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(54) **PRECIOUS METAL RECOVERY**

EDELMETALLRÜCKGEWINNUNG

RECUPERATION DE METAL PRECIEUX

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## Description

**[0001]** The invention relates to a method and a device for the plating of work pieces with a fluid containing palladium. The invention is especially applicable in processes for producing electrical circuit carriers.

**[0002]** To electroplate work pieces, surfaces thereof must first be treated in such a manner that they are made electrically conductive if the surfaces of the work pieces are non-conductive. For this purpose, the work pieces are immersed into a solution containing ionic, ionogenic or colloidal palladium. Ionic palladium may more specifically be present in the form of a salt, such as palladium chloride for example, which is generally dissolved in a hydrochloric acidic solution. Ionogenic palladium is present as a complex, an aminopyridine complex for example. Colloidal palladium may contain diverse protective colloids, e.g., a protective colloid formed from tin(II) chloride or consisting of an organic polymer. The palladium nuclei which are thereupon adsorbed on the surfaces of the work pieces serve for example as activators to initiate an electroless metal deposition that causes an electrically conductive layer to form on the surfaces so that the surfaces are then ready to be metal-plated with any metal. This method is utilized for producing printed circuit boards and other circuit carriers as well as metal-plated parts in the sanitary, automotive and furniture industry for example and more specifically for chromium-plating plastic parts.

**[0003]** The palladium containing solution may also be used for forming an electrically conductive layer. In this direct electroplating method, further metal is electrolytically deposited after palladium treatment without a metal layer being previously formed with an electroless metal coating method.

**[0004]** In treating the work pieces having electrically non-conductive surfaces, part of the palladium containing solution still adheres to the work pieces when the previously immersed work pieces are emersed from the solution. The adhering solution is usually rinsed with water.

**[0005]** With known activating methods using colloidal palladium for example, a solution is used that usually contains 50 - 400 mg/l of palladium. In treating plastic parts with a geometrical surface of one square meter, about 5 - 10 mg of palladium are typically adsorbed. This quantity is necessary to activate the plastic surface. When the work pieces to be treated leave the corresponding processing station, about 0.2 1 activating solution per square meter is carried over from the bath and is still left on the surfaces. Therefore, approximately 10 - 50 mg of palladium get lost to the bath because the adhering solution is entrained out of the processing bath, then rinsed and transferred to waste water treatment.

**[0006]** In direct electroplating electrically non-conductive surfaces without electroless metal-plating palladium containing solutions are also utilized. In this case, a higher concentration of palladium, of e.g., 400 mg/l, in the solution is needed.

**[0007]** In carrying out the known direct metal-plating methods, the palladium entrained from the processing solution amounts to about 50 mg/$m^2$. By taking appropriate measures such as the previous adsorption of polyelectrolyte compounds to the non-conductive surfaces, the adsorption of the palladium particles may be increased from a relatively low value to about 50 mg/$m^2$ of the surface of the work pieces. Even though, about 60 - 70% of the palladium utilized in the solution gets lost by being entrained. 40 - 30% only can actually be used for metal-plating the surfaces of the work pieces.

**[0008]** It has been known for example to recover palladium from processing solutions. U.S. Patent No. 4,078,918 e.g., describes a recovery process for reclaiming e.g., palladium from various materials that contain dissolved or non-dissolved palladium. The materials are at first treated with an oxidizing agent to destroy possible organic components and are then treated with ammonium hydroxide in order to form amine complexes. The thus obtained palladium complexes are next reduced with ascorbic acid so that palladium deposits from the processing solution as a metal and may be filtered.

**[0009]** Furthermore, in "Reclamation of palladium from colloidal seeder solutions" in Chemical Abstracts, 1990: 462908 HCAPLUS there is described a method of reclaiming palladium from solutions of colloidal Pd/$SnCl_2$ as a pretreatment prior to electroless metal-plating in which the solution is air-gassed for 24 hours so that palladium is caused to flocculate. The deposit is separated, dried and further processed.

**[0010]** In "Recovery of palladium and tin dichloride from waste solutions of colloidal palladium in tin dichloride" in Chemical Abstracts, 1985:580341 HCAPLUS there is described a method of precipitating palladium by the addition of metallic tin at 90°C.

**[0011]** U.S. Patent No. 4,435,258 discloses another method for recovering palladium from spent baths that are utilized for activating electrically non-conductive surfaces for the subsequent electroless metal-plating process. The activating solutions are reprocessed by causing the colloidal palladium to oxidize into the solution by adding an oxidizing agent such as hydrogen peroxide for example, by subsequently heating the solution to destroy the residual hydrogen peroxide and by thereafter electrolytically depositing palladium from these solutions onto a cathode.

**[0012]** In "Recovery of the colloidal palladium content of exhausted activating solutions used for the current-free metal coating of resin surfaces" in Chemical Abstracts, 1976:481575 HCAPLUS finally there is described a method of obtaining palladium from Pd/$SnCl_2$ in which palladium is precipitated by the addition of concentrated nitric acid and is filtered.

**[0013]** DE 100 24 239 C1 describes a method of electroplating work pieces with a palladium colloid solution by contacting the work pieces with the colloid solution according to which palladium is recovered after the colloid solution was used, by separating palladium colloid particles from the colloid solution by means of a membrane filter. Materials made from ceramics for example may be used for filtration. The pore exclusion size of the membranes amounts to 200

to 10,000 Dalton. It is stated therein that the palladium particles pass through the membrane filter when the pore exclusion size used is in excess of 10,000 Dalton.

**[0014]** The prior art methods for electroplating work pieces with a palladium colloid solution are complicated and expensive.

**[0015]** The basic problem the present invention faces is to avoid the drawbacks of the known methods and to find a method for plating work pieces with a fluid containing palladium that may be carried out at low cost. Small quantities of additional chemicals only should be necessary to carry out the method. Furthermore, the method should involve little expense of energy and time and should more specifically require low maintenance.

**[0016]** This problem is overcome by the method according to claim 1. Preferred embodiments of the invention are indicated in the subordinate claims.

**[0017]** The method in accordance with the invention serves to plate work pieces with a fluid, said fluid containing palladium, the method comprising contacting the work pieces with the fluid. For the purpose of recovering the precious metal from the fluid, said fluid is mixed with chemical substances selected from the group comprising pH adjusting agents, reducing agents, sulfur compounds, selenium compounds and tellurium compounds such that the palladium is altered in such a manner that it is substantially entirely retained during filtration and is thereafter filtered through at least one ceramic membrane filter to separate the palladium from the fluid, the ceramic membrane filter having an exclusion pore size in excess of 10,000 Dalton. Due to the filtering the palladium is separated from the fluid.

**[0018]** By plating, any treatment with fluids is meant that is directed to alter the surface of the work pieces, the fluid having to contain palladium. Not included therein though are methods of coating work pieces with polymer coatings, more specifically enamelling methods.

**[0019]** The work pieces to be plated include metallic work pieces, non-metallic work pieces and work pieces consisting of both metallic and non-metallic materials. The work pieces may have all conceivable forms and be intended for all conceivable utilizations. Preferred pieces are semi-finished products for producing circuit carriers, more specifically for producing printed circuit boards and hybrid circuit carriers such as multichip modules for example.

**[0020]** More specifically the fluid may be a solution. This is more specifically the case when the palladium is present in ionic or ionogenic form. By ionic form of the palladium, salts of palladium dissolved in water or in another solvent that promotes the dissociation of said salts is more specifically meant. By ionogenic form of the palladium, palladium complexes are meant, more specifically.complexes of the palladium ions with organic complex ligands. The complexes may be uncharged or be present in the form of ions. The fluid may be present in the form of a colloid, more specifically of a colloid of the elemental palladium.

