Patented Mar. 5, 1935

1,993,623

UNITED STATES PATENT OFFICE

1,993,623

ELECTRODEPOSITION OF PLATINUM METALS

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No Drawing. Application July 9, 1932, Serial No. 621,754. Renewed July 24, 1934. In Great Britain July 11, 1931

5 Claims. (Cl. 204—1)

This invention relates to an improved method for the electrodeposition of platinum group metals like palladium and to a bath for use in carrying out said method.

It is well known that heretofore in the plating of platinum group metals such as palladium, a salt of the platinum metal has been added to the plating bath from time to time as the palladium or platinum metal content has become depleted. In this manner the platinum metal content is maintained at the proper concentration.

The investigators in the art were searching for a process to eliminate the foregoing procedure but, as far as I am aware, no method has been provided which is wholly satisfactory, acceptable and practical when operated on a commercial scale.

I have discovered a method which overcomes the disadvantages of prior procedures and which avoids the necessity of adding salts or compounds of platinum metals to the plating bath.

It is an object of the present invention to eliminate the need for periodical additions of platinum metal compounds, such as palladium salts to plating baths by the use of platinum metal anodes like a palladium anode.

It is a further object of the invention to provide a bath containing an electrolyte capable of anodically dissolving platinum metal anode at a rate substantially equal to that at which platinum metal like palladium is deposited cathodically on articles immersed in the electrolyte.

It is also within the contemplation of the invention to provide an improved method of maintaining substantially constant the platinum metal (palladium) concentration of the electrolytic baths used, while yielding satisfactory and acceptacle deposits of the platinum metal.

Other objects and advantages of the invention will become apparent from the following description of a preferred procedure of carrying the invention into practice.

Broadly stated I have found that the most advantageous results of the invention are obtained by using an electrolyte containing a complex nitrite of a platinum metal, such as palladonitrite of an alkali metal or an alkaline earth metal in solution in water and also containing an alkali or alkaline earth metal halide, like a chloride or bromide of an alkali metal or alkaline earth metal. The palladonitrite or other platinum metal nitrite may be replaced by a mixture of two or more such nitrites and the halide may be replaced by a mixture of two or more such halides. The anode is constituted of a platinum metal, such as a hard rolled palladium sheet which is dissolved anodically by the aforesaid electrolyte.

For the purpose of giving those skilled in the art a better understanding of the invention, the following description is given of a preferred procedure of carrying the invention into practice. For illustration palladium has been referred to as the metal of the platinum group, although it is to be understood that the invention is not limited thereto.

One method of forming a palladium electrolyte which may be described by way of example is as follows:—

About 38 grams of potassium palladonitrite $K_2Pd(NO_2)_4.2H_2O$, a well known salt of palladium containing 26.36 per cent of palladium by weight, is dissolved in about one liter of hot water and to the solution so obtained is added about 25 grams of a halide like potassium bromide. The mixture is boiled and allowed to cool to about 40°–50° C., which is a suitable temperature for the subsequent plating operations.

As another example, the electrolyte may be made by taking for each liter of electrolyte desired about 10 grams of palladium, dissolving this in aqua regia, evaporating the product with hydrochloric acid one or two times to remove nitric acid and to convert the palladium to palladous chloride, treating this with a solution containing about 26 grams of sodium nitrite which is a quantity sufficient to convert the palladium in the solution to sodium palladonitrite, boiling the mixture, dissolving sufficient sodium chloride to bring the concentration thereof in the final electrolyte to about 25 grams per liter and then making up the solution to one liter with distilled water. Although it is preferred to convert all the palladium to the palladonitrite by the addition of about 26 grams, that is the theoretical amount of sodium nitrite, it is found that good results may be obtained if from about 22 to 30 grams are added, that is if there is either a small deficiency in or a small excess of nitrite in the electrolyte.

The sodium salts may be replaced by potassium or lithium salts or by, for example, calcium or magnesium salts, and the palladium concentration may be varied from that set forth above, but with higher palladium concentrations it is preferred to use sodium salts rather than those of potassium, for example, since the former are more soluble. The halides may be varied in quantity, but it is preferred to keep their concentration between the limits of about 10 to 30 grams per liter.

The anodes are preferably made of hard rolled palladium sheet. Cast palladium anodes are practically as good while soft annealed palladium sheet may also be used. Soft annealed sheets, however, tend to dissolve non-uniformly, giving a much greater quantity of anode sludge than hard rolled or cast material and such sheets are consequently not so economical in use. The anodes should be made of practically pure metal in order to obtain the best results and to prevent contamination of the electrolyte.

In order to prevent contamination of the electrolyte by any anode sludge which may be formed during the process, the anodes may be placed in, for example, unbleached calico bags. The electrolyte should be operated above room temperature, preferably at temperatures of from 40 degrees to 50 degrees C., to obtain the best deposits but the solutions work well at higher or lower temperatures than these.

The current density may conveniently be maintained at about 0.1 ampere per square decimeter and at this density the current efficiencies of the anodic and cathodic processes are both very high, being in the order of 95 to 100 per cent. The current density may rise to about 0.5 amperes per square decimeter if desired.

As one example of a method of carrying out the process and as an illustration of the high efficiency of the process when the necessary working conditions are observed, the following may be given:

About 400 cubic centimeters of a solution containing about 4.25 grams of palladium as sodium palladonitrite and about 10 grams of sodium chloride were prepared. This solution was used for some time for plating a variety of articles. The temperature of the electrolyte was maintained at about 40°–50° C. and the anode and cathode current densities were varied from 0.1 to 0.4 amperes per square decimeter. After about 4.62 grams of palladium had been deposited from the electrolyte the latter was found to contain about 4.26 grams of palladium. From these figures, it is evident that the palladium anode had dissolved anodically and had fully maintained, and even very slightly increased, the palladium content of the electrolyte.

While the process is particularly suitable for the deposition of palladium on silver, it may also be used for the deposition of palladium on surfaces of gold, copper, brass, bronze, palladium, and nickel-silver. Surfaces such as those of nickel, iron, and steel should first be coated with copper or silver or both from a bath of an alkali metal cyanide. If base metals such as copper are to be plated and the electrolytes contain bromides, it is found to be advisable to work at room temperatures, since at a temperature of about 40° C. local action occurs when the base metal is placed in the electrolyte and dark non-adherent deposits are obtained. However, if the base metal is given a preliminary strike of palladium from one of the known ammoniacal solutions, the process can be carried out at from about 40°–50° C. with good results.

It has been found that the deposits of palladium obtained by means of the invention are very bright, and in general no buffing is needed after the plated articles have been removed from the bath.

Although the present invention has been described in conjunction with a preferred embodiment and certain specific reagents, temperatures, current densities, etc., have been given, it is to be understood that the invention is not limited thereto and that modifications and variations may be resorted to without departing from the spirit and scope of the invention as defined in the appended claims.

I claim:—

1. The method of depositing palladium electrolytically which comprises establishing a bath containing a palladium anode soluble in an electrolyte containing palladonitrite of an "alkali" metal, making the article to be plated the cathode, and passing a current through said soluble palladium anode, said electrolyte and said article to be plated whereby palladium metal is electrodeposited on the article to be plated and the electrolyte anodically dissolves the palladium anode during the electrolysis at a rate substantially equal to that at which palladium is deposited cathodically on articles immersed in the electrolyte.

2. The method of depositing palladium electrolytically which comprises establishing a bath containing a soluble palladium anode and an electrolyte containing palladonitrite of an "alkali" metal and a halide of an "alkali" metal, making the article to be plated the cathode, and passing a current through said soluble palladium anode, said electrolyte and said article to be plated whereby palladium metal is electrodeposited on the article to be plated and the electrolyte anodically dissolves the palladium anode during the electrolysis at a rate substantially equal to that at which palladium is deposited cathodically on articles immersed in the electrolyte.

3. The method of depositing palladium electrolytically which comprises establishing a bath containing a soluble, hard-rolled, palladium sheet anode and an electrolyte containing palladonitrite of an "alkali" metal, making the article to be plated the cathode, and passing a current through said soluble, hard-rolled palladium sheet anode, said electrolyte and said article to be plated whereby palladium metal is electrodeposited on the article to be plated and the electrolyte anodically dissolves the hard-rolled, palladium sheet anode during the electrolysis at a rate substantially equal to that at which hard-rolled, palladium sheet is deposited cathodically on articles immersed in the electrolyte.

4. The method of depositing palladium electrolytically which comprises establishing a bath containing palladonitrite of an "alkali" metal, adjusting the concentration of palladonitrite in the electrolyte to give about 10 grams of palladium per liter, making the article to be plated the cathode, and passing a current through said soluble palladium anode, said electrolyte and said article to be plated whereby palladium metal is electrodeposited on the article to be plated and the electrolyte anodically dissolves the palladium anode during the electrolysis at a rate substantially equal to that at which palladium is de-

posited cathodically on articles immersed in the electrolyte.

5. The method of depositing palladium electrolytically which comprises establishing a bath containing a soluble palladium anode and an electrolyte containing palladonitrite of an "alkali" metal and a halide of an "alkali" metal, adjusting the concentration of halide in the electrolyte to about 10 to about 30 grams per liter, making the article to be plated the cathode, and passing a current through said soluble palladium anode, said electrolyte and said article to be plated whereby palladium metal is electrodeposited on the article to be plated and the electrolyte anodically dissolves the palladium anode during the electrolysis at a rate substantially equal to that at which palladium is deposited cathodically on articles immersed in the electrolyte.

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