

SPECIFICATION

Palladium electrodeposition compositions and process

This invention relates to the electrodeposition of palladium on substrates, and more particularly palladium electrodeposition baths having stabilized bath efficiencies.

Processes for electrodepositing metal in various thicknesses on substrates, also sometimes referred to as electrolytic deposition and electroplating, are well known in the metallizing art. Typically, a deposition bath comprising ions of the metal to be deposited and a suitable electrolyte is provided, the article or object to be plated is immersed in or otherwise contacted with the bath while connected as the cathode to an external current source, and a metal electrode is connected as the anode to the same current source. During operation, ions of the metal to be deposited are reduced in the bath to zero valent metal which plates out on the workpiece surface.

Special mention is made of methods for electrodepositing metallic palladium on substrates, particularly metallic surfaces. In such cases, the palladium deposition bath tends to be unstable and cannot be used continuously for extended periods without undergoing significant losses in bath efficiency. The term "bath efficiency" herein refers to the comparison at a given current density between the actual bath plating rate and the theoretical bath plating rate as determined mathematically from Faraday's Law.

Whilst the invention is not dependent on any particular theory, it is believed that the palladium ions in the bath are oxidized to higher valence states during operation, thus making it more difficult to reduce the palladium ions to metallic palladium, which plates out, without supplying more current to the bath.

Although conventional palladium electrodeposition baths may display good efficiency initially and shortly after plating has begun, this efficiency often decreases sharply within a few hours, in some cases dropping off to less than 50% of the original value after only about twenty four hours of continuous use. To maintain the palladium plating rate at or reasonably near original levels, it is usually necessary to supply more current to the plating bath which is a costly procedure.

It is an object of this invention to provide compositions which, when subjected to electrodeposition techniques, are capable of depositing metallic palladium at substantially constant bath efficiencies for extended periods of use.

It is another object of this invention to provide compositions for replenishing palladium electrodeposition baths which also serve to maintain the bath at substantially constant bath efficiencies.

It is a further object of this invention to provide improved methods for electrodepositing metallic palladium from an aqueous deposition bath.

Compositions in accordance with the invention comprise A) a water soluble palladium compound capable of dissociating in water to provide palladium ions, B) a source of free nitrite ions in an amount sufficient to provide free nitrite ions not complexed with the palladium ions and optionally C) a further electrolyte compound.

The constituents may be added separately to water to form the bath or they may be premixed, for example as a commercial product, and then added to water. The pH of the bath preferably being adjusted to be above 7.

The foregoing compositions are capable, when subjected to electrolytic deposition techniques, of depositing metallic palladium on a substrate for prolonged periods without the need to adjust the current upwards to maintain the plating rate.

This invention also provides compositions useful in replenishing the palladium bath and helping to maintain bath efficiency over extended periods. Such compositions comprise an admixture, without an electrolyte, of a water soluble palladium compound and a water soluble nitrite compound, the latter being present in an amount sufficient to provide free nitrite ions not complexed with the palladium ions in the mixture when dissolved in water.

The present invention also provides an improved method of electrodepositing palladium from a bath comprising an aqueous solution of a palladium (II) compound, comprising maintaining in the bath free nitrite ions not complexed with the palladium ions and thus stabilizing the bath efficiency.

The present invention also extends to a method of electrodepositing metallic palladium on a substrate, which method comprises contacting the substrate as a cathode with a bath composition comprising A) a water soluble palladium compound capable of dissociating in water to provide palladium ions, B) a bath soluble source of free nitrite ions to provide free nitrite ions not complexed with the palladium ions and optionally C) a further electrolyte compound and passing an electroplating current through the said cathode, there being free nitrite ions present in the bath throughout plating.

Bath efficiency begins to fall off almost as soon as operation of the bath begins. Thus, it is important that the free nitrite ions be present in the bath at the outset and maintained in the bath throughout the plating cycle. A water soluble palladium compound, such as palladium diamine dinitrite, is suitable as a source of palladium ions in the bath. However, while containing nitrite such a compound does not serve as a source of "free" nitrite because the nitrite remains complexed even after the compound is dissolved in the bath. Thus, it is necessary to include initially in the bath some other

nitrite compound which is capable of dissociating in water to provide free, i.e. uncomplexed, nitrite ions.