**[0021]** The palladium containing fluid may be both a processing fluid for treating the work pieces or a rinsing fluid. By processing fluid a fluid is meant that serves to alter the surface properties of the work pieces, e.g., a coating fluid, including an activating fluid, a cleansing fluid, an etching fluid or the like. By contrast, a rinsing fluid only serves, after treatment of a work piece with the processing fluid, to rinse off the processing fluid still adhering on the surface of the work piece.

**[0022]** After use of the fluid for plating the work pieces, the palladium is filtered in the at least one ceramic membrane filter. This means that the fluid is at first utilized for plating and is only filtered afterwards in the membrane filter for the purpose of recovering the palladium that it contains. The fluid can for example be contacted with a work piece by spraying, jetting, flooding or blasting, the fluid dripping off the work piece collected and the collected fluid be conducted to the membrane filter immediately thereafter. The collected fluid may also be first retained in a reservoir from where it is delivered back to the work piece, though. In this case, the fluid may be either conducted to the membrane filter after having been collected for a predetermined period of time (intermittent method), or part of the fluid may be tapped continuously from the reservoir and be transferred to the membrane filter (continuous method). To achieve a stationary filling condition in the reservoir in this case, new processing fluid is permanently introduced into the reservoir in a quantity per unit of time that equals the quantity of the fluid permeating the membrane filter per unit of time. The work pieces may also be contacted with processing fluid contained in a treatment container by immersing them thereinto. In this case, the processing fluid is, after use, either conducted to the membrane filter after having been collected for a predetermined period of time (intermittent method), or part of the fluid in the reservoir may be tapped continuously from the treatment container and be transferred to the membrane filter (continuous method).

**[0023]** The method of the invention permits to achieve in a simple manner and with little expense of chemicals, energy and time as well as with little maintenance, a far-reaching separation of palladium from the exhausted processing solutions under continuous operation. It more specifically permits to regenerate the exhausted processing solutions after the fraction containing the palladium has been separated so that the entire palladium may be recirculated into the process.

**[0024]** Over the method described in Chemical Abstracts, 1990:462908 HCAPLUS for reclaiming palladium from colloidal $Pd/SnCl_2$, the present method has the advantage that the fractions are completely separated whereas with the precipitation method described in Chemical Abstracts a non-negligible part of the palladium is oxidized to form the bivalent, soluble stage thereof so that it cannot be completely separated from the solution by filtration. Accordingly, this part of the palladium cannot be recovered and will be lost.

**[0025]** Another advantage of the method of the invention over the method described in Chemical Abstracts, 1985: 580341 HCAPLUS is that there is no need for considerable expense of additional chemicals like metallic tin and of energy and time as they are required for the known method for the purpose of heating the colloid solution.

**[0026]** The method in accordance with the invention also has substantial advantages over the method described in U.S. Patent No. 4,435,258, namely that palladium may be removed almost entirely from the solutions, whereas, by the method according to U.S. Patent No. 4,435,258, only an extremely low current efficiency may be achieved, especially when the palladium concentration is low, which occurs after a long period of electrolysis. Therefore, it is either very complicated or not possible at all to completely remove palladium with this prior art method.

**[0027]** In contrast to the method described in Chemical Abstracts, 1976:481575 HCAPLUS, the method and the device in accordance with the present invention are more specifically suited for continuous operation. Furthermore, the method presented in this publication imperatively needs additional chemicals.

**[0028]** Surprisingly, and as contrasted with the properties of membrane filters having a pore exclusion size clearly in excess of 10,000 Dalton as they are indicated in DE 100 24 239 C1 and according to which the palladium particles of colloidal palladium colloid solutions permeate the filter, the separating properties of ceramic filters having a pore exclusion size of e.g., 20,000 Dalton proved excellent with regard to colloidal palladium. In this connection, reference is made to the tests No. 1 and 2 in Example 1.

**[0029]** The method and the device in accordance to the present invention have the following advantages over known methods and devices:

a. Palladium, may be recovered from ionic, ionogenic and colloidal solutions with but one device. It is not necessary to use several matched devices. As a result thereof, the solutions may be mixed and collected prior to being regenerated. The same also applies to the processing and rinsing fluids: processing fluids with a high concentration of palladium can be mixed with rinsing fluids containing palladium in a very low concentration and then be processed together.

b. Ceramic membrane filters that are largely resistant to chemicals and to the effects of temperature may be utilized since separation of palladium is also successful with the larger pores of ceramic membrane filters. Maintenance is low as a result thereof as the filters do not need cleaning very often. Ceramic membrane filters also have a long durable life. Moreover, palladium does not adsorb to the membrane material.

c. The fluid to be treated can be reprocessed with a very simple method. It is e.g., not necessary to work in a protective atmosphere to prevent colloidal particles from dissolving in the fluid.

**[0030]** Colloidal activators on the basis of palladium comprise palladium particles that are surrounded by a protective coating (protective colloid). Tests using high resolution transmission electron microscopy (HTEM) and atomic force microscopy (AFM) showed that the palladium particles have a diameter of at least 2.5 nm. The mean particle diameter amounts to approximately 4 nm, which corresponds to the gaussian distribution of particles. In testing a rinsing fluid that was obtained after treatment of work pieces with the colloidal activator, a wide particle size distribution that showed particles with a maximum size of about 18 nm as well as smaller particles (from 2 to 18 nm) was determined.

**[0031]** In practical utilization, colloid solutions are acidic, often highly hydrochloric acidic, and contain chloride ions as well as possibly tin in the oxidation stages (II) and (IV) or organic, polymeric stabilizers like gelatine or polyvinyl pyrrolidone and reducing agents. Except for the polymers, which are utilized in small quantities, all the other substances contained therein are ionic. It is presumed that these ionic constituents are much smaller than the palladium particles.

**[0032]** Surprisingly, palladium particles may be removed very selectively and completely from these colloid solutions by means of appropriate membrane filters comprising different porosities, although, in the case of the tin containing colloidal solutions, tin, which is simultaneously present, is contained in a high concentration (usually more than 70 times the palladium concentration) and although the tin compounds are known to form colloidal solutions that are difficult to filter.

**[0033]** For ultrafiltration, diverse types of membranes made of various materials have been tested. The tests showed that what matters in selecting the membrane filter is more specifically that it be sufficiently stable to the fluid that contains the palladium and that may contain 15 percent by weight of hydrochloric acid for example.

**[0034]** To separate the palladium colloid particles, ceramic membrane filters may be utilized that have an exclusion pore size of from about 15,000 Dalton to about 25,000 Dalton, more specifically an exclusion pore size of from about 17,500 Dalton to about 22,500 Dalton and most preferably of approximately 20,000 Dalton.

**[0035]** A preferably utilized ceramic membrane filter is made of a ceramic material containing aluminum oxide, more specifically $\alpha$-$Al_2O_3$, titanium dioxide and possibly zirconium dioxide. In principle, other filter materials may also be utilized. As a rule, the filter material is deposited onto a highly porous supporting body that provides the filter with the required mechanical stability. This supporting body may consist of $\alpha$-$Al_2O_3$ or of SiC (silicon carbide) for example.

**[0036]** The filter may be configured in the form of a disc or as a tube. In the first case, a flow is directed onto the disc,

approximately normal to the surface thereof, said flow being deviated in radial direction. A pressure difference is built up between the two surfaces of the disc so that permeate may pervade the disc. If the filter has the shape of a tube, the fluid is conveyed through the tube in axial direction, a pressure difference being built up between the inner space and the outer space of the tube. As a result thereof, permeate can pervade the wall of the tube e.g., from the interior volume of the tube to the space external of the tube. This second method is called dynamic filtration. In this case, the palladium is retained within the inner space of the tube, whereas the fluid, which has been largely freed from palladium permeates through the wall of the tube from the inner volume of the tube to the space external of the tube.

