United States Patent Office

2,915,406

Patented Dec. 1, 1959

2,915,406

PALLADIUM PLATING BY CHEMICAL REDUCTION

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No Drawing. Application March 3, 1958
Serial No. 718,455

21 Claims. (Cl. 106—1)

The present invention relates to the deposition of smooth, adherent coatings of palladium and, more particularly, to the chemical deposition of smooth, adherent deposits of palladium on metallic surfaces.

It is well known how to produce smooth and adherent deposits of palladium on metallic surfaces by electroplating techniques. When electrodeposition is used, extensive and sometimes elaborate equipment is necessary to control the process in order to obtain satisfactory deposits. A source of direct current external to the plating bath and electrical conductive means connecting therewith are the absolute minimum in equipment required by electrochemical processes. Further refinements entail, among other things, voltage and amperage regulating devices. The capital expense involved in providing and maintaining such equipment contributes to the cost of depositing the metal. In addition, the baths used in electrodeposition must be large enough to accommodate the necessary electrode structures, thus requiring relatively large amounts of expensive electroplating solutions. As far as is known at the present time, with the exception of electrodeposition, no satisfactory method of producing smooth, thick, adherent deposits of palladium from aqueous baths has heretofore been developed.

Although attempts were made to overcome the foregoing difficulties and other disadvantages, none, as far as we are aware, was entirely successful when carried into practice.

It has now been discovered that continuous, smooth, adherent plates of palladium may be chemically deposited by means of a special bath.

It is an object of the present invention to provide an autocatalytic process for the production of smooth and adherent deposits of palladium from an aqueous bath.

A further object is to provide a bath from which smooth and adherent deposits of palladium may be produced by catalyzed chemical means.

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

Generally speaking, the present invention contemplates the production of smooth, adherent deposits of palladium on objects having a catalytic metal surface by catalyzed chemical deposition from water-containing plating baths. The baths contemplated in accordance with the present invention contain in solution about 0.001 to about 0.25 mole per liter (m.p.l.) of divalent palladium, about 2.5 up to about 14 m.p.l. of ammonia which may be partly or entirely replaced mole for mole by one or more materials selected from the group consisting of aliphatic organic compounds having a primary amine group and having up to 5 carbon atoms per mole, about 0.002 to about 0.05 m.p.l. of hydrazine, about 0.005 up to about 0.25 m.p.l. of a stabilizing agent and the balance essentially water including sufficient ions to complement the aforementioned divalent palladium with the water being in a concentration of at least greater than 2 m.p.l. and up to at least about 50 m.p.l. In practice, the aforementioned bath is maintained at a temperature between about 30° C. to about 80° C. When an object made of, or having a surface layer of, a substance which catalyzes the reduction of divalent palladium by hydrazine is introduced into the bath, palladium is reduced at or near the surface of the object and a deposit of palladium is produced thereon. As the deposition proceeds, the palladium surface thus produced is itself a catalyst for the reduction of palladium ion by hydrazine.

Among the substances which catalyze the reduction of divalent palladium by hydrazine and thus may be coated in the aforementioned bath are the metals aluminum, chromium, cobalt, gold, iron, molybdenum, nickel, palladium, platinum, ruthenium, silver, steel, tin, tungsten and alloys rich in nickel or cobalt. Alloys rich in nickel and cobalt include austenitic nickel-chromium alloys, including nickel-chromium-iron and nickel-chromium-cobalt and cobalt-chromium alloys, including cobalt-chromium-iron alloys, which contain a total of at least about 25% nickel plus chromium, cobalt plus chromium or nickel plus chromium plus cobalt (i.e., a total of at least about 25% of chromium plus nickel and/or cobalt), in addition to small amounts of aluminum, titanium, molybdenum, tungsten, niobium, tantalum, silicon, manganese, zirconium and boron which may optionally be present in the alloys. Such alloys include the nickel-chromium-cobalt alloys and nickel-chromium alloys which are sold commercially under the trademarks of Inconel "700" and Inconel "X." Substances which satisfactorily catalyze the reduction of palladium in accordance with the invention are generally metals which are not chemically attacked by the bath. It is to be noted, however, that substances which do not catalyze the reduction of divalent palladium by hydrazine may be plated with palladium in the aforementioned chemical deposition bath by coating them with a preliminary deposit of a catalytic metal. For example, glass and ceramics may be coated by this technique. In this manner it is possible to chemically deposit smooth and adherent plates of palladium on the surface of any object.

