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(54) Title: PALLADIUM COLLOID SOLUTION AND ITS UTILISATION

(57) **Abrégé/Abstract:**

The invention relates to a palladium colloid solution, which, in addition to a palladium compound, a protective colloid for stabilising the colloid and a reducing agent, additionally contains noble metals from the group rhodium, iridium and platinum. The solution can be used to treat electrically non-conductive substrate surfaces, particularly in order to metalise the substrate surfaces directly and electrolytically. By means of this method, the non-conductive areas of the holes in printed circuit boards can be directly electrolytically metallised.



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ABSTRACT

The invention relates to a palladium colloid solution, which, in addition to a palladium compound, a
15 protective colloid for stabilising the colloid and a reducing agent, additionally contains noble metals from the group rhodium, iridium and platinum.

The solution can be used to treat electrically non-
20 conductive substrate surfaces, particularly in order to metalise the substrate surfaces directly and electrolytically. By means of this method, the non-conductive areas of the holes in printed circuit boards can be directly electrolytically metallised.

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PALLADIUM COLLOID SOLUTION AND ITS UTILISATION

The invention relates to a palladium colloid solution,
a utilisation of the solution for coating electrically
5 non-conductive substrate surfaces with metallic
coverings, and a printed circuit board produced by
using the solution.

Metallisation of electrically non-conductive substrate
10 surfaces is known per se. Electrolytic processes are
used for metallising printed circuit boards, plastics
parts for decorative applications and also for
functional purposes. To this end the substrate
surfaces, after an appropriate pre-treatment, are
15 activated with a solution normally containing noble
metal, and then metallised in a currentless manner. If
necessary, further metal layers may be applied to this
first metal layer by means of an electrolytic coating
process.

20

The currentless metallisation process however has
considerable disadvantages (difficulty of monitoring
the process in currentless metallising baths, use of
formaldehyde as a reducing agent, which is suspected of
25 being carcinogenic , utilisation of complex formers
which are difficult to handle in terms of waste water

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disposal). For this purpose, efforts were made in the

past to develop better processes. In some processes, the process step of currentless metallisation needed to generate the electrical surface conductivity, is no longer necessary.

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The electrical surface conductivity necessary for electrolytic metallisation is in this case for example generated by means of intrinsically conductive organic polymers, these being applied as a thin layer to the
10 surfaces. In DE 38 06 884 C1, DE 39 28 832 A1, DE 39 31 003 A1, EP 0 206 133 A1 and EP 0 413 109 A2, there are described methods which use such polymer layers and subsequent metallisation. In these methods the conductive form of the polymer is generated by an
15 acidic or oxidising subsequent treatment of the monomer adsorbed on the substrate surface, in which the monomer is polymerised. A disadvantage however is that the conductive polymer layer is applied not only to the non-conductive substrate surfaces, but is also
20 deposited on metallic surfaces such for example as the copper surfaces on printed circuit boards, so that subsequently deposited metal layers do not adhere sufficiently securely on these metal surfaces.

25 In another variant of the method, the surfaces with the conductive organic polymer layer are coated after

treatment with an activator containing noble metal (DE 42 11 152 C1).

In another alternative method, disclosed in the
5 documents DE 39 39 676 C1, DE 41 12 462 A1, DE 42 27
836 A1 and GB 22 43 833A, the conductive polymer layer
is formed only on the non-conductive surfaces, the non-
conductive monomer reacting in an acidic solution
directly with the oxidation agent adsorbed on the non-
10 conductive substrate surfaces. However, the monomer
compounds used, from which the conductive polymer film
is generated, is, as in the preceding variant of the
method, relatively volatile, so that special
precautionary measures have to be taken in order to
15 protect working personnel.

Furthermore, as disclosed in US-PS 46 31 117, US-PS 48
74 477, DE 41 41 416 A1 and WO 92/19092, thin carbon
layers may be applied to the substrate surfaces in
20 order to generate the surface conductivity. In this
case also the conductive layers form not only on the
non-conductive areas of the substrate surfaces, but on
metallic surface areas. Therefore the carbon layers
must be removed from these areas before metallisation.
25 This requires an additional process step.

In a further alternative method, the first conductive layer required for electrolytic metallisation is generated by treatment in solutions containing noble metal. Various alternative methods are described for
5 this purpose.

According to US-PS 30 99 608, the substrate surfaces are firstly treated with a palladium/tin oxide-colloid solution and then with a solution by means of which the
10 adsorbed tin compounds are again removed from the surfaces. The surfaces can then be metallised with a copper solution containing pyrophosphate.

According to DE 33 04 004 A1, the surfaces are likewise
15 treated with a palladium/tin oxide-colloid solution and then with a solution for removing the tin compounds. Thereafter electrolytic metallisation can take place.

According to DE 33 23 476 C2 the surfaces are also
20 treated with a palladium/tin oxide-colloid solution and then with a solution by means of which adsorbed tin compounds are removed from the surfaces. The surfaces are metallised with copper baths with special organic compounds which enable the preferred separation of the
25 surface areas coated with palladium colloid.

According to DE 37 41 459 C1 the substrate surfaces,
after a catalytic activation, for example with a
palladium/tin oxide-colloid solution. are treated with
a solution containing nitrogenous compounds, for
5 example polyvinylpyrrolidone, and are thereafter
electrolytically metallised.

According to US-PS 47 90 913 and US-PS 48 91 069 the
surfaces are treated with a palladium/tin oxide-colloid
10 solution which additionally contains a stabiliser and a
promoter, the hydrogen occurring during the
electrolytic deposition being taken up by the adsorbed
palladium colloid and reinforcing the electrolytic
metallisation. Salts of aluminium, titanium, zirconium
15 and hafnium and as promoter materials such as organic
hydroxy, thiourea compounds, surface-active compounds,
amino acids, polycarboxylic acids, and water-soluble
polymers are used. Thereafter electrolytic
metallisation can take place.

20

According to US-PS 50 71 517, the surfaces are treated
with a palladium/tin oxide-colloid solution and then
with a weakly alkaline solution for removing the tin
compounds. Thereafter electrolytic metallisation can
25 take place.

According to EP 0 398 019 A1 the substrate surfaces,
before treatment with a solution containing metal, such
for example as a palladium/tin oxide-colloid solution,
are treated with a solution which contains a surface-
5 active compound and which reinforces the adsorption of
metal.

The abovenamed methods have the disadvantage that a
sufficiently dense and pore-free metal coating can only
10 be deposited, and a sufficiently high degree of
adhesion of the deposited metal film on the metallic
areas, for example on the copper surfaces of a printed
circuit board, can only be achieved which can scarcely
be maintained during industrial application of the
15 methods.

According to US-PS 39 84 290, in a further alternative
method, there is deposited on the entire surface of the
substrate a more electropositive (nobler) metal than
20 the metal present on the substrate in specific areas.
During metallisation of printed circuit boards, for
example, palladium or silver is applied to the copper
surfaces and the non-conductive areas. Then the metal
coating formed is treated with an etching solution,
25 which attacks only the original metal surfaces
(copper), so that the nobler metal film formed is again
removed from the original metal surfaces. Thereafter

electrolytic metallisation can take place. According to a variant of the method the substrate surfaces are treated, in conjunction with coating with the nobler metal, with a solution containing chalcogen compounds.

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In a further variant of the method, the substrate surfaces are firstly treated with a colloid solution containing a noble metal, and then with a solution containing chalcogenide compounds. In this way the
10 adsorbed noble metal is converted into a highly conductive noble metal-chalcogenide compound which is stable against chemical influences. More typically, a palladium/tin oxide-colloid solution is used as an activator and sodium sulphide as a chalcogenide
15 compound (US-PS 48 95 739, US-PS 49 52 286, US-PS 50 07 990, US-PS 50 17 742).

According to US-PS 48 10 333, the substrate surfaces are first treated with an alkaline permanganate
20 solution. There then forms on the substrate surfaces a manganese dioxide layer to a reaction of the permanganate with the organic material of the substrate. This layer is subsequently treated with a chalcogenide solution and then with a noble metal
25 solution. Thereafter electrolytic metallisation is carried out.

The treatment with the chalcogenide solution however leads, on metallic areas of the substrate surfaces, to a formation of metallic chalcogenides, so that these metallic chalcogenide layers must be removed before the subsequent electrolytic metallisation by an etching process, from the metal surfaces, in order to obtain sufficient adhesion of the deposited metal on the metal substrate. The etching process must be carried out within narrow parameter limits, in order on the one hand not to damage the formed conductive layer, and on the other hand to remove the entire metallic chalcogenide layer from the metal surfaces.

According to US-PS 49 19 768, the surfaces to be coated are firstly treated with a solution containing tin (II) ions, then with a chalcogenide solution and thereafter with a solution of a noble metal, for example with palladium chloride. Then the pre-treated substrate surfaces can be electrolytically metallised. In this case also the metallic chalcogenide layer formed must be removed from the metallic areas of the substrate in an etching process. The same problems arise as in the first case mentioned.

In all processes in which colloidal noble metal solutions and in particular palladium/tin oxide-colloid solutions are used, there exists the problem that the

colloidal solutions are oxidation-sensitive. This is due above all to the easy oxidation of the tin (II) compounds into tin (IV) compounds. Due to oxidation of the tin compounds, the stabilising effect on the
5 colloid solution of the tin (II) ions is lost, as tin (IV) ions do not have a stabilising effect. In this way the colloid coagulates, and palladium is precipitated.

10 In addition, only a limited palladium concentration can be adsorbed on the substrate surfaces from palladium/tin oxide-colloid solutions. Therefore the capacity for metallisation of palladium layers, which are adsorbed from these colloids, is less than that of
15 colloid solutions stabilised with organic protective colloids.

Another noble metal colloid solution is described in DE 42 03 577 A1. In this case there are involved colloids
20 of the noble metal oxides which, after adsorption on the non-conductive substrate surfaces, must be reduced by a further treatment step to the corresponding metals.

25 Noble metal solutions stabilised with organic protective colloids are less sensitive to oxidation than the palladium/tin oxide-colloid solutions

mentioned above. In US-PS 40 04 051, US-PS 46 34 468, US-PS 46, 52 311 and US-PS 47 25 314, such noble metal solutions are described for processes with currentless metallisation baths, preferably with alkaline copper
5 baths.

In a further alternative method for direct electrolytic metallisation, the substrate surfaces according to DE 42 06 680 C2 are treated with noble metal colloid
10 solutions stabilised with organic protective colloids instead of with tin compounds. In addition, in order to remove the adsorbed protective colloid compounds from the substrate surfaces, a solution is used which contains sulphur compounds with sulphur in the
15 oxidation stage of +1 to +5. This method has the advantage that coating of the non-conductive surface areas with the noble metal colloid is successful without deposition of a disturbing layer on the metallic areas of the surfaces to be coated.

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However, the noble metal colloid solutions stabilised with organic protective colloids are also oxidation-sensitive, as the colloidal noble metal reacts with atmospheric oxygen, which is carried into the solution.
25 In an acidic solution, the colloidal palladium is transferred by oxidation into soluble palladium salts, so that the noble metal colloid is destroyed. The

colloid solutions react particularly in the use of continuous installations used for manufacturing printed circuit boards and in which the treatment solutions are sprayed or splashed on to the horizontally guided
5 printed circuit boards, with oxygen, as the solutions in this case are intensively moved, and they therefore come more intensively into contact with air than when a dipping process is used.

10 Therefore the problem underlying the present invention is to avoid the disadvantages of prior art and to find a palladium colloid solution with low oxidation sensitivity and a method enabling electrically non-conductive substrate surfaces to be coated with metal
15 by a direct electrolytic deposition of metal.

According to one aspect of the invention, there is provided a palladium colloid solution with low oxidation sensitivity, containing at least one tin-free
20 reducing agent and at least one organic protective colloid for stabilising the colloid solution, and in addition at least one noble metal selected from the group rhodium, iridium and platinum, or at least one compound of these noble metals or a mixture of these
25 noble metals and of these compounds.

According to one aspect of the invention, there is provided utilisation characterised by electrolytic metallisation.

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According to yet another aspect of the invention, there is provided utilisation of a palladium colloid solution characterised by individual or all new features or combinations of the disclosed features.

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According to one aspect of the invention, there is provided a method of manufacturing a palladium colloid solution with low oxidation sensitivity, containing palladium, at least one tin-free reducing agent and at least one organic protective colloid for stabilising the colloid solution, and at least one second noble metal selected from the group consisting of rhodium, iridium, platinum, compounds thereof and mixtures thereof, characterised by the following process steps:

10 producing a parent solution from a palladium compound, the organic protective colloid and the reducing agent in diluted aqueous hydrochloric acid; heating the solution to a temperature of 50°C. to 70°C., and maintaining the temperature of the solution for approximately 24 hours; and cooling the solution to a temperature of 20°C. to 40°C., and adding at least one of the second noble metal selected from the group consisting of rhodium, iridium, platinum, compounds thereof and mixtures thereof.

25

According to another aspect of the invention, there is provided a method for coating electrically non-conductive substrate surfaces with metallic layers by direct metallisation of said surfaces with a palladium

12b

colloid solution with low oxidation sensitivity
consisting of palladium, at least one tin-free reducing
agent and at least one organic protective colloid for
stabilising the colloid solution, and at least one
5 second noble metal selected from the group consisting
of rhodium, iridium, platinum, compounds thereof and
mixtures thereof, wherein the weight ratio of the
second noble metal to palladium is from about 0.01:10
to 1.0:10, comprising the process steps of treating the
10 substrate surfaces with the palladium colloid solution;
rinsing off disturbing colloidal residues of the
palladium colloid solution from the substrate surfaces;
and metallising the substrate surfaces with a
metallising solution electrolytically and without a
15 currentless metal layer being previously applied.

According to yet another aspect of the invention, there
is provided a method of manufacturing a palladium
colloid solution with low oxidation sensitivity,
20 containing palladium, at least one tin-free reducing
agent and at least one organic protective colloid for
stabilising the colloid solution, and at least one
noble metal selected from the group consisting of
rhodium, iridium, platinum, compounds thereof and
25 mixtures thereof, wherein compounds of the noble metals
are selected from the group consisting of trivalent
rhodium, iridium, and bivalent platinum compounds,
characterised by the following process steps: producing
a parent solution containing the palladium, the organic
30 protective colloid and the reducing agent in diluted

12c

aqueous hydrochloric acid; heating the parent solution to a temperature of 50°C. to 70°C., and maintaining the temperature of the solution for approximately 24 hours; and cooling the solution to a temperature of 20°C. to
5 40°C., and adding at least one of said noble metal.

According to a further aspect of the invention, there is provided a method for coating electrically non-conductive substrate surfaces with metallic layers by
10 direct metallisation of said surfaces with a palladium colloid solution with low oxidation sensitivity consisting of palladium, at least one tin-free reducing agent and at least one organic protective colloid for stabilising the colloid solution, and at least one
15 second noble metal selected from the group consisting of rhodium, iridium, platinum, compounds thereof and mixtures thereof, wherein the weight ratio of the second noble metal to palladium is from about 0.01:10 to 1.0:10, comprising the process steps of (a) treating
20 said substrate surfaces by spraying or splashing onto said substrate surfaces, the palladium colloid solution; (b) removing colloidal residues of the palladium colloid solution from the substrate surfaces after treatment in step (a); and (c) metallising the
25 substrate surfaces with a metallising solution electrolytically and without a currentless metal layer being previously applied.

12d

According to yet another aspect of the invention, there is provided a method of coating electrically non-conductive substrate surfaces with metallic coatings, having the following method steps: treating the

5 substrate surfaces with a palladium colloid solution, having a low sensitivity to oxidation and containing at least one tin-free reducing agent and at least one organic protective colloid for stabilising the colloid solution and additionally at least one noble metal,

10 selected from the group including rhodium, iridium and platinum, or at least one compound of these noble metals, or a mixture of these noble metals and these compounds; rinsing, if necessary, undesirable residues of the palladium colloid solution from the substrate

15 surfaces; and metallising the substrate surfaces with a metallising solution.

According to a further aspect of the invention, there is provided a method of producing a palladium colloid

20 solution having a low sensitivity to oxidation and containing at least one tin-free reducing agent and at least one organic protective colloid for stabilising the colloid solution and additionally at least one noble metal, selected from the group including rhodium,

25 iridium and platinum, or at least one compound of these noble metals, or a mixture of these noble metals and these compounds, characterised by the following method steps: producing a prefabricated stock solution from a

12e

palladium compound, from at least one organic protective colloid and from at least one reducing agent in dilute aqueous hydrochloric acid; heating the solution to between 50°C and 70°C, possibly

5 additionally adding reducing agent to the solution and maintaining the temperature of the solution for substantially 24 hours; and after cooling the solution to between 20°C and 40°C, adding at least one of the additional noble metal compounds.

10

According to another aspect, there is provided a method of directly depositing a metal to electrically non-conductive substrate surfaces comprising the steps of:

(a) treating the substrate surfaces with a palladium
15 colloid solution with low oxidation sensitivity, containing at least one tin-free reducing agent and at least one organic protective colloid for stabilising the colloid solution, and in addition at least one noble metal selected from the group rhodium, iridium
20 and platinum, or at least one compound of these noble metals or a mixture of these noble metals and of these compounds and (b) electrolytically metallising the substrate surfaces with a metal plating solution.

25 According to yet another aspect, there is provided the method wherein palladium colloid solution is characterised by protective colloids selected from the group of compounds: polyvinylpyrrolidon, polyvinylpyridine, polyvinylmethyleketone, polyvinyl
30 alcohol, polyvinyl acetate, polyacrylic acid and its

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derivatives, polyethylene glycol, polyimine, alkyl and hydroxyalkylcellulose, and its copolymers.

According to yet another aspect, there is provided the
5 method further comprising the step of rinsing off the solution containing at least one compound selected from the group consisting of quaternary and polyquaternary compounds after the solution is brought into a pH value of 1 to 3.

10

According to a further aspect, there is provided a method characterised in that protective colloids are used, selected from the group comprising
polyvinylpyrrolidone, polyvinylpyridine,
15 polyvinylmethylketone, polyvinylalcohol, polyvinylacetate, polyacrylic acid and its derivatives, polyethylene glycol, polyimine, and alkyl and hydroxyalkyl cellulose and its copolymers.

20 The palladium colloid solution according to the invention is characterised by additional contents of noble metals, selected from the group rhodium, iridium and platinum or compounds of these metals or their mixtures. By means of these additionally contained
25 noble metals, the problem of oxidation sensitivity of such noble metal colloid solutions is avoided. These

solutions may without difficulty be brought intensely into contact with atmospheric oxygen even over a lengthy period without their effectiveness being thereby impaired. For example in continuously-
5 operating plants used in the manufacture of printed circuit boards, these solutions come intensively into contact with oxygen, as the solutions are applied to the material to be coated through spray or splash nozzles, the oxygen being taken up by the solution in
10 the spray or splash jet. In the same installations, these solutions are also returned from the printed circuit boards again into the liquid reservoir which is usually disposed underneath, the liquid, depending on the construction of the treatment device, passing back
15 for example in free fall or over guide planes into the liquid reservoir. Here also there is an intimate contact of the solution with atmospheric oxygen.

As the solutions are less oxidation-sensitive than the
20 known colloid solutions, far less reducing agent is necessary in the use and supplementation of the colloid solutions containing additional noble metal, without the electrochemical reduction/oxidation potential in the solution, necessary for the function of the colloid
25 solution, being displaced from a negative operating value to a positive value. From this there arises the

further advantage that during use of the solutions, fewer chemicals are consumed.

Moreover, the proportion of copper ions in these
5 solutions, which arises through slow dissolution of copper substrates in contact with the solution, for example of printed circuit boards, is less critical than in the case of known palladium colloid solutions. In these colloid solutions, the consumption of
10 reduction agent increases in the solutions, in order to obtain their efficiency, as soon as a critical upper limit of the copper concentration is exceeded. Therefore the consumption of reducing agents in over solutions, in which a large printed circuit board
15 surface has been processed, is considerable. As soon as the critical upper limit of the copper concentration in these solutions has been reached, a negative electrochemical reduction/oxidation potential can no longer be maintained in the colloid solution, even by
20 further addition of reducing agents, so that the colloid solution becomes ineffective for substrate treatment.

The critical upper limit of copper concentration
25 therefore lies very much higher for the solutions according to the invention than for colloid solutions without additional noble metals. A large printed

circuit board surface can be treated in the colloid solution before this concentration limit is reached. Therefore fewer of the chemicals, which are expensive particularly because of the noble metal content in the
5 colloid solution, is necessary for the reconstitution of such baths.

In colloid solutions containing hypophosphite as a reducing agent, phosphate, in addition to
10 hypophosphite, is also active, which forms in these colloid solutions from hypophosphite as a reducing agent, when the additional noble metals are added to the palladium colloid solution. In this way the degree of effectiveness of the added hypophosphite as a
15 reducing agent is appreciably increased.

The advantages obtained by the addition of the additional noble metals to the palladium colloid solution are extraordinarily surprising as it is not
20 possible successfully to metallise electrically non-conductive substrate surfaces in a directly electrolytic manner, as, for the pre-treatment of these substrate surfaces, colloid solutions produced only with the noble metals rhodium, iridium or platinum are
25 used. In addition, colloid solutions of the additional noble metals cannot be produced without palladium under

the conditions preferred for formation of palladium colloid.

In order to produce the novel colloid solution, firstly
5 a palladium colloid parent solution is prepared
according to known methods. For this purpose for
example a solution of a palladium compound is combined
with an organic protective colloid and then mixed with
a solution of a reducing agent. In this case the
10 organic protective colloid serves to stabilise the
palladium colloid solution against undesirable
palladium flocculation. Aqueous solutions are
preferably used, which can in addition contain organic
solvents, for example in order to enable the solubility
15 of specific compounds in the colloid solution or the
initial materials required for manufacture of the
colloid solution to be achieved in their initial
solutions. Such colloid solutions are described also
in the publications US-PS 40 04 051, US-PS 46 34 468,
20 US-PS 46 52 311 and US-PS 47 25 314. Therefore the
procedure for manufacturing the palladium colloid
parent solution can be seen in these documents.

There may be used as palladium compounds all materials
25 which are reducible to metallic palladium by reducing
agents, which are easy to handle and which dissolve
sufficiently well in the initial solution or by

dissolution in the initial solution into soluble compounds. Suitable materials are inorganic salts such for example as chlorides, sulphates, nitrates, phosphates, pyrophosphates, cyanides and fluoroborates, organic salts, for example of carboxylic acids, such as
5 formic, ethanoic, succinic, malic, lactic, citric, ascorbic, oxalic, benzoic and vanillic acids, and complex compounds such for example as ammin, halogen complexes and complexes with organic complex formers.
10 Palladium (II) chloride and palladium (II) sulphate in an aqueous hydrochloric solution have proved particularly suitable.

Palladium compounds can be dissolved in an aqueous
15 solution, if necessary with proportions of organic solvents. Water is preferred for economic reasons as a solvent in the colloid solution.

The palladium concentration in the colloid solution
20 lies in the range from 50 mg/l to 1000 mg/l solution, preferably from 1000 mg/l to 5000 mg/l solution. It is advantageous to set as small a palladium concentration as possible, approximately from 250 mg/l solution, in order to minimise the loss of expensive palladium by
25 carry-over of the solution when dipping and retrieving the substrates to be coated. On the other hand, the concentration selected must be of such a height that

sufficient absorption of the palladium is obtained on the substrate surfaces in order to enable the surfaces to be metallised subsequently without difficulty.

5 In order to stabilise the colloid solution to be manufactured, organic compounds are used as protective colloids. For this purpose either ionic or non-ionic, preferably water-soluble polymers are used. On the one hand, natural polymers such for example as proteins,
10 peptides, polysaccharides, gelatines, agar-agar, gum arabic, tannin, and on the other hand synthetic polymers such for example as alkyl or hydroxyalkylcellulose, polyvinyl pyridine, pyrroladon, methylketone, alcohol, acetate, polyamine, polyacrylic
15 acid, polyacrylamide, polyacrylates and their other derivates, polyethylene glycol, its derivates and its copolymers, and the mixtures of these compounds with one another are suitable. Polyvinylpyrrolidon and in particular poly(4-vinylpyrrolidon) is particularly
20 suitable. The molecular weight of these materials should be within a range of 1.000 g/mol to 10.000.000 g/mol, preferably however within the range of 2.000 g/mol to 2.000.000 g/mol and particularly preferably within a range of 3.000 g/mol to 1000.000 g/mol. The
25 weight ratio of these materials to palladium in the colloid solution should be set within a range of 1 : 1

to 100 : 1 and preferably within a range of 3 : 1 to 10 : 1.

There are used as reducing agents compounds which are
5 capable of reducing the palladium compounds to metallic
palladium. The function of the reduction agents
however consists in maintaining the electrochemical
reduction/oxidation potential in the colloid solution
within a specific negative range, while preventing
10 undesired side reactions, for example oxidation of the
colloid, by means of the reducing agent. The
concentration of the reducing agent is therefore so
selected that a sufficiently negative
reduction/oxidation potential value in the solution is
15 obtained.

Among others, suitable reducing agents are compounds
from the compound classes of the low alkylaminboric
hydrides (mono-, di-, trialkylaminboric hydrides), such
20 for example as dimethylaminboric hydride, alkali metal
boric hydrides such as lithium, sodium, potassium boric
hydrides and in particular sodium boric hydride,
ascorbic acid, isoascorbic acid, metal hypophosphite,
preferably alkali metal hypophosphite, such for example
25 as sodium hypophosphite, hypophosphorous acid, metal
phosphite, preferably alkali metal phosphite, such for
example as sodium phosphite, phosphorous acid, formic

acid, formaldehyde, hydrazine and its derivatives, such
for example as hydrazine hydrate and its salts
hydrazine sulphate, formiate, dichloride, mononitrate,
monochloride, oxalate, hypophosphite, phosphite,
5 orthophosphate, and tartrate and its derivatives 1, 1-
dimethylhydrazine, 1, 2- dimethylhydrazine, methyl
hydrazine, ethylhydrazine, phenylhydrazine, iso-
propylhydrazine and its hydrochlorides and
hydrazoethanic acid, further hydroxylamine and its
10 derivatives such for example as alpha- and beta-
hydroxylamines. Among the latter there belong the
compounds of the alpha and beta alkylhydroxylamines
with 1 to 5 carbon atoms in the either linear or
branched alkyl group, such for example as alpha- and
15 beta- methylhydroxylamine, alpha, and beta,
ethylhydroxylamine, and further alpha- and beta-
arylhydroxylamine, aryl being phenyl, benzyl or
naphthyl, and substituted with one or a plurality of
low alkyl groups, such for example as alpha- and beta-
20 phenylhydroxylamine.

The colloid solution can further contain halogenide
ions, for example chloride ions, in a concentration of
0.1 to 50 g/l solution, their proportion arising via
25 the stoichiometric ratio to palladium in the palladium
compound. In this way the stability of the colloid
solution is increased and the electrolytic metal

deposition carried out after treatment with the colloid solution is simplified. It has become apparent that an increased proportion of halogenide ions in the colloid solution leads to an accelerated metal coating. If, based on the stoichiometric ratio in the palladium compound, halogenised ions are contained in the palladium solution required for producing the colloid solution, these also stabilise the solution against undesired precipitation of palladium compounds.

The pH value of the colloid solution likewise has an influence on the subsequent electrolytic metallisation. The solution should preferably be set in the acidic range, preferably in the pH range from 1 to 3 and particularly in the pH range from 1.2 to 2.0. As soon as the colloid solution has been set at acidic, the palladium colloid becomes more effectively adsorbed on the substrate surfaces. Moreover, the colloid stability against flocculation of palladium is increased.

In order to produce the palladium colloid parent solution, the initial solution containing palladium is mixed with the preferably aqueous solution of the reducing agent. After mixing, the solution is heated to an increased temperature, for example to a temperature of 50 to 70°C, and if necessary further

reducing agent is added. During mixing, a presented solution is intensively agitated/stirred, in order to favour the formation of smaller colloid particles. It is assumed that colloid particles will form in a range of magnitude from 50 Angstrom to approximately 2000 Angstrom. The precise size is not known. Presumably particles which attain a size of approximately 10 μm , no longer adhere securely to the substrate surfaces. Therefore a colloid with particle sizes in this order of magnitude may no longer be effective. On the other hand, smaller particles are particularly oxidation-sensitive, as their specific surface is greater than that of larger particles.

The particle size in the colloid solutions depends on various external influences and is controlled by the competition between nuclear formation and nuclear growth speed. It is generally known that the particles are smaller the more rapidly the solutions are mixed, and the higher the temperature during mixture of the solutions and the higher the concentration of reducing agents and palladium in the solutions. Further, no colloid particles arise particularly when strong reducing agents are used.

25

After mixture of the individual ingredients of the colloid solution, the increased temperature is

maintained for several hours longer, for example for a further 24 hours. Thereafter the additional noble metals are added, preferably after the solution has been cooled to a temperature of 20 to 54°C. Rhodium, 5 iridium and platinum are used as additional noble metals. Preferably the trivalent rhodium iridium and the bivalent platinum compounds, basically however also other compounds of these metals, may be used. The noble metals may be added to the solution for example 10 as salts. More typically there are used for this purpose halogenide salts, sulphates, hydroxides, cyanides, phosphates, pyrophosphates, phosphites, hypophosphites, fluoroborates, carboxylic acid salts, such for example as the salts of formic, ethanoic, 15 succinic, malic, lactic, citric, ascorbic, oxalyic, benzoic or vanillic acid, and complex compounds such for example as ammin, halogen complexes and complexes with organic complex formers.

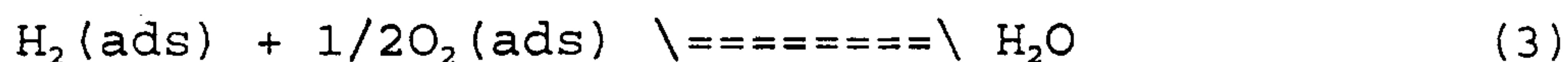
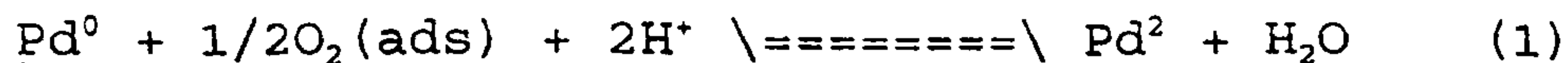
20 The concentration of the additional noble metals in the colloid solution is set in dependence on the palladium content. Preferred weight ratios of additional noble metal to palladium are 0.01 : 10 to 1.0 : 10.

25 Specific surface structures of the additional noble metal on the colloid particles are possibly responsible for achieving the resistance of the colloid solution to

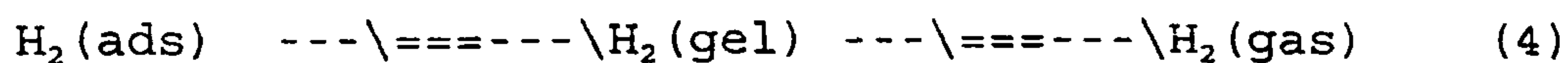
oxidation. In order to understand the effect of these structures, the possible reactions are represented in a hypocolloid solution containing hypophosphite as a reducing agent. In this respect reference is made to
5 the reaction diagram given below (the following meanings are indicated: (ads): adsorbed compound (gel): compound dissolved in solution, (gas): compound in the gas phase):

10 Reaction (1) describes the de-activating effect of the dissolved oxygen for the colloid solution, in which palladium is oxidised into palladium (II) ions. According to reaction (5) hypophosphite is oxidised catalytically into phosphite, forming hydrogen.

15 Reactions (2) and (3) illustrate possible consumption reactions for dissolved oxygen. It should be noted in this respect that according to reaction (4) hydrogen probably desorbs very quickly from the palladium colloid particle surface, so that the surface-catalysed
20 oxidation of the hydrogen by means of oxygen to water according to reaction (3) is only possible to a secondary degree. On the other hand, according to reaction (2) phosphite is only very slowly oxidised to orthophosphate. Therefore, in the stationary
25 condition, a high content of dissolved hydrogen occurs. This reinforces reaction (1).

Reaction diagram:

rapid rapid



10 Copper ions in the colloid solution, which for example
can increase in the presence of hydrogen by dissolution
of copper from the surfaces of the printed circuit
boards in the solution, clearly reinforce reaction (1)
and inhibit reactions (2) and (3).

15

One effect of the surface structures of the additional
metal on the colloid particles could for example
consist in catalysing the oxidation of the phosphite to
orthophosphate with oxygen according to reaction (2),
20 in order to accelerate the consumption of dissolved
oxygen. In this way the stationary concentration of
dissolved oxygen would be clearly reduced. In fact a
negative electrochemical reduction/oxidation potential
can be maintained by the addition of phosphite to the
25 colloid solution even during the action of atmospheric
oxygen. This effect on the other hand is not observed

without additional noble metals in the colloid solution.

After addition of the additional noble metals, the
5 colloid solution may be used in a metallisation process.

It has proved advantageous to monitor the colloid solution by measuring the electrochemical
10 reduction/oxidation potential. This is particularly necessary when using reducing agents which decompose catalytically in the colloid solution, such for example as with borohydride and hypophosphite compounds, in order to achieve the required process reliability. In
15 order to measure the electrochemical reduction/oxidation potential, the voltage between a metal electrode submerged in the colloid solution, for example a gold or platinum electrode, and a second electrode which adopts a predetermined potential in the
20 solution, is measured. Any electrochemical standard electrode such for example as a silver/ silver chloride or calomel electrode may be used as a second electrode. The potential which occurs after production of the colloid solution at the measurement electrode, measured
25 against a silver/silver chloride standard electrode, should lie in the range between approximately -170 mV to approximately -300mV. Under this measurement, the

colloid solution can be monitored. If necessary, the reducing agent can be automatically supplemented, as soon as the potential becomes more positive for example than -170 mV.

5

In order to provide metal coating on substrate surfaces, the latter are pre-treated according to known methods. For example, resin impurities of copper surfaces on printed circuit boards are removed by resin etching methods (for example by a permanganate process with the process steps pre-swelling/etching in alkaline permanganate solution/reducing the formed manganese dioxide (and oxide layers from the copper surfaces by copper-etching (for example with hydrogenperoxide/ sulphuric acid solutions). Further, a solution containing a wetting agent may be used to wet the resin surfaces. Suitable for this among other things are non-ionic wetting agents such for example as ethoxylised alkyphenol ether and polyethylene glycol (Handbook of Printed Circuit Technology, 1993, Volume 3, Pages 61 to 69).

After this pre-treatment, in which the surfaces achieve hydrophilic properties, the latter are conditioned in order to reinforce the subsequent adsorption of the palladium colloid. Complex forming and/or cationic surface active compounds are used as conditioning

agents. Typical cationic surface active compounds are quoted in US-PS 43 59 537. These involve emulsion copolymers which are converted by generally known methods into positively-charged ion exchanger resins by
5 chemical reaction.

There may be used as complex-forming compounds which have a conditioning action, those compounds which for example are quoted in Kirk-Other, Encyclopaedia of
10 Chemical Technology, Third Edition, Volume 5, Pages 339 to 368.

Compounds containing nitrogen and with a chemical affinity to noble metal are preferably used as
15 conditioning compounds. These involve in particular cationic wetting agents, such for example as trimethyl-alkyl-ammonium halogenides with a short chain length of the alkyl residue, polyelectrolytes, for example quaternary compounds (for example the polyquaternary
20 compounds named in DE 37 43 740 A1, DE 37 43 741 A1, DE 37 43 742 A1, DE 37 43 743 A1, DE 37 43 744 A1, and DE 35 30 617 A1), and in particular the polyquaternary polyvinylimidazoles, and complex formers containing nitrogen such for example as the lower alkanolamines,
25 the alkyl group containing 1 to 5 carbon atoms and being linear or branched. Further low alkanolamines, which may be used as conditioning agents, include

diethanolamine, triethanolamine, monoisopropanolamine,
disopropanolamine, trisopropanolamine, mono-sec-
butanolamine, di-sec-butanolamine, 2-amino-2-methyl-1-
propandiol, 2-amino-2-ethyl-1,3-propandiol, 2-
5 dimethylamino-2-methyl-1-propanol, tris
(hydroxylmethyl)- amino methane, and various mixtures
of the alkanolamines.

During substrate treatment, a temperature of 35°C to
10 60°C is preferably set in the conditioning solution.
However, a higher temperature, up to the boiling point
of the solution, or a lower temperature, may be
selected. The treatment time can be extraordinarily
short; basically, a few seconds are sufficient for
15 conditioning the substrate surfaces. An upper
threshold arises only from economic considerations.
Treatment times of about 5 minutes are advantageous.

After conditioning and the subsequent rinsing of the
20 substrate surfaces, the latter are preferably treated
in a solution which substantially contains reducing
agents. In this way the loss of reducing agent in the
colloid solution by carry-over upon dipping and
removing the substrate is minimised. The temperature
25 of this solution can likewise be at room temperature.
However, a higher temperature up to the boiling point
of the solution can be selected.

Thereafter the substrate is brought into contact directly with the colloid solution without further rinsing processes. In this case the palladium colloid particles are adsorbed on to the conditioned
5 electrically non-conductive substrate surfaces and prepare these for metallisation. The colloid solution is heated to a temperature increased in comparison to room temperature, for example 40°C; the treatment time should not be considerably less than 20 seconds. An
10 advantageous treatment time lies between 2 and 7 minutes.

If necessary, the substrate surfaces are then again rinsed and thereafter brought into contact with a
15 treatment solution, in which there is a chalcogen compound with chalcogen in the oxidation stages +1 to +5. Preferably suitable are sulphur compounds and in particular the compounds from the substance classes of the sulphinic acids, particularly with 1 to 5 carbon
20 atoms with a linear or branched alkyl chain, sulphites, thiosulphates, sulphides, sulphones, dithionite, dithionate and other compounds. In this respect, particularly suitable materials have proved to be the compounds hydroxymethansulphinic acid, alkalisulphite
25 and alkalithiosulphate. Mixtures of these compounds may also be advantageously used. Basically, the corresponding selenium and tellurium compounds are

suitable. A particularly suitable solution for after treatment of substrate surfaces contains basically in addition to sodium thiosulphate, also sodium citrate.

5 A temperature of this solution increased above room temperature (25°C) is not necessary. The treatment time can be selected within wide ranges, without any influence on the result of treatment. Therefore times of at least a few seconds are sufficient. A favourable
10 treatment time lies between 1 and 2 minutes.

Probably, the organic protective colloid layer, which has been adsorbed by the treatment with the colloid solution on the substrate surfaces, is removed
15 therefrom by treatment with this solution, so that the palladium colloid particles are released and thus can develop their action for the subsequent metallisation.

After this treatment and the subsequent rinsing of the
20 substrate surfaces, the latter can be metallised. The metal layer may be deposited electrolytically, without a currentless metal layer being previously applied. Basically all electrically depositable metals, such for example as the metals copper, nickel, silver, gold,
25 palladium, cobalt, tin, lead, zinc, chromium, cadmium, iron and their alloys and their mixtures with one another and with other elements, for example phosphorus

and boron, can be considered as metals. For deposition of copper, for example a sulphuric acid copper sulphate solution (for example electrolytic copper bath CUPRACID® of the firm Atotech Deutschland GmbH, Berlin, 5 Germany) is used. Naturally, further metals may also be deposited on the first metal layer.

Furthermore, the colloid solution containing the additional noble metals may also be used as an 10 activator for the previously known currentless metallisation. Such methods are described for example in the US Patent 46 34 468. An additional variant of the method, which is not disclosed in the above document, consists in treating the substrate according 15 to the above statements after treatment with the colloid solution with the chalcogen solution described above.

For metallisation, the substrate surfaces may be 20 treated in a dipping process. The advantages of the colloid solution containing the additional noble metals become apparent in particular however when using spray and splash jets, as the oxidation-sensitivity of the known palladium colloid solutions has a particularly 25 disadvantageous effect above all in these treatment methods.

By means of the advantageous effect of the additional noble metals in the colloid solution, the new palladium colloid solutions are clearly more stable against oxidation than the known colloid solutions.

5

In order to metallise drilled, stamped holes or holes produced in any other way in printed circuit boards, these are treated both in the conventional dipping process and also in continuous processes with the
10 colloid solutions according to the invention. In continuous-flow installations, the printed circuit boards are moved horizontally in the treatment plant, and brought into contact with the treatment solutions by means of splash or spray nozzles. therefore the
15 novel colloid solution is particularly suitable for this application. With treatment of the printed circuit boards in continuous-flow installations without addition of the additional noble metals to the palladium colloid solution is industrially and
20 economically impossible.

The palladium colloid solution containing the additional noble metals can be used to metalise various substrates. In addition to metallising holes in
25 printed circuit boards, other substrates for electronics, such for example as hybrid carriers or integrated circuits and multi-chip modules, as well as

plastics for the range of decorative applications, such
for example as in automobile trimming, in sanitary
technology, for furniture fittings, costume jewellery,
and in the functional regions such for example as for
5 casings shielded against electromagnetic radiation and
reflectors, can be coated with this solution for
subsequent metallisation.

The following examples are intended to explain the
10 invention in more detail:

EXAMPLE 1:

A palladium colloid solution was produced by mixing two
15 solutions:

Solution 1: dissolution of 4g palladium (II) chloride
in 27 ml aqueous concentrated hydrochloric acid (37% by
weight),
20

Supplementation of the solution with de-ionised water
to 1 litre solution,

Dissolution of 20 g poly (4-vinylpyrrolidon) in the
25 solution.

Solution 2: provision of 1 litre de-ionised water

Dissolution of 50 g sodium hypophosphite, $\text{NaH}_2\text{PO}_2\text{H}_2\text{O}$.

Firstly 800 ml de-ionised water was placed in a container, then 100 ml of solution 1 was added to the water and thereafter 30 ml of solution 2 was added. Then the solution was heated to 70°C . During heating, a further 70 ml of solution 2 was added slowly and with continuous stirring. Then the solution became slowly dark in colour.

10

Solution 3: dissolution of 1.5 g rhodium (III) chloride or 1.0 g rhodium (III) oxide hydrate in 25 ml aqueous concentrated hydrochloric acid (37% by weight),

15 supplementation of the solution with de-ionised water to a final volume of 1 litre.

Thereafter the solution was left for a further 24 hours at the temperature of 70°C . After cooling the solution to approximately 40°C , 10 ml of solution 3 and then a further 2 ml of solution 2 were added. Thereafter the solution was ready for use.

EXAMPLE 2:

25

Solution 4: placing of 1 litre de-ionised water, addition of 50 ml hypophosphorous acid (50% by weight).

Solution 5: dissolution of 1.5 g platinum (II) chloride in 25 ml aqueous concentrated hydrochloric acid (37% by weight), filling of the solution with de-ionised water to a final volume of 1 litre.

5

A colloidal solution as in example 1 was produced, yet instead of solution 2 solution 4, and instead of solution 3, solution 5 were used.

10 EXAMPLE 3:

Solution 6: dissolution of 2.5 g iridium (III) chloride in 25 ml aqueous concentrated hydrochloric
15 acid (37% by weight),

filling of the solution with de-ionised water to a final volume of 1 litre.

20 A colloidal solution as in example 1 was produced, yet instead of solution 3, solution 6 was used.

EXAMPLE 4:

25 Solution 7: dissolution of 0.05 g rhodium (III) oxide hydrate and 0.08 g platinum (II) chloride in 25 ml aqueous concentrated hydrochloric acid (37% by weight),

filling of the solution with de-ionised water to a final volume of 1 litre.

A colloid solution as in example 1 was produced, yet
5 instead of solution 3, solution 7 was used.

The colloid solution obtained has a slightly higher oxidation sensitivity than the solutions obtained in examples 1 to 3.

10

EXAMPLE 5:

Solution 8: dissolution of 0.08 g rhodium (III) chloride and 0.13 g iridium (III) chloride in 25 ml
15 aqueous concentrated hydrochloric acid (37% by weight),

filling of the solution with de-ionised water to a final volume of litre.

20 A colloidal solution as in example 1 was produced, yet instead of solution 3, solution 8 was used.

The colloid solution obtained has a slightly higher oxidation sensitivity than the solutions obtained in
25 examples 1 to 3.

EXAMPLE 6:

A perforated printed circuit board was metallised in a dipping process according to the following procedure:

		Treatment time	Temp.
5	1. Pre-treatment with a solution containing a wetting agent Rinsing	2-5 min. 1-2 min.	50°C
10	2. Etching of copper surfaces in a hydrogen peroxide/sulphuric acid solution Rinsing	2 min. 2 min.	25°C
15	3. Conditioning with quaternary polyelectrolyte (e.g. polyvinylimidazol (pH value:8-9) Rinsing	5 min.	35-60°C
20	4. Treatment with a hydrochloric sodium hypophosphite solution	1 min.	25°C
25	5. Treatment with the solution in Example 1 Rinsing	4-7 min.	30-50°C
	6. Treatment in an aqueous sodium thiosulphate/sodium citrate solution	1-2 min.	25°C
30	7. Cleaning of copper surfaces with diluted sulphuric acid Rinsing	1 min.	
35	8. Electrolytic coppering e.g. with sulphuric copper sulphate electrolyte)		

40 A dense and pore-free copper layer was obtained on the bore hole walls, which was enclosed after a few minutes of electrolysis time.

EXAMPLES 7 AND 8:

A perforated printed circuit board was metallised in the dipping process according to example 6. In process stage 5, instead of the palladium colloid solution from example 1, the palladium colloid solutions from examples 2 and 3 were used.

A dense and pore-free copper layer was obtained on the bore hole walls, which was closed after a few minutes of electrolysis time.

10

EXAMPLES 9 TO 11:

100 ml of the palladium colloid solutions, produced in accordance with examples 1 to 3, were respectively stirred in a beaker at 600 rpm on a magnetic stirrer and in this way exposed to a reinforced action of air. The electrochemical reduction/oxidation potential of the solutions was measured with a platinum electrode with reference to a silver/silver chloride reference electrode. The potential at the platinum electrode after a few minutes came to values between -170 and -250 mV and remained constant within this range.

20

EXAMPLE 12:

25

Example 6 was repeated in a continuous-flow installation, in which the printed circuit board is

guided continuously in a horizontal position between rollers, and is transported from one treatment station to the next. The treatment solutions were sprayed on to the printed circuit board and into the bore holes through nozzles. The treatment times were shorter than in example 6; they came to only 20% of the times there given. Although the palladium colloid solution in the continuous-flow installation came more intensively into contact with air due to the intensive movement of the solution, it remained stable over a long period. Even after a continuous execution of the method over a period of several days the electric chemical reduction/oxidation potential measured in the palladium colloid solution at approximately - 250 mV, measured against a silver/silver chloride standard electrode, was kept approximately constant. After passing through all the stations, a dense and pore-free copper layer was obtained on the bore hole walls, which was closed after a few minutes of treatment time in the coppering solution. This result could be obtained even when the test was carried on for several days operation.

EXAMPLE 13 (COMPARATIVE EXAMPLE):

A previously known palladium colloid, not additionally stabilised with noble metals, was produced from 870 ml de-ionised water, 100 ml of the solution 1 obtained

according to example 1, and 30 ml of the solution 2
obtained according to example 2. This colloid was
exposed, as in examples 9 to 11, to a reinforced action
of air, and the electrochemical reduction/oxidation
5 potential in the solution was measured. Within a few
minutes after the start of the action of air, the
potential changed from originally approximately -300 mV
to positive values. After a short action time values
of approximately +400 mV were measured at the platinum
10 electrode.

15

20

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Claims:

1. A method of directly depositing a metal to electrically non-conductive substrate surfaces comprising the steps of:

- (a) treating the substrate surfaces with a palladium colloid solution with low oxidation sensitivity, containing at least one tin-free reducing agent and at least one organic protective colloid for stabilising the colloid solution, and in addition at least one noble metal selected from the group rhodium, iridium and platinum, or at least one compound of these noble metals or a mixture of these noble metals and of these compounds; and
- (b) electrolytically metallising the substrate surfaces with a metal plating solution.

2. The method according to claim 1, wherein the palladium colloid solution is characterised by compounds of the noble metals selected from the group of trivalent rhodium, iridium and bivalent platinum compounds.

3. The method according to claim 1 or 2, wherein the palladium colloid solution is characterised by a palladium concentration of 50 mg/l to 1000 mg/l solution.

4. The method according to any one of claims 1 to 3, wherein the palladium colloid solution is characterised by a weight ratio of the additional noble metals to palladium of 0.01:10 to 1.0:10.

5. The method according to any one of claims 1 to 4, wherein the palladium colloid solution is characterised by reducing agents selected from the group of compounds:

metal hypophosphite, metal phosphite and their acids,
alkali-metal boric hydride,
monoalkylamine boron hydride,
dialkylamine boric hydride,
trialkylamine boric hydride,
ascorbic acid, iso-ascorbic acid,
hydrazine and its derivatives,
hydroxylamine and its derivatives, and
formaldehyde.

6. The method according to any one of claims 1 to 5, wherein the palladium colloid solution comprises organic compounds as protective colloids in a weight ratio of the protective colloid to palladium of 1:1 to 100:1.

7. The method according to any one of claims 1 to 6, wherein the palladium colloid solution is characterised by protective colloids selected from the group of compounds:

polyvinylpyrrolidon,
polyvinylpyridine,
polyvinylmethylketone,
polyvinyl alcohol,
polyvinyl acetate,
polyacrylic acid and its derivatives,
polyethylene glycol,
polyimine,
alkyl and hydroxyalkylcellulose,
and its copolymers.

8. The method according to any one of claims 1 to 7, wherein the palladium colloid solution is characterised by a pH value of 1 to 3.

9. The method according to any one of claims 1 to 8, wherein the palladium colloid solution is characterised by a negative electrochemical reduction/oxidation potential in the solution measured against a silver/silver chloride standard electrode.

10. A method of manufacturing a solution according to any one of claims 1 to 9, characterised by the following process steps:

a. production of a previously-prepared parent solution from a palladium compound, an organic protective colloid and a reducing agent in diluted aqueous hydrochloric acid;

b. heating the solution to 50°C to 70°C; and

c. after cooling the solution to 20°C to 40°C, adding at least one of the additional noble metal compounds.

11. The method of claim 10, wherein step b. further comprises adding at least one reducing agent to the solution, the temperature of the solution being maintained for approximately 24 hours.

12. Utilisation of the palladium colloid solution according to one of claims 1 to 11 for coating electrically non-conductive substrate surfaces with metallic layers according to a method with the process steps:

a. treating the substrate surfaces with the palladium colloid solution; and

b. electrolytically metallising the substrate surfaces with an electrolytic metallising solution.

13. Utilisation according to claim 12 further comprising the process step of rinsing off disturbing colloidal residues of the palladium colloid solution from the substrate surfaces, after step a. and before step b.

14. Utilisation according to claim 12, characterised by treatment of the substrate surfaces between process steps a. and b. with a solution containing a sulphur compound with sulphur in the oxidation stage of at least +1 to at most +5.

15. Utilisation according to any one of claims 12 to 14, characterised in that the substrate surfaces, before treatment according to process step a., are brought into contact with a solution containing at least one quaternary compound.

16. Utilisation according to claim 15, wherein the substrate surfaces are rinsed off with the solution containing at least one quaternary compound.

17. Utilisation according to any one of claims 12 to 15, characterised in that the substrate surfaces are metallised with a copper solution.

18. Utilisation according to any one of claims 12 to 17 for metallising holes in printed circuit boards.

19. Printed circuit board manufactured by utilising the palladium colloid solution according to one of claims 17 to 18.

20. A method of manufacturing a palladium colloid solution with low oxidation sensitivity, containing palladium, at least one tin-free reducing agent and at least one organic protective colloid for stabilising the colloid solution, and at least one second noble metal selected from the group consisting of rhodium, iridium, platinum, compounds thereof and mixtures thereof, characterised by the following process steps:

a. producing a parent solution from a palladium compound, the organic protective colloid and the reducing agent in diluted aqueous hydrochloric acid,

b. heating the solution to a temperature of 50°C. to 70°C., and maintaining the temperature of the solution for approximately 24 hours, and

c. cooling the solution to a temperature of 20°C. to 40°C., and adding at least one of the second noble metal selected from the group consisting of rhodium, iridium, platinum, compounds thereof and mixtures thereof.

21. The method of claim 20, wherein step b. further comprises a further addition of reducing agents to the solution.

22. A method for coating electrically non-conductive substrate surfaces with metallic layers by direct metallisation of said surfaces with a palladium colloid

solution with low oxidation sensitivity consisting of palladium, at least one tin-free reducing agent and at least one organic protective colloid for stabilising the colloid solution, and at least one second noble metal selected from the group consisting of rhodium, iridium, platinum, compounds thereof and mixtures thereof, wherein the weight ratio of the second noble metal to palladium is from 0.01:10 to 1.0:10, comprising the process steps of:

a. treating the substrate surfaces with the palladium colloid solution,

b. rinsing off disturbing colloidal residues of the palladium colloid solution from the substrate surfaces, and

c. metallising the substrate surfaces with a metallising solution electrolytically and without a currentless metal layer being previously applied.

23. The method according to claim 22, further comprising the step of treating the substrate surfaces between process steps b. and c. with a solution containing a sulphur compound with sulphur in the oxidation stage of at least +1 to at most +5.

24. The method of claim 23, wherein said solution containing a sulphur compound with sulphur in the oxidation stage of at least +1 to at most +5 is an aqueous solution of sodium thiosulphate and sodium citrate.

25. The method according to claim 22, characterised in that the substrate surfaces, before treatment according to process step a., are brought into contact with a solution

containing at least one compound selected from the group consisting of quaternary and polyquaternary compounds.

26. The method of claim 25, further comprising the step of rinsing off the solution containing at least one compound selected from the group consisting of quaternary and polyquaternary compounds after said solution containing at least one compound selected from the group consisting of quaternary and polyquaternary compounds is brought into a pH value of 1 to 3.

27. The method according to claim 22, characterised in that the substrate surfaces are metallized with a copper solution.

28. The method according to claim 22, wherein the method comprises a method for metallising holes in printed circuit boards.

29. A method of manufacturing a palladium colloid solution with low oxidation sensitivity, containing palladium, at least one tin-free reducing agent and at least one organic protective colloid for stabilising the colloid solution, and at least one noble metal selected from the group consisting of rhodium, iridium, platinum, compounds thereof and mixtures thereof, wherein compounds of the noble metals are selected from the group consisting of trivalent rhodium, iridium, and bivalent platinum compounds, characterised by the following process steps:

a. producing a parent solution containing the palladium, the organic protective colloid and the reducing agent in diluted aqueous hydrochloric acid,

b. heating the parent solution to a temperature of 50°C. to 70°C., and maintaining the temperature of the solution for approximately 24 hours, and

c. cooling the solution to a temperature of 20°C. to 40°C., and adding at least one of said noble metals.

30. The method according to claim 29, wherein step b. further comprises a further addition of reducing agents to the solution.

31. A method for coating electrically non-conductive substrate surfaces with metallic layers by direct metallisation of said surfaces with a palladium colloid solution with low oxidation sensitivity consisting of palladium, at least one tin-free reducing agent and at least one organic protective colloid for stabilising the colloid solution, and at least one second noble metal selected from the group consisting of rhodium, iridium, platinum, compounds thereof and mixtures thereof, wherein the weight ratio of the second noble metal to palladium is from 0.01:10 to 1.0:10, comprising the process steps of:

a. treating said substrate surfaces by spraying or splashing onto said substrate surfaces, the palladium colloid solution;

b. removing colloidal residues of the palladium colloid solution from the substrate surfaces after treatment in step a.; and

c. metallising the substrate surfaces with a metallising solution electrolytically and without a currentless metal layer being previously applied.

32. Method of coating electrically non-conductive substrate surfaces with metallic coatings, having the following method steps:

a. treating the substrate surfaces with a palladium colloid solution, having a low sensitivity to oxidation and containing at least one tin-free reducing agent and at least one organic protective colloid for stabilising the colloid solution and additionally at least one noble metal, selected from the group comprising rhodium, iridium and platinum, or at least one compound of these noble metals, or a mixture of these noble metals and these compounds, and

b. electrolytically metallising the substrate surfaces with an electrolytic metallising solution.

33. Method according to claim 32, wherein undesirable residues of the palladium colloid solution are rinsed from the substrate surfaces after step a. and before step b.

34. Method according to claim 32, characterised in that compounds of the noble metals are used, selected from the group comprising trivalent rhodium and iridium and bivalent platinum compounds.

35. Method according to claim 32 or 34, characterised in that a palladium concentration is set between 50 mg/l and 1000 mg/l solution.

36. Method according to any one of claims 32 to 35, characterised in that a weight ratio of the additional noble metals to palladium is set between 0.01:10 and 1.0:10.

37. Method according to any one of claims 32 to 36, characterised in that reducing agents are used, selected from the group comprising:

metal hypophosphite, metal phosphite and their acids,
alkali-metal boron hydride,
monoalkylamine borane,
dialkylamine borane,
trialkylamine borane,
ascorbic acid, iso-ascorbic acid,
hydrazine and its derivatives,
hydroxylamine and its derivatives, and
formaldehyde.

38. Method according to any one of claims 32 to 37, characterised in that the organic protective colloids are used in the weight ratio of the protective colloid to palladium of between 1:1 and 100:1.

39. Method according to any one of claims 32 to 38, characterised in that protective colloids are used, selected from the group comprising:

polyvinylpyrrolidone,
polyvinylpyridine,
polyvinylmethylketone,
polyvinylalcohol,
polyvinylacetate,
polyacrylic acid and its derivatives,
polyethylene glycol,
polyimine, and

alkyl and hydroxyalkyl cellulose
and its copolymers.

40. Method according to any one of claims 32 to 39,
characterised in that a pH value of between 1 and 3 is set
in the palladium colloid solution.

41. Method according to any one of claims 32 to 40,
characterised in that a negative electrochemical
reduction/oxidation potential is set in the palladium
colloid solution, measured relative to a silver/silver
chloride standard electrode.

42. Method according to any one of claims 32 to 41,
characterised in that, between the method steps a. and b.,
the substrate surfaces are treated with a solution
containing a sulphur compound with sulphur in the oxidation
stage of between at least +1 and at most +5.

43. Method according to any one of claims 32 to 42
characterised in that, prior to the treatment according to
method step a., the substrate surfaces are brought into
contact with a solution containing at least one quaternary
compound.

44. Method according to claim 43, wherein the substrate
surfaces are subsequently rinsed with the solution,
containing at least one compound selected from quaternary
compounds.

45. Method according to any one of claims 32 to 44,
characterised in that the substrate surfaces are metallised
with a copper solution.

46. Use of the method according to any one of claims 32 to 45 for metallising holes in printed circuit boards.

47. Method of producing a palladium colloid solution having a low sensitivity to oxidation and containing at least one tin-free reducing agent and at least one organic protective colloid for stabilising the colloid solution and additionally at least one noble metal, selected from the group comprising rhodium, iridium and platinum, or at least one compound of these noble metals, or a mixture of these noble metals and these compounds, characterised by the following method steps:

a. producing a prefabricated stock solution from a palladium compound, from at least one organic protective colloid and from at least one reducing agent in dilute aqueous hydrochloric acid,

b. heating the solution to between 50°C and 70°C, and

c. after cooling the solution to between 20°C and 40°C, adding at least one of the additional noble metal compounds.

48. The method according to claim 47, wherein step b. further comprises adding at least one reducing agent to the solution and maintaining the temperature of the solution for substantially 24 hours.

49. The method according to any one of claims 3 to 11, wherein the palladium concentration is 100 mg/l to 500 mg/l solution.

50. The method according to any one of claims 3 to 11, wherein the palladium concentration is approximately 250 mg/1 solution.

51. The method according to any one of claims 8 to 11, wherein the pH value is 1.2 to 2.0.

52. The method according to claim 9, wherein the negative electrochemical reduction/oxidation potential in the solution, is in the range from -170mV to -300mV.

53. Utilisation according to claim 14 or any one of claims 15 to 18 when dependent on claim 14, wherein the solution containing a sulphur compound is an aqueous solution of sodium thiosulphate and sodium nitrate.

54. Utilisation according to claim 15 or any one of claims 16 to 18 when dependent on claim 15, wherein the quaternary compound is a polyquaternary compound.

55. Method according to claim 35 or any one of claims 36 to 45 when dependent on claim 35, wherein the palladium concentration is set between 100 mg/1 and 500 mg/1 solution.

56. Method according to claim 35 or any one of claims 36 to 45 when dependent on claim 35, wherein the palladium concentration is substantially 250 mg/1 solution.

57. Method according to claim 40 or any one of claims 41 to 45 when dependent on claim 40, wherein the pH value is between 1.2 and 2.0.

58. Method according to claim 41 or any one of claims 42 to 45 when dependent on claim 41, characterised in that the negative electrochemical reduction/oxidation potential is set in the palladium colloid solution, in the range of between -170 mV and -300 mV.

59. Method according to claim 42 or any one of claims 43 to 45 when dependent on claim 42, characterised in that the solution containing a sulphur compound is an aqueous solution of sodium thiosulphate and sodium citrate.

60. Method according to claim 43 or claim 44 or claim 45 when dependent on claim 43, characterised in that, the quaternary compound is a polyquaternary compound.