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PROCESS OF PLATING PALLADIUM AND
PLATING BATH THEREFOR

George C. Lambros, New York, N. Y.

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This application is a continuation-in-part of my application Serial No. 443,222, filed May 16, 1942, which has been abandoned, and this invention relates to a process of electrodepositing metals of the platinum group, particularly palladium, a plating bath for use in carrying out said process, and a method of preparing said bath.

Until recently there has been practically no industrial or commercial application for electrodeposits of pure palladium. However the present plentiful supply of the metal resulting from rapid developments in the extraction of nickel from sulfidic ores, and the relatively low price of palladium as compared with platinum and gold, coupled with the fact that a given weight of palladium will plate about twice as much surface area as will the same weight of gold or platinum, have created a substantial demand for palladium plating.

Difficulty has been encountered in producing satisfactory methods and baths for electrodepositing palladium. Several attempts have been made including the proposal to use a bath formed by dissolving a crystallized amino-cyanide of palladium in water and adding ammonia or sodium hydroxide, but the known methods and baths have serious disadvantages or shortcomings, such as instability or rapid deterioration of the bath, inefficiency in the plating operation and lack of coherency in the deposit.

Therefore, prime objects of my invention are to provide a method of electroplating palladium and a bath therefor which shall embody novel and improved features whereby the bath shall be substantially more stable than known palladium plating baths and the plating operation can be carried on for exceptionally long periods of time without series deterioration of the bath; and to provide a simple, efficient, and relatively inexpensive method and bath for electrolytically producing exceptionally coherent deposits of palladium with either brilliant or matte surfaces.

Other objects, advantages and results of the invention will be brought out by the following description.

I have discovered that the above-mentioned disadvantages of the prior methods and baths may be overcome, and that the foregoing objects may be attained, by electroplating from a bath prepared by dissolving dichlorodiamine palladium $[Pd(NH_3)_2Cl_2]$ in a solution of sodium or potassium cyanide.

More particularly I have found that best results can be obtained when the weight of sodium or potassium cyanide bears a specific ratio

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to the weight of palladium metal in the form of dichlorodiamine salt.

Furthermore, it is desirable that the dichlorodiamine palladium be freshly prepared immediately before the addition of the sodium or potassium cyanide.

In preparing the bath, the preliminary steps may closely follow the method advocated by the United States Bureau of Standards for the purification of palladium metal. More specifically stated, a weighed sample of palladium is dissolved in nitric acid and the solution is evaporated to a syrupy consistency in a covered porcelain dish. The syrupy residue is dissolved in water by a little hydrochloric acid, and the solution is diluted to 40 to 50 grams of palladium per liter. Ammonium hydroxide is then added until no further precipitation of the flesh-colored palladium compound occurs. The solution is then heated on a steam bath for 15 to 20 minutes to redissolve the precipitate, whereafter a little more ammonium hydroxide is added with care to avoid excess, and the solution is allowed to cool. Hydrochloric acid is then added until no more precipitation of the yellow salt occurs, but an excess of hydrochloric acid should be avoided.

To this freshly prepared solution, C. P. sodium or potassium cyanide is added in water solution. It is necessary to add not less than 1.2 grams and not more than 1.8 grams of sodium cyanide, or at least 1.6 grams and at most 2.4 grams of potassium cyanide, for each gram of palladium in the form of the dichlorodiamine salt, which of course produces an excess of cyanide within definite limits. If less than the above stated minimum is used, the precipitate will not completely dissolve, while if more than the stated maximum is added, the bath will not operate satisfactorily.

This ratio may be expressed in terms of weight of cyanide (CN) to weight of palladium metal as follows: from 0.63 gram to 0.96 gram of cyanide (CN) for every gram of palladium metal.

No attempt is made to explain the chemical compounds that are formed upon the addition of the cyanide, or why an excess of cyanide deleteriously affects the bath. However, it is my belief that my bath has free chloride ions (Cl) and that these in large measure account for the stability and long life of the bath.

The solution is made up in concentrated form of about forty (40) grams of palladium metal per liter, and thereafter diluted with water to make the bath. This concentrated solution is also used as a replenisher and is added to the bath from

time to time to replace the palladium that is plated out.