The term "stabilizing agent" as used herein, refers to a group of substances which inhibit the spontaneous decomposition of the bath to form spongy palladium. Stabilizing agents include substances which form soluble complexes with divalent palladium. Such substances include the di-sodium salt of ethylene-diaminetetraacetic acid (EDTA), aliphatic ketones containing from 3 up to about 5 carbon atoms per molecule and dihydroxy-dialkyl sulfides having up to 5 carbon atoms per molecule. 3-pentanone, di-[2-hydroxyethyl] sulfide otherwise known as 2,2'-thiodiethanol ($HOC_2H_4—S—C_2H_4OH$), acetone and methylethyl ketone have proven satisfactory.

In addition, similar amounts of ammonium salts of mono-basic and di-basic mineral acids such as ammonium chloride, ammonium nitrate and ammonium sulfate have been found to stabilize the baths and thus, are also included in the term "stabilizing agents."

As was mentioned hereinbefore, primary aliphatic amines having up to about 5 carbon atoms per molecule can be used in the bath to replace ammonia on a mole for mole basis. It will be obvious, however, to one skilled in the art that this replacement may occur only to the extent that it is possible to concentrate the particular amine. Thus, if normal amylamine is used to replace ammonia it is clear to one skilled in the art that the absolute limit of mole concentration of normal amylamine is about 8.5 moles per liter. Accordingly, normal amylamine may replace ammonia up to somewhat less than 8.5 moles per liter. Primary amines which have proven satisfactory include ammonia as ammonium hydroxide, ethylamine and aminoethyl ethanolamine. Aminoethyl ethanolamine otherwise known as N-(2 hydroxyethyl) ethylene diamine, ($NH_2CH_2CH_2NHCH_2CH_2OH$), may be present in the bath only in a concentration up to about 9 moles per liter.

In carrying the invention into practice, it is advantageous to maintain the bath composition within the following range of composition:

Constituent:	Moles/liter
Divalent palladium	0.03–0.20
NH_3 or amine	7–10
Hydrazine	0.005–0.01
Stabilizing agent	0.01–0.10
Water	Balance >2

The pH of these baths lies between about 9 and 11 and the baths are advantageously maintained at a temperature of about 30° C. to about 70° C. during deposition. Divalent palladium may be introduced into the bath as the chloride, the chloropalladite and the amminochloride. A typical bath contains about 3.2 to about 21.2 g.p.l. of divalent palladium (about 0.03 to about 0.2 m.p.l.), about 245 to about 350 g.p.l. of ammonium hydroxide (about 7 to about 10 m.p.l.), about 0.16 to about 0.32 g.p.l. of hydrazine (about 0.005 to about 0.01 m.p.l.), about 3.36 to about 33.6 g.p.l. of the di-sodium salt of EDTA (about 0.01 to about 0.1 m.p.l.) and the balance being essentially water. It is preferred to maintain the bath at a temperature of about 30° C. to about 70° C. and the pH range should be about 9 to 11. It is to be observed that the reduction of divalent palladium by hydrazine is catalyzed by a large number of substances. Accordingly, since it is undesirable that the reduction take place in any location other than on the catalytic surface, the bath should be free of suspended solid particles. Advantageously, before it is used for plating, the bath is filtered through a fine filter in order to eliminate centers or nuclei of reduction. A filter made of a fine grade of fritted glass is preferred over a filter made of organic material, since organic material may tend to reduce palladium and thus provide possible centers for continuing reduction.