**[0037]** Some fluids may be filtered directly without any further pretreatment. In this case, very good results are obtained with the ceramic membrane filters.

**[0038]** The fluids to be reprocessed are chemically pretreated first. After having been used for plating and prior to being filtered through the membrane filter, the fluid is mixed for this purpose with chemical substances that are suited to alter the palladium in such a manner that it is almost completely retained during filtration. It is presumed that, by adding these chemical substances, the particle size of the palladium is altered in such a manner that the particles that contain palladium cannot pass through the pores of the membrane filter. For this purpose it should be sufficient to adjust the average particle size to a value in excess of about 10 nm when the particle size fits the Gaussian distribution. In this case, a membrane filter with an exclusion pore size in excess of 10,000 Dalton would already retain almost the entire quantity of palladium in the concentrate. Larger particles may be set accordingly by adding these chemical substances when membrane filters with a greater exclusion pore size are being used.

**[0039]** If palladium is present in the solution in ionic and/or ionogenic form, the fluid may be mixed with chemical substances selected from the group comprised of reducing agents, sulfur compounds, selenium compounds and tellurium compounds. The chemical substances for pretreatment are most preferably selected from the group comprised of boron hydrides, amine boranes, hypophosphites, inorganic sulfides and organic thio compounds, more specifically the alkali and ammonium salts of dimethyl dithiocarbamate, of sulfides, of boron hydrides such as tetrahydroboranate for example, and of hypophosphites. The organic thio compounds considered are more specifically organic compounds in which sulfur is bonded to one or to two atoms of carbon to form a single or a double bond therewith i.e., thioles, sulfides, disulfides and polysulfides, thioamides and thioaldehydes for example.

**[0040]** If palladium is present in the fluid in colloidal form, pH adjusting agents are used as chemical substances. The fluid is mixed with the pH adjusting agents in such a manner that solution pH ranges from 3 to 12.

**[0041]** In both cases, a solution is obtained that is very well suited for separating the palladium.

**[0042]** The following advantages derive from this improvement of the present invention:

a. the pretreatment is very simple. It suffices to mix the fluids containing the palladium with the required substances or with the pH adjusting agent respectively.

b. The expense of additional chemicals is very low. To process 200 l of rinsing water from the treatment with an aqueous solution of an organic palladium complex (7 mg/l of Pd), only 7.5 ml of a solution containing 467 g/l of sodium dimethyl dithiocarbamate are needed. If rinsing waters originating from the treatment with a palladium colloid (organic protective colloid, 25 mg/l Pd) are to be processed, mere 0.5 l of an aqueous solution of 432 g/l of NaOH will suffice.

**[0043]** It could be inferred from the observations and tests that led to the present invention that it is possible to recover palladium from rinsing fluids and/or processing fluids by means of membrane filters. For this purpose

a. the work pieces are contacted with a palladium containing processing fluid,
b. then, the processing fluid still adhering to the surfaces of the work pieces is removed with rinsing fluid, and
c. the processing fluid and/or the rinsing fluid are passed (preferably under pressure) through the at least one ceramic membrane filter for filtration thereof, the fluid being passed through the at least one membrane filter being a permeate fluid and the fluid that has not passed through the at least one membrane filter being a concentrate fluid.

**[0044]** After treatment with a palladium containing fluid, the work pieces, which are preferably made of an electrically non-conductive material, are rinsed in a suitable device with a rinsing fluid by immersing them into it, by flooding or preferably by spraying said rinsing fluid onto said work pieces in order to keep the volume of rinsing solution as small as possible. The rinsing fluid is next conducted through a ceramic membrane filter by means of a pressure pump, said filter retaining the palladium particles and allowing the rinsing water to permeate. Said permeate may then be transferred to waste water treatment.

**[0045]** Prior to being conducted through the membrane filter, the processing fluid and/or the rinsing fluid may be mixed with the chemical substances such as for example the reducing agents, sulfur compounds, selenium compounds, tellurium compounds or the pH adjusting agents.

**[0046]** In a particularly preferred embodiment of the invention, only the rinsing fluid, or a rinsing fluid containing preferably up to 5 percent by volume of processing fluid, is conducted through the membrane filter (preferably under pressure). The work pieces are contacted with fresh rinsing solution, a predetermined quantity of fresh rinsing solution per unit of time being permanently available. The quantity of the permeate fluid formed per unit of time may be more specifically adjusted to approximately equal the quantity of the rinsing fluid that is contacted with the work pieces per unit of time. As a result thereof, a stationary condition is achieved in the processing plant: in that the amount of fresh rinsing fluid delivered to the work pieces is exactly the same as the amount of permeate fluid drained from the plant, the result obtained is a constant flow of substances. This, of course, only applies if the amount of added chemical substances is negligible and if no further influencing variables affect the process. For, in practice, evaporation of rinsing fluid could play a major part.

**[0047]** Retained palladium, which is present as a concentrate in the form of a homogeneous dispersion of metal or of a metal compound, e.g., in the form of a PdS dispersion, may be recycled. The retained palladium may e.g., be dissolved, converted to palladium chloride and be utilized to synthesize a new palladium containing processing fluid or for any other application. The palladium containing concentrate solution may also be concentrated to near dryness in a filter press. For this purpose, the concentrate fluid coming from the membrane filter is directed into a container in which palladium containing slurry that has formed during concentration deposits, the slurry suspension being directed to the filter press. The palladium containing filter cake obtained by means of the filter press may be utilized as a base substance for producing pure palladium and palladium compounds.

**[0048]** The device for plating work pieces with a fluid containing palladium is typically provided with means for contacting the work pieces with the fluid as well as with holding means for the work pieces.

**[0049]** The means for contacting the fluid with the work pieces are e.g., nozzles by means of which processing or rinsing fluid is sprayed, jetted, flooded or discharged onto the surfaces of the work pieces. This arrangement is used for example when the fluid is to reach the surface at a high flow velocity or when the quantity of the fluid needed is to be minimized. In another embodiment of the invention, the contacting means are treatment containers in which the processing fluid is disposed and into which the work pieces are immersed.

**[0050]** The holding means for the work pieces may also be embodied in very diverse forms: the work pieces may for example be retained in a conventional way by means of cramps, clamps, tongs or screw fastenings. Furthermore, the work pieces may also simply be held, transported and conducted in a horizontal position on rolls, wheels or cylinders or they may be clamped therein between.

**[0051]** Aside from the features mentioned, the device also comprises a facility for separating the palladium from the fluid. This facility comprises at least one ceramic membrane having an exclusion pore size in excess of 10,000 Dalton. Further the facility comprises at least one pump for delivering the fluid to the at least one membrane and fluid conduits for conducting the fluid from the means for contacting the work pieces with the fluid to the at least one ceramic membrane. By a pump, any pump which is not motor operated or simply delivery of the fluid by gravity is also meant.

**[0052]** In accordance with the explanations given herein above, the facility for separating the palladium from the fluid is furthermore provided with a mixing facility. In this mixing facility, fluid coming from the means for contacting the work pieces with the fluid can be mixed with chemical substances. For this purpose, any conventional mixing facility known in the chemical reaction technique, such as e.g., stirring facilities and mixing zones in flow reactors, may be utilized.

**[0053]** Furthermore, the facility for separating the palladium from the fluid may also be provided with a multiphase separating unit in which slurry may deposit which is produced during separation from the fluid and which comes from the facility for separating the palladium from the fluid. A multiphase separating unit of this type is formed by a sedimentation tank for example in which virtually no fluid convection is taking place. Said slurry suspension may then be directed into a filter press in order to largely purify and dry the slurry, which mainly contains palladium.

