

NEW PATENTS

METALS AND ALLOYS

Production of a Sintered Palladium-Silver Alloy Membrane

NISSHIN STEEL K.K. *Japanese Appl. 3/267,327*

A Pd-Ag sintered alloy membrane is produced by mixing a metallic Pd powder with a Ag-Pd composite powder containing 50–95 wt.% Ag and 10–70 wt.% Pd, (both powders having an average particle diameter of 0.01–5 μm), compacting the mixture into the desired shape, and sintering at 500–700°C. The porous sintered alloy membrane produced is useful for separation of hydrogen isotopes and has a higher separation factor and permeability than a non-porous Pd alloy membrane.

Permanent Magnet Composition Containing Platinum

SEIKO EPSON CORP. *Japanese Appl. 4/26,103*

A rare earth-Fe permanent magnet is obtained by melting an alloy containing a rare earth metal, Fe, B and Cu as the base composition, and one or more of Pt, Au and Ag, casting the melt, hot working the ingot to refine the crystal grains, orienting the crystal axis in a specified direction and making the cast alloy magnetically anisotropic. The method is used to make rare earth-Fe permanent magnets having improved corrosion resistance without reducing the magnetic characteristics.

CHEMICAL COMPOUNDS

Organic Palladium Compound Used for Laminated Ceramic Capacitors

DOWA MINING CO. LTD. *Japanese Appl. 4/19,906*

A Pd tertiary alkyl(phenyl) mercaptide is synthesised by reacting an alkyl sulphide complex compound of Pd chloride with a tertiary alkyl(phenyl) mercaptan (4–20C alkyl). The organic Pd compound produced is used as an electrode material for a laminated ceramic capacitor, or as a material for a resinate paste. A uniform, thin Pd film can be obtained.

ELECTROCHEMISTRY

Platinum Coated Anode for Ozone Manufacture

JOHNSON MATTHEY P.L.C. *European Appl. 470,761A*

An electrode used in the manufacture of ozone consists of one or more of W, Ti, Ta and Nb in contact with at least one area, up to 30 mm^2 , of Pt or a Pt containing material, which is itself in contact with the electrolyte. The Pt coating prevents oxide formation which would otherwise render the surface inactive. The electrode is preferably used as the anode in an electrolytic cell to manufacture ozone.

Bipyridyl Ruthenium Complex for Electrochemiluminescent Electrode

CAPE COD RES. *U.S. Patent 5,075,172*

An electrochemiluminescent (ECL) electrode has an ECL layer consisting of a homogeneous mixture of a tris (2,2'-bipyridyl) Ru complex and a polytetrafluoroethylene polymer backbone, deposited on an etched glass substrate layered with a light transparent, conducting, fine grained substance for supporting and activating the ECL layer. The electrodes are used in apparatus for monitoring the concentration of organic material in H_2O , and the improved ECL layers are especially useful for monitoring petroleum contaminated ground waters.

Palladium-Tin Coated Anodes for Electrolysis of Chloride Solutions

M.F. REZNIK *Russian Patent 1,638,208*

Anodes for electrolysis of chloride solutions to produce chlorine, hypochlorites and chlorates are prepared by depositing a catalytically active coating of SnO_2 and PdO on a Ti substrate. The coating is applied in layers by electrolytic deposition from a solution containing 100–150 g/l $\text{Sn}(\text{BF}_4)_4$ and 0.1–0.5 g/l PdCl_2 at the current density of 50–100 mA/cm^2 , and each layer is heat treated to give a uniform, adherent and active coating. Stable anode operation is achieved, with a high level of electrocatalytic activity.

ELECTRODEPOSITION AND SURFACE COATINGS

Platinum Plating Bath for Jewellery Manufacture

ELECTROPLATING ENG. *European Appl. 465,073A*

A plating bath for electroplating or electroforming consists of 2–100 g/l Pt as a Pt compound, 20–100 g/l of an alkali metal hydroxide, a compound selected from soluble carboxylates, phosphates and sulphates, and an alloying metal salt of Pd, Ir, Ru, Au or Ag. Materials with high hardness, thickness and improved corrosion and scratch resistance are produced.

Chemical Vapour Deposition of Superior Quality Metal Films

IBM CORP. *U.S. Patent 5,096,737*

Chemical vapour deposition of Rh, Ir, Ag or Cu from a ligand stabilised (+1) β -diketone co-ordination complex of the metal is effected by heating the substrate, producing a vapour from the metal-containing precursor, and decomposing the vapour to deposit metal on the substrate in the (0) oxidation state. The method deposits metal films of superior conformity, surface smoothness and vertical hole-filling, allowing the fabrication of multilayer structures.

