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(54) **Catalyst for electroless plating process.**

(57) Complexes comprising X palladium atoms and Y nitrogen-containing ligands wherein $X/Y >= 1$ are useful as sensitisers in rendering substrates catalytic to the deposition of electroless metal. The compounds can be prepared by reacting A moles of a nitrogen-containing compound with B moles of palladium where $A/B <= 4$ at a pH of 6 or above.

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CATALYST FOR ELECTROLESS PLATING PROCESS

This invention relates to palladium complexes suitable for catalysing the deposition of a metal from a solution of that metal onto a substrate, for example in an electroless plating process, and to a composition and a process for rendering the substrate catalytic. The invention may find particular use where copper is to be deposited on an at least partially conductive substrate (e.g. on a circuit board) as a thin layer before more copper is deposited by an electroless or electroplating process, although the invention is not limited to this use.

Before the plating of non conductive substrates in electroless plating solutions can proceed, the substrate surfaces need to be rendered catalytic or "catalysed", that is coated with a thin layer of a metal which will initiate electroless deposition when bought into contact with the electroless plating solution. The most commonly used catalytic metal for this purpose is palladium.

US-A-3011920 and US-A-3672923 describe aqueous palladium catalysts produced by reaction of palladium and tin salts in acidic chloride media. This type of catalyst may contain elemental palladium and a thin catalytic deposit of palladium may be produced on a substrate by the single step of immersion of the substrate in the catalyst. This type of catalyst is therefore termed a "one step" catalyst. Before plating substrates which have been treated in a "one step" catalyst it is desirable but not essential to remove tin residues by treatment in a solution which at the simplest level may be regarded as dissolving the tin salts but not the palladium.

The tin-palladium catalyst is widely used but suffers from disadvantages which include:-

1. The need for a chloride based pre-dip to maintain chloride levels in the catalyst.
2. The precipitation of tin hydroxides in water rinses after treatment in the catalyst.
3. In the manufacture of printed circuit boards, which are through-plated by the subtractive technique the aggressive nature of the catalyst causes the catalyst to become contaminated with copper which leads to a shortened process life.
4. The catalyst can become "overactive" resulting in diminished adhesion of the subsequent electroless deposit on the substrate.
5. When used in multilayer circuitboard manufacture the aggressive nature of the catalyst can result in dissolution of the oxide coating present on the metal surface of circuit innerlayers, thus giving rise to the unwelcome phenomenon known as the pink (or red) ring effect around plated through holes.

In addition to the tin-palladium "one step" process, various "two step" processes are known. In a two step process the substrate to be catalysed is immersed in a solution containing palladium which is not in its elemental state and then in a solution of a reducing agent capable of reducing the palladium species left on the surface to catalytic palladium metal.

In this two step process the solution containing palladium may be referred to as the "sensitiser" whilst the solution containing the reducing agent may be referred to as the "reducer". The order of process steps may be either sensitiser followed by reducer (which is the most common), or vice versa.

DE-A-1621207 describes such a two step process. The sensitiser contains palladium in its +2 valency state complexed with organic 3 valent nitrogen compounds. There is a considerable molar excess of nitrogen compound as compared to palladium.

EP-A-0167326 describes a two step catalysing system in which the sensitiser comprises a palladium compound dissolved in an amide, typically a 1% or 2% solution. In such a solution the amide is necessarily in a high molar excess. When using formamide for example, a 2% solution of palladium chloride has a 250 molar excess of formamide.

Although two step sensitiser and reducer systems do not suffer from some of the disadvantages of the one step process, they do suffer from the major disadvantage that if rinsing is included between the two steps then the coverage of the subsequent electroless plated deposit tends to be incomplete. This is because either the sensitiser or reducer is rinsed off the substrate. Large concentrations of palladium in the sensitiser may overcome this effect but with the penalty of greatly increased process costs. If rinsing is not employed between the two steps then good coverage can be achieved. However, no rinsing inevitably means contamination of one solution with another, producing undesired metallic palladium precipitation in the second solution. The two step processes described in DE-A-1621207 and EP-A-0167326 suffer from this disadvantage.

GB-A-1394164 and GB-A-1394165 disclose a process for activating a surface of a non-conductor for chemical metallisation using a solution containing a complex of the formula:

$M - (L)_X - A$

where M can be palladium, L is a nitrogen-containing radical and A is an inorganic or organic acid radical. X is an integer of at least one, preferably 2, 3 or 4. Palladium complexes that are exemplified include dichloro-2,2′- dipyridyl palladium (II) and dichlorobis (2-aminopyridine) palladium (II). These complexes are prepared by reacting the metal salt with a large excess of nitrogen-containing compound (molar ratios of nitrogen containing compound: palladium exceed 4.2:1) at low pH and have ligand:metal ratios of at least 1:1. The solutions may be, or can adjusted to be, at pH 7.0. At higher pH's with less nitrogen-containing compound present, it is expected that the palladium would precipitate as $PdO.nH_2O$ (see "Advanced Inorganic Chemistry", Cotton and Wilkinson, 4th Edtn. p.905).

The inventors of the present invention have realised that some complexes are capable of being used as metal (eg. palladium) sensitisers which are water soluble under alkaline conditions, stable and very active and that the useful complexes contain nitrogen compounds or ligands in a low molar ratio to palladium.

Therefore, according to one aspect of the present invention there is provided a complex which comprises 2 palladium atoms and Y nitrogen-containing ligands wherein $X/Y>=1$, the complex being formable by reacting A moles of a nitrogen-containing ligand-forming species with B moles of a palladium compound wherein $A/B<=4$, at a pH of 6 or above. However, it is advantageous if the pH is 7, 9 or even 12 and above.

The ratio X/Y may range from 1 to 20, but it is preferred that X/Y ranges from 1 to 5, and it has been found that best results can be obtained with the X/Y ratio from 1 to 2.

The palladium will generally be in its +2 oxidation state.

Preferably the nitrogen-containing ligand is urea, a mono-, di-, tri- or tetra- C_1-C_6 alkyl N-substituted urea, a C_2-C_7 acyl amide, a C_1-C_6 alkyl (mono- or di-) substituted C_2-C_7 acyl amide, a C_1-C_6 alkyl cyanide, a compound where the nitrogen atom forms part of an aromatic (such as pyridine or quinoline) ring optionally substituted with one or more amino, C_1-C_6 alkyl, hydroxy or other substituents, an amino acid, such as an alpha-amino acid, sulphamic acid or a nitrite or cyanate ion.

The palladium compound is preferably a salt. The salt may be a halide such as a chloride, bromide or iodide, or any other suitable salt such as nitrate.

Examples of alpha amino acids include: alanine, valine, leucine, isoleucine, proline, phenylalanine, tryptophan, methionine, glycine, serine, threonine, cysteine, tyrosine, asparagine, glutamine, aspartic acid, glutamic acid, lysine, arginine and histidine. It is to be understood that weak acids such as amino acids may exist as salts. The exact nature of the species present will depend on the pH.

Other suitable nitrogen-containing ligands include polymeric nitrogen-containing compounds including polyvinylpyrrolidinone (PVP) , polyacrylamide and polymers of urea (optionally substituted as before) with epichlorohydrin. The term "polymer" includes homopolymers and copolymers. Polymers of (optionally substituted) urea and epichlorohydrin may be prepared by reacting the urea and epichlorohydrin together (for example in equimolar proportions or with a molar excess of epichlorohydrin) under alkaline conditions. Other suitable polymeric nitrogen-containing compounds include the the reaction products of epichlorohydrin and other amine monomers such as imidazole.

More preferably the nitrogen-containing ligand is glycine, dimethylamine, acetamide, formamide, N,N-dimethylformamide, acetonitrile, 2-hydroxypyridine, 2-aminopyridine, 2-methylpyridine, pyridine or nitrite. The most preferred nitrogen-containing ligands are urea and mono-, di-, tri- and tetra-N-(C_1-C_4)alkyl substituted ureas.

In the reaction it is preferable that $A/B<=1.5$ but may be $<=0.5$ or even $<=0.2$.

As a starting point in preparing palladium complexes it is common to use palladium chloride dissolved in hydrochloric acid. Such a solution contains the palladium in the form of a square planar ion $PdCl_4^{2-}$ - (tetrachloropalladate). If a solution of tetrachloropalladate is made alkaline, palladium is precipitated as a hydrous oxide $PdO.nH_2O$. If the procedure is repeated in the presence of an excess of amine a complex $Pd(amine)_2Cl_2$ is formed (see Advanced Inorganic Chemistry, Cotton and Wilkinson, 4th Edition, pages 905 and 911). If urea is used, again in excess, a yellow complex, $Pd(NH_2CONH_2)2_2Cl_2$ is precipitated. This complex, which is thought to have the urea bonded through a nitrogen atom, [see The Chemistry of Platinum and Palladium, F.R. Hartley, page 183], and containing 36% by weight of palladium, has been used as the basis of a palladium electroplating solution [US-A- 3637474].

If this procedure is repeated with only a very small quantity of urea present then a different result is obtained. If the molar ratio of urea to palladium is 1:1 then the yellow colouration of $Pd(NH_2CONH_2)_2Cl_2$ is not formed, neither is the excess palladium precipitated as $PdO.nH_2O$ as might be expected. Instead as the pH goes above 4.5 a deep red colouration is formed and the final result at pH values above 10 is a red-orange solution. In this solution each molecule of urea appears to complex only one atom of palladium.

If the procedure is repeated but with the urea concentration reduced by a factor of 2, 4 or 8 the result is the same. All the palladium remains in the solution which attains a red-orange colouration.

Nitrogen ligands that behave in a similar manner to urea include C_1-C_6 alkyl N-substituted ureas, C_2-C_7 acyl amides, a C_1-C_6 alkyl (mono- or di-) substituted C_2-C_7 acyl amides, C_1-C_6 alkyl cyanides, compounds where nitrogen is part of an aromatic (eg C_6 or C_{10}) ring optionally substituted with one or more amino, C_1-C_6 alkyl hydroxy or other substitutents, amino acids such as glycine, sulphamic acid and nitrite. The common themes that seem to be present amongst the (generally three valent) nitrogen ligands that are most effective are:-

1. The nitrogen atom is either adjacent to or forms part of the ligand, which is pi bonded.
2. The nitrogen-containing ligand-forming species gives rise to low molar ratio complexes which are sufficiently soluble to be effective.
3. The nitrogen-containing ligand should not reduce palladium ions to elemental palladium.

Pi-bonded nitrogen-containing ligands may allow pi back-bonding to occur and thus to stabilise the palladium complexes.

It should be noted the invention is not limited to these theories or possible explanations for the results observed.

The low molar ratio nitrogen-containing ligand palladium complexes are evidently quite stable and appear to be more catalytically active than species such as PdL_2X_2 (L = nitrogen ligand; X = halogen). The presence of too many such species will tend to lead to a loss of catalytic performance of the solution.

Complexes in accordance with the first aspect are therefore generally substantially free of complexes in which the ratio of palladium atoms to nitrogen-containing ligand X/Y <1, and/or containing only one palladium atom. By "substantially free" is meant being in association with less than 50%, 40%, 30%, 20%, 10% or even 5% by weight of the single palladium atom containing complexes.

A complex in accordance with the first aspect of the invention may be prepared by reacting A moles of a nitrogen-containing ligand-forming species with B moles of a palladium compound wherein A/B< = 4 at a pH of 6 or above. This process forms a second aspect of the invention.

Palladium compounds such as palladium halides and nitrogen-containing ligand-forming species are available commercially or may be synthesised appropriately.

The process of preparing the complex is in at least some embodiments essentially simple. A source of palladium can be a palladium salt e.g. palladous chloride or nitrate. The palladium salt may be dissolved in a small quantity of hydrochloric, hydrobromic or hydroiodic acid and then diluted with water. To this dilute solution, which may contain up to 5 gram/litre of palladium, can then be added a quantity of a nitrogen-containing ligand-forming species up to 4 x the molar quantity of palladium. Alternatively, the palladium salt may be in solution free of halide.

Once the nitrogen-containing ligand-forming species has dissolved, the solution can be stirred and gradually made alkaline, for example by additions of an alkali metal hydroxide such as sodium or potassium hydroxide, or a quaternary ammonium hydroxide $N^+R^1R^2R^3R^4$ (where R^1 to R^4 are all alkyl eg. C_1-C_6 alkyl or aryl groups). Once the pH of the mixture reaches about 4.5 the solution usually deepens in colour to a dark red, indicating formation of a complex. The hydroxide addition is allowed to continue to the desired final value which is preferably above 6.

An alternative and preferred method of producing a palladium complex is to predissolve a palladium source, generally under acid conditions, add to this a nitrogen-containing ligand-forming species and then add this mixture with stirring to a dilute alkali hydroxide solution. This procedure generally produces a yellow solution which is believed to contain the palladite (PdO_2^{2-}) anion. Heating this solution, for example at 60°C to 80°C for l to 3 hours results in the development of the red-orange colour and generates the complex in solution. (It is not known whether this is a true solution or a fine colloid.) It should be noted that the nitrogen-containing ligand-forming species can be added at any time prior to, or less preferably during, early stages of heating.

Compositions according to a third aspect of the present invention are usually aqueous and may be prepared by admixing a complex in accordance with the first aspect or an aqueous solution of such a complex, with an aqueous pH adjusting solution such as aqueous alkali.

Since the composition may contain very low concentrations of palladium, nitrogen-containing ligands and hydroxide it may be beneficial to incorporate a buffer. The buffer may be incorporated into either a concentrate, a working solution or both in order to stabilise the pH when in use. Suitable buffers can be selected dependent on the pH desired but may comprise carbonate, phosphate, borate or phthalate ions.

The buffer may be at a concentration from 0.1 g/l to saturation. Preferably the buffer is provided at a concentration of 1.0 to 50 g/l and more preferably at a concentration of 5 to 10 g/l.

Since the complex will in the majority of instances be used as a sensitiser under alkaline conditions it may be beneficial to incorporate a chelating agent. This may prevent the precipitation of insoluble metal hydroxides should the sensitiser become contaminated with metals such as calcium, magnesium, manganese or copper. Suitable chelating agents include EDTA, gluconates, glucoheptonates and the like. The chelating agent is preferebly provided at a concentration of from 0.1 to 50 g/l, more preferably at about 5 g/l.

The pH of the composition is usually alkaline, ie above 7. A pH of from 9 to 14, especially from 12 to 13, is preferred.

If copper clad printed circuit boards are to be processed through an aqueous composition as described above, the final pH should be above 10 to prevent immersion palladium deposits occuring on the copper surface. If, during the procedure a precipitate is formed, particularly a dark red or orange precipitate, then this can be avoided by either reducing the palladium concentration, or reducing the molar ratio of nitrogen containing compound to palladium, by adding the nitrogen containing compound concurrently with the hydroxide addition, by reducing the initial hydroxide concentration or by more rapid stirring during the mixing of the ingredients.

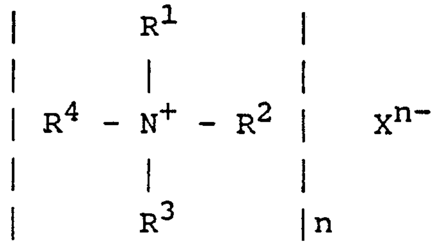
The procedures described can be used to prepare working solutions of the palladium complex in the concentration range of from 1.0 to 0.001g/l, or to prepare more concentrated solutions which may be diluted prior to use.

It is preferred that the palladium concentration in the working composition is from 0.02 g/l to 0.3 g/l, or more preferably 0.05 g/l to 0.15 g/l.

According to a fourth aspect of the invention, there is provided a method of rendering a substrate catalytic to the electroless deposition of a metal, the method comprising contacting at least part of a surface of the substrate with a complex or composition in accordance with the first or third aspects of the invention.

The surface will preferably previously have been conditioned, that is to say contacted with a cationic wetting agent such as a quaternary ammonium wetting agent.

The purpose of the quaternary wetting agent is to make the surface(s) of the laminate receptive to a catalyst which, in turn, serves the purpose of rendering the surface(s) catalytic to the deposit of copper. The quaternary wetting agent may be a quaternary ammonium wetting agent of general formula (I):



$$\left|\begin{array}{c} R^1 \\ | \\ R^4 - N^+ - R^2 \\ | \\ R^3 \end{array}\right|_n X^{n-} \qquad (I)$$

wherein each of R^1, R^2, R^3 and R^4 independently represents a C_1 to C_{20}, preferably C_{1-8}, alkyl group, a C_6 or C_{10} aryl or a C_7 to C_{30} arylalkyl or alkylaryl group, each optionally substituted with a group $-OR^5$, $-NHR^5R^6$, where each of R^5 and R^6 independently represents a hydrogen atom or a C_1 to C_{20}, preferably C_{1-8}, alkyl group;

and X^{n-} represents a compatible anion of acidity n, where n is an integer, generally 1 to 4 but preferably 1.

The nature of the substituents on the quaternary ammonium cation will in general be selected so that the cation is sufficiently soluble in and otherwise compatible with the solution. At least two of the substituents R^1, R^2, R^3 and R^4 will preferably represent a C_1 to C_4 alkyl or substituted alkyl group, especially methyl, ethyl or propyl. But it is also preferred that at least one of the substituents R^1, R^2, R^3 and R^4 be substituted as described, and that at least one of R^5 and R^6 represents a C_6 to C_{20} alkyl group such as stearyl.

Preferred cations include stearylamidopropyldimethyl-2-hydroxyethylammonium and oxyethylalkylammonium. Stearylamidopropyldimethyl-2-hydroxyethylammonium phosphate is sold by Ciba-Geigy under the trade mark CYASTAT-SP.

The cation may alternatively be a C_1-C_{20} alkyl pyridinium moiety, such as cetyl pyridinium. The cation may alternatively be an imidazolinium cation or be a recurring part of a polymer such as an imidazolinium polymer species.

The anion will generally be selected so that it too is sufficiently soluble in and otherwise compatible with the solution. It may be a halide ion such as chloride or bromide, or a nitrate, phosphate, sulphate, hydrogen phosphate or dihydrogen phosphate ion. Preferred anions are nitrate and dihydrogen phosphate.

The wetting agent may be present in an amount of 0.1 to 10 g/l, typically 0.5 to 5 g/l, for example 1 to 3 g/l.

The aqueous conditioning solution will also preferably contain a complexing agent, which functions to clean the surface by removing oxides. The complexing agent will generally be an amine or amine derivative. Suitable complexing agents include soluble amines, alkanolamines (especially C_1-C_6 alkanolamines such as monoethanolamine, diethanolamine, triethanolamine), amine carboxylic acids, hydroxycarboxylic acids and amine phosphoric acids. Improved results may be obtainable by using such complexing agents, of which soluble amine carboxylic acids are preferred. Tetraethylene pentamine may also be used. In general it should be noted that the complexing agent should be non-volatile if the composition containing them is to be used above room temperature.

The complexing agent may be present in an amount of 1 to 50 g/l, typically 5 to 30 g/l, for example 10 to 20 g/l.

Another preferred component of the conditioning solution is a nonionic surfactant. Examples of compatible and suitable nonionic surfactants are ethoxylated linear alkyl alcohols, such as an ethoxylated nonyl phenol containing for example about 12 moles of ethylene oxide. The nonionic surfactant acts as a wetting agent generally to provide a water-break free surface.

The nonionic surfactant may be present in an amount of 0.1 to 20 g/l, typically 0.5 to 5 g/l, for example 1 to 3 g/l.

The pH of the conditioning solution is not believed to be critical but may range from 1 to 14; preferably the pH is below 7 as better results appear to be obtained in acid conditions.

According to a fifth aspect of the invention, there is provided a method of depositing a metal onto a substrate (which will generally be at least partially non-conductive), the method comprising rendering the substrate (or part of it) catalytic to the electroless deposition of a metal by a method in accordance with the fourth aspect and subsequently depositing metal on the so-catalysed substrate by an electroless deposition process.

Methods in accordance with the fourth and fifth aspects find particular application in the manufacture of printed circuit boards for the electronics industry.

The fourth and fifth aspects of the invention are therefore embodied in a process for the electroless deposition of a metal (such as copper, nickel, cobalt or gold) onto a substrate, such as treating a board in the manufacture of a printed circuit board, the process comprising the steps of:

(a) cleaning and/or conditioning a substrate, followed by a water rinse,
(b) optionally etching copper on the substrate followed by a water rinse,
(c) contacting the substrate with a complex of the first aspect of the invention, or a composition as in the third aspect of the invention,
(d) optionally rinsing with water,
(e) contacting the substrate with a reducing agent composition and optionally rinsing with water,
(f) electroless plating the substrate.

Cleaning the substrate to remove stains, soil and unwanted copper oxide deposits may be achieved by means of a copper complexor such as EDTA, tartrate, citrate, nitrilotriacetic acid, gluconate, N-ethanolamine or HEDTA. If step (a) comprises only cleaning, conditioning may be left until after step (b) and before step (c). As an optional variant a "pre-dip" may be included directly before step (c) in order to prevent the sensitiser becoming unduly contaminated with, for example, hard water salts. The pre-dip, which may be acid or alkali, may contain a metal ion complex or may simply be distilled water.

The reducing solution contains at least one compound capable of reducing catalytic metal complexes remaining on the surface of the substrate to elemental metal. Preferably the reducing agent is a dimethylamine-borane complex, an alkali metal borohydride (eg. sodium borohydride) or hydrazine, and it is preferred that the reducing agent is present in an amount from 0.1 to 100 g/l, or more preferably at about 10 g/l. The reducing agent composition may be aqueous and alkaline; it may contain sodium hydroxide, e.g. in an amount of about 10 g/l.

A typical treatment sequence for the electroless plating of a totally non-conductive substrate (which may require prior etching to ensure adhesion of the plated deposit) or a mixed substrate such as a drilled copper clad printed circuit board (which may be a multilayer printed circuit board and/or which may have been pre-treated in a hole resin desmearing or etchback process with or without glass etching) is as follows:-

FUNCTION		TIME	EXAMPLE
1.	Clean/Condition Water Rinse	3-5 mins 1 min	CIRCUITPREP 1017 -
2.	Copper Etch (only for copper clad substrates) Water Rinse	1.3 mins 1 min	100g/l sodium persulphate + 20 ml/l sulphuric acid -
3.	Palladium Sensitiser Water Rinse	2-6 mins 1 min	See Examples -
4.	Reducer Water Rinse	2-6 mins 1 min	Alkaline sodium borohydride solution -
5.	Electroless Plate	As required	CIRCUITPREP 5540 Electroless Copper
The word "CIRCUITPREP" is a registered trade mark.			

Gentle to moderate agitation of the substrate in all the process steps including the palladium sensitiser is beneficial and may be effected by either solution movement (for example by air agitation or by means of a pump) or by substrate movement or both as is suitable.

The performance of the sensitiser can be determined by visually observing the coverage of the electroless deposit. On most substrates any areas of misplating can be readily observed.

In the plating of through holes in printed circuit boards however it is the coverage of the hole walls with, for example, copper which is of primary importance. In this case the "backlight test" is used to determine the degree of coverage achieved. After plating, a few chosen holes are cut through longitudinally so that about 50% of the hole wall remains. The sample is then arranged on a microscope so that the hole wall can be observed at a right angle from above whilst a powerful light is placed directly below the sample. The non-conductive substrate, from which a circuit board is normally fabricated, is generally a very good light transmitter. Any discontinuities in the copper deposit on the hole wall will allow light transmission and will show up as bright areas. In this way areas of misplating from tiny pinholes to large voids may be seen.

Since an electroless deposit will in general only form where a catalytic metal has been previously deposited, the results of the backlight test will reflect the performance of the catalytic treatment if other parameters are maintained unchanged. The results of backlight tests can be graded as follows:-

A+	perfect	
A	less than 3 pinholes	excellent
B	less than 6 pinholes	acceptable
C	less than 5% voiding	unacceptable
D	less than 15% voiding	unacceptable
E	more than 15% voiding	unacceptable

The results of at least 5 holes are averaged in order to reach an overall rating ie. A+ or A/B etc.

In the plating of through holes in printed circuit boards it has been found that sensitiser compositions according to the invention can give backlight tests graded A+ at palladium concentrations as low as 20mg/l. This is remarkable in comparison to the performance of the tin-palladium system which operates at palladium concentrations within the much higher range of 100-300mg/l. The difference between the two systems is even more evident when desmeared or etchback treated circuit boards are processed since these are more difficult to plate completely void free in an electroless copper process.

The reasons why these sensitiser compositions are particularly effective at low palladium concentrations, even if rinsing is employed between the sensitiser and reducer steps are unclear but may be attributed to the following:-

1. The species contain high percentages of palladium, 44% or greater in the case of urea as the complexor.

2. In the rinsing step the species may be hydrolysed and become insoluble thus remaining on the surface of the substrate. (This occurs in the case of the tin-palladium catalyst where the tin-chloride is hydrolysed thus retaining palladium on the surface entrapped in insoluble tin hydroxides).

3. The species whether hydrolysed or not are readily reduced to elemental palladium.

4. The species may exist as a colloid.

However, it should be realised that the invention is not limited by these possible explanations. The invention will now be described by way of example only.

EXAMPLE 1

Palladous chloride 1.67g (0.0095 mole) was dissolved in 30 ml of H_2O containing 6 ml of concentrated hydrochloric acid by heating to 50 °C and stirring until a clear yellow brown solution was obtained. This solution was diluted to 1 litre and then urea 0.6g (0.01 mole) was added and dissolved. The solution was made alkaline by the gradual addition of solid sodium hydroxide. As the pH reached values above 4.5 the solution became very dark red in colour. The sodium hydroxide addition was stopped when the pH reached 12 by which time the solution, which remained clear, had attained an orange-red colouration. 50 ml of this solution, which contained 1g/l of palladium, was diluted to 500 ml with distilled water so as to contain 100 mg/l of palladium. The molar ratio of palladium to urea in the complex was 1:1. This solution was used as the sensitiser in the following sequence to plate a 0.5 dm_2 piece of double sided copper clad epoxy glass laminate with previously drilled holes of 1 mm diameter with an electroless copper deposit.