I have found that the bath operates most satisfactorily at temperatures ranging from 40° to 90° C. or above, preferable about 90° C., or close to the boiling point, and with a cathode current density of from 0.1 to 0.5 ampere per square decimeter at a bath potential of from 1 to 2 volts. Platinum or palladium anodes are preferred. The palladium metal content of the bath is maintained within the range of 0.5 gram to 15 grams, preferably from 1 to 5 grams palladium, per liter, by periodic additions of the concentrated solution of the dichlorodiamine palladium and cyanide.

In preparation of the concentrated solution, I have found that the stability of the solution is improved and more of the palladium is made available in plating form, by heating the mixture for about four hours at a temperature of from about 60° C. to about 95° C., and the improvement is substantially greater when an amount of hydroxide of sodium or potassium substantially equal to the amount of potassium cyanide or sodium cyanide, is added with the cyanide to the freshly prepared dichlorodiamine palladium salt.

The bath remains exceptionally stable and has been found to operate for many weeks, more or less constantly and uniformly satisfactorily, with only periodic additions of the concentrated solution. This is remarkable because the quantity of cyanide would be expected to be reduced, especially with the bath operating at close to boiling temperatures.

The color or composition of the palladium deposit may be varied to suit the taste, purpose or use of the plated articles, by the addition to the bath of small amounts of metals such as tin, cobalt, nickel, zinc, copper, gold or indium. The addition of sodium stannite, for example, to the palladium cyanide bath in small quantities until the desired effect is obtained, results, in a deposit comprising both palladium and tin. Preferably the second metal is added to the bath in the form of an alkaline solution of that metal and in small quantities until the desired change in the palladium plate is effected. Bright or matte surfaces and plating of various colors can be produced in this simple manner.

Similar baths for electrodepositing other metals of the platinum group may be prepared by dissolving in a water solution of sodium or potassium cyanide, salts of those metals that will form amino-cyanides of the platinum metals in such solutions.

Although the present invention has been described in connection with certain preferred embodiments thereof, it is to be understood that variations and modifications may be resorted to which will be within the spirit and scope of the invention.

Having thus described the invention, what I claim is:

1. A process of electrodepositing palladium which comprises dissolving freshly prepared dichlorodiamine palladium in an aqueous solution of a cyanide of the group consisting of sodium cyanide and potassium cyanide, said solution con-

taining cyanide in an amount ranging from 0.63 to 0.96 gram of cyanide (CN) per gram of palladium in the form of dichlorodiamine palladium, and from 0.5 to 15 grams of palladium metal per liter, and electrolyzing said solution in the presence of said cyanide.

2. A process of electrodepositing palladium which comprises dissolving freshly precipitated dichlorodiamine palladium in an aqueous solution of cyanide of the group consisting of sodium cyanide and potassium cyanide, said solution containing cyanide in an amount ranging from 0.63 to 0.96 gram of cyanide (CN) per gram of palladium in the form of dichlorodiamine palladium, and from 0.5 to 15 grams of palladium metal per liter, and electrolyzing said solution in the presence of said cyanide at a temperature of about 90° C., and replenishing the solution periodically to maintain the palladium content of the solution from 0.5 to 15 grams of metal per liter.

3. A bath for the electrodeposition of palladium which comprises a solution of freshly precipitated dichlorodiamine palladium in an aqueous solution of a cyanide of the group consisting of sodium cyanide and potassium cyanide, said solution containing cyanide in an amount ranging from 0.63 to 0.96 gram of cyanide (CN) per gram of palladium in the form of dichlorodiamine palladium, and from 0.5 to 15 grams of palladium metal per liter.

4. The method of preparing a concentrated solution for use in preparing baths for electrodeposition of palladium comprising the steps of dissolving freshly precipitated dichlorodiamine palladium in a solution of a cyanide of the group consisting of sodium cyanide and potassium cyanide, said solution containing about forty grams of palladium metal per liter and from 0.63 gram to 0.96 gram of cyanide for each gram of palladium, and heating said solution for about four hours at a temperature of from about 60° C. to about 95° C.

5. The method as defined in claim 4 with the additional step of adding to the mixture during heating thereof an amount of sodium or potassium hydroxide substantially equal to the amount of cyanide.

GEORGE C. LAMBROS.

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