When it is desired to deposit palladium on the surface of a metal object, for example, an object made of a metal which catalyzes the reduction of divalent palladium by hydrazine, a bath within the composition limits set forth hereinbefore is preferred. Advantageously, the bath is made up by the addition of two stock reagents, the first being an aqueous solution containing dissolved palladium, ammonium hydroxide and the di-sodium salt of EDTA and the second being an aqueous solution containing hydrazine as hydrazine sulfate, $N_2H_4.H_2SO_4$, or hydrazine hydrate, $N_2H_4.H_2O$. Hydrazine may also be added in the form of a commercially available aqueous solution. The palladium in the first solution is in the form of tetramminepalladium (II) chloride

$$(Pd(NH_3)_4Cl_2)$$

This complex palladium salt is prepared by adding concentrated ammonium hydroxide to an aqueous solution of palladous chloride. A precipitate of diamminepalladium (II) chloride ($Pd(NH_3)_2Cl_2$) is formed thereby. Upon further addition of ammonium hydroxide this precipitate is redissolved forming, with an excess of ammonium hydroxide, a substantially colorless solution containing the aforementioned tetramminepalladium (II) chloride. Preferably, the hydrazine stock solution is added to the palladium containing stock solution immediately before the plating operation is to begin. The object to be plated is thoroughly cleansed, taking care that the surface is free from such material as lubricating oils, etc., which would interfere with the chemical reduction. These interfering materials are for the most part identical to those materials which cause imperfections in electrodeposits and are well known to those skilled in the art of electroplating. After the object has

been thoroughly cleaned, it is rinsed in distilled water and immersed in the aforementioned palladium chemical plating bath. The initiation of chemical plating of palladium is indicated by the appearance of a multiplicity of small bubbles on the surface of the object. The object is kept in the bath until a sufficient thickness of palladium is obtained thereon, or until there is no further indication of plating on the surface of the object due to depletion of the bath. If deposition ceases and the bath still contains dissolved palladium, plating may again be initiated, usually by the introduction of additional hydrazine solution. This addition should be made after the bath has been cooled to about 10° C. An additional filtration of the bath at this stage is often advisable. If a black precipitate appears in the bath, the object should be removed and the use of the bath discontinued. When decomposition of the bath, as indicated by the aforementioned black precipitate, takes place, the precipitate consisting of finely divided palladium, may be allowed to settle and the supernatant liquid may be decanted. The finely divided palladium may then be recovered and can be redissolved by processes well known to those skilled in the art, for example, by subjecting the material to the action of aqua regia. In operating the bath as described hereinbefore, care should be taken that substances such as iodide ion, stannous ion and other divalent palladium precipitants (e.g., dimethylglyoxime, cyanides, thionalide, pyridine and hydroxyquinolines), should be absent from the bath. Neither metallic zinc nor magnesium should be introduced into or brought in contact with the bath since they cause the precipitation of the palladium ion as spongy palladium metal.

When operating the aforementioned baths, it is to be noted that the rate of deposition of palladium is dependent upon a number of variables. With increasing content of dissolved palladium, all other factors being equal, the rate of deposition increases. The rate of deposition, however, depends upon the nature of the complexing agent and the specific amine used. The rate of deposition likewise increases as the ratio of hydrazine to divalent palladium increases. As the temperature increases, the rate of deposition also increases. All other factors being equal the rate of agitation will also affect the rate of deposition. A particular advantage of the baths of the present invention is afforded by the fact that all surfaces of objects which are exposed to the bath may be coated with palladium through the use thereof. The agitation of the bath by the evolution of gas at the catalytic surface of the object tends to minimize the depletion of the bath at or near interior surfaces such as in blind depressions.

