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(71) Applicant (for all designated States except US): **COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH** [IN/IN]; Rafi Marg, 110 001 New Delhi (IN).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **BORICHA, Arvindkumar, Balvantrai** [IN/IN]; Central Salt and Marine Research Institute, Bhavnagar, 364 002 Gujarat (IN). **BAJAJ, Hari, Chand** [IN/IN]; Central Salt and Marine Research Institute, Bhavnagar, 364 002 Gujarat (IN). **JASRA, Raksh, Vir** [IN/IN]; Central Salt and Marine Research Institute, Bhavnagar, 364 002 Gujarat (IN). **GHOSH, Pradyut** [IN/IN]; Central Salt and Marine Research Institute, Bhavnagar, 364 002 Gujarat (IN). **GHOSH, Pushipito, Kumar** [IN/IN]; Central Salt and Marine Research Institute, Bhavnagar, 364 002 Gujarat (IN).

(74) Agent: **GABRIEL, Devadoss, Calab**; K & S Partners, 84-C C6 Lane, Off Central Avenue, Sainik Farms, 110 062 New Delhi (IN).

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(54) Title: A PROCESS FOR THE RECOVERY OF ADSORBED PALLADIUM FROM SPENT SILICA

(57) Abstract: The present invention relates to a process for the recovery of precious metals from spent catalysts or adsorbent or inorganic waste. More specifically a process is provided for the recovery of palladium from silica, which is used as an adsorbent in column chromatography or as a catalyst support in many catalysts. The process includes burning the spent silica to oxidize the organic component of the adsorbed Pd-complex, digesting the cooled residue with a mineral acid, filtering the obtained solution to separate out silica residue, adjusting the pH of the filtrate to remove precipitate impurities and raising the pH of the purified filtrate to recover a palladium salt.

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## A PROCESS FOR THE RECOVERY OF ADSORBED PALLADIUM FROM SPENT SILICA

**TECHNICAL FIELD**

The present invention relates to the recovery of precious metals from spent  
5 catalysts or adsorbent or inorganic waste, specifically the process concerns with the  
recovery of Pd from silica, which is used as an adsorbent in column chromatography or  
as a catalyst support in many catalysts.

**BACKGROUND ART**

Precious transition metal irons and their coordination complexes find industrial  
10 applications as supported catalysts and performance chemicals in fine chemicals  
industries. For example, metals like Ag, Au, Pd, Pt and Rh are used in a variety of  
industrial applications as catalysts for oxidation, hydrogenation and dehydrogenation  
reactions. Various polymeric materials modified silica, zeolite or/and various clay  
materials are used as support for these metals. Similarly, coordination metal complexes  
15 of Pd, Pt and Rh are used as commercial catalysts in homogeneous conditions for  
hydroformylation and hydrogenation reaction. However, owing to difficulties in  
separation of metal complexes from product mixtures, there is growing need to  
developed heterogenized catalysts where coordination metal complexes are supported on  
polymeric or inorganic solid support like silica, carbon, zeolite and alumina.  
20 Commercially, it is important to recover the precious metals from the support to the  
maximum extent possible once the catalyst is deactivated.

In certain situations, the catalysts are degraded during the reaction cycle or  
subsequent work-up and the reaction effluent may comprise of various remnants, e.g.,  
complexes of various valence states for the metal ions. In many cases, the presence of  
25 excessive contaminants reduces the feasibility of recycling of the catalyst. However, the  
problem related to degradation of catalysts over the repeated cycles, contaminants over  
the repeated cycles, contaminants arise from side reaction and leaching of the effective  
catalyst for the solid support are common in some cases of heterogeneous catalysis. In  
view of the environmentally stipulated restrictions on disposal of metal containing waste,  
30 effective recovery of the residual precious metals from the reaction effluent is of  
paramount importance for a process to be environmentally acceptable and economically  
viable.

Furthermore, during the recovery of precious metals from ore or scrap including  
spent catalysts, the use of solvent extraction to separate the precious metals from one

another and from base metals that may also be present is becoming more widespread. The hydrometallurgical processes employed for the separation and recovery of the platinum group metals, (e.g., platinum, palladium and rhodium), typically involve dissolving the metal ions by some type of oxidative acidic chloride leach, typically with  
5 aqua regia or hydrochloric acid/ $\text{Cl}_2$  followed by solvent extraction.

The application of coordination complexes of precious metals in fine chemicals industries also requires prior purification of these complexes using silica gel as a stationary phase. For example Pd-pythalocyanine complexes namely Palladium phthalocyanine complex, Bromo phthalocyanine complex and Irgaphor green, which find  
10 applications as pigment material for compact disc coating are purified using silica gel.

Significant quantity of these complexes (up to 0.5 wt % Pd) is adsorbed in the pores of silica gel and is difficult to dislodge from the pores of silica (spent silica) by conventional elution with a solvent. Many technologies, at times specific to support and metal are used for recovery of precious metals from spent catalysts, effluent solutions.