**[0054]** The invention will be understood better upon reading the description of the Figs. More specifically,

**Fig. 1:** is a perspective, schematic view of a ceramic membrane filter;

**Fig. 2:** is a schematic representation of a device for plating work pieces in accordance with the invention.

**[0055]** **Fig. 1** illustrates a ceramic membrane filter in the form of a tube **1**. The tube is made of a highly porous ceramic material that serves as support **3** and that is, in the present case, of aluminum oxide. The support **3** is provided, on its inner side, with another ceramic layer of an oxide that serves as a membrane filter layer **2**. Said membrane filter layer **2** in turn consists of two layers (not specifically shown), i.e., a first microfiltration layer made of $\alpha$-$Al_2O_3$ and of a second ultrafiltration layer made of $ZrO_2$ and $TiO_2$, $TiO_2$ having the finest pore size so that filtration is also possible with an exclusion pore size of e.g., 20,000 Dalton. The membrane filter layer **2** has an exclusion pore size of about 20,000 Dalton. Accordingly, the mean pore size amounts to approximately 20 nm.

**[0056]** The tube has an inside diameter of about 6 mm. The tube is about 1000 mm in length. The flow passes therethrough under pressure in the direction of flow referred to be reference numeral **4**. The pressure difference between

the entrance and the exit of the tube ranges from 1.5 to 3 bar.

**[0057]** In order to collect the permeate passing through the internal wall of the tube, the ceramic tube is positioned concentrically within another tube.

**[0058]** **Fig. 2** comprises two of the filter tubes **1** represented in **Fig. 1** in the lower part of the figure, the filter tubes **1** being part of ceramic tubes with several bores of the type shown in **Fig. 1.** For this purpose 19 axial bores are for example drilled in a ceramic tube consisting of a highly porous ceramic material, said axial bores being paralleled.

**[0059]** In the upper part of **Fig. 2**, the processing stations of a processing plant for printed circuit boards is partially shown. The printed circuit boards are successively conveyed through the different processing stations in the processing direction **R**. A typical example of such a method is described, *inter alia,* in WO 93/17153 A1.

**[0060]** After having already performed the pretreatment steps, the printed circuit boards (which are not shown herein) are immersed, in activating station **A-Pd**, into an activating bath containing palladium in colloidal form. For this purpose, the fluid is contained in an immersion bath tank.

**[0061]** Then, the printed circuit boards are conveyed through three successive rinsing stations $\mathbf{S_1}$, $\mathbf{S_2}$ and $\mathbf{S_3}$. There, the activating fluid that adheres to the surfaces of the printed circuit boards is successively rinsed off. The different rinsing stations $\mathbf{S_1}$, $\mathbf{S_2}$ and $\mathbf{S_3}$ are provided with spray nozzles to serve this purpose. The rinsing stations $\mathbf{S_1}$, $\mathbf{S_2}$ and $\mathbf{S_3}$ are configured as open top containers that are provided with nozzles arranged on the walls of the long sides thereof. In order to rinse off the adhering activating fluid, rinsing fluid is sprayed onto the surfaces of the printed circuit boards as the printed circuit boards are lowered into and/or are raised out of the stations $\mathbf{S_1}$, $\mathbf{S_2}$ and $\mathbf{S_3}$. The rinsing fluid is collected at the bottom of a container in the respective one of the rinsing stations $\mathbf{S_1}$, $\mathbf{S_2}$ and $\mathbf{S_3}$. Fresh rinsing fluid is dispensed to the rinsing station $\mathbf{S_3}$ at an average flow rate of 200 l/h, from there it is conducted in a direction counter to the processing direction **R** of the printed circuit boards to the rinsing station $\mathbf{S_2}$ arranged upstream thereof from where it is brought into the rinsing station $\mathbf{S_1}$, the flow rate remaining the same. Each rinsing station $\mathbf{S_1}$, $\mathbf{S_2}$ and $\mathbf{S_3}$ is also allocated a collecting tank (not shown) in which the respective rinsing fluid is collected. The collected rinsing fluid is drained at a flow rate of 200 l/h from the collecting tank of rinsing station $\mathbf{S_1}$ toward further processing.

**[0062]** After the surfaces of the printed circuit boards have been freed from adhering activating fluid by rinsing, they are subjected to posttreatment. Such processing fluids are for example solutions of sulphinic acids. In the posttreatment station **B**, the printed circuit boards are immersed for treatment into these solutions which are contained in the treatment containers.

**[0063]** Then, adhering posttreatment solution is rinsed off again in the further rinsing stations $\mathbf{S_4}$, $\mathbf{S_5}$ and $\mathbf{S_6}$. Again, the rinsing fluid is sprayed from nozzles arranged in the stations $\mathbf{S_4}$, $\mathbf{S_5}$ and $\mathbf{S_6}$ onto the surfaces of the printed circuit boards. The collected rinsing fluid is directed to collecting tanks (not shown) from where it is conducted successively back, in a direction counter to the processing direction of the printed circuit boards **R**, to the rinsing stations $\mathbf{S_5}$ and $\mathbf{S_4}$ which are arranged upstream thereof. The rinsing fluid is drained from rinsing station $\mathbf{S_4}$ toward subsequent waste water treatment.

**[0064]** The printed circuit boards are next immersed into an etch solution contained in a container in etch station **C-Pd**. There, palladium adsorbed to the copper surfaces is removed from activation by etching slightly the copper surfaces. In this case as well, the printed circuit boards are immersed into the etch solution.

**[0065]** After that, adhering processing fluid is again rinsed off the surfaces of the printed circuit boards. For this purpose, the printed circuit boards are conveyed to the rinsing stations $\mathbf{S_7}$, $\mathbf{S_8}$ and $\mathbf{S_9}$. Etch solution adhering to the surfaces of the printed circuit boards is removed by means of rinsing fluid that is sprayed from nozzles onto the surfaces. For this purpose, fresh rinsing fluid is conducted into rinsing station $\mathbf{S_9}$ at a flow rate of 200 l/h and the rinsing fluid gathering in this rinsing station is collected in collecting tanks (not shown). Again, the collected rinsing fluid is conducted in a direction counter to the processing direction of the printed circuit boards **R**, from rinsing station $\mathbf{S_9}$ to rinsing station $\mathbf{S_8}$ and from there into rinsing station $\mathbf{S_7}$. From rinsing station $\mathbf{S_7}$ the palladium enriched rinsing fluid is conducted to a regenerating arrangement at a flow rate of 200 l/h.

**[0066]** The afore mentioned way of treating the printed circuit boards is but one possible alternative. The printed circuit boards may also be processed in a so called horizontal plant. The boards are hereby conducted through the various stations in a horizontal direction of transport and in a horizontal or vertical orientation. In the diverse stations, the fluids may be delivered to the surfaces by nozzles.

**[0067]** The rinsing fluid originating from rinsing station $\mathbf{S_4}$ contains virtually no precious metal and can be dispensed to the conventional waste water processing system. By contrast, the rinsing fluid originating from the rinsing stations $\mathbf{S_1}$ and $\mathbf{S_7}$ contains palladium and is regenerated in the inventive way:

**[0068]** In the first place, the various rinsing waters are collected in buffer tanks **11.1** and **11.2**, respectively. Rinsing fluid drained from the buffer tanks **11.1** and **11.2** at a flow rate of 200 l/h is next conducted into the conduits **13.1** and **13.2**, respectively, by means of pumps **12.1** and **12.2**, respectively, and is delivered to a common conduit **13.3**. To adjust the pH, the combined rinsing fluids are - if necessary - mixed with a pH adjusting agent, in the present case with NaOH. For this purpose, NaOH solution is added from a reservoir **14** to the combined rinsing fluids. An electric control circuit (not shown) serves to control the dosage of the NaOH solution. Said control circuit comprises a pH probe **15**, a pH

measuring electrode for example, for controlling a dosing pump (not shown) for the NaOH solution. In case the pH of the rinsing fluid is near 7, the pH needs not be adjusted to the precise value of 7.

**[0069]** If, instead of a palladium colloid fluid, an ionic or ionogenic palladium solution is utilized, solutions of other suitable chemical substances are added to the flow of fluid in place of a pH adjusting agent in order to make certain the palladium containing fluid is filtrable.

**[0070]** The rinsing fluid, the pH of which is now adjusted to a value of about 7, is then directed by means of another pump **12.3** through a conduit **13.4** into a collecting tank **16**.

**[0071]** A lower fill level sensor **17.1** and an upper fill level sensor **17.2** are provided in collecting tank **16**. If the fluid level is higher than the upper fill level sensor **17.2**, fluid is directed through conduit **13.5** from container **16** to pump **18**. If, by contrast, the fill level of the collecting tank **16** is below the lower fill level sensor **17.1**, the rinsing fluid is not pumped out of the collecting tank **16**.

**[0072]** By means of pump **18**, the fluid is conducted, under a pressure ranging from 1.5 to 3 bar, through two membrane filter tubes **1** connected in series. The permeate fluid pervading the walls of the tube is drained toward further waste water treatment **A**. The concentrate fluid remaining in the filter tube is recirculated via the closed circular conduit **13.6** so that the fluid is permanently and increasingly concentrated with regard to palladium. Via the branching **13.7**, part of the concentrated rinsing fluid is permanently circulated back to the collecting tank **16** from where it is directed to the membrane filters by way of pump **18** so that palladium gradually enriches in this fluid.

**[0073]** In collecting tank **16**, palladium containing slurry, which results from concentration, deposits in a multiphase separating zone. Said slurry suspension may be drained into another container **19**.

**[0074]** Fluid coming directly from the activating station **A-Pd** can also be discharged directly for regeneration and be directed toward ultrafiltration. For this purpose, said fluid may be either transferred by hand into a collecting tank **20** using the path referred to by reference numeral **M** or small quantities thereof may be conducted to the buffer tank **11.1** by means of a pump **12.4**. Fluid that has been removed and transferred by hand to collecting tank **20** may then be dispensed to collecting tank **16** by way of another pump **12.5** for example.

**[0075]** The slurry suspension contained within the container **16** in the multiphase separating unit is directed to a filter press **21** for further separation of palladium. The filter press **21** is shown in dashed lines in **Fig. 2**. It contains filter material having a pore size of about 50 $\mu$m. The pressure in the press amounts to about 4 bar. Excess fluid can either be circulated back to the collecting tank **16** by way of the additional conduit **22** or be dispensed to waste water treatment **A**.

**[0076]** The following examples will serve to explain the invention:

**Example 1:**

**[0077]** To perform a test, printed circuit boards were treated with a colloidal, acidic activating fluid that contained 400 mg/l of colloidal palladium, a protective colloid in the form of a polymer and a reducing agent in the form of sodium hypophosphite. The mean particle diameter of the palladium colloid particles was about 4 nm.

**[0078]** After rinsing, the printed circuit boards were treated with an posttreatment solution containing an organic sulphinic acid, were then rinsed again and finally treated in an etch solution containing 300 g/l of sodium persulfate. The amounts of palladium thereby removed from the copper surfaces were dispensed to the etch solution and, via the etch solution adhering to the surfaces of the printed circuit boards, to the subsequent rinsing fluid.

**[0079]** The rinsing fluids obtained in the rinsing stations $\mathbf{S_1}$ to $\mathbf{S_3}$ and $\mathbf{S_7}$ to $\mathbf{S_9}$ (see **Fig. 2**) under the afore mentioned conditions were dispensed to the regeneration arrangement described at a flow rate of 200 l/h respectively. The fluids were separated at a filter membrane made of ceramic ($\alpha$-$Al_2O_3$ as a support material with two ultrafiltration layers of $ZrO_2$ and $TiO_2$ applied thereon, $TiO_2$ being provided with the finest pore size and effecting a filtration with a pore exclusion size of approximately 20,000 Dalton; the $TiO_2$ layer was applied by a Sol Gel method). The concentration of palladium in the rinsing fluids as well as the pH of these fluids are indicated in Table 1 (tests No. 1 and 2).

**[0080]** The pH of the fluids originating from rinsing stations $\mathbf{S_1}$ to $\mathbf{S_3}$ and $\mathbf{S_7}$ to $\mathbf{S_9}$ were not adjusted with pH adjusting agents.

**[0081]** During ultrafiltration, the concentrate fluid was conducted through the ceramic membrane filter at a flow rate of 2,800 l/h. The permeate flow rate obtained was of 40 to 45 l/h.

**[0082]** After ultrafiltration, a permeate fluid and a concentrate fluid were obtained. The concentrations of palladium in the permeate and in the concentrate according to the tests No. 1 and 2 are also indicated in Table 1.

**Example 2:**

**[0083]** In another test, a mixture of rinsing fluids from the colloidal activating fluid and from the etch solution was prepared at a volume ratio of 1 : 1 (test No. 3). The same ceramic membrane filter was used as in Example 1. The initial palladium concentration in the combined rinsing fluids and the pH of the mixture are indicated in Table 1. To adjust the pH of the combined rinsing fluids to 7, a NaOH solution was added to the rinsing fluid.

**[0084]** The permeate solution obtained after having carried out ultrafiltration had a palladium concentration of < 0.5 mg/l. The palladium concentration in the concentrate was > 1 g/l (see Table 1).

**Example 3:**

**[0085]** In another test No. 4, the same ceramic membrane filter as in Example 1 was used. Colloidal activating fluid was added at a volume ratio of 1 : 100 to the mixture of rinsing fluids obtained according to Example 2. The palladium concentration in this fluid was equal to 15.0 mg/l. The pH of this fluid was adjusted to 7 by means of NaOH solution. The palladium concentrations in the permeate and in the concentrate after ultrafiltration was performed are indicated in Table 1.

**Example 4:**

**[0086]** In another test No. 5, the same ceramic membrane filter as in Example 1 was used. In this test, the solution of an ionogenic activator was used in place of a colloidal activating solution. The activator contained an organic palladium complex (Neoganth® Activator, Atotech Deutschland GmbH, Germany), the palladium concentration in this solution was 250 mg/l.

**[0087]** The printed circuit boards activated with this solution were again treated in a rinsing cascade of three rinsing stations $\mathbf{S_1}$, $\mathbf{S_2}$ and $\mathbf{S_3}$, the direction of flow of the rinsing water corresponding to that shown in **Fig. 2**. The palladium concentration in the rinsing water originating from rinsing station $\mathbf{S_1}$ was about 1.5 mg/l. For adjusting the ultrafiltrability of the rinsing water, an aqueous solution of 467 g/l of sodium dimethyl dithiocarbamate was added to the rinsing water. The palladium concentrations obtained in the permeate and in the concentrate as a result of ultrafiltration of this solution are indicated in Table 1 (Test No. 5).

**Example 5:**

**[0088]** In another test No. 6, the same ceramic membrane filter as in Example 1 was used. In this test, the rinsing water obtained according to Example 4 was mixed at a volume ratio of 100 : 1 with the solution of the activating bath. An aqueous solution of 10 g/l of sodium sulfide was added to the mixture. The initial palladium concentration was 8.0 mg/l. The palladium concentrations in the filtrate and in the concentrate after ultrafiltration are indicated in Table 1.

**[0089]** The tests described herein above yielded concentrate fluids that had a considerable amount of slurry. After the slurry had settled, the concentrate was dispensed to a filter press. The palladium concentration in the enriched concentrate amounted to 2 to 5 g/l. The filter cake obtained during compression had a palladium concentration of 2 to 15 percent by weight.

**Example 6:**

**[0090]** In another test No. 7, the same ceramic membrane filter as in Example 1 was used. A mixture according to Example 5 was added at a volume ratio of 2 : 1 to the mixture of rinsing fluids obtained according to Example 2.

**[0091]** The palladium concentration in this fluid was 4.2 mg/l. The pH was adjusted to 7 by means of NaOH solution. Furthermore, an aqueous solution of 467 g/l of sodium dimethyl dithiocarbamate was added to the fluid. The palladium concentrations in the permeate and in the concentrate after ultrafiltration had been performed are shown in Table 1.

**[0092]** It is understood that the examples and embodiments described herein are for illustrative purpose only and that various modifications and changes in light thereof as well as combinations of features described in this application will be suggested to persons skilled in the art and are to be included within the spirit and purview of the described invention and within the scope of the appended claims. All publications, patents and patent applications cited herein are hereby incorporated by reference.

Table 1:

| Test No. | Mixture of the product | Initial Pd-concentration [mg/l] | pH | Pd conc. in the permeate [mg/l] | Pd conc. in the concentrate [mg/l] | Addition of chemicals |
|---|---|---|---|---|---|---|
| 1 | rinsing fluid colloid. activator | 5.5 | 5 | < 0.5 | > 1,000 | no addition |
| 2 | rinsing fluid etch solution | 2.5 | 3 | < 0.5 | > 1,000 | no addition |

(continued)

| Test No. | Mixture of the product | Initial Pd-concentration [mg/l] | pH | Pd conc. in the permeate [mg/l] | Pd conc. in the concentrate [mg/l] | Addition of chemicals |
|---|---|---|---|---|---|---|
| 3 | rinsing fluid coll. act. + etch sol.: 1:1 | 4.0 | 7 | < 0.5 | > 1,000 | NaOH |
| 4 | rinsing fluid coll. act. + etch sol.: 1:1 + 1 % by vol. coll. act. | 15.0 | 7 | < 0.5 | > 1,000 | NaOH |
| 5 | rinsing fluid ionogenic activator | 1.5 | 8 | <0.5 | > 1,000 | Na dimethyl dithiocarbamate |
| 6 | rinsing fluid ionogenic activator + 1 %-vol. ionog. act. | 8.0 | 8 | < 0.5 | > 1,000 | $Na_2S$ |
| 7 | (rinsing fluid ionogenic activator + 1 % by vol. ionog. act.) + rinsing fluid coll. act. + rins. fluid etch sol.:1:1:1 | 4.2 | 7 | < 0.5 | > 1,000 | NaOH Na dimethyl dithiocarbamate |

**Listing of numerals:**

**[0093]**

| | |
|---|---|
| **1** | ceramic membrane filter |
| **2** | ceramic filter layer |
| **3** | highly porous ceramic supporting tube |
| **4** | direction of flow |
| **10** | processing plant for printed circuit boards |
| **11.1, 11.2** | buffer tanks |
| **12.1 -12.5** | pumps |
| **13.1 -13.7** | conduits |
| **14** | reservoir |
| **15** | pH probe |
| **16** | collecting tank |
| **17.1** | lower fill level sensor |
| **17.2** | upper fill level sensor |
| **18** | pump |
| **19** | container |
| **20** | collecting tank |
| **21** | filter press |
| **22** | conduit |
| **A-Pd** | activating station |
| **B** | posttreatment station |
| **$S_1$ - $S_9$** | rinsing stations |

| | |
|---|---|
| **C-Pd** | etch station |
| **M** | removal by hand |
| **A** | waste water treatment |
| **R** | processing direction of the printed circuit boards |

## Claims

1. A method for plating work pieces with a fluid, said fluid containing palladium, said method comprising contacting said work pieces with said fluid, thereafter mixing said fluid with chemical substances selected from the group comprising pH adjusting agents, reducing agents, sulfur compounds, selenium compounds and tellurium compounds and thereafter filtering said fluid through at least one ceramic membrane filter to separate the palladium from said fluid, wherein said ceramic membrane filter has an exclusion pore size in excess of 10,000 Dalton, the chemical substances being selected such that palladium particles are formed the particle size thereof being such that the particles cannot pass through the pores of the at least one ceramic membrane filter.

2. The method of claim 1, wherein said at least one ceramic membrane filter has an exclusion pore size ranging from about 15,000 Dalton to about 25,000 Dalton.

3. The method of claim 2, wherein said at least one ceramic membrane filter has an exclusion pore size of about 20,000 Dalton.

4. The method of any one of the previous claims, wherein said at least one ceramic membrane filter is made of an aluminum oxide/titanium dioxide/zirconium dioxide ceramic material.

5. The method of any one of the previous claims, wherein said work pieces are suited for manufacturing electric circuit carriers.

6. The method of any one of the previous claims, wherein palladium is present in ionic and/or ionogenic form and wherein said fluid is mixed with said chemical substances selected from the group comprised of reducing agents, sulfur compounds, selenium compounds and tellurium compounds.

7. The method of claim 6, wherein said chemical substances are selected from the group comprised of boron hydrides, amine boranes, hypophosphites, inorganic sulfides and organic thio compounds.

8. The method of claim 7, wherein palladium is present in colloidal form and wherein said chemical substances are pH adjusting agents that are mixed with said fluid in such a manner that solution pH ranges from 3 to 12.

9. The method of any one of claims 6-8, comprising the following method steps:

   a. said work pieces are contacted with a palladium containing processing fluid,
   b. then, said processing fluid adhering to the surfaces of said work pieces is removed with rinsing fluid, and
   c. said processing fluid and/or said rinsing fluid are passed through said at least one ceramic membrane filter for filtration thereof, the fluid being passed through said at least one ceramic membrane filter being a permeate fluid and the fluid that has not passed through said at least one ceramic membrane filter being a concentrate fluid.

10. The method of claim 9, wherein said processing fluid and/or said rinsing fluid are mixed with said chemical substances prior to being conducted through said at least one ceramic membrane filter.

11. The method of any one of claims 9 and 10, wherein a rinsing fluid containing a maximum of 5 percent by volume of said processing fluid is conducted through said at least one ceramic membrane filter.

12. The method of claim 11, wherein said work pieces are contacted per unit of time with a predetermined quantity of fresh rinsing fluid and wherein the quantity of said permeate fluid formed per unit of time approximately equals the quantity of the rinsing fluid contacted with said work pieces per unit of time.

## Patentansprüche

1. Verfahren zum Beschichten von Werkstücken mit einer Flüssigkeit, wobei die Flüssigkeit Palladium enthält und wobei das Verfahren umfasst: In-Kontakt-Bringen der Werkstücke mit der Flüssigkeit, danach Mischen der Flüssigkeit mit chemischen Substanzen, die ausgewählt sind aus der Gruppe, umfassend pH-Einstellmittel, Reduktionsmittel, Schwefelverbindungen, Selenverbindungen und Tellurverbindungen, und danach Filtrieren der Flüssigkeit durch mindestens einen Keramikmembran-Filter, um das Palladium von der Flüssigkeit zu trennen, wobei der Keramikmembran-Filter eine Ausschlussporengröße von über 10 000 Dalton hat und wobei die chemischen Substanzen so ausgewählt sind, dass Palladiumteilchen gebildet werden, deren Teilchengröße so groß ist, dass die Teilchen durch die Poren des mindestens einen Keramikmembran-Filters nicht passieren können.

2. Verfahren nach Anspruch 1, wobei der mindestens eine Keramikmembran-Filter eine Ausschlussporengröße im Bereich von ungefähr 15 000 Dalton bis ungefähr 25 000 Dalton hat.

3. Verfahren nach Anspruch 2, wobei der mindestens eine Keramikmembran-Filter eine Ausschlussporengröße von ungefähr 20 000 Dalton hat.

4. Verfahren nach einem der vorstehenden Ansprüche, wobei der mindestens eine Keramikmembran-Filter aus einem Aluminiumoxid/Titandioxid/Zirkondioxid-Keramikmaterial hergestellt ist.

5. Verfahren nach einem der vorstehenden Ansprüche, wobei die Werkstücke zur Herstellung von elektrischen Schaltungsträgern geeignet sind.

6. Verfahren nach einem der vorstehenden Ansprüche, wobei Palladium in ionischer und/oder ionogener Form vorliegt und wobei die Flüssigkeit mit den chemischen Substanzen, die ausgewählt sind aus der Gruppe, umfassend Reduktionsmittel, Schwefelverbindungen, Selenverbindungen und Tellurverbindungen, gemischt wird.

7. Verfahren nach Anspruch 6, wobei die chemischen Substanzen ausgewählt sind aus der Gruppe, umfassend Borhydride, Aminborane, Hypophosphite, anorganische Sulfide und organische Thioverbindungen.

8. Verfahren nach Anspruch 7, wobei Palladium in kolloidaler Form vorliegt und wobei die chemischen Substanzen pH-Einstellmittel sind, die mit der Flüssigkeit in einer Art und Weise gemischt werden, dass der pH-Wert der Flüssigkeit im Bereich von 3 bis 12 liegt.

9. Verfahren nach einem der Ansprüche 6-8, umfassend die folgenden Verfahrensschritte:

   a. die Werkstücke werden mit einer Palladium enthaltenden Behandlungsflüssigkeit in Kontakt gebracht,
   b. dann wird die an den Oberflächen der Werkstücke anhaftende Behandlungsflüssigkeit mit einer Spülflüssigkeit entfernt, und
   c. die Behandlungsflüssigkeit und/oder die Spülflüssigkeit werden durch den mindestens einen Keramikmembran-Filter zu deren Filtration geleitet, wobei die Flüssigkeit, die den mindestens einen Keramikmembran-Filter passiert hat, eine Permeatflüssigkeit ist und die Flüssigkeit, die den mindestens einen Keramikmembran-Filter nicht passiert hat, eine Konzentratflüssigkeit ist.

10. Verfahren nach Anspruch 9, wobei die Behandlungsflüssigkeit und/oder Spülflüssigkeit mit den chemischen Substanzen gemischt wird, bevor sie durch den mindestens einen Keramikmembran-Filter geleitet wird.

11. Verfahren nach einem der Ansprüche 9 und 10, wobei eine Spülflüssigkeit, die höchstens 5 Vol.-% der Behandlungsflüssigkeit enthält, durch den mindestens einen Keramikmembran-Filter geleitet wird.

12. Verfahren nach Anspruch 11, wobei die Werkstücke pro Zeiteinheit mit einer vorbestimmten Menge von frischer Spülflüssigkeit in Kontakt gebracht werden und wobei die Menge der pro Zeiteinheit gebildeten Permeatflüssigkeit ungefähr zur Menge der Spülflüssigkeit gleich ist, die pro Zeiteinheit mit den Werkstücken in Kontakt gebracht wird.

## Revendications

1. Procédé de placage de pièces de fabrication avec un fluide, ledit fluide contenant du palladium, ledit procédé

consistant en outre à mettre en contact lesdites pièces de fabrication avec ledit fluide, à mélanger ensuite ledit fluide avec des substances chimiques choisies dans le groupe comprenant les correcteurs de pH, les agents réducteurs, les composés de soufre, les composés de sélénium et les composés de tellure, et à filtrer ensuite ledit fluide à travers au moins un filtre à membrane céramique pour séparer le palladium dudit fluide, dans lequel ledit filtre à membrane céramique possède des pores d'exclusion ayant une dimension supérieure à 10 000 Daltons, les substances chimiques étant choisies de telle sorte que les particules de palladium soient formées avec une dimension telle que les particules ne puissent pas passer à travers les pores de l'au moins un filtre à membrane céramique.

**2.** Procédé selon la revendication 1, dans lequel ledit au moins un filtre à membrane céramique possède des pores d'exclusion ayant une dimension allant d'environ 15 000 Daltons à environ 25 000 Daltons.

**3.** Procédé selon la revendication 2, dans lequel ledit au moins un filtre à membrane céramique possède des pores d'exclusion ayant une dimension d'environ 20 000 Daltons.

**4.** Procédé selon l'une quelconque des revendications précédentes, dans lequel l'au moins un filtre à membrane céramique est fabriqué à partir d'un matériau céramique à l'oxyde d'aluminium/dioxyde de titane/dioxyde de zirconium.

**5.** Procédé selon l'une quelconque des revendications précédentes, dans lequel lesdites pièces de fabrication sont adaptées à la fabrication de supports de circuits électriques.

**6.** Procédé selon l'une quelconque des revendications précédentes, dans lequel du palladium est présent sous forme ionique et/ou ionogénique et dans lequel ledit fluide est mélangé auxdites substances chimiques choisies dans le groupe comprenant les agents réducteurs, les composés de soufre, les composés de sélénium et les composés de tellure.

**7.** Procédé selon la revendication 6, dans lequel lesdites substances chimiques sont choisies dans le groupe comprenant les hydrides de bore, les amine-boranes, les hypophosphites, les sulfides inorganiques et les composés thio-organiques.

**8.** Procédé selon la revendication 7, dans lequel du palladium est présent sous forme colloïdale et dans lequel lesdites substances chimiques sont des correcteurs de pH qui sont mélangés audit fluide de telle manière que le pH de la solution aille de 3 à 12.

**9.** Procédé selon l'une quelconque des revendications 6 à 8, comprenant les étapes de procédé suivantes :

a. lesdites pièces de fabrication sont en contact avec un fluide de traitement contenant du palladium,
b. ensuite, ledit fluide de traitement adhérant aux surfaces desdites pièces de fabrication est éliminé avec du fluide de rinçage, et
c. ledit fluide de traitement et/ou ledit fluide de rinçage sont passés à travers ledit au moins un filtre à membrane céramique pour filtration, le fluide étant passé à travers ledit au moins un filtre à membrane céramique étant un fluide pénétrant et le fluide n'étant pas passé à travers ledit au moins un filtre à membrane céramique étant un fluide concentré.

**10.** Procédé selon la revendication 9, dans lequel ledit fluide de traitement et/ou ledit fluide de rinçage sont mélangés avec lesdites substances chimiques avant d'être conduits à travers ledit au moins un filtre à membrane céramique.

**11.** Procédé selon l'une quelconque des revendications 9 et 10, dans lequel un fluide de rinçage contenant un maximum de 5 % en volume dudit fluide de traitement est conduit à travers ledit au moins un filtre à membrane céramique.

**12.** Procédé selon la revendication 11, dans lequel lesdites pièces de fabrication sont en contact par unité de temps avec une quantité prédéterminée de fluide de rinçage frais et dans lequel la quantité dudit fluide pénétrant formée par unité de temps est approximativement égale à la quantité de fluide de rinçage en contact avec lesdites pièces de fabrication par unité de temps.