STEP	PROCESS	TIME	T$^{\circ}$C
1	CIRCUITPREP 1017 cleaner/conditioner	5 mins	60°
2	water rinse		
	100 g/l sodium persulphate	1 min	room temp.
3	20ml/l sulphuric acid	2 mins	" "
4	water rinse	1 min	" "
5	sensitiser (100mg/l Pd)	5 mins	" "
6	water rinse	1 min	" "
7	10 g/l sodium borohydride 10 g/l sodium hydroxide	4 mins	" "
8	water rinse	1 min	" "
9	CIRCUITPREP 5540 electroless copper	30 mins	40°C

(2-2.5 microns deposited)

(The word CIRCUITPREP is a registered trade mark)

In the backlight test the copper coverage in the holes was graded A*

EXAMPLE 2 (A comparison example)

The procedure of Example 1 was followed execpt that the addition of urea was omitted. As the pH increased the palladium precipitated as a light brown solid. The catalytic activity of the supernatant liquid was not investigated.

EXAMPLE 3

Palladous chloride 0.835 g (0.0047 mole) was dissolved in 10 ml of water containing 2 ml of concentrated hydrochloric acid by heating to 50° C. This solution was diluted to 500 ml and 0.15 g urea (0.0025 mole) was added and dissolved. The pH adjustment, dilution for plating test and plating test procedure were as in Example 1. In the backlight test the copper coverage in the holes was graded A^+/A.

EXAMPLE 4

Palladous chloride 0.167 g (0.00095 mole) was dissolved in 10 ml of water containing 2 ml of concentrated hydrochloric acid. This solution was made up to 1 litre and 0.045 g of dimethylamine (0.00098 mole) added. The pH was increased to 11.5 g by gradual addition of solid sodium hydroxide. This solution which contained 100 mg/litre of palladium was tested as a sensitiser using the procedure given in Example 1. In the backlight test, the copper coverage in the holes was graded A^+.

EXAMPLE 5

The procedure for Example 3 was followed except that acetamide 0.3 g (0.005 mole) was used in place of urea. In the backlight test, the copper coverage in the holes was graded A^+.

EXAMPLE 6

Palladous chloride 10 g (0.057 mole) was dissolved in 25 ml of concentrated hydrochloric acid diluted to 100 ml with distilled water. 4.17 ml (0.0024 mole) of the above solution was diluted to 250 ml to give a 1g/litre palladium solution. Glycine, 0.188 g (0.0025 mole) was added with stirring. The pH was increased to 12 by the gradual addition of solid sodium hydroxide. The solution produced was dark orange. The solution dilution and plating procedure were as described in Example 1. In the backlight test, the copper coverage in the holes was graded A^+.

EXAMPLE 7

The procedure for Example 6 was followed except that acetonitrile 0.102 g (0.0025 mole) was used instead of glycine. In the backlight test, the copper coverage in the holes was graded A/B.

EXAMPLE 8

Palladous bromide 0.625 g (0.0024 mole) was dissolved in 10 ml of water containing 1.5 ml of 40% hydrochloric acid. The solution was heated to 60 °C until all the palladous bromide had dissolved. The solution was then diluted to 250 ml. Urea 0.15 g (0.0025 mole) was added and dissolved with stirring. Solid sodium hydroxide was added slowly until the pH reached 12. The solution was orange/red in colour. This solution which contained 1g/l palladium was diluted and tested as in Example 1. In the backlight test, the copper coverage in the holes was graded A.

EXAMPLE 9

Palladous chloride 0.417 g (0.0024 mole) was dissolved in 30 ml of water containing 2 ml of concentrated hydrochloric acid by heating to 50° C. This solution was diluted to 250 ml and sulphamic acid

25mg, (0.00026 mole) added and dissolved. The molar ratio of palladous chloride to sulphamic acid was thus 9.2:1. Solid sodium hydroxide was added gradually and dissolved until the pH reached 12. The solution produced was dark red/orange. This solution which contained 1g/l palladium was diluted and tested as in Example 1. In the backlight test the copper coverage in the hole was graded A^+.

EXAMPLE 10

The procedure of Example 8 was followed except that sulphamic acid 12.5mg (0.00013 mole) was used in place of urea. The molar ratio of palladous bromide to sulphamic acid was thus 18.5:1. In the backlight test the copper coverage in the holes was graded A^+/A.