15 Reference is made to the patent (Great Britain Patent no. A-2127001, 1984) wherein precious metals are recovered rapidly and efficiently from cyanide containing leach solution by loading onto an activated carbon fibre body. The main limitation of the process is that cyanide ligand should have high affinity and should form stable complexes with the metal ions to be leached out.

20 Reference is made to the patent CS-B-251467 (1988); Chemical Abstract 109 (24): 213964) wherein palladium is recovered from acidified wastewater by sorption on activated carbon, pre-treated with an alkali metal salt of Ethylene diamine tetra acetic acid (EDTA). However, this is useful for homogenous aqueous catalyst waste and is not directly applicable to non-aqueous systems.

25 Reference is made to the patent JP 54 9597 (1978) wherein, the regeneration and recovery of precious metal like palladium involves a burning step. It is disclosed in that patent, that the spent residue obtained from a catalyzed reaction performed in homogeneous condition is subjected to heating to burn out the organic fragment and then by subsequent dissolution of the palladium species in acid to the corresponding  
30 palladium salt. However, this invention has a limited scope in the sense that it is only concerned with degradation of metal complex having lower aliphatic mono-carboxylic acids as the organic moiety.

Reference is made to the US Patent 4, 331, 634 (1982) wherein strongly acidic solution of sulfuric, hydrochloric, perchloric or nitric acid is used as stripping solvent for

the extraction of the palladium from the organic acidic solution containing oxime as extracting reagent. The organic phase may also contain an anionic phase transfer material or catalyst to aid the extraction process. In this patent, the oximes employed for the extraction of palladium are hydroxyoxime and derivatives, which are expensive  
5 considering the industrial application.

Reference is also made to the US Patent 4, 578, 250 (1986) wherein aqueous ammonia is used as the stripping solution and along with oxime as an extracting solvent similar to those of the U.S. Patent No. 4,331, 634 (1982) but here oxime used is ether oxime, in which, the hydroxy group of the oximes are converted to ether groups. In this,  
10 case also, the oximes employed for the extraction of palladium is expensive and not user friendly considering the industrial application. Furthermore, it is reported that after recycling certain oxime containing solvents over a period of time (e.g., ten extractions of palladium followed each time by stripping with 6M hydrochloric acid solution), the rate of palladium extraction deteriorates considerably.

Reference is made to the JP Patent 61-238, 927 (1996) wherein palladium is recovered by extraction using an aldoxime. The main limitation of these processes is the use of expensive organic ligands and organic solvents, which are difficult to recover.  
15

Y. Baba, K. Inoue, K. Yoshizuka and T Furusawa, (Industrial engineering Chemistry - Research, Volume 29, (1990), page 21111) have described the use of non-  
20 chelating oximes such as dodecanal oxime, decanal, oxime, octanal oxime and hexanol oxime for the extraction of palladium metal. This report also has drawback in the sense that the oximes employed for the extraction are expensive considering the industrial application.

In exchange resins can also be used to recover precious metal ions, but it is difficult to achieve 100% metal recovery in this method and all precious metals are not also not present in the ionic state or too much of contaminants is present in the effluents to be treated.  
25

According to the above prior art, most of the metal recovery methods are applicable to the homogeneous reaction mixtures and employs chelating agents for extracting metal ions. Process known in the prior art for recovery of metals from supported catalysts also makes use of mineral acids and invariably destroyed the support structure.  
30

## OBJECTS OF THE INVENTION

The main object of the present invention is to provide a process for the recovery of palladium from spent silica, which obviates the drawbacks as detailed above.

Another objective of the present invention is to provide a process for the recovery of precious metals or their complexes supported on solid support as in adsorbent / catalysts, specially palladium from spent silica wherein palladium is present as a mixture of palladium phthalocyanine complexes adsorbed on silica gel.

Yet another objective of the present invention is to provide a process for enabling 100% recovery of palladium with more than 99% purity.

Yet, another objective of the present invention is to recover phthalocyanine from silica along with Pd metal.

Yet another objective of the present invention to provide a process wherein silica is recovered as a value added product that can be reused.

## SUMMARY OF THE PRESENT INVENTION

Accordingly, the present invention provides a process for the recovery of precious metals from spent catalysts or adsorbent or inorganic waste, specifically the process concerns with the recovery of Pd from silica, which is used as an adsorbent in column chromatography or as a catalyst support in many catalysts.

## DESCRIPTION OF THE INVENTION

Accordingly, the present invention provides a process for the recovery of palladium as its salt from palladium complex adsorbed on spent silica gel, said process comprising:

- a) burning the spent silica gel with palladium complex adsorbed on its surface, in a furnace in the temperature range of 300-700 °C in presence of air for a period ranging between 2 and 8 hours to oxidize the organic compound in the complex;
- b) cooling the burnt residue of step (a), digesting with a mineral acid at a temperature range of 70-100 °C for a time period of 1-6 hours;

- c) cooling the solution of step (b) to an ambient temperature;
- d) filtering the cooled solution of step (c) to obtain a filtrate and a residue;
- e) washing the residue of step (d) with a mineral acid and drying at 60 – 100 °C to recover silica;
- 5 f) adjusting the pH of the filtrate of step (d) to obtain a precipitate, filtering to remove the precipitate; and
- g) further raising the pH of the filtrate obtained in step (f) to obtain a palladium salt

In an embodiment, the invention provides a process, wherein the complex is burnt  
10 in order to oxidize the organic compound, preferably in the temperature range of 350-450 °C and more preferably in the range of 350-400 °C.