For the purpose of giving those skilled in the art a better understanding of the invention and/or a better appreciation of the advantages of the invention the following illustrative examples are given:

Example I

A bath containing 4.3 g.p.l. of divalent palladium, 0.29 g.p.l. of hydrazine, 33.6 g.p.l. of the di-sodium salt of EDTA, 350 g.p.l. of ammonium hydroxide and the balance essentially water was provided. The pH of the bath was 10.5. A platinum wire to be plated having the dimensions of 0.04 inch diameter and 2 inches long was inserted in this bath while the bath was maintained at a temperature of 80° C. After a few minutes, the wire increased in weight by 0.0076 gram, indicating the deposition of a palladium plate 0.00015 inch thick. The plate was smooth, bright and adherent and had a Knoop hardness number of 257 K.H.N.$_{25g}$.

Example II

A bath containing 0.04 m.p.l. of divalent palladium, 7 m.p.l. of aminoethyl ethanolamine, 0.0075 m.p.l. of hydrazine, 0.05 m.p.l. of the disodium salt of EDTA, with the balance water, was provided. The bath had a pH in excess of 12.5 and was maintained at a temperature of about 60° C. A nickel wire 0.040 inch in diameter and 2 inches long was inserted in the bath. After 30 minutes a ductile, adherent gray deposit of palladium was obtained on the nickel wire.

Example III

A bath containing 0.20 m.p.l. of divalent palladium, 7 m.p.l. of ammonia introduced in the form of ammonium hydroxide, 0.0075 m.p.l. of hydrazine, 0.025 m.p.l. of the disodium salt of EDTA, with the balance water, was provided. The bath was maintained at a temperature of about 30° C. A nickel wire having the same dimensions as the wire of Example II was inserted in the bath. After about 2½ hours, the wire gained 128.0 milligrams in weight through the formation of an adherent, semi-ductile, gray deposit of palladium. The deposit had a hardness of 230 K.H.N.$_{25g}$ and was 2.5 mils thick.

Example IV

A bath containing 0.06 m.p.l. of divalent palladium, 10 m.p.l. of ammonia introduced in the form of ammonium hydroxide, 0.005 m.p.l. of hydrazine, 0.01 m.p.l. of the disodium salt of EDTA, with the balance water, was provided. The bath had a pH of about 10.3 and was maintained at a temperature of 60° C. A platinum wire having the same dimensions as the nickel wire used in Examples II and III was inserted in the bath. After about an hour, a bright, adherent, ductile deposit of palladium weighing 12.5 milligrams was obtained. The deposit had a hardness of 157 K.H.N.$_{25g}$ and was 0.25 mil thick.

Example V

An aqueous palladium plating bath containing 0.03 m.p.l. of divalent palladium, 8 m.p.l. of ammonia, 0.0075 m.p.l. of hydrazine, 0.075 m.p.l. of ammonium sulfate, with the balance water, was provided. The bath had a pH of 11.0 and was maintained at a temperature of about 70° C. A stainless steel square 1 inch on the side and 0.040 inch thick was inserted in the bath. After 30 minutes a bright, adherent, ductile deposit of palladium was obtained. The deposit had a hardness of 235 K.H.N.$_{25g}$.

Example VI

A palladium plating bath containing 0.04 m.p.l. of divalent palladium, 9 m.p.l. of ethylamine, 0.0075 m.p.l. of hydrazine, 0.05 m.p.l. of the disodium salt of EDTA, with the balance water, was provided. The bath had a pH of 9.0 and was maintained at a temperature of 70° C. A nickel wire having the same dimensions as the wire used in Examples II and III was inserted in the bath. After 10 minutes, an adherent, gray, ductile deposit of palladium was obtained.

Example VII

A palladium plating bath containing 0.1 m.p.l. of divalent palladium, 7 m.p.l. of ammonia, 0.01 m.p.l. of hydrazine, 0.05 m.p.l. of 2-2'-thiodiethanol, with the balance water was established. The bath had a pH of 10.0 and was maintained at a temperature of 50° C. A nickel wire similar to the wire used in Example VI was inserted in the bath. After 15 minutes, a gray, adherent, ductile deposit of palladium having a hardness of 242 K.H.N.$_{25g}$ was obtained. The deposit had a weight of 3.5 milligrams and was 0.07 mil thick.

Example VIII

An aqueous palladium plating bath containing 0.04 m.p.l. of divalent palladium, 8 m.p.l. of ammonia, 0.010 m.p.l. of hydrazine, 0.05 m.p.l. of 3-pentanone, with the balance water, was provided. The bath had a pH of 9.2 and was maintained at a temperature of 70° C. A platinum square 1 inch on the side and 0.040 inch thick was inserted in the bath for 30 minutes. A bright, adherent, ductile deposit of palladium was obtained.

Example IX

A palladium plating bath containing 0.16 m.p.l. of divalent palladium, 9 m.p.l. of ammonia, 0.0075 m.p.l. of hydrazine, 0.075 m.p.l. of the disodium salt of EDTA, with the balance water, was maintained at a temperature of 40° C. The pH of this bath was 10.6 A nickel wire similar to the wire used in Example II was inserted in this bath. After 90 minutes, a gray, adherent, semi-ductile deposit of palladium was formed upon the wire. The hardness of the deposit was 224 K.H.N.$_{25g}$ and the deposit weighed 14.8 milligrams and was 0.30 mil thick.

Example X

An aqueous ammoniacal plating bath containing 0.04 m.p.l. of divalent palladium, 8 m.p.l. of ammonia, 0.010 m.p.l. of hydrazine, 0.05 m.p.l. of acetone, with the balance water, was provided. The bath had a pH of 9.2 and was maintained at a temperature of 70° C. A nickel wire similar to the wire used in Example II was inserted in the bath. After about one-half hour a bright, ductile, adherent deposit of palladium was obtained on the wire.

The present invention is particularly applicable to the production of palladium deposits on metallic objects. Palladium deposits on molybdenum formed in the manner contemplated by the present invention are particularly advantageous in electronic applications such as grids and other parts in electron tubes.

The present invention is also applicable to the production of electrical contacts and connectors, electrical components for glass-to-metal seals and printed circuits, diffusion barriers, protective coatings, corrosion protection and tarnish protection.

Although the present invention has been described in conjunction with preferred embodiment, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the 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. A bath for depositing palladium comprising a single-phase, water-containing liquid having in solution about 0.001 to about 0.25 mole per liter or divalent palladium, about 0.002 up to about 0.05 mole per liter of hydrazine, about 0.005 up to about 0.25 mole per liter of a stabilizing agent selected from the group consisting of aliphatic ketones containing from 3 to about 5 carbon atoms per molecule, ammonium salts of mono and di-basic mineral acids, the disodium salt of ethylenediaminetetraacetic acid and 2,2'-thiodiethanol, about 2.5 up to about 14 moles per liter of at least one substance selected from the group consisting of ammonia and aliphatic organic compounds containing a primary amine group and having up to 5 carbon atoms per molecule and the balance essentially water, said water being in a concentration of at least 2 moles per liter.

2. A bath for depositing palladium comprising a single-phase, water-containing liquid having in solution about 0.03 to about 0.20 mole per liter of divalent palladium, about 0.005 up to about 0.01 mole per liter of hydrazine, about 0.01 up to about 0.10 mole per liter of a stabilizing agent selected from the group consisting of aliphatic ketones containing from 3 to about 5 carbon atoms per molecule, ammonium salts of mono and di-basic mineral acids, the disodium salt of ethylenediaminetetraacetic acid and 2,2'-thiodiethanol, about 7 up to about 10 moles per liter of at least one substance selected from the group consisting of ammonia and aliphatic organic compounds containing a primary amine group and having up to 5 carbon atoms per molecule and the balance essentially water, said water being in a concentration of at least 2 moles per liter.