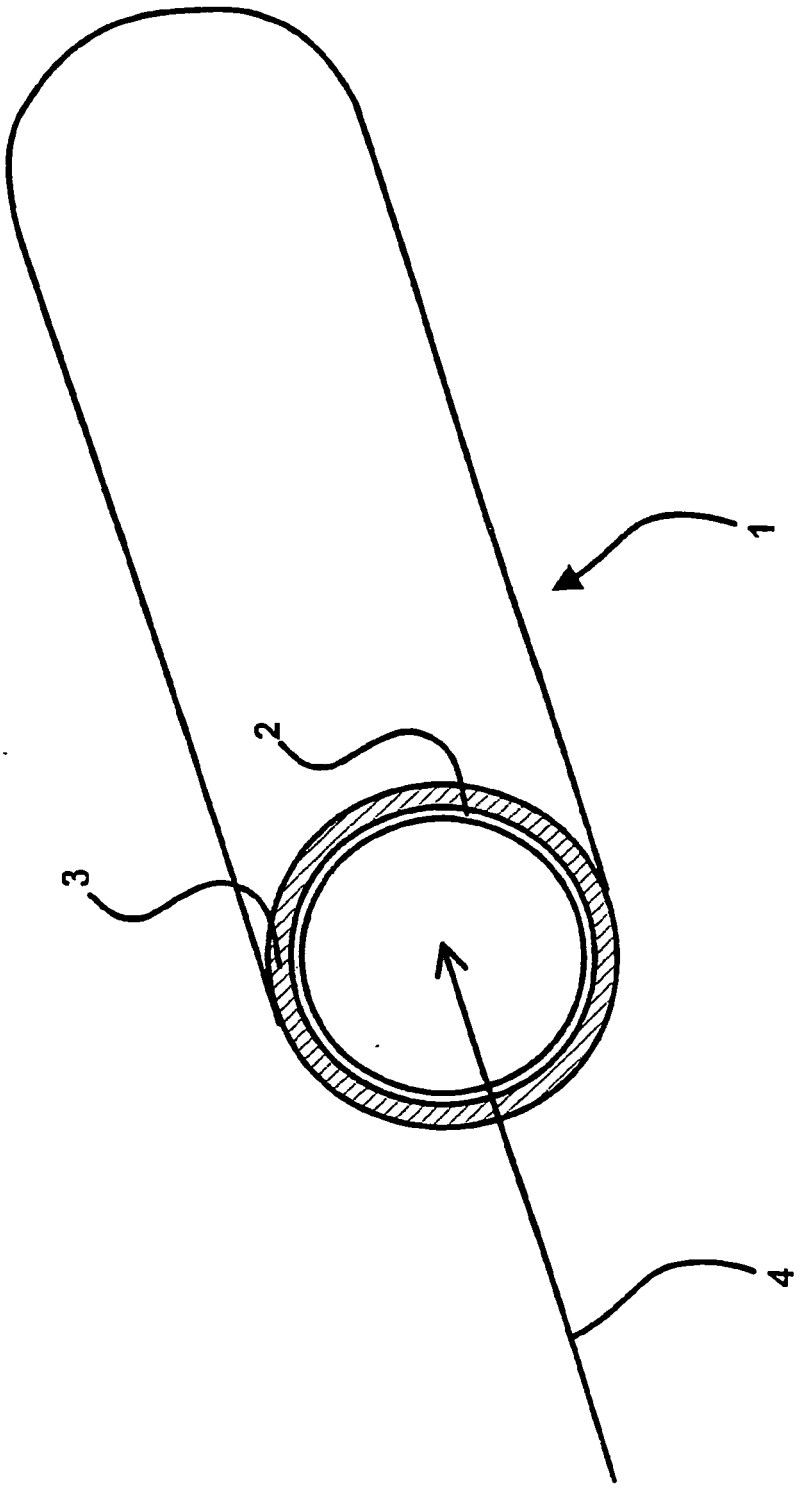



Fig. 1

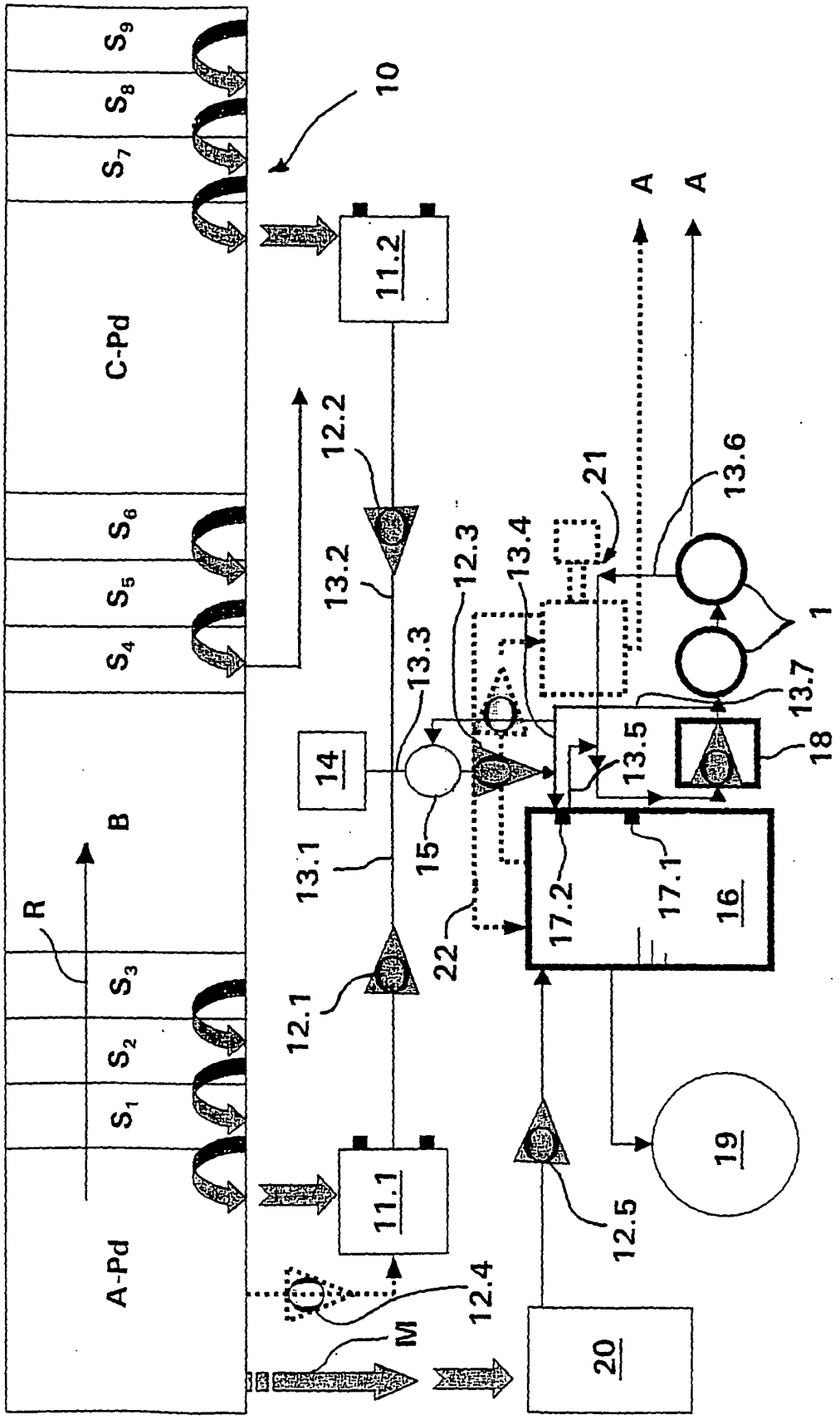

A-Pd
C-Pd
B
R
S1
S2
S3
S4
S5
S6
S7
S8
S9
10
11.1
11.2
12.1
12.2
12.3
12.4
12.5
13.1
13.2
13.3
13.4
13.5
13.6
13.7
14
15
16
17.1
17.2
18
19
20
21
22
1
A
A
M

Fig. 2

## REFERENCES CITED IN THE DESCRIPTION

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