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3,544,435

**ELECTRODEPOSITION OF PALLADIUM**

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9 Claims

**ABSTRACT OF THE DISCLOSURE**

Directed to a method for electrodepositing palladium in a single compartment cell using a bath consisting of an aqueous ammoniacal solution of tetramminopalladous bromide having a pH of at least about 9 up to pH 10 to produce ductile palladium coatings highly useful in electrical contact service.

The present invention is directed to a method for producing palladium electrodeposits of high ductility and, more particularly, to the provision of electrical contacts made of a ductile metal having thereon a surface coating of ductile palladium.

In recent years palladium has become widely adopted as a surface coating for electrical contacts on account of the desirable properties of such coatings which include high electrical conductivity and high resistance to both corrosion and mechanical wear.

The coatings are conveniently formed by electrodeposition from aqueous baths but it is a disadvantage of palladium coatings electrodeposited from commercially available baths that they exhibit high internal stress and low ductility and have a tendency to crack if the coating is thick. Even if a stressed coating is free of cracks when initially deposited, it may develop cracks in service if its ductility is low. Cracking of the coating reduces the protection it affords against corrosion.

We have now discovered a method for providing palladium coatings of high ductility and excellent protective value which may be employed upon ductile metal substrate materials to provide electrical contacts having improved characteristics.

It is an object of the present invention to provide a method for electrodepositing palladium which yields sound, essentially crack-free, highly ductile palladium coatings, particularly in conjunction with a single-compartment or nondiaphragm cell.

It is a further object of the invention to provide electrical contacts made of ductile metal and having on the contact surfaces thereof a coating of highly ductile and essentially crack-free palladium.

Other objects and advantages of the invention will become apparent from the following description.

According to the invention, palladium coatings on electrical contacts are formed by the electrodeposition of palladium in a single-compartment cell from a bath consisting of an aqueous ammoniacal solution of tetramminopalladous bromide,  $(\text{Pd}(\text{NH}_3)_4)\text{Br}_2$ , and this invention includes coated contacts so produced. We find that such coatings have remarkably high ductility and are wholly or substantially wholly free from cracks as determined by an electrographic test at thicknesses even as great as 10 microns or more. Moreover, at thicknesses even as low as 2 microns, the protection afforded by the coating is very good. The electrographic test referred to

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comprises placing a sheet of cadmium sulfide paper with a moistened backing pad against a plated specimen and making the specimen anodic. Blackening of the cadmium sulfide paper occurs at the pores and cracks.

The ductility of the coating depends upon the concentration of palladium in the solution and upon the current density used, and to obtain the highest ductility these must be suitably correlated. The palladium concentration may be as low as 2 grams per liter (g.p.l.) but advantageously, the bath contains at least 10 g.p.l. palladium, since at lower concentrations, ductile coatings are obtained only within a narrow range of current densities not exceeding 0.5 ampere per square decimeter when the bath is used without agitation. Preferably, the palladium concentration is from 15 to 30 g.p.l. As the concentration increases, the range of current densities that may be used widens and at a concentration of 30 g.p.l., it extends up to 2.5 amperes per square decimeter. Advantageously, however, it does not exceed 1.5 amperes per square decimeter, since above this the ductility of the coating falls off. The upper limit of palladium concentration is determined by the solubility of tetramminopalladous bromide in the bath and is thus about 35 g.p.l.

The ductility of the deposit is also affected by agitation of the bath. At palladium concentrations above about 10 g.p.l. vigorous agitation of the bath reduces the ductility of the coating produced. Surprisingly, however, we find that at lower palladium concentrations, e.g., about 5 g.p.l., this is not the case, and at such concentrations the ductility may even be improved, so that a bath containing about 5 g.p.l. palladium may advantageously be employed for barrel plating. Baths containing more than 10 g.p.l. of palladium may also be employed with agitation, e.g. for barrel plating, provided the current density used is such that the ductility of the deposit is not reduced below an acceptable value. Thus provided the operating conditions are suitable chosen, coatings of palladium have been obtained according to the invention by the process of barrel plating which possess better ductility than those obtained from currently used standard plating baths under these conditions. Agitation of the bath has the advantage of increasing its operating life, since the tendency to deposit sludge is reduced.

Ammonia is employed in the bath to control pH in the range between 9 and 10 and, more advantageously, pH is from 9 to 9.5. Control of the bath pH within this range permits electrodeposition of ductile palladium in a single-compartment cell. This practice is advantageous since apparatus difficulties associated with the diaphragm cell are avoided and, in addition, a further improvement in ductility of the deposits is achieved as compared to the instance in which the diaphragm cell is employed. Insoluble anodes, for example of platinum or palladium, are employed. It is to be appreciated that when the bath pH is below 9, the life of the bath is limited since large amounts of palladium-containing sludge separate from the solution after only a short period of operation with consequent wastage of palladium.

The bath may be used at temperatures from room temperature up to about 60° C.

The bath does not attack any of the common base metals and the substrate on which the palladium is supported may consist, for example, of copper, brass, a beryllium-copper alloy, nickel or nickel-silver.

The bath may conveniently be prepared by dissolving palladium sponge in an excess of concentrated aqueous hydrobromic acid, with the addition of small amounts of bromine to promote solution and evaporating the resulting solution to dryness to remove excess hydrobromic acid and reduce any tetravalent palladium to the divalent

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state. The dry palladium bromide thus obtained is dissolved in the minimum amount of dilute hydrobromic acid. Ammonia is added and the solution heated until the precipitate first formed just redissolves. The solution is filtered and diluted as required, the pH being adjusted to a value within the required range of 9 to 10 by the further addition of ammonia.

Some examples will now be given.

#### EXAMPLE I

To illustrate the variation of the ductility of the deposits with changes in palladium concentration and cathode current density, copper specimens were coated with a 5 micron thick deposit of palladium from baths having palladium concentrations from 5 to 30 g.p.l. operated without agitation in a nondiaphragm, i.e., single-compartment, cell at a pH of 9.2 and a temperature of 24° C., using cathode current densities in the range of 0.25 to 2.5 amperes per square decimeter. The anode current density in each case was 1 ampere per square decimeter and the cathode efficiency was higher than 90%. The results are set forth in Table I below, in which the figure zero indicates that the deposits were cracked before elongation occurred.

TABLE I

| Palladium concentration, g.p.l.: | Ductility (percent elongation), cathode current density, A./dm. <sup>2</sup> — |      |      |      |      |
|----------------------------------|--|------|------|------|------|
|                                  | 0.25   | 0.50 | 1.00 | 1.75 | 2.50 |
| 30.....                          | 0  | 6    | 13   | 6    | 2    |
| 20.....                          | 2  | 11   | 11   | 0    | 0    |
| 15.....                          | 2.5  | 13   | 12   | 0    | 0    |
| 10.....                          | 6.5  | 15   | 0    | 0    | 0    |
| 5.....                           | 6  | 0    | 0    | 0    | 0    |

NOTE.—A./dm.<sup>2</sup>=amperes per square decimeter.

#### EXAMPLE II

This is an example of barrel plating using a bath with a high concentration of palladium. 300 milliliters of tetramminopalladous bromide solution, containing 30 g.p.l. of palladium, was placed in an oblique rotating barrel set at 45° to the horizontal. Sixty copper-beryllium alloy spring strips were pretreated by degreasing, etching in 1.5% phosphoric acid and coated with copper. These strips were then plated at room temperature in the barrel to a thickness of 5 microns using a cathode current density of 1.0 ampere per square decimeter. A platinum anode was used and the speed of rotation of the barrel was 24 revolutions per minute. The resulting coatings had a ductility (percent elongation) of 2.5%. Solution pH was adjusted to about 9.2 by ammonia additions.

#### EXAMPLE III

This is an example of barrel plating with a bath containing a low concentration of palladium. 300 milliliters of tetramminopalladous bromide solution containing 5 g.p.l. of palladium and having a pH of 9.2 was placed in an oblique rotating barrel set at an angle of 45° to the horizontal. Twenty-four beryllium-copper alloy spring strips were plated at room temperature, using a current density of 1.0 A./dm.<sup>2</sup> and a platinum anode, the speed of rotation of the barrel being 20 r.p.m. Coatings 5 microns thick produced in this way had a ductility (percent elongation) of 5%.

#### EXAMPLE IV

This is an example of plating from an agitated bath containing a low concentration of palladium. Copper specimens were plated with palladium to a thickness of 5 microns in a tetramminopalladous bromide bath containing 5 g.p.l. of palladium operated in a nondiaphragm cell at a pH of 9.2. Plating was carried out at room temperature and at a cathode current density of 1.0 A./dm.<sup>2</sup>. The bath was agitated by means of a motor-driven glass stirrer and the resulting coatings had ductility (percent elongation) of 5%.

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It will be observed that the ductility of the deposits obtained in both of Examples III and IV was substantially higher than that obtained in Example I from an unstirred bath under the same conditions of palladium concentration, pH and current density.

#### EXAMPLE V

In order to demonstrate the improvement in results particularly with regard to ductility of the deposits by employing a single-compartment cell with the special pH control as contemplated in accordance with the invention as compared with use of a similar electrolyte in a diaphragm cell, two solutions were made up having palladium concentrations, respectively, of 15 g.p.l. and 30 g.p.l. The solutions were prepared by dissolving palladium in concentrated hydrobromic acid and warming with small additions of bromine until all the palladium was dissolved. The solutions were evaporated to dryness to give palladium bromide which was dissolved in hot 50% hydrobromic acid. The clear solutions in each case were treated with ammonia and diluted to one liter to provide baths containing, respectively, 15 and 30 g.p.l. of palladium as tetramminopalladous bromide each having a pH adjusted to 9.2 by additions of ammonia. Palladium deposits 5 microns thick were produced on copper substrates at room temperature from the solutions in the diaphragm cell and in the nondiaphragm cell at the current densities and with the results set forth in the following Table II.

TABLE II

| Solution and type of cell                                 | Ductility (percent elongation) | Appearance of deposit |
|---|--------------------------------|-----------------------|
| 15 g.p.l. Pd at current density 1.0 A./dm. <sup>2</sup> : |                                |                       |
| With diaphragm.....                                       | 35                             | Matte.                |
| Without diaphragm.....                                    | 19                             | Dull.                 |
| 30 g.p.l. Pd at current density 1.5 A./dm. <sup>2</sup> : |                                |                       |
| With diaphragm.....                                       | 8                              | Matte.                |
| Without diaphragm.....                                    | 16                             | Dull.                 |

The high ductility of palladium electrodeposited from a tetramminopalladous bromide bath is most surprising since deposits formed from otherwise similar baths in which the bromide is replaced by chloride or sulfate are much less ductile and appreciably harder. Moreover, despite the high cathode efficiency of the bath, hydrogen, which is known to have a very embrittling effect upon palladium, is evolved to some extent at the cathode.

Palladium deposits formed from similar ammoniacal solutions of tetramminopalladous phosphate, nitrate, tartrate, citrate, oxalate and carbonate are also unsatisfactory for use on electrical contacts since they fail to give useful protection to the basis metal within the thickness range of 2 to 10 microns.

Tetramminopalladous iodide solutions decompose spontaneously and are therefore useless.

Deposits from a modified chloride bath containing 10 g.p.l. of palladium as tetramminopalladous chloride, 10 g.p.l. ammonium chloride, 50 milliliters per liter ammonia, and 25 milliliters per liter ammonium sulfate, used in a single-compartment cell, have also been tested and found to have a ductility of only 1.4%.

Palladium-plated electrical contacts according to the invention are particularly useful for the spring components of plug-and-socket contacts, which often have to withstand severe deformation on crimping, as well as repeated flexing during insertion and withdrawal in service. The high ductility of the coatings makes it possible to employ much thicker coatings than hitherto, thereby increasing protection. Coatings 8 microns thick have proved satisfactory. If desired, however, the coatings can be built to greater thicknesses, e.g., 30 microns or even 100 microns.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the

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invention as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the invention and appended claims.

We claim:

1. The method for electrodepositing ductile palladium in a single-compartment cell which comprises establishing an aqueous ammoniacal bath containing about 2 to about 35 grams per liter of palladium as tetramminopalladous bromide, containing ammonia to control the pH thereof in the range of at least 9 to about 10, and having a temperature between room temperature and 60° C., and electrodepositing palladium therefrom at a cathode current density of at least about 0.25 but not exceeding about 2.5 amperes per square decimeter upon a cathode immersed in said to provide a ductile, substantially crack-free palladium coating upon said cathode.

2. The method according to claim 1 wherein the palladium content is at least about 10 grams per liter.

3. The method according to claim 1 wherein the palladium concentration is about 5 grams per liter and the bath is agitated.

4. The method according to claim 2 wherein the palladium content is about 15 to about 30 grams per liter.

5. The method according to claim 2 wherein the bath pH does not exceed about 9.5.

6. The method according to claim 2 wherein the cathode material is a ductile metal from the group consist-

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ing of copper, brass, beryllium-copper, nickel and nickel-silver and the plated cathode is then formed into an electrical contact.

7. The method according to claim 4 wherein the cathode current density does not exceed about 1.5 amperes per square decimeter.

8. The method according to claim 4 wherein the cathode current density is about 0.5 to about 1 ampere per square decimeter.

9. The method according to claim 3 wherein the cathode material is a ductile metal from the group consisting of copper, brass, beryllium-copper, nickel and nickel-silver and the plated cathode is then formed into an electrical contact.

#### References Cited

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ROBERT K. MIHALEK, Primary Examiner

R. L. ANDREWS, Assistant Examiner

UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 3,544,435

Dated December 1, 1970

Inventor(s) HAMISH CHARMICHAEL ANGUS and JOHN MICHAEL STEVENS

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Col. 1, 6th line of the heading, after "England" insert the following --assignors to The International Nickel Company, Inc., New York, N.Y., a corporation of Delaware

Col. 2, line 38, for "suitable" read -- suitably--.

Col. 4, line 35, (Table II, Col. 2) under "Ductility (perc elongation)", first number, for "35" read --15--.

Col. 5, line 16, (line 11 of claim 1) after "said" insert --bath--.

Signed and sealed this 14th day of September 1971.

(SEAL)  
Attest:

EDWARD M. FLETCHER, JR.  
Attesting Officer

ROBERT GOTTSCHALK  
Acting Commissioner of Patents