3. A bath for depositing palladium comprising a single-phase, water-containing liquid having in solution about

0.03 to about 0.20 mole per liter of divalent palladium, about 0.005 up to about 0.01 mole per liter of hydrazine, about 0.01 up to about 0.10 mole per liter of a stabilizing agent selected from the group consisting of aliphatic ketones containing from 3 to about 5 carbon atoms per molecule, ammonium salts of mono and di-basic mineral acids, the disodium salt of ethylenediaminetetraacetic acid and 2,2'-thiodiethanol, about 7 up to about 10 moles per liter of ammonia and the balance essentially water, said water being in a concentration of at least 2 moles per liter.

4. A bath for depositing palladium comprising a single-phase, water-containing liquid having in solution about 0.001 to about 0.25 mole per liter of divalent palladium, about 0.002 up to about 0.05 mole per liter of hydrazine, about 0.005 up to about 0.25 mole per liter of a stabilizing agent selected from the group consisting of aliphatic ketones containing from 3 to about 5 carbon atoms per molecule, ammonium salts of mono and di-basic mineral acids, the disodium salt of ethylenediaminetetraacetic acid, and 2,2'-thiodiethanol, about 2.5 up to about 14 moles per liter of ethylamine and the balance essentially water.

5. A bath for depositing palladium comprising a single-phase, water-containing liquid having in solution about 0.03 to about 0.20 mole per liter of divalent palladium, about 0.005 up to about 0.01 mole per liter of hydrazine, about 0.01 up to about 0.10 mole per liter of a stabilizing agent selected from the group consisting of aliphatic ketones containing from 3 to about 5 carbon atoms per molecule, ammonium salts of mono and di-basic mineral acids, the disodium salt of ethylenediaminetetraacetic acid and 2,2'-thiodiethanol, about 7 up to about 10 moles per liter of ethylamine and the balance essentially water.

6. A bath for depositing palladium comprising a single-phase, water-containing liquid having in solution about 0.03 to about 0.20 mole per liter of divalent palladium, about 0.005 up to about 0.01 mole per liter of hydrazine, about 0.01 up to about 0.10 mole per liter of a stabilizing agent selected from the group consisting of aliphatic ketones containing from 3 to about 5 carbon atoms per molecule, ammonium salts of mono and di-basic mineral acids, the disodium salt of ethylenediaminetetraacetic acid and 2,2'-thiodiethanol, about 7 up to about 9 moles per liter of aminoethyl ethanolamine and the balance essentially water, said water being in a concentration of at least 2 moles per liter.

7. A bath for depositing palladium comprising a single-phase, water-containing liquid having in solution about 0.001 to about 0.25 mole per liter of divalent palladium, about 0.002 up to about 0.05 mole per liter of hydrazine, about 0.005 to about 0.25 mole per liter of the disodium salt of ethylenediaminetetraacetic acid, about 2.5 up to about 14 moles per liter of at least one substance selected from the group consisting of ammonia and aliphatic organic compounds containing a primary amine group and having up to 5 carbon atoms per molecule and the balance essentially water, said water being in a concentration of at least 2 moles per liter.

8. A bath for depositing palladium comprising a single-phase, water-containing liquid having in solution about 0.03 to about 0.20 mole per liter of divalent palladium, about 0.005 up to about 0.01 mole per liter of hydrazine, about 0.01 up to about 0.10 mole per liter of the disodium salt of ethylenediaminetetraacetic acid, about 7 up to about 10 moles per liter of at least one substance selected from the group consisting of ammonia and aliphatic organic compounds containing a primary amine group and having up to 5 carbon atoms per molecule and the balance essentially water, said water being in a concentration of at least 2 moles per liter.