Catalyst Solution Used in Electroless Plating

HITACHI CHEMICAL K.K. *Japanese Appl.* 4/26,774

A catalyst used for electroless plating is obtained by mixing a divalent Pd compound and at least two lower alkylamines into a buffer solution consisting of 0.001–0.5 mol/l Na citrate and 0.001–0.5 mol/l NaOH, where the Pd:alkylamine molar ratio is 1:1 to 1:10. The catalyst is used for electroless plating high density multilayer printed circuit boards, by dipping insulating materials in the catalyst solution, then dipping in reducing agent and electroless plating.

Composite Plating by Laser Irradiation

MITSUBISHI HEAVY IND. K.K. *Japanese Appl.* 4/26,791

Composite plating of layers of one or more kinds of ion is effected by immersing a Pt anode and the work-piece into a plating solution containing one kind or different kinds of ion, and irradiating with a variable wavelength laser beam. The plating procedure is simple and gives a desirable composite electroplating.

Platinum-Tungsten Alloy Electroplating Bath

TANAKA KIKINZOKU KOGYO *Japanese Appl.* 4/32,595

An electroplating bath used for electroplating Pt-W alloy objects contains a Pt compound and tungstic acid and/or a tungstate, and has a pH of at least 3. A novel Pt alloy plated film is obtained which is preferably amorphous, and has high corrosion resistance even to aqua regia. The Pt-W alloy plated film is useful for electrodes, sensors and ornamental goods for which high corrosion resistance is required.

APPARATUS AND TECHNIQUE

Electrode for Measuring pH

TOA ELECTRONICS K.K. *European Appl.* 472,398A

A measuring electrode consists of an electrically conductive support such as Al, Ta or Pt, mostly covered with an insulating film of Al_2O_3 , Ta_2O_5 or Si_3N_4 , with a coating of sensitive metal oxide film on the exposed region. Oxides of Pt, Pd, Rh, Ir or Sn are suitable for the sensitive film, especially with an O:Ir ratio of 2.5–3.5. The electrode is used as a pH electrode and is durable, stable, effective for pH 0–14, has a quick response time and has minimised interference.

Oxygen Sensor Element for Internal Combustion Engine Exhaust

JAPAN ELTRN. CONTROL SYST. *Japanese Appl.* 3/264,857

An O_2 sensor element is obtained by coating the inner and outer surfaces of an oxygen ion conductive solid electrolyte substrate with a Pt electrode, firing at high temperature, dissolving the oxide film formed during firing with HF, and forming a Pt catalyst layer on the outside surface of the substrate. The O_2 concentration of internal combustion engine exhaust gas is derived from the electromotive force generated by the O_2 concentration difference between the inside and outside surfaces. The controlled air/fuel ratio becoming lean due to the oxide film is prevented.

Liquid-Gas Sensor for Rocket Fuel

OKAZAKI SEISAKUSHO *Japanese Appl.* 3/276,053

A liquid-gas sensor consists of a high purity thin Pt wire contacted and wound on an insulating spool to produce a resistor, which is coated with a ceramic. The sensor has good response resulting from the use of a small spool and the high purity thin Pt wire, and has high mechanical strength resulting from the ceramic coating. The liquid-gas sensor is especially useful for detecting liquid H_2 used as rocket fuel.

Humidity Sensor with Platinum-Silica Sensitive Film

SEIKO EPSON CORP. *Japanese Appl.* 3/295,457

The humidity sensitive film of a humidity sensor consists of Pt particles dispersed in a silica film. In an example an Al substrate having screen printed Pt-Pd comb-type electrodes was coated with a silica sol containing dispersed Pt particles, then dried and sintered to form a silica film. Humidity sensors of low resistance, low cost and high accuracy can be obtained.

Oxygen Sensors

JAPAN ELTRN CONTROL SYST.

Japanese Appls. 3/295,461 and 4/19,555

O_2 sensors have a zirconia tube or other ceramic tube having oxygen ion conductivity, a pair of Pt electrodes formed on the inner and outer surfaces of the tube, and an optional Pt catalyst layer formed on the outside surface so that it contacts the engine exhaust. After the Pt electrodes are adhered, the tube may be given a high temperature and pressure treatment at 1000°C (or more) and 10–1000 atm in Ar, in which case a sensor having high heat resistance is obtained.

Gas Sensor with Excellent Reliability

FUJI KASUI ENG. K.K. *Japanese Appl.* 4/55,747

A gas sensor consists of two separate electrodes formed directly on a base plate, a gas sensitive layer of Sn oxide carrying 0.5–2.0 wt.% Pd formed over the base plate and in contact with the electrodes, and covering this layer a coating layer which is formed by a reaction of Sn oxide and Al_2O_3 carrying 1.5–3.0 wt.% Pt. The coating layer removes the interfering alcohol gas and eliminates the temperature dependency for gases containing CH_4 and H_2 . Thus the sensor has excellent reliability and does not require a stabilised voltage source.

Palladium Alloy Membrane for Hydrogen Purification

TOPCHIEV. PETROCHEM. SYNTH.

Russian Patent 1,643,450

H_2 purification is effected by diffusion through a Pd alloy membrane at 400–900°C, where the alloy contains 6–8 wt.% In and 0.5–1.0 wt.% Ru, with a surface Ru concentration of $(0.01–0.6) \times 10^{-4}$ g/cm². The membrane has an extended working life of at least 2000 h, and the process has twice the throughput of the previous method at 600°C.

Production of a Moisture Indicator Using Ruthenium or Osmium Complexes

MOSCOW LOMONOSOV UNIV. *Russian Patent* 1,644,024
A moisture indicator is produced by treating silica with a solution of Ru(II) or Os(II) tris-(1,10-phenanthroline) chloride, bromide or iodide, or complexes of Ru(II) or Os(II) tris-(2,2'-dipyridyl) chloride, bromide or iodide, then removing the water and drying. An increased rate of colour change is achieved using this indicator, to determine the moisture in gases.

JOINING

Palladium Solder for Improved Bonding of Carbon and Metal Materials

NISSAN MOTOR K.K. *Japanese Appl.* 4/6,178
A method for bonding C and metal materials involves applying an active metal (such as Ti, Zr) or active metal hydride on one or both surfaces, and then soldering at 1100°C in a vacuum with a Pd solder containing 4.0–7.0 wt.% Si. A stress-relaxing layer is preferably formed between the materials. The method enables strong chemical bonding instead of mechanical joints and improves high bonding strength.

HETEROGENEOUS CATALYSIS

Catalytic Converter for Alcohol Fuelled Engines

GENERAL MOTORS CORP. *European Appl.* 470,653A
A monolithic catalytic converter for use with automobile exhaust gas from engines using alcohol-containing fuels has a first, upstream region with Pd deposited on the surface, and a second, downstream region having a uniform loading of one or more of Pt, Pd or Rh on the surface. The catalytic converter minimises the formation of aldehydes, and is characterised by a rapid heat-up period and a correspondingly lower light-off time.

Diesel or Petrol Engine Combustion Catalyst

STTS SPECIALITES *World Appl.* 92/1,505A
A perovskite based catalyst suitable for treatment of diesel or petrol engine exhaust preferably consists of La, Y, Nd or Pr; Sr; Mn or Co; Pt, Pd, Rh or Ru; cationic vacancies; and oxygen, and can be extruded or deposited on a honeycomb support. One of the compounds particularly claimed for treatment of diesel exhaust containing soot is $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{0.9}\text{Pd}_{0.001}\text{O}_3$.

Supported Palladium Catalyst for Butene Isomerisation

CHEMICAL RES. & LICENSING *U.S. Patent* 5,087,780
2-Butene is isomerised to 1-butene by contacting a feed containing 2-butene, 1-butene and H_2 with a fixed bed of a PdO/ Al_2O_3 catalyst in a distillation column, at 150–180°F and 100–150 psig. An overhead stream rich in 1-butene and a bottoms stream rich in 2-butene are obtained, and any butadiene present is simultaneously hydrogenated to butenes.

Catalyst for Removal of Nitrogen Oxides

OSAKA GAS K.K. *Japanese Appl.* 3/293,035
A catalyst for NO_x removal consists of at least one of Pt, Rh or Ir on a porous carrier which is at least one of Al_2O_3 , ZrO_2 or Ti oxide; with the carrier having a pore diameter distribution maximum at 50–1000 Å. The catalyst is used for decomposing and removing NO_x in combustion exhaust gas from gas fuel such as LNG or LPG, and can be used in combustion tools such as dryers, engines or generators. NO_x can be removed stably, over a long period, at low temperature, without a reducing agent even in the presence of O_2 .

Palladium-Antimony-Vanadium Catalyst for Preparation of Unsaturated Diesters

TOSOH CORP. *Japanese Appl.* 3/294,244
An unsaturated diester is prepared by the gas phase reaction of a conjugated diene with a carboxylic acid and O_2 in the presence of a catalyst and a 4–5C unsaturated halogenated hydrocarbon. The catalyst consists of a carrier having 0.1–10 wt.% Pd, Sb and V, and also supporting 0.1–40 mmol/g (total) of an alkali metal carboxylate and alkali metal halide as promoter.

Metal Catalyst with Well-Adhered Noble Metal

N. ECHEM CAT. K.K. *Japanese Appl.* 4/4,042
A noble metal catalyst is prepared by treating a metal material such as honeycomb, net or wire with a solution containing 0.5–20 wt.% of a noble metal as a Pt, Pd, Rh, Ir, Ru, Au, Ag or Re salt containing no halogen, 0.05–10 wt.% of a refractory metal oxide as a compound containing no halogen (such as alumina sol), and 1–50 wt.% of an alkyl alcohol such as CH_3OH , and then heating. A metal catalyst with supported noble metal is easily produced at low cost, with the noble metal well adhered to the support.

Exhaust Purification Catalyst with High Oxygen Storage Capacity

NISSAN MOTOR K.K. *Japanese Appl.* 4/4,043
A heat resistant catalyst for purifying exhaust gas consists of at least one of Pt, Pd and Rh on a supporting layer obtained by co-precipitation and containing Al_2O_3 , Ce oxide and Zr oxide. The support has high O_2 storage capacity and a large specific surface area, and the catalyst maintains high activity after using for a long period at high temperature.

Palladium-Iron Catalyst for Dealkylation Process

JGC CORP. *Japanese Appl.* 4/18,039
Dealkylation of alkyl aromatic compounds to produce dealkylated aromatic compounds and synthesis gas is effected by contacting with CO_2 in the presence of a Pd-Fe catalyst. The catalyst is prepared by impregnating 0.01–50 wt.% Pd and Fe on a carrier such as Al_2O_3 , SiO_2 , zeolite, and so on, with a Pd:Fe wt. ratio of 10:1–1:10, sintering and reducing.

Catalytic Converters for Lean Burn Engines

MITSUBISHI MOTOR CORP. *Japanese Appl.* 4/22,706-07

Catalytic converters for use with a lean burn engine consist of (a) at least one of Pt, Pd and Rh directly supported on a metal support, with a Cu/zeolite washcoat layer formed on at least the front side of the metal support; or (b) Pt, Pd and/or Rh supported on a Cu/zeolite washcoat layer formed on a support. NO_x from a lean burn engine is decomposed at the active sites of the Cu/zeolite structure, and the hydrocarbons, CO and NO_x released during transient operation are reduced at the active sites. The catalytic converters give improved purification efficiency for NO_x.

Durable High Temperature Combustion Catalyst

BABCOCK-HITACHI K.K. *Japanese Appl.* 4/27,433

A high temperature combustion catalyst consists of a refractory inorganic support loaded with Pd oxide and a double oxide of Pd and La, with La:Pd atomic ratio 0.01–0.4:1. In an example the catalyst was produced by loading La/Al₂O₃ on a honeycomb support and firing at 900°C, then impregnating with an aqueous solution of La and Pd nitrates and firing at 800°C. The catalyst has an extended operating life.

Multipurpose Palladium-Magnesium Carbonate Catalyst

JENAPHARM VEB. *East German Patent* 294,430

A supported Pd catalyst is produced by precipitation of Pd metal or oxide onto basic Mg carbonate from Pd salt solutions or suspensions, at room temperature. The catalyst has higher activity and selectivity, reproducible properties, low toxicity, and easy recovery of Pd. The catalyst is useful for selective and quantitative reduction of a substituted nitroketone.

HOMOGENEOUS CATALYSIS

Rhodium Hydroformylation Catalysts with Phosphite Ligands

BASF A.G. *European Appl.* 472,071A

Rh catalysts used for hydroformylation of 2–20C olefins contain bis-phosphite ligands, and show higher activity and greater hydrolysis resistance than previous Rh complexes. The catalysts show low volatility and allow easy separation of the catalyst and products.

Pollution Reduction

B.J. ROBINSON *U.S. Patent* 5,085,841

A method for reducing the pollution emitted from a combustion chamber involves introducing a mixture of precious metals homogeneously to the flame zone of the combustion chamber for simultaneously enhancing oxidation of C in the fuel and inhibiting oxidation of N₂ in the air. The mixture contains 1–9 mg Pt, 0.2–3 mg Rh and 0.3–3 mg Re, with no more than 15 mg metal per 24 kg fuel. The method is used for diesel and gasoline motor vehicle engines.

Production of Alkylarylcarbinols

MITSUBISHI KASEI CORP. *Japanese Appl.* 4/21,644

Alkylarylcarbinols are produced by hydrogenating aromatic ketones at 50–250°C under 0.1–200 kg/cm² pressure, for 1–20 h, in a homogeneous liquid medium, in the presence of 0.0001–100 mol/l of a Ru compound, an organophosphine and a P compound. The products are produced in high yield, under milder conditions and are useful as starting compounds for drugs and agrochemicals.

FUEL CELLS

Fuel Cell for Electricity Generation with Noble Metal Anode

PHYSICAL SCI. INC. *World Appl.* 92/2,965A

A fuel cell anode has a first fluid-permeable face and a second face in contact with the electrolyte which has as electrocatalyst a crystalline particulate alloy consisting of Au as the main component and a Group VIII noble metal. Electricity is generated in the compact fuel cell by oxidising a lower primary alcohol to CO₂ and H₂O at the anode and reducing a reducible gas at the cathode. Using this method, poisoning by adsorbed reaction intermediates is avoided or minimised.

Catalyst Powder for Hydrogen Fuel Cell Electrode

DAIKI GUM KOGYO K.K. *Japanese Appl.* 4/18,933

A highly active electrode is prepared by mixing highly active catalyst powder with C powder and hydrophobic fluoride resin, coating on a conductive base, and heating. The catalyst powder is prepared by soaking an alloy containing at least one of Ti, Zr, Nb or Ta, at least one of Pt, Pd, Rh, Ir or Ru, and at least one of Ni or Co, in hydrofluoric acid. The catalyst powder and electrode have excellent activity for H₂ oxidation, can be made without a complicated or expensive process and can be used for a H₂ fuel cell electrode.

ELECTRICAL AND ELECTRONIC ENGINEERING

Ceramic Coatings Suitable for Electronic Devices

DOW CORNING CORP. *U.S. Patent* 5,091,162

A perhydrosiloxane copolymer is dissolved in a solvent to give a 0.1–50 wt.% solution which optionally includes 5–500 ppm of a Pt or Rh catalyst (based on the weight of copolymer), and a modifying ceramic oxide precursor. The copolymers are converted to ceramic coatings having low defect density by coating the solution on a substrate, evaporating and heating at 20–1000°C for up to 6 h in an atmosphere of NH₃ or amines. The coatings are used on electronic devices for protection, as dielectric layers and as diffusion barriers against ionic impurities.

Conductor Containing Ruthenium

TANAKA MASSEI K.K. *Japanese Appl. 4/39,812*

A conductor composition consists of a metal powder containing at least Ag and an inorganic binder powder dispersed in a vehicle, where the inorganic binder contains 0.1–12 wt.% glass frit, a Bi compound and a Ru compound (0.05–3 wt.% as oxide) as an additive. The conductor composition has improved adherence and wettability of solder.

Manufacture of Low Resistance Platinum Heating Elements

TANAKA KIKINZOKU KOGYO *Japanese Appl. 4/43,586*

A Pt resistance heating element is made by forming heating element circuits on a heat resisting matrix using a photoresist; by electroless Pt plating and heat treatment at 450–600°C. The method is used for making Pt resistance heating elements having low electrical resistance, and uses less Pt.

Ultra High Density Photomagnetic Recording Medium

HITACHI K.K. *Japanese Appl. 4/53,045*

The recording film of a magneto-optical recording medium is up to 500 Å thick and is made of two magnetically bound layers, one of which is an alloy of Tb, Dy or Ho and Fe or Co, while the other is a reciprocal laminate of a Pt group element and an Fe group element, for example Pt and Co. The medium has a larger Kerr rotating angle at the short wavelength domain, and is used for ultra high density recording.

TEMPERATURE MEASUREMENT

High Temperature Thermocouple with Noble Metal Sheath

JGC CORP. *Japanese Appl. 4/38,429*

The outer surface of the temperature measuring part of a thermocouple body is covered with a first sheath tube of at least one of Pt, Rh and Ir; which is itself covered with a second sheath tube of heat resisting ceramics including 50 wt.% or more of Cr oxide. The thermocouple can withstand continuous use for temperature measurement in high temperature furnaces including molten material, for one year (8000 h) or more.

Measuring Resistor for Resistance Thermometer

HERAEUS SENSOR G.m.b.H. *German Appl. 4,026,061*

An electrical resistor for resistance thermometer is prepared by depositing a Pt thin film on a substrate by vapour deposition or sputtering, applying a layer of Pt resinate and Rh sulpho-resinate by screen printing, drying, firing and heat treating at 1000–1400°C. This method gives a uniform distribution of 0.01–10 wt.% Rh in the resistor layer. The temperature coefficient is obtained in the range 1600–3860 ppm/K.

MEDICAL USES

Diagnosis of Cells Resistant to Platinum Anti-Neoplastic Agents

ONