United States Patent Office 3,206,382 Patented Sept. 14, 1965

3,206,382

ELECTRODEPOSITION OF PLATINUM OR PALLADIUM

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No Drawing. Filed Sept. 28, 1960, Ser. No. 58,890
Claims priority, application Great Britain, Sept. 30, 1959, 33,207/59
9 Claims. (Cl. 204—47)

This invention relates to improvements in and relating to the electrodeposition of platinum or palladium from aqueous solutions and is more particularly concerned with the provision of an improved plating bath for electrodepositing these metals on to the noble metals, such as gold or silver or on to the base metals, such as copper, nickel, or titanium.

An object of the invention is to provide an improved plating bath for the electrodeposition of platinum or palladium which will give consistently good results over a wider range of thicknesses than hitherto found possible.

Another object is to enable bright adherent deposits of platinum or palladium to be obtained on noble metals, such as silver or gold, or on base metals, such as copper, nickel or titanium, over a wide range of thicknesses varying from 0.00001" to at least 0.001".

Alkaline plating baths have been proposed in the past for the electrodeposition of platinum which contain complex compounds of platinum, such as sodium hexahydroxy platinate, $Na_2Pt(OH)_6$, or diammine dinitrito-platinum, $(NH_3)_2Pt(NO_2)_2$. Such baths have, however, proved inefficient mainly owing to the fact that, whilst the initial deposit is satisfactory, the baths gradually deteriorate for various reasons with consequent reduction in efficiency and are thus only suitable for the deposition of thin or "flash" deposits of the order of 0.00001" to 0.0001" thick, heavier deposits tending to be dull and liable to crack or chip off.

Such baths are operated at about 70° C. and have a pH of about 8–10.

In an attempt to avoid the disadvantages accompanying the use of alkaline plating baths, it has been suggested, for the electrodeposition of platinum, to employ an essentially acid bath consisting of a solution of chloroplatinic acid in concentrated hydrochloric acid operating at temperatures above 70° C.

Such a bath is, however, difficult to operate owing to the evolution of hydrochloric acid fumes at the high temperatures employed and, moreover, is only suitable for plating on to noble metals, base metals being attacked by the acid present in the bath.

The deposition of platinum, palladium or rhodium from a plating bath comprising a solution of a double nitrite of the metal, such as sodium platino-nitrite or sodium pallado-nitrite, has also been suggested, but, so far as we are aware, the suggestion has found no practical application.

We have now found that the disadvantages inherent in the use of electrolytic baths, hitherto used or proposed for the electrodeposition of platinum or palladium, can be readily overcome by the use, as the plating bath or electrolyte of an aqueous solution of a complex nitrito-platinite compound or nitrito-palladite compound of the general formula:

$$A_2[X(NO_2)_aR'_{4-a}] \text{ or } A_2\left[X(NO_2)_aR''_{\frac{4-a}{2}}\right]$$

wherein

A represents an alkali metal, alkaline earth metal, an ammonium or hydrogen cation;

X represents platinum or palladium;

R′ represents a monovalent acid radicle or a hydroxide ion;

R″ represents a divalent acid radicle, and

a is 1, 2 or 3.

The acid radicle may advantageously be the sulphate, chloride, perchlorate, oxalate or sulphamate ion.

When an alkali metal is used to form the cation constituent, the latter is preferably derived from sodium or potassium. In practice, however, we have found that the most satisfactory results are obtained by the use of a hydrogen cation.

Suitable compounds which may be employed in carrying out our invention are:

(1) Potassium-dichloro-dinitrito-platinite, $K_2Pt(NO_2)_2Cl_2$.

(2) Potassium-dichloro-dinitrito-palladite, $K_2Pd(NO_2)_2Cl_2$.

(3) Potassium-sulphato-dinitrito-platinite, $K_2Pt(NO_2)_2SO_4$.

(4) Potassium-sulphato-dinitrito-palladite, $K_2Pd(NO_2)_2SO_4$.

The corresponding complex compounds of sodium may also be used.

The compound we prefer to use, however, consists of dinitrito-sulphato-platinous acid, $H_2Pt(NO_2)_2SO_4$, or dinitrito-sulphato-palladous acid, $H_2Pd(NO_2)_2SO_4$.

The following are examples of methods of preparing complex nitrito-platinite compounds for use in carrying out our invention, it being understood that no limitation is intended thereby either as regards the complex compound itself or its manner of manufacture.