9. A bath for depositing palladium comprising a single-phase, water-containing liquid having in solution about 0.03 to about 0.20 mole per liter of divalent palladium, about 0.005 up to about 0.01 mole per liter of hydrazine, about 0.01 to about 0.10 mole per liter of the disodium salt of ethylenediaminetetraacetic acid, about 7 up to about 10 moles per liter of ammonia and the balance essentially water, said water being in a concentration of at least 2 moles per liter.

10. A bath for depositing palladium comprising a single-phase, water-containing liquid having in solution about 0.03 to about 0.20 mole per liter of divalent palladium, about 0.005 up to about 0.01 mole per liter of hydrazine, about 0.01 to about 0.10 mole per liter of the disodium salt of ethylenediaminetetraacetic acid, about 7 up to about 10 moles per liter of ethylamine and the balance essentially water, said water being in a concentration of at least 2 moles per liter.

11. A bath for depositing palladium comprising a single-phase, water-containing liquid having in solution about 0.03 to about 0.20 mole per liter of divalent palladium, about 0.005 up to about 0.01 mole per liter of hydrazine, about 0.01 to about 0.10 mole per liter of the disodium salt of ethylenediaminetetraacetic acid, about 7 up to about 9 moles per liter of aminoethyl ethanolamine and the balance essentially water, said water being in a concentration of at least 2 moles per liter.

12. A bath for depositing palladium comprising a single-phase, water-containing liquid having in solution about 0.03 to about 0.20 mole per liter of divalent palladium, about 0.005 up to about 0.01 mole per liter of hydrazine, about 0.01 to about 0.10 mole per liter of 3-pentanone, about 7 up to about 10 moles per liter of ammonia and the balance essentially water.

13. A bath for depositing palladium comprising a single-phase, water-containing liquid having in solution about 0.03 to about 0.20 mole per liter of divalent palladium, about 0.005 up to about 0.01 mole per liter of hydrazine, about 0.01 to about 0.10 mole per liter of 2,2'-thiodiethanol, about 7 up to about 10 moles per liter of ammonia and the balance essentially water.

14. An auto-catalytic process for the production of adherent deposits of palladium on objects which comprises providing an object having at least a surface layer of catalytic metal and immersing said object in a single-phase liquid bath having a pH from about 9 to about 11 and containing from about 0.03 to about 0.20 mole per liter of divalent palladium, about 7 up to about 10 moles per liter of a substance selected from the group consisting of ammonia and aliphatic primary amines containing up to about 5 carbon atoms per molecule, about 0.01 to about 0.10 mole per liter of a stabilizing agent selected from the group consisting of aliphatic ketones containing from 3 to about 5 carbon atoms per molecule, ammonium salts of mono and di-basic mineral acids, the disodium salt of ethylenediaminetetraacetic acid and 2,2'-thiodiethanol, from about 0.005 to about 0.01 mole per liter of hydrazine with the balance at least 2 moles per liter essentially water while maintaining said bath at a temperature between about 30° C. to about 80° C.

15. An auto-catalytic process for the production of adherent deposits of palladium on objects which comprises providing an object having at least a surface layer of catalytic metal and immersing said object in a single-phase liquid bath having a pH from about 9 to about 11 and containing from about 0.03 to about 0.20 mole per liter of divalent palladium, about 7 up to about 10 moles per liter of a substance selected from the group consisting of ammonia and aliphatic primary amines containing up to about 5 carbon atoms per molecule, about 0.01 to about 0.10 mole per liter of a stabilizing agent selected from the group consisting of aliphatic ketones containing from 3 to about 5 carbon atoms per molecule, ammonium salts of mono and di-basic mineral acids, the disodium salt of ethylenediaminetetraacetic acid and 2,2'-thiodiethanol, from about 0.005 to about 0.01 mole per liter of hydrazine with the balance at least 2 moles per liter essentially water while maintaining

said bath at a temperature between about 30° C. to about 70° C.