EXAMPLES 11 and 12

Palladous chloride, 0.835 g (0.0047 mole) was dissolved in 10 ml of water containing 2 ml of concentrated hydrochloric acid and diluted to 250 ml. Urea, 0.3 g (0.0050 mole) was added and dissolved in this solution. Solid sodium hydroxide was then added gradually and dissolved until the solution pH was in the range 6.0-6.5. The solution, which had become very dark red in colour was then added dropwise with stirring to 250ml of a solution containing 100g/litre boric acid and 100g/litre sodium hydroxide. The final volume was 500 ml of a red/orange solution containing 1g/litre palladium. This solution was diluted to 100 mg/litre palladium (Example 11) and also to 20 mg/litre palladium (Example 12) and these dilute solutions were tested as sensitisers according to the procedure of Example 1. The copper coverage in the holes in the backlight test was graded as follows:
Example 11: A at 100 mg/litre palladium
Example 12: A/B at 20 mg/litre palladium

EXAMPLE 13

Palladous chloride, 0.835 g (0.0047 mole) was dissolved in 10 ml of water containing 2 ml of concentrated hydrochloric acid and diluted to 250 ml. Urea, 0.3 g (0.0050 mole), was added and dissolved in this solution, which was added dropwise to 250 ml of a solution containing 100 g/litre boric acid and 100 g/litre sodium hydroxide. The final volume was 500 ml of a light yellow solution. A sample of this solution was diluted to give a palladium concentration of 100mg/litre. After 1 day standing, the light yellow solution had begun to turn red-orange. This process was accelerated by heating to 60° C for 3 hours by which time the solution colour was the same as that of Examples 11 and 12. A sample was again diluted to 100 mg/litre of palladium and used as a sensitiser in the procedure of Example 1. The copper coverage in the holes was graded A^+/A.

EXAMPLE 14

A 250 ml sample of the concentrated solution produced in Examples 11 and 12 was taken and 5 g/litre tetrasodium EDTA added and dissolved. The solution colour did not change and no precipitate was formed. After dilution to 100 mg/litre palladium concentration the solution was tested as a sensitiser according to the procedure given in Example 1. The copper coverage in the holes was graded A.

EXAMPLE 15

A sample of the solution produced in Example 3 was taken and diluted to 100 mg/litre palladium concentration. This solution was tested as a sensitiser using the procedure of Example 1 except for the following:

1. The test piece was a 0.5 dm^2 coupon of epoxy glass laminate without copper cladding.
2. An alkaline electroless nickel plating solution (UDIQUE 891) was used in place of an electroless copper solution. (The word "UDIQUE" is a trade mark).

Nickel had deposited over the entire surface of the coupon within 30 seconds of immersion. After 10 minutes plating the nickel thickness was determined by strip and weigh technique to be 1.2 microns. The adhesion of the deposit to the substrate was excellent.

EXAMPLE 16

Palladous chloride 0.417g (0.0024 mole) was dissolved in 10 ml of water containing 2 ml of concentrated hydrochloric acid and diluted to 250 ml. The solution pH was adjusted to 2.5 with the addition of solid sodium hydroxide. Sodium nitrite 0.1g, (0.00126 mole) was added and dissolved and then the solution pH increased to 12 with solid sodium hydroxide. The solution became dark red/orange in colour. A sample of this solution which contained 1g/litre of palladium was diluted to 100 mg/litre palladium and tested as a sensitiser following the procedure of Example 1. In the backlight test the copper coverage in the holes was graded A^+.

EXAMPLE 17

6.44 ml of a palladium nitrate solution (from Johnson Matthey Chemicals) containing 0.50 g of palladium (0.0047 mole) was diluted to 100 ml. This diluted solution was added dropwise to a solution of 400 ml of water containing 6 g of sodium hydroxide. After the addition was complete, a slightly cloudy yellow solution was obtained. This solution was divided into three parts:

Part A: (250 ml). To this was added urea 0.15 g (0.0025 mole) and the solution heated to 90° C. This solution became very dark brown/red in colouration and remained clear.

Part B: (150 ml). This solution was heated to 90° C. A dark brown precipitate was obtained.

Part C: (100 ml). This solution was retained.

The solution from Part A (which contained 1 g/l palladium) was diluted with water to a palladium concentration of 100 mg/l and used as a sensitiser in the sequence described in Example 1, except that the substrate used was bare epoxy glass (after stripping the copper cladding) and also except that the following composition was used (at 40° C) in place of the CIRCUITPREP 5540 composition:

12 g/l $CuSO_4.5H_2O$
10 g/l NaOH
20 g/l Ethylenediamine tetra-2-hydroxy propyl
3 g/l formaldehyde
5 mg/l 2,2′-bipyridyl

After 10 minutes plating, the substrate was completely covered with copper.

EXAMPLE 18

(A) Palladous chloride 0.835 g (0.0047 mole) was dissolved in 10 ml of water containing 2 ml of concentrated hydrochloric acid and diluted to 125 ml.

(B) Sodium hydroxide (5 g) and urea (0.3 g, 0.005 mole) was dissolved in 125 ml water.

(C) Solution (A) was then added dropwise to solution (B) with stirring. The solution was then heated to 70° C until the solution became very dark red.

(D) The solution obtained in (C) was then diluted to give a 100 mg/l Pd sensitiser solution.

An electroless plating line as described in Example 1 was then prepared with two exceptions:

(i) CIRCUITPREP 1017 was replaced with a cleaner/conditioner of the following formulation:

20 g/l HEDTA - tri-sodium salt
20 ml/l stearamidopropyldimethyl-2-hydroxyethylammonium nitrate (50% solution)
5 ml/l ethoxylated linear secondary alcohol (C_{11}-C_{15})

(ii) The sensitiser solution was that described in (D).

A drilled copper clad laminate panel was then processed through the electroless plating line. The panel was conditioned first. The copper coverage in the holes in the backlight test was graded A.