Another embodiment, the concentration of mineral acid used is in the range of 2-3 molar hydrochloric acid.

Still another embodiment, the original structural properties, namely surface area  
15 and pore volumes are maintained in the recovered silica and is reusable.

Still another embodiment, the concentration of the mineral acid used to wash the residue is about 0.5 M.

Yet another embodiment, the pH of the filtrate in step (e) is adjusted to about 6.0.

Yet another embodiment, the pH of the filtrate in step (e) is adjusted in the range of  
20 8.5-9.3 and preferably 9.3.

Yet another embodiment, purity of palladium recovered in the said process is about 97-100% and the percentage yield of the palladium salt recovered in step (d) is in the range of about 95-100%.

One more embodiment of the present invention provides a process for the recovery  
25 of palladium as its salt from palladium phthalocyanine complex adsorbed on spent silica gel, the said process comprising:

- a) treating spent silica containing organic material with hydrofluoric acid;
- b) filtering the solution of step (a) to obtain a solution containing  $H_2SiF_6$  and suspended palladium phthalocyanine complex;
- 30 c) recovering palladium phthalocyanine complex of step (b) by gravity separation, digesting it by refluxing with an aqueous mineral acid for a time period of 2-4 hours;
- d) filtering the digested mixture of step (c) to remove phthalocyanine to obtain aqueous acidic filtrate solution;

e) recovering palladium as its salt of the mineral acid by evaporation of the aqueous acidic filtrate solution of step (d); and

f) recovering phthalocyanine ligands by solvent extraction.

Another embodiment of the invention relates to the concentration of mineral acid used in step (c), which is in the range of 2-3 molar hydrochloric acid.

Still another embodiment, the concentration of the mineral acid used in step (e) is 5-10 molar hydrochloric acid.

Still another embodiment, the preferable solvent used for extracting the phthalocyanine ligand is chloroform and is reusable.

Yet another embodiment, the spent silica is recovered as a value added product namely  $\text{H}_2\text{SiF}_6$ .

The present invention provides a process for the 95 - 100 % recovery with 97 - 100 % purity of palladium as palladium chloride from spent silica wherein organic moiety is fully or partially oxidized by heat treatment at 350 - 450<sup>0</sup>C in air for 3 - 5 hours followed by noble metals recovery as metal salt by its digestion with mineral acid like hydrochloric, sulfuric and nitric acid in the range 2 - 6 molar aqueous solution at 70 - 90<sup>0</sup>C under constant stirring for 4 - 6 hours; cooling to ambient temperature and filtration and washing to recover silica and further recovery and purification of palladium metal from filtrate and precipitation of the metal salt at different pH in the range of 6 to 9.5 and washing and drying of recovered silica in oven form 80 to 110<sup>0</sup>C alternatively process wherein the spent silica is treated with hydrofluoric acid to dissolve silica to form  $\text{H}_2\text{SiF}_6$  and recovery of palladium phthalocyanine complexes by filtration followed by extraction of palladium by digestion with 2 molar aqueous hydrochloric acid and further recovery and purification of palladium metal from filtrate by precipitation of the metal salt at different pH in the range of 6 to 9.5 and recovering phthalocyanine ligands by solvent extraction using chloroform as solvent.

In an embodiment of the present invention spent silica-containing palladium is in the range 0.1 to 0.5 wt % may be calcined in air in the temperature range 350 to 450<sup>0</sup>C for 4 - 6 hours.

In an embodiment of the present invention, calcined silica may be refluxed with 2-6 molar aqueous hydrochloric acid solution for 4 - 6 hours to leach out palladium.

In an embodiment of the present invention, silica is filtered and the pH of the filtrate may be maintained in the range 9.5 to 10.5 to precipitate palladium as palladium chloride.

In an embodiment of the present invention, silica may be dissolved in 40 % hydrofluoric acid under stirring as  $\text{H}_2\text{SiF}_6$  whereas palladium phthalocyanine complex, which is insoluble in hydrofluoric acid, is recovered by filtration.

In an embodiment of the present invention, suspended Pd-complex may be recovered by solvent extraction process using organic solvent like chloroform and dichloromethane.

In an embodiment of the present invention, the extracted palladium phthalocyanine complex may be de-metallated using aqueous hydrochloric acid under reflux conditions. Subsequently, phthalocyanine ligands were recovered by solvent extraction using organic solvents like chloroform and dichloromethane, and palladium was recovered as palladium chloride from aqueous phase by precipitation.

In an embodiment of the present invention phthalocyanine fragments remaining in organic phase may be recovered by distillation.

In an embodiment of the present invention, chloroform and dichloromethane used may also be recovered in the process by distillation.

In the process invented, spent silica is thermally treated in air to partially burn the organic moiety of the palladium phthalocyanine complex followed by palladium extraction by acid digestion and purification by judiciously adjusting the pH of filtrate obtained. Recovered silica retains its structure and can be re-used. Analysis of Pd in the silica and after its recovery was done by ICP - Inductively Coupled Plasma Emission Spectrometer (ICP-spectrometer) and Spectrophotometrically as  $[\text{PdI}_4]^{2-}$  complex.

Palladium is estimated, in acidic aqueous solution as brown-red complex,  $[\text{PdI}_4]^{2-}$ . In an acid medium (hydrochloric acid,  $\text{H}_2\text{SO}_4$ ) containing excess of iodide, palladium forms a brown-red complex,  $[\text{PdI}_4]^{2-}$ . The molar absorptivity of the complex is  $1.02 \times 10^4$  at  $\lambda_{\text{max}} = 410 \text{ nm}$  ( $a=0.096$ ). A calibration curve is obtained by preparing a palladium iodide complex solution by dissolving the known amounts of palladium chloride and other reagent, like concentrated hydrochloric acid, ascorbic acid and potassium iodide. The detailed procedure is as follow:

Accurately measured volume / weight of the sample solution / solid containing (2 w/v) not more than 1 mg of Pd was taken in a 100 ml volumetric flask. To this was added 10 ml of 6N hydrochloric acid, 20 ml of 20 % (w/v) potassium iodide solution and 4 ml of 1% (w/v) ascorbic acid solution. The volume was made up to 100 ml with water in a 100 ml volumetric flask and absorbance 410 nm, against water was measured



Wt of Palladium in the diluted solution can be obtained as:

Weight of Pd % 100 ml =  $(A/E)$ . (Mol. Wt of Palladium)

**A = Absorbance of the 100 ml solution at 410 nm**

**E = Extinction coefficient,  $1.02 E^4 \text{ cm}^{-1}$  for species at 410 nm**

5

Palladium has also be estimated spectrophotometrically using inductively coupled plasma emission spectrometer (ICP - This is most accurate method of estimation of metals ions at PPM / ppb levels. A calibration curve was obtained, by dissolving a known amount of palladium chloride in hydrochloric acid and recording its intensity on ICP spectrometer for palladium at 340.458 nm, using Perkin Elmer's Inductively Coupled Plasma Emission Spectrometer.

- 15
- a) Thermal treatment of spent silica at an appropriate temperature such that organic moiety is only partially oxidized without the formation of metal oxide. Scientifically speaking, during thermal treatment, palladium phthalocyanine complex, which is trapped in the pores of silica, is disrobed and organically rich phthalocyanine moiety is partially oxidized to volatile compounds. Partially oxidized palladium complex gets deposited on the external surface of silica and can easily react with mineral acid used for digestion. The major inventive step involved in the present invention is selectively partially oxidizing palladium phthalocyanine complex so that it does not form palladium oxide, which is difficult to react with mineral acid under normal processing conditions.
- 20
- b) Recovery of pure palladium with 99 - 100 % purity and 95 - 100 % recovery as palladium chloride by judiciously adjusting the pH of the aqueous solution and thereby removing the impurities namely iron, zinc, nickel and silica.
- 25
- c) Recovery of pure palladium without resorting to the use expensive and hazardous organic solvent and complexing ligands.
- 30
- d) Recovery of pure palladium without destroying structure of the inorganic support namely silica in the present case.

The following examples are given by way of illustration and therefore should not be constructed to limit the scope of the present invention.

### Example 1

500 g of spent silica, wherein palladium is present as a mixture of palladium phthalocyanine complexes adsorbed on silica gel, was taken in a china dish and kept at 400<sup>0</sup>C in a muffle furnace in air atmosphere for three hour and than allowed to cool to ambient temperature. 1000 ml 2M aqueous hydrochloric acid solution was taken in a 5 liters round bottom flask equipped with heating mantle and thermocouple to heat the content of the round bottom flask at constant temperature. To this was added above treated silica and the whole content of the round bottom flask at constant temperature. To this was added above treated silica and the whole content was refluxed at 90<sup>0</sup>C for five hours. It was filtered with Buckner funnel after cooling to ambient temperature followed by washing with 0.5M aqueous hydrochloric acid and then dried at 100<sup>0</sup>C in an oven. The pH of the filtrate, which contained palladium, was raised to 6 and precipitate formed filtered to remove impurity especially of silica, iron and other metals. The precipitates were collected and dried. The pH of the filtrate obtained at pH 6 was raised to 9.3 and precipitate collected and dried.

The precipitates obtained at pH 6 and 9.3 were analyzed for palladium content. 0.745 g, of the precipitate was obtained at pH 6, which contains no palladium. 0.228g of precipitate collected at pH 9.3 contains 98.67% palladium determine spectrophotometrically. The total palladium content adsorbed on the silica, estimably separately using known procedure of repeatedly treating with aqua regia and hydrochloric acid finally estimating Pd by ICP spectrometry) was 0.23 g showing 99 - 100 % recovery by above process.

### Example 2

500 g of spent silica was taken in a china dish and kept at 700<sup>0</sup> C in a muffle furnace in air atmosphere for three hour and than allowed to cool to ambient temperature. 1000 ml 2 M aqueous HCl solution was taken in a 5 liters round bottom flask equipped with heating mantle and thermocouple to heat the content of the round bottom flask at constant temperature. To this was added above treated silica and the whole content was refluxed at 90<sup>0</sup> C for five hours. It was filtered with Buckner funnel after cooling to ambient temperature followed by washing with 0.5-M aqueous hydrochloric acid solution. Silica was dried at 100<sup>0</sup>C in an oven. The pH of the filtrate, which contained palladium, was raised to 6 and precipitate formed filtered to remove impurity especially of silica, iron and other metals. The precipitates were collected and dried. The pH of the filtrate obtained at pH 6 was raised to 9.3 and precipitate collected and dried.

The precipitated obtained at pH 6 and 9.3 were analyzed for palladium content. 0.745 g, of the precipitate was obtained at pH 6 contains nil palladium, 0.226 g of precipitate collected at pH 9.3 also contains nil palladium and 0.25 g of the precipitate collected at pH 11 also contains nil palladium as determined spectrophotometrically.

5

### Example 3

The above experiment was repeated except that the silica was calcined at 300°C. There was nil recovery of palladium from precipitates obtained after adjusting pH at different value of 6, 9 and 11 of the filtrate obtained after acid digestion.

### Example 4

10 500 g silica waste was calcined at 400°C in a muffle furnace in air atmosphere for three hours. After cooling the sample to ambient temperature, it was digested with 1000 ml 2M aqueous hydrochloric acid solution. Filtered and washed the content to remove silica and finally filtrated was evaporated it to dryness on water bath / hot place to get solid mass. It gave 2.07 g inorganic solid, which contained 122.5 mg of palladium chloride.

15

### Example 5

500 g silica waste was calcined at 400°C in a muffle furnace in air atmosphere for three hours and after that it was digested with 1000 ml aqua regia (750 ml concentrated hydrochloric and 250 ml concentrated nitric acid). The content was filtered and pH of the filtrated was adjusted to 6 and filtered again. It gave 208 mg brown colored solid with nil PdCl<sub>2</sub> content. The pH of the filtered was raised to 9.5 and again filtered. It gave 740 mg solid, again with nil palladium in it.

20

### Example 6

100 g silica wastes, as such was treated with 100 ml aqua regia ( 75 ml concentrated hydrochloric acid and 25 ml concentrated nitric acid) and mixture kept for 3- 4 hours, then decanted and the filtrate was analyzed for Pd spectrophotometrically. It gave no test for palladium.

25

### Example 7

770 g of spent silica (crude deep green in colour) was added to 3500 g HF (40 %) and stirred by magnetic stirrer. SiO<sub>2</sub> dissolves in HF solution as H<sub>2</sub>SiF<sub>6</sub> and palladium phthalocyanine complex, being insoluble in aqueous HF media remains suspended. Palladium phthalocyanine complex (1.950 g) was recovered from aqueous HF media by gravity filtrations and washed with water. Finally, it was extracted with chloroform. Chloroform was removed on rotaevaporater. It gave 1.95 g of green color palladium phthalocyanine complex.

30

**Example 8**

100 g spent silica (crude deep green in color) was added to 500 g HF (40 %) and stirred by magnetic stirrer. SiO<sub>2</sub> dissolve in HF solution as H<sub>2</sub>SiF<sub>6</sub> and palladium phthalocyanine complex, being insoluble in aqueous HF media remain suspended.

5 Palladium phthalocyanine complex (200 mg) was recovered from aqueous HF media by gravity filtration and washed with water and dried. Palladium phthalocyanine complex so recovered was refluxed with 100 ml 2 M hydrochloric acid for 2 hours, than it was filtered to remove phthalocyanine. Palladium was recovered as PdCl<sub>2</sub> (39 mg) by evaporation of aqueous acidic solution.

10

**Example 9**

500 g of spent silica was taken in a china dish and kept at 400<sup>0</sup> C in a muffle furnace in air atmosphere for three hours and then allowed to cool to ambient temperature. 1000 ml 2M aq. HCl solution was taken in a 5 liters round bottom flask equipped with heating mantle and thermocouple to heat the content of the round bottom

15 flask at constant temperature.

To this was added above treated silica and the whole content was refluxed at 90°C for five hours. It was filtered with Buckner funnel after cooling to ambient temperature followed by washing with 0.5-M aqueous HCl solution. Silica was dried at 100°C in an oven. Recovered silica following heat treatment and acid digestion showed no difference

20 in XRD, IR and surface area with respect to original silica.