The source of free nitrite ions is preferably a water soluble inorganic nitrite compound. Alkali metal nitrites, such as sodium nitrite, potassium nitrite, or ammonium nitrite are especially preferable.

5 Mixtures of compounds may also be used.

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A small amount (by weight) of free nitrite ions is sufficient to maintain bath stability, usually at least about 0.05% by weight relative to the palladium ions in the bath. In most cases, the bath is formulated to provide free nitrite ions, initially, of from about 0.1 to about 50% by weight relative to the palladium ions in the bath.

10 As the bath is operated and palladium is consumed by plating out, some of the free nitrite ions in the bath simultaneously undergo oxidation to the nitrate form. Thus, even if a large amount is provided in the bath initially, the free nitrite will eventually exhaust itself as the bath is operated. To ensure that an amount of free nitrite is maintained throughout plating, fresh amounts of free nitrite should be added to the bath from time to time. A convenient way of doing this is to add the nitrite compound to

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15 the bath with each periodic addition of the palladium compound used to replenish the palladium consumed. As a general rule, in each case the nitrite compound is added in an amount sufficient to provide at least about a 10% by weight amount of nitrite ions relative to the palladium ions provided by the palladium compound.

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20 The palladium is supplied to the bath, initially and upon replenishment, preferably in the form of a water soluble organic or inorganic palladium (II) compound selected from among materials conventionally employed for such purposes in palladium electrodeposition baths. Examples include palladium diamine dinitrite [$\text{Pd}(\text{NH}_3)_2(\text{NO}_2)_2$], palladium chloride (PdCl_2), palladium sulphate, palladosamine chloride, diamine palladium hydroxide, tetramine palladium chloride and dichlorodiamine palladium chloride. Among these, palladium diamine dinitrite and palladium chloride

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25 are especially preferred for use in this invention.

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The electrolyte for the bath may be any water soluble compound capable of dissolving in water to form an electrically conductive ionic medium. These may be selected from among the conventional materials. In the usual case, this is a water soluble nitrate compound, and preferably ammonium nitrate or an alkali metal nitrate, for example, potassium nitrate or sodium nitrate.

30 The constituents of the compositions according to the present invention may be present in a wide range of amounts. Preferably, however, prior to addition to water the compositions comprise an admixture as described in Table 1.

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Table 1

	<i>Ingredients</i>	<i>Amount, parts by weight</i>	
35	Water soluble palladium (II) compound, preferably palladium diamine dinitrite or palladium chloride	30—40 equivalent to 14—18% Pd (for palladium diamine dinitrite) or 18—24% Pd (for palladium chloride)	35
40	Water soluble electrolyte compound, preferably alkali metal nitrate or ammonium nitrate	65—75	40
45	Water soluble source of free nitrite, preferably alkali metal nitrite	5—15	45

These may be formulated into a palladium deposition bath having the following preferred ranges and which are operated under the conditions described in Table 2.

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Table 2

	Ingredients	Amount	
5	Water soluble palladium (II) compound, preferably palladium diamine dinitrite or palladium chloride	40—60 grams per litre equivalent to 18—27 g/l palladium (for palladium diamine dinitrite) or 24—36 g/l palladium (for palladium chloride)	5
10	Water soluble electrolyte compound, preferably alkali metal nitrate or ammonium nitrate	85—95 grams per litre	10
	Water soluble source of free nitrite, preferably alkali metal nitrite	5—15 grams per litre	
15	Water	To make 1 litre	15
	Temperature	50—70°C	
	pH	8—9	
20	Current density	1—500 amperes per square foot (0.11—55 amperes per square decimetre (ASD))	20

The bath pH may be adjusted before or during operation or both in the usual manner such as by addition of suitable amounts of an acid, for example nitric acid, or a base, for example ammonium hydroxide.

Other ingredients may also be included in the compositions for their conventionally employed purposes. By way of illustration, such materials include brightening agents, wetting agents or surfactants, complexing agents for palladium ions, or antioxidants all of which are well known to those skilled in the art.

In carrying out the electrodeposition process of the present invention, the bath may be operated over a wide range of temperatures, such as from room temperature, for example 25°C, almost up to but below the boiling point of the bath, for example 100°C.

Plating times will vary depending on factors such as the supplied current density, bath temperature and thickness of palladium deposit desired. For the particular current density and temperature ranges indicated above, i.e. 1—500 amps per square foot (0.11—55 ASD) and 50—70°C, a plating period of about 10 minutes or less is usually sufficient to yield a palladium deposit thickness of about one thousandth of an inch, 0.00254 cms (25.4 microns).

According to this invention, metallic palladium is deposited on a metallic substrate in substantially smooth, bright and adherent layers. Examples of metal surfaces on which palladium may be deposited include copper, nickel, silver and steel, e.g. stainless steel or alloys such as brass, or bronze.

Bath efficiencies of greater than 90% may be achieved by use of the present invention and efficiencies of from 80 to 95% can be achieved even when the baths are operated over extended periods. Additionally, it is found that these high bath efficiencies are obtained when operating the baths at high current densities of 300—350 amps per square foot (33—38.5 ASD). Moreover, even at current densities as high as 450—500 amps per square foot (49.5—55 ASD), bath efficiencies of 60—70% are still obtained.

The invention may be put into practice in various ways and a number of specific embodiments will be described to illustrate the invention with reference to the accompanying examples.

Example 1

A small piece of flat copper was pretreated to remove any surface dirt and grease, preweighed and immersed in a palladium electrodeposition bath having the following composition:

	Palladium diamino dinitrite, $\text{Pd}(\text{NH}_3)_2(\text{NO}_2)_2$	50 grams/litre (23 g/l as Pd^{2+})	
	Ammonium nitrate, NH_4NO_3	90 grams/litre	
55	Sodium nitrite, NaNO_2	10 grams/litre (6.7 g/l as NO_2^-)	55
	Water	(to make 1 litre)	

A piece of platinized tantalum/titanium was immersed in the bath and connected as the anode to the positive side of a D.C. power supply unit. The copper workpiece was connected as the cathode to the negative supply of the D.C. power supply, and plating commenced.

The bath had an initial weight ratio of nitrite ions to palladium ions of 1.5:1. The initial bath pH was between 8 and 9. The temperature of the bath was adjusted to and maintained at 70°C.

The current supply was regulated to deposit palladium at a current density of 150 amperes per square foot (16.5 ASD). At this current density, metallic palladium plated out on the surface of the copper workpiece at a rate of 30 milligrams per ampere-minute.

From time to time, the bath was replenished by adding more palladium diamine dinitrite in amounts so as to maintain the initial palladium concentration in the bath. Upon each addition of the palladium compound, the sodium nitrite was also added in an amount providing a 10% amount of free nitrite ion relative to the palladium ion of the diamine dinitrite compound.

A palladium deposit having a thickness of about 0.001 inch, 0.00254 cms (25.4 microns) was obtained after about six minutes of operation. As calculated from the known current density, plating time and palladium deposit thickness, the bath efficiency was found to be 95%.

Thereafter, plating was resumed and the consumable bath ingredients were periodically replaced in the bath in the manner previously described. In this way, the bath was operated continuously for several days with bath efficiency being maintained at or near 95%.

Example 2

This is a comparison example.

The plating procedure of Example 1 was repeated except that fresh amounts of the nitrite compound were not added to the bath after operation had begun. It was observed that the bath efficiency began to fall off after several hours and the amount of palladium being deposited decreased significantly.

Example 3

The procedure of Example 1 was repeated at several different current densities and the following results were obtained:

Table 3

Current density (amps per square foot)	ASD	Bath efficiency (%)
25	2.75	97
50	5.5	97
100	11	94
200	22	86
300	33	80
350	38.5	77
400	44	73
450	49.5	67
500	55	60

Example 4

This is a comparison Example.