16. An auto-catalytic process for the production of adherent deposits of palladium on objects which comprises providing an object having at least a surface layer of catalytic metal and immersing said object in a single-phase liquid bath containing from about 0.001 to about 0.25 mole per liter of divalent palladium, about 2.5 up to about 14 moles per liter of a substance selected from the group consisting of ammonia and aliphatic primary amines containing up to about 5 carbon atoms per molecule, about 0.005 to about 0.25 mole per liter of a stabilizing agent selected from the group consisting of aliphatic ketones containing from 3 to about 5 carbon atoms per molecule, ammonium salts of mono and di-basic mineral acids, the disodium salt of ethylenediaminetetraacetic acid and 2,2′-thiodiethanol, from about 0.002 to about 0.05 mole per liter of hydrazine with the balance at least 2 moles per liter essentially water while maintaining said bath at a temperature between about 30° C. to about 80° C.

17. A bath for depositing palladium comprising a single-phase, water-containing liquid having in solution about 0.03 to about 0.2 mole per liter of divalent palladium, about 0.005 up to about 0.01 mole per liter of hydrazine, about 0.01 up to about 0.10 mole per liter of 3-pentanone, about 7 up to about 10 moles per liter of at least one substance selected from the group consisting of ammonia and aliphatic organic compounds containing a primary amine group and having up to 5 carbon atoms per molecule and the balance essentially water, said water being in a concentration of at least 2 moles per liter.

18. A bath for depositing palladium comprising a single-phase, water-containing liquid having in solution about 0.03 to about 0.2 mole per liter of divalent palladium, about 0.005 up to about 0.01 mole per liter of hydrazine, about 0.01 up to about 0.10 mole per liter of 2,2′-thiodiethanol, about 7 up to about 10 moles per liter of at least one substance selected from the group consisting of ammonia and aliphatic organic compounds containing a primary amine group and having up to 5 carbon atoms per molecule and the balance essentially water, said water being in a concentration of at least 2 moles per liter.

19. A bath for depositing palladium comprising a single-phase, water-containing liquid having in solution about 0.03 to about 0.20 mole per liter of divalent palladium, about 0.005 up to about 0.01 mole per liter of hydrazine, about 0.01 up to about 0.10 mole per liter of ammonium salts of di-basic mineral acids, about 7 up to about 10 moles per liter of at least one substance selected from the group consisting of ammonia and aliphatic organic compounds containing a primary amine group and having up to 5 carbon atoms per molecule and the balance essentially water, said water being in a concentration of at least 2 moles per liter.

20. An auto-catalytic process for the production of adherent deposits of palladium on objects which comprises providing an object having at least a surface layer of catalytic metal and immersing said object in a single-phase liquid bath having a pH from about 9 to about 11 and containing from about 0.03 to about 0.20 mole per liter of divalent palladium, about 7 up to about 10 moles per liter of a substance selected from the group consisting of ammonia and aliphatic primary amines containing up to about 5 carbon atoms per molecule, about 0.01 to about 0.10 mole per liter of the disodium salt of ethylenediaminetetraacetic acid, from about 0.005 to about 0.01 mole per liter of hydrazine with the balance at least 2 moles per liter essentially water while maintaining said bath at a temperature between about 30° C. to about 80° C.

21. An auto-catalytic process for the production of adherent deposits of palladium on objects which comprises providing an object having at least a surface layer of catalytic metal and immersing said object in a single-phase liquid bath having a pH from about 9 to about 11 and containing from about 0.03 to about 0.20 mole per liter of divalent palladium, about 7 up to about 10 moles per liter of ammonia, about 0.01 to about 0.10 mole per liter of a stabilizing agent selected from the group consisting of aliphatic ketones containing from 3 to about 5 carbon atoms per molecule, ammonium salts of mono and di-basic mineral acids, the disodium salt of ethylenediaminetetraacetic acid and 2,2′-thiodiethanol, from about 0.005 to about 0.01 mole per liter of hydrazine with the balance at least 2 moles per liter essentially water while maintaining said bath at a temperature between about 30° C. to about 80° C.

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