**Example 10**

10 kg calcimined spend silica, calcination was done in indirect fixed calciner, which can calcine the material at 400 to 700<sup>0</sup> C in a continuous process at 2 - 10 kg per hour rate depending upon the residence time was placed in a 50 - liters capacity round

25 bottom flask equipped with heating and stirring facilities. To this, were added 3.33 liters of concentrated hydrochloric acid and 16.5 liter of de-ionised water. The content of flask was refluxed at 90°C for 5 hours. After it cools down, it was filter off with Buckner funnel to remove silica and the filtrate was collected in a container. The silica was washed with de-ionized water and the washing was mixed with the filtrate. The pH of

30 the filtrate containing Palladium was adjusted to 6.0 with sodium hydroxide and it was filtered to remove non-palladium metal impurities. Again the pH of this filtrate is adjusted to 9.3 - 9.5 with sodium hydroxide solution, wherein palladium metal is precipitated as palladium chloride. This was filtered off and washed with de-ionised water till it is chloride free. The precipitate after washing are dried in oven night and

analyzed for palladium content. If required the sample can be further purified by re-dissolving the impure Pd containing sample in slightly warm 1M HCl solution and then adjusting its pH to 6.3 and filtering off the impurity (if any) and then finally precipitating the pure PdCl<sub>2</sub> at pH 9.3. By the above procedure, it gave 12.5 g-palladium chloride of 5 97- 99 % purity.

**The main advantages of the present invention include:**

- a) Thermal treatment of spent silica at reasonably lower temperature of less than 450<sup>0</sup>C.
- 10 b) Recovery of palladium with 99 - 100 % recovery as palladium chloride.
- c) Recovery of palladium without resorting to the use expensive and hazardous organic solvent and complexing ligands.
- d) Recovery of pure palladium without destroying structure of the inorganic support silica.
- 15 e) Possibility of recovering expensive phthalocyanine ligands as well as silica as a value added product.

**Claims**

- 1.) A process for the recovery of palladium as its salt from palladium complex adsorbed on spent silica gel, said process comprising steps of :
  - a) burning the spent silica gel with palladium complex adsorbed on its surface, in  
5 a furnace in the temperature range of 300-700 °C in presence of air for a period ranging between 2 and 8 hours to oxidize the organic compound in the complex;
  - b) cooling the burnt residue of step (a), digesting with a mineral acid at a temperature range of 70-100 °C for a time period of 1-6 hours;
  - 10 c) cooling the solution of step (b) to an ambient temperature;
  - d) filtering the cooled solution of step (c) to obtain a filtrate and a residue;
  - e) washing the residue of step (d) with a mineral acid and drying at 60 – 100 °C to recover silica;
  - f) adjusting the pH of the filtrate of step (d) to obtain a precipitate, filtering to  
15 remove the precipitate; and
  - g) further raising the pH of the filtrate obtained in step (f) to obtain a palladium salt.
- 2.) A process as claimed in claim 1, wherein in step (a), the palladium complex is burnt preferably in the temperature range of 350-450°C and more preferably in the  
20 range of 350–400°C.
- 3.) A process as claimed in claim 1, wherein in step (b) the concentration of mineral acid used is in the range of 2-3 molar hydrochloric acid.
- 4.) A process as claimed in claim 1, wherein in step (d), the original structural properties namely surface area and pore volumes are maintained in the recovered  
25 silica.
- 5.) A process as claimed in claim 1, wherein in step (d), the recovered silica is reusable.
- 6.) A process as claimed in claim 1, wherein in step (d), the mineral acid used to wash the residue is 0.5-M hydrochloric acid.
- 30 7.) A process as claimed in claim 1, wherein in step (d), the pH of the filtrate is adjusted to about 6.0.
- 8.) A process as claimed in claim 1, wherein in step (f), the pH of the filtrate is adjusted in the range of 8.5-9.3, preferably pH 9.3.

- 9.) A process as claimed in claim 1, wherein in step (g), the purity of palladium salt obtained is about 97-100%.
- 10.) A process as claimed in claim 1, wherein the percentage yield of the palladium salt recovered in step (d) is in the range of about 95-100%.
- 5 11.) A process for the recovery of palladium as its salt from palladium phthalocyanine complex adsorbed on spent silica gel, the said process comprising steps of:
- a) treating spent silica containing organic material with hydrofluoric acid;
  - b) filtering the solution of step (a) to obtain a solution containing  $H_2SiF_6$  and suspended palladium phthalocyanine complex;
  - 10 c) recovering palladium phthalocyanine complex of step (b) by gravity separation, digesting it by refluxing with an aqueous mineral acid for a time period of 2-4 hours;
  - d) filtering the digested mixture of step (c) to remove phthalocyanine to obtain aqueous acidic filtrate solution;
  - 15 e) recovering palladium as its salt of the mineral acid by evaporation of the aqueous acidic filtrate solution of step (d); and
  - f) recovering phthalocyanine ligands by solvent extraction.
- 12.) A process as claimed in claim 11, wherein in step (c) the concentration of mineral acid used is in the range of 2-3 molar hydrochloric acid.
- 20 13.) A process as claimed in claim 11, wherein in step (e) the mineral acid used is 5-10 molar hydrochloric acid.
- 14.) A process as claimed in claim 11, wherein in step (f) the solvent used is preferably chloroform.
- 15.) A process as claimed in claim 11, wherein in step (b) the spent silica is recovered  
25 as a value added product namely  $H_2SiF_6$ .
- 16.) A process as claimed in claim 11, wherein the solvent used in step (f) is reusable.

**AMENDED CLAIMS**

[received by the International Bureau on 12 February 2004 (12.02.04);  
original claims 1-16 replaced by new claims 1-12 (2 pages)]

- 1) A process for the recovery of palladium as its salt from spent silica gel having organic palladium complex adsorbed thereto, said process comprising steps:
  - a) burning the spent silica gel having organic palladium complex adsorbed thereto, in a furnace in the temperature range of 300-700 °C in presence of air for a period ranging between 2 and 8 hours to partially oxidize the organic compound in the complex without formation of metal oxide thereby to obtain a burnt residue;
  - b) cooling the burnt residue of step (a), digesting the same with a mineral acid at a temperature range of 70-100 °C for a time period of 1-6 hours to obtain a solution;
  - c) cooling the solution of step (b) to an ambient temperature;
  - d) filtering the cooled solution of step (c) to obtain a filtrate and a residue;
  - e) washing the residue of step (d) with a mineral acid and drying at 60 – 100 °C;
  - f) adjusting the pH of the filtrate of step (d) to obtain a precipitate, filtering to remove the precipitate; and
  - g) further raising the pH of the filtrate obtained in step (f) to obtain a palladium salt.
- 2.) A process as claimed in claim 1, wherein in step (a), the palladium complex is burnt in the temperature range of 350-450°C
- 3.) A process as claimed in claim 1 wherein in step (a), the palladium complex is burnt in the temperature range of 350–400°C.
- 4.) A process as claimed in claim 1, wherein in step (b) the concentration of mineral acid used is in the range of 2-3 molar hydrochloric acid.
- 5.) A process as claimed in claim 1, wherein in step (d), the mineral acid used to wash the residue is 0.5-M hydrochloric acid.
- 6.) A process as claimed in claim 1, wherein in step (f), the pH value of the filtrate is adjusted in the range of 8.5-9.3.
- 7.) A process as claimed in claim 1, wherein in step (f), the pH value of the filtrate is adjusted to pH 9.3.



- 8.) A process as claimed in claim 1, wherein in step (g), the purity of palladium salt obtained is about 97-100%.
- 9.) A process as claimed in claim 1, wherein the percentage yield of the palladium salt recovered in step (d) is in the range of about 95-100%.
- 10.) A process for the recovery of palladium as its salt from palladium phthalocyanine complex adsorbed on spent silica gel, the said process comprising steps of:
  - a) treating spent silica containing organic material with hydrofluoric acid;
  - b) filtering the solution of step (a) to obtain a solution containing  $H_2SiF_6$  and suspended palladium phthalocyanine complex;
  - c) recovering the suspended palladium phthalocyanine complex of step (b) by gravity separation, digesting it by refluxing with an aqueous mineral acid for a time period of 2-4 hours;
  - d) filtering the digested mixture of step (c) to remove phthalocyanine and obtain aqueous acidic filtrate solution, and
  - e) recovering palladium as its salt of the mineral acid by evaporation of the aqueous acidic filtrate solution of step (d).
- 11.) A process as claimed in claim 10, wherein in step (c) the concentration of mineral acid used is in the range of 2-3 molar hydrochloric acid.
- 12.) A process as claimed in claim 10, wherein in step (e) the mineral acid used is 5-10 molar hydrochloric acid.

**STATEMENT UNDER ARTICLE 19(1)**

Claim 1 has been revised to reflect that the process of the present invention is directed towards a process for recovering palladium from spent silica gel having organic palladium complex absorbed thereto. Step (a) of claim 1 has been further amended to indicate that the organic palladium complex is partially oxidized without formation of metal oxides which is a novel and inventive feature of the present invention.

**XP 002247763** which has been considered to destroy the novelty of the present invention teaches a process for recovery of Pd from Pd/Al<sub>2</sub>O<sub>3</sub> spent catalyst comprising the steps of calcining the catalyst to insolubilize Al<sub>2</sub>O<sub>3</sub>, treating the same with 1:1 HCl to obtain a solution, reducing the solution thus obtained with 80% hydrazine hydrate and filtering the reaction mixture to obtain Pd black. **XP 002247764** teaches a process similar to that described by XP 002247763 with the additional use of formic acid and H<sub>2</sub>O<sub>2</sub>. **XP 002247766** also teaches a process similar to that described by the above two documents which comprises ashing the catalyst, treating the same with HCl and sodium hypochlorite to obtain a sludge and boiling the sludge with nitric and hydrochloric acids. **XP 002247767** also teaches a process of treating the calcined catalyst with HCl along with a reducing agent. **XP 002247768** teaches a process which involves reducing steps such treatment with sodium formate or formaldehyde.

The process of the present invention on the other hand does not involve any reducing step and palladium is recovered by simple precipitation technique. Thus, the technique

adopted in the present process is entirely different from that being adopted in the aforesaid documents.

GB 1,578,123 teaches a process for preparation of a supported palladium catalyst and not recovery of Pd from spent catalyst.

In view of the above, it is respectfully submitted that the claims of the present invention are both novel and non-obvious over the cited document.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/IB 02/05198

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC 7 C22B11/00 C22B7/00 C22B3/06 C22B3/26 C01B33/14  
C01B33/10

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C22B C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal, PAJ, COMPENDEX

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Section Ch, Week 198430 Derwent Publications Ltd., London, GB; Class J04, AN 1984-186497 XP002247763 & RO 83 032 A (COMB INGRAS CHIM PI), 30 January 1984 (1984-01-30)	1, 3
Y	abstract ---	2, 4, 5
Y	US 3 947 543 A (THIEL REINHOLD ET AL) 30 March 1976 (1976-03-30) abstract; claims 1-3; example 2 ---	1-3, 5, 6, 9, 10
Y	GB 798 712 A (UNIVERSAL OIL PROD CO) 23 July 1958 (1958-07-23) page 1, line 53 - line 59; claim 2 --- -/--	2, 4, 5

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

° Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*&\* document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
16 September 2003	29. 10. 2003

Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer  Bombeke, M
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## INTERNATIONAL SEARCH REPORT

International Application No

PCT/IB 02/05198

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4 360 380 A (ZARUR GEORGE L) 23 November 1982 (1982-11-23) abstract; claims 1,3-5; figure 1 ---	1-5
Y	DATABASE WPI Section Ch, Week 200007 Derwent Publications Ltd., London, GB; Class J04, AN 2000-084587 XP002247764 & RO 115 067 B (INST CHIM CLUJ-NAPOCA), 29 October 1999 (1999-10-29) abstract ---	1-5
Y	DATABASE WPI Section Ch, Week 199826 Derwent Publications Ltd., London, GB; Class J04, AN 1998-295869 XP002247765 & RU 2 095 442 C (AS USSR KOLA RARE ELEMENTS), 10 November 1997 (1997-11-10) abstract ---	1-5
Y	DATABASE WPI Section Ch, Week 199301 Derwent Publications Ltd., London, GB; Class J04, AN 1993-000460 XP002247766 & CS 9 006 696 A (VU CHEM TECHNOLOGIE SP), 15 July 1992 (1992-07-15) abstract ---	1
Y	DATABASE WPI Section Ch, Week 198218 Derwent Publications Ltd., London, GB; Class J04, AN 1982-004827 XP002247767 & RO 77 670 A (INST CHIM CLUJ-NAPO), 30 October 1981 (1981-10-30) abstract ---	1,3,9,10
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## INTERNATIONAL SEARCH REPORT

International Application No

PCT/IB 02/05198

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Section Ch, Week 197727 Derwent Publications Ltd., London, GB; Class J04, AN 1977-48282Y XP002247768 & SU 525 469 A (BUSHKANETS A S), 5 November 1976 (1976-11-05) abstract ---	2,9,10
Y	GB 1 578 123 A (JOHNSON MATTHEY CO LTD) 5 November 1980 (1980-11-05) claims 3,5 ---	1,3
Y	GB 1 090 294 A (LAPORTE CHEMICAL) 8 November 1967 (1967-11-08) page 1, line 63 -page 2, line 23; claims 1-3,10-12 ---	1,3-6
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A	DATABASE WPI Section Ch, Week 199209 Derwent Publications Ltd., London, GB; Class E12, AN 1992-069969 XP002254677 & JP 04 015266 A (MITSUI TOATSU CHEM INC), 20 January 1992 (1992-01-20) abstract ---	14
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# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/IB 02/05198

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1.  Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
  
2.  Claims Nos.:  
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
  
3.  Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1.  As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2.  As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3.  As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4.  No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

### Remark on Protest

- The additional search fees were accompanied by the applicant's protest.
- No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1-10

Process for the recovery of palladium from palladium complex adsorbed on spent silica comprising a burning (calcining) step to oxidize the organic compound in the Pd-complex, digesting the burnt residue with mineral acid, filtering the digested mixture to obtain a Pd-filtrate and a silica residue, recovery of Pd-salt from the filtrate by pH adjustments and washing and drying the residue to recover silica.

2. Claims: 11-16

A process for the recovery of palladium from palladium phthalocyanine complex adsorbed on spent silica gel comprising:  
treating the spent silica gel with hydrofluoric acid and filtering the liquid to obtain a solution containing  $H_2SiF_6$  and suspended Pd-phthalocyanine complex, gravity separation of solution to recover Pd-complex, digesting it with mineral acid and filtering to remove phthalocyanine and to obtain aqueous acidic filtrate Pd-solution, recovery of Pd-salt by evaporation of filtrate and recovery of phthalocyanine ligands by solvent extraction.



## INTERNATIONAL SEARCH REPORT

International Application No

PCT/IB 02/05198

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