A plating bath was made up with the following composition and concentrations in accordance with Example 1 of U.S. Patent 4,092,225:

10 g/l Pd⁰,
150 g/l Potassium Pyrophosphate,
130°F Temperature,
pH=9 adjusted by pyrophosphate or potassium hydroxide.

This bath was used to rack plate copper coupons with good mechanical agitation at several different current densities. The following results were obtained:

Table 4

Current density (amp per square foot)	ASD	Bath efficiency (%)
10	1.1	94
20	2.2	94
30	3.3	94
40	4.4	94
50	5.5	77

From a comparison of Examples 3 and 4 it is apparent that not only does the composition and method of the present invention provide high bath efficiencies over prolonged periods of operation, but additionally, the current density at which such efficiencies are obtained is extended, very substantially, as compared with a prior art bath and process.



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Claims

1. A composition of matter for use in a bath for the electrodeposition of metallic palladium on a substrate comprising A) a water soluble palladium compound capable of dissociating in water to provide palladium ions B) a bath soluble source of free nitrite ions in an amount sufficient to provide free nitrite ions not complexed with the palladium ions and optionally C) a further electrolyte compound. 5
2. A composition as claimed in Claim 1 in which the amount of free nitrite ions is at least 0.05% by weight relative to the palladium ions in the bath.
3. A composition of matter as claimed in Claim 1 or Claim 2 which comprises a mixture of a water soluble palladium (II) compound and an alkali metal nitrite in an amount to provide at least 0.05% by weight free nitrite ions relative to the palladium (II) ions. 10
4. A composition as claimed in Claim 1, 2 or 3 in which the amount of free nitrite ions is in the range of 0.1 to 50% by weight relative to the palladium ions in the bath.
5. A composition of matter as claimed in Claim 1 comprising 30—40% by weight of a water soluble palladium (II) compound, 65 to 75% by weight of a water soluble electrolyte compound and 5 to 15% by weight of a water soluble source of free nitrite ions. 15
6. A composition as claimed in any one of Claims 1 to 5 in which the palladium compound is palladium diamine dinitrite or palladium chloride.
7. A composition as claimed in any one of Claims 1 to 6 in which the bath soluble source of free nitrite ions is an alkali metal or ammonium nitrite. 20
8. A composition as claimed in any one of Claims 1 to 7 in which the free nitrite compound is sodium nitrite or potassium nitrite.
9. A composition as claimed in Claim 1 substantially as specifically described herein with reference to Example 1 or Example 3.
10. An electrodeposition bath for depositing metallic palladium on a substrate comprising an aqueous solution of a composition as claimed in any one of Claims 1 to 9 the bath having a pH of above 7. 25
11. A bath as claimed in Claim 10 containing 40 to 60 g/l of water soluble palladium (II) compound, 85 to 95 g/l of water soluble electrolyte compound and 5 to 15 g/l of water soluble source of free nitrite ions so that there are free nitrite ions not complexed with palladium (II) ions, the bath having a pH in the range 8—9. 30
12. A bath as claimed in Claim 10 substantially as specifically described herein with reference to Example 1 or Example 3.
13. A method of electrodepositing metallic palladium on a substrate which comprises contacting the substrate as the cathode with a bath composition as claimed in Claim 10, 11 or 12 and passing an electroplating current through the said cathode. 35
14. A method of electrodepositing metallic palladium on a substrate, which method comprises contacting the substrate as a cathode with a bath composition comprising A) a water soluble palladium compound capable of dissociating in water to provide palladium ions, B) a bath soluble source of free nitrite ions to provide free nitrite ions not complexed with the palladium ions and optionally C) a further electrolyte compound and passing an electroplating current through the said cathode, there being free nitrite ions present in the bath throughout plating. 40
15. A method of electrodepositing metallic palladium on a succession of substrates which comprises carrying out the method of Claim 13 or 14 on each of the substrates whilst maintaining in the bath free nitrite ions not complexed with the palladium ions. 45
16. A method as claimed in Claim 13 or 14 substantially as specifically described herein with reference to Example 1 or Example 3.
17. An article whenever provided with a palladium electrodeposit by a method as claimed in any one of Claims 13 to 16.