EXAMPLE 19

Palladous chloride, 1.2525g (0.0071 mole) was dissolved in 5 ml of concentrated hydrochloric acid and 5 ml of water. This solution was diluted to 250 ml with water. Urea, 0.42g (0.007 mole) was then added and dissolved. Solid sodium hydroxide, 4g was then added and the solution rapidly stirred until all the sodium hydroxide had dissolved. The clear dark red-brown solution obtained was then heated to 60 °C for 1 hour, cooled to room temperature and filtered. (No precipitate was obtained). Evaporation losses were made up to the original volume of 250 ml to give a solution containing 3 g/l Pd. A portion of this solution was diluted with water to a palladium concentration of 100 mg/l and tested as a sensitizer following the procedure of Example 1. In the backlight test the copper coverage in the holes was graded A+.

EXAMPLE 20

A sample of the sensitiser produced in Example 3 was taken and diluted to 150mg/l Pd concentration. 5g/l sodium hydroxide was added to the resulting solution. The solution was tested as a sensitiser using the procedure of Example 1 except for the following.

1. The test piece was a 0.5 dm^2 coupon of epoxy glass laminate without copper cladding.
2. The cleaner/conditioner pre-treatment step was omitted and the first step became immersion in the sensitiser sample.
3. The reducer solution was 1g/l sodium borohydride.
4. An alkaline electroless cobalt plating solution (ENPLATE CO-7473) was used in place of an electroless copper plating solution. (The word "ENPLATE" is a trade mark).

After 1 minute plating cobalt had deposited on 90% of the surface of the substrate. The adhesion of the deposit to the substrate was excellent.

Claims

1. A complex comprising X palladium atoms and Y nitrogen-containing ligands wherein X/Y> =1, the complex being formable by reacting A moles of a nitrogen-containing ligand-forming species with B moles of a palladium compound wherein A/B< =4 at a pH of 6 or above.

2. A compound as claimed in claim 1, wherein the nitrogen-containing ligand is urea, a mono-, di-, tri-or tetra- C_1-C_6 alkyl N-substituted urea, a C_2-C_7 acyl amide, a C_1-C_6 alkyl (mono- or di-) substituted C_2-C_7 acyl amide, a C_1-C_6 alkyl cyanide, a compound where the nitrogen atom forms part of an aromatic ring (optionally substituted with one or more amino, C_1-C_6 alkyl, hydroxy or other substituents, an amino acid, sulphamic acid or a nitrite or cyanate ion.

. A compound as claimed in claim 1 or 2 wherein the nitrogen-containing ligand is glycine, dimethylamine, acetamide, formamide, N,N-dimethylformamide, acetonitrile, 2-hydroxypyridine, 2-aminopyridine, 2-methylpyridine , pyridine or nitrite.

4. A compound as claimed in any of claims 1 to 3 wherein A/B< =1.5.

5. A composition for use in an electroless plating process comprising a solution of a compound as claimed in any of claims 1 to 4.

6. A method of rendering a substrate catalytic to the electroless deposition of a metal, the method comprising contacting at least part of a surface of the substrate with a compound as claimed in any one of claims 1 to 4 and/or a composition as claimed in claim 5.

7. A method of depositing a metal onto a substrate, the method comprising rendering the substrate (or part of it) catalytic to the electroless deposition of a metal by a method as claimed in claim 6 and subsequently depositing metal on the so-catalysed substrate by an electroless deposition process.

8. A process for the electroless deposition of a metal onto a substrate comprising the steps of;

(a) cleaning and/or conditioning the substrate, followed by a water rinse,

(b) optionally etching with copper followed by a water rise,

(c) contacting the substrate with a compound as claimed in any of claims 1 to 4 and/or a composition as claimed in claim 5,

(d) optionally rinsing with water,

(e) contacting the substrate with a reducing agent composition and optionally rinsing with water,

(f) electroless plating the substrate.

9. A process as claimed in claim 8 wherein the reducing agent is a dimethylamine-borane complex, alkali metal borohydride or hydrazine.

10. A process for preparing a complex comprising palladium and a nitrogen-containing compound, the process comprising reacting A moles of a nitrogen-containing ligand-forming species with B moles of a palladium compound wherein A/B< =4 at a pH of 6 or above.

European Patent
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EUROPEAN SEARCH REPORT

Application Number

EP 88 31 0037

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
D,X	EP-A-0 167 326 (HITACHI CHEMICAL CO., LTD) * Claims 1,2,5,6-10; example 1 * ---	1-7,9,10	C 23 C 18/28
X	FR-A-2 132 172 (SCHERING AG) * Claims 1-8,11,15,16 * ---	1-3,5,6,7,9	
X	PATENT ABSTRACTS OF JAPAN, vol. 9, no. 166 (C-290)[1889], 11th July 1985; & JP-A-60 36 672 (HITACHI KASEI KOGYO K.K.) 25-02-1985 * Abstract * ---	1	
X	METALLOBERFLÄCHE, vol. 31, no. 11, 1977, page 521; J. ANSCHÜTZ: "Aktivierung von elektrischen Nichtleitern mit palladiumhaltigen Katalysator-Lösungen" * Page 521, left-hand column, lines 18-29 * ---	8	
A	FR-A-1 481 700 (PHOTOCIRCUITS CORP.) -----		**TECHNICAL FIELDS SEARCHED (Int. Cl.4)** C 23 C H 05 K

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	27-02-1989	DE ANNA P.L.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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