing the body in 70% nitric acid solution for 2.0 minutes at a temperature of 80° ± 10° F. after the anodic treatment and before the first water rinse.

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