Example I

POTASSIUM-SULPHATO-DINITRITO-PLATINITE, $K_2Pt(NO_2)_2SO_4$

This complex compound was prepared by reacting potassium-platino-nitrite with sulphuric acid, according to the following equation:

$$K_2Pt(NO_2)_4+H_2SO_4\rightarrow K_2Pt(NO_2)_2SO_4$$

Example II

The same complex compound as in Example I was prepared by reacting potassium-chloro-platinite with silver nitrite and silver sulphate.

The reaction involved is illustrated by the following equation:

$$K_2PtCl_4+2AgNO_2+AgSO_4\rightarrow K_2Pt(NO_2)_2SO_4+4AgCl$$

Example III

POTASSIUM-DICHLORO-DINITRITO-PLATINITE, $K_2Pt(NO_2)_2Cl_2$

This compound was prepared by reacting potassium-platino-nitrite with hydrochloric acid, according to the following equation:

$$K_2Pt(NO_2)_4+2HCl\rightarrow K_2Pt(NO_2)_2Cl_2$$

Example IV

The compound of Example III was prepared by reacting potassium chloroplatinite with silver nitrite according to the following equation:

$$K_2PtCl_4+2AgNO_2\rightarrow K_2Pt(NO_2)_2Cl_2+2AgCl$$

Example V

DINITRITO-SULPHATO-PLATINOUS ACID, $H_2Pt(NO_2)_2SO_4$

This compound was prepared by boiling a solution of platino-nitrous acid, $H_2Pt(NO_2)_4$, prepared by passing a solution of potassium platino-nitrite, $K_2Pt(NO_2)_4$, through

a cation exchange column, with sulphuric acid. This reaction is exemplified by the following:

$$H_2Pt(NO_2)_4 + H_2SO_4 \rightarrow H_2Pt(NO_2)_2SO_4 + 2HNO_2$$

It will be readily appreciated that the corresponding complex palladite compounds may be prepared in a similar manner by substituting potassium-pallado-nitrite for potassium-platino-nitrite in Examples I and III, by substituting potassium-chloro-palladite for potassium chloroplatinite in Examples II and IV, and by substituting a solution of pallado-nitrous acid for a solution of platino-nitrous acid in Example V.

Moreover, the potassium constituent in the above examples may readily be replaced by sodium to give the corresponding salts of sodium.

Our invention, thus also includes a method of electrodepositing platinum or palladium which method comprises electrolysing an electrolyte comprising an aqueous solution of a complex nitrito-platinite compound or nitrito-palladite compound of the general formula:

$$A_2[X(NO_2)_nR'_{4-n}] \text{ or } A_2\left[X(NO_2)_nR''_{\frac{4-a}{2}}\right]$$

wherein

A represents an alkali metal, alkaline earth metal, an ammonium or hydrogen cation;
X represents platinum or palladium;
R′ represents a monovalent acid radicle or a hydroxide ion;
R″ represents a divalent acid radicle, and
a is 1, 2, or 3

In carrying out the invention in practice our improved bath preferably contains 5–20 grams per litre of platinum or palladium as the nitrite, 5 gms./litre being found particularly suitable for general use. If a lower concentration be used, it will be found that the deposits are liable to be uneven and dark in appearance.

The solution should preferably have a pH of below 2, as, above this figure, black powdery deposits result and there is heavy gassing at the cathode.

The bath is advantageously operated at a current density of 5–25 amps/sq. ft. the lower figure being recommended for building up heavy deposits.

The temperature of the bath should preferably be within the range of 30°–70° C. as within this range the smooth bright appearance of the deposits remains unchanged. If the bath be operated below this temperature range, the deposits are liable to be rough and have a "frosted" appearance.

The following examples illustrate the manner in which the invention may be carried out, it being understood that the invention is in no way limited thereto or thereby.

Example VI

A flat copper base member was plated with platinum to a thickness of 0.0001″ thick by the use of a bath comprising an aqueous solution containing 5 gms. per litre of platinum as dinitrito-sulphato-platinous acid, the bath being operated at a temperature of 30° C. and a current density of 5 amps/sq. ft. with the use of insoluble platinum anodes. The resulting deposit was bright and the absence of porosity and cracking was proved by electrographic tests.

Example VII

A copper base member was plated with platinum to a thickness of 0.0005″ thick by the use of a plating bath similar to that used in Example I, but containing 15 gms./litre of platinum as dinitrito-sulphato-platinous acid. A current density of 20 amps./sq. ft. was used and the bath was operated at a temperature of 60° C. The resulting platinum deposit remained unaffected after treatment with 25% nitric acid for a period of 16 hours.

Whilst the invention will be found to be particularly suitable for the electro-deposition of platinum and has been so specifically referred to above, it is to be understood that the invention is equally applicable to the electrodeposition of palladium, it merely being necessary to use the corresponding complex palladium compound instead of the platinum compound.

Electro-deposits made in accordance with this invention will be found to be bright and smooth up to thicknesses of at least 0.001″ and to require no polishing.

Electrographic tests of platinum deposited on polished copper up to 0.0005″ thick in accordance with the teachings of the invention, show that the deposits are free from porosity but that above 0.001″ thick they are liable to show cracking. This tendency to cracking is, however, considerably reduced if etched copper, instead of polished copper, surfaces are used.

The plating bath of the invention will, moreover, be found to be stable, to give consistent results and not to deteriorate on standing.

The invention may be applied to the plating of noble metals, such as silver or gold and also to base metals, particularly efficient results being obtained on copper, brass, silver, nickel, lead and titanium. Owing to the acid nature of the bath, it cannot be used for plating platinum or palladium directly on to iron, tin, zinc or cadmium, and with these metals, an underlayer of nickel or silver is recommended.

It is to be understood that the invention is intended to include within its scope any articles composed of, or comprising, a noble metal or base metal member when plated with platinum or palladium by the method of, or with the use of a bath in accordance with, the invention.

What we claim is:

1. A method of electrodepositing a metal selected from the group consisting of platinum and palladium which method comprises electrolysing an electrolyte having a pH value below 2 and consisting essentially of an aqueous solution of a complex nitrito compound of the selected metal, said compound having a general formula selected from the group:

$$A_2\left[X(NO_2)_2R'_{4-n}\right] \text{ and } A_2\left[X(NO_2)_nR''_{\frac{4-a}{2}}\right]$$

wherein

A represents a cation selected from the group consisting of alkali metal and hydrogen cations;
X represents the selected metal;
R′ represents an ion selected from the group consisting of monovalent acid radicles;
R″ represents a divalent acid radicle, and
a is a number selected from the group of numbers 1, 2, and 3, and electrodepositing the selected metal from said electrolyte at a current density of 5–25 amps/sq. ft. and at a temperature of 30–70° C.

2. A method according to claim 1 in which the acid radicle is selected from the group of ions consisting of the sulphate, chloride, perchlorate and oxalate ions.

3. A method according to claim 1 in which A is an alkali metal cation derived from the group consisting of potassium and sodium.

4. A method of electrodepositing platinum metal which comprises electrolysing an electrolyte having a pH value below 2 and consisting essentially of an aqueous solution consisting essentially of potassium-dichloro-dinitrito-platinite, $K_2Pt(NO_2)_2Cl_2$, and remainder water, said electrolysis being carried out at a temperature of 30–70° C. and at a current density of 5–25 amps/sq. ft.

5. A method of electrodepositing palladium metal which comprises electrolysing an electrolyte having a pH value below 2 and consisting essentially of an aqueous solution consisting essentially of potassium-dichloro-dinitrito-palladite, $K_2Pd(NO_2)_2Cl_2$, and remainder water, said electrolysis being carried out at a temperature of 30–70° C. and at a current density of 5–25 amps/sq. ft.

6. A method of electrodepositing platinum metal which

comprises electrolysing an electrolyte having a pH value below 2 and consisting essentially of an aqueous solution consisting essentially of potassium-sulphato-dinitrito-platinite, $K_2Pt(NO_2)_2SO_4$, and remainder water, said electrolysis being carried out at a temperature of 30–70° C. and at a current density of 5–25 amps/sq. ft.

7. A method of electrodepositing palladium metal which comprises electrolysing an electrolyte having a pH value below 2 and consisting essentially of an aqueous solution consisting essentially of potassium-sulphato-dinitrito-palladite, $K_2Pd(NO_2)_2SO_4$, and remainder water, said electrolysis being carried out at a temperature of 30–70° C. and at a current density of 5–25 amps/sq. ft.

8. A method of electrodepositing platinum metal which comprises electrolysing an electrolyte having a pH value below 2 and consisting essentially of an aqueous solution consisting essentially of dinitrito-sulphato-platinous acid, $H_2Pt(NO_2)_2SO_4$, and remainder water, said electrolysis being carried out at a temperature of 30–70° C. and at a current density of 5–25 amps/sq. ft.

9. A method of electrodepositing palladium metal

which comprises electrolysing an electrolyte having a pH value below 2 and consisting essentially of an aqueous solution consisting essentially of dinitrito-sulphato-palladous acid, $H_2Pd(NO_2)_2SO_4$, and remainder water, said electrolysis being carried out at a temperature of 30–70° C. and at a current density of 5–25 amps/sq. ft.

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