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METHOD OF MAKING PALLADIUM COATED ELECTRICAL CONTACTS

Hamish Carmichael Angus, High Wycombe, Bucks., England, assignor to The International Nickel Company, Inc., New York, N.Y., a corporation of Delaware
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3 Claims

ABSTRACT OF THE DISCLOSURE

A method of making corrosion resistant electrical contacts coated with palladium. The palladium is electrodeposited from an aqueous ammoniacal bath comprising tetrammino-palladous bromide and having a pH of about 8-10. The resulting palladium deposit is highly ductile and thus permits subsequent deformation of the coated article to form electrical contacts.

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.

I 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 diaphragm 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 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. I 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 comprises placing a sheet of cadmium sulfide paper with a moistened backing pad against a plated specimen and making the specimen anodic.

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Blackening of the cadmium sulfide paper occurs at the pores and cracks.

The bath advantageously contains from 15 to 30 grams per liter (g.p.l.) of palladium as tetramminopalladous bromide, and has a pH of from 8 to 9. Higher or lower palladium concentrations may, however, be used and, broadly speaking, the palladium content may be from 2 to 35 g.p.l. With low palladium concentrations below about 15 g.p.l., only a narrow range of current densities can be employed while still obtaining high ductility in the deposits and it is for this reason that palladium concentrations of 15 g.p.l. and higher are advantageously employed. On the other hand, the pH of the bath is quite critical. If the pH drops much below 8, for example, to 7, a precipitate is formed while to maintain a higher pH than 9 would require the continuous addition of ammonia even at room temperature. The bath is operative in the diaphragm cell at a pH up to 10 provided that ammonia is continuously added to the bath. The ammonia concentration of the bath may be 20 to 70 g.p.l. expressed as ammonium bromide, with advantageous results being obtained using 50 to 60 g.p.l. ammonium bromide.

The efficiency of the bath and the ductility of the deposits falls as the cathode current density is increased above 2.0 amperes per square decimeter, and the current density is advantageously not more than 1.5 amperes per square decimeter to obtain best efficiency and ductility. Deposition proceeds at a satisfactory rate at room temperature when the cathode current density is at least 0.5 ampere per square decimeter, or advantageously, at least about 1 ampere per square decimeter. The bath may be operated in the temperature range of about 18° C. to about 60° C.

The bath is preferably employed as the catholyte in a cell divided into cathode and anode compartments by a porous diaphragm, the electrolyte in the anode compartment conveniently being composed of ammonium carbonate, ammonium sulfate and ammonia. Insoluble anodes, for example, of platinum, are used.

The bath solution does not attack any of the common base metals and the substrate on which the palladium is supported may consist, for example, of a ductile metal such as copper, brass, beryllium-copper, 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 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.

By way of example, a bath was prepared by dissolving 15 grams of palladium in 150 milliliters concentrated hydrobromic acid and warming with small additions of bromine till all the palladium was dissolved. The solution was evaporated to dryness to give palladium bromide, which was dissolved in approximately 75 milliliters of hot 50% hydrobromic acid. The clear solution was treated with approximately 100 milliliters of ammonia and diluted to 1 liter. The resulting bath contained 15 g.p.l. of palladium and had a pH of 8.5. It was used at room temperature in the cathode compartment of a diaphragm cell with anodes of palladium and an anolyte consisting of an aqueous solution of 20 g.p.l. ammonium sulfate, 10 g.p.l. ammonium carbonate and 50 milliliters per liter ammonia (s.g. 0.88), to deposit palladium on cathodes consisting of copper electrical contact parts using a current density of

1.0 ampere per square decimeter. A coating 5 microns thick was obtained in 21 minutes, the cathode efficiency being 88%. The deposit was smooth, had a hardness of 187 D.P.N., a stress of 10 long tons per square inch tensile and was so ductile that it had an elongation of 14%. The deposit was essentially crack-free. An identical bath used in a single-compartment cell with anodes in the electrolyte had a very limited life, owing to sludging, but deposits of ductility as high as 20% could be obtained from it.

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. In operation, hydrogen is evolved at the cathode despite the high cathode efficiency of the bath. It is known that hydrogen hardens and reduces the ductility of palladium but, nevertheless, palladium deposits produced in accordance with the invention have high ductility.

The improved ductility and lower hardness of the deposits obtained in accordance with the invention are shown by the following table, in which their properties are compared with those of deposits from similar chloride and sulfate baths and also of a deposit from a commercial bath consisting of an ammoniacal solution of tetramminopalladous nitrate. In each of the solutions, the concentration of palladium was within the range of 10 to 20 g.p.l. The substrate material was copper.

Where three individual results are given in the table, coatings were obtained from at least two similar electrolytes. Hardness and ductility were measured on different specimens. The ductility was measured on specimens having a coating 5 microns thick and the hardness on specimens having a coating 10 microns thick.

TABLE

Electrolyte	Ductility (percent elongation)	Hardness D.P.N. (30 gram load)
Tetramminopalladous bromide.....	12, 14, 15.....	204, 187, 162.
Tetramminopalladous chloride.....	2.1, 2.3, 2.6.....	280, 270, 250.
Tetramminopalladous sulfate.....	2.8.....	250.
Tetramminopalladous nitrate.....	0.9.....	310.

Palladium deposits formed from similar ammoniacal solutions of tetramminopalladous phosphate, nitrate, tartrate, citrate, oxalate and carbonate are 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%.

The high ductility of palladium coatings produced from

the tetramminopalladous bromide baths in accordance with the invention makes these coatings particularly useful in electrical contact service since this ductility permits forming of a plated ductile metal into contact configuration after plating whereas plated coatings from other tetramminopalladous baths, including the chloride and sulfate baths, are insufficiently ductile to permit forming.

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.

I claim:

1. In the production of corrosion resistant spring components for electrical contact service, the improvement which comprises electrodepositing ductile palladium upon such a component made of a ductile metal from the group consisting of copper, brass, beryllium-copper, nickel, and nickel-silver immersed as a cathode in a diaphragm cell provided in the cathode compartment thereof with an aqueous ammoniacal bath containing about 2 to about 35 grams per liter of palladium as tetramminopalladous bromide and having a pH of about 8 to about 10 using a cathode current density of about 0.5 to about 2 amperes per square decimeter to provide a palladium coating at least about 2 microns thick upon said component and thereafter deforming said plated component to produce an electrical contact.

2. The method according to claim 1 wherein the palladium concentration of the bath is about 15 to about 30 grams per liter and the current density is about 1 to 1.5 amperes per square decimeter.

3. The method according to claim 1 wherein the bath pH does not exceed about 9.

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JOHN H. MACK, Primary Examiner

G. L. KAPLAN, Assistant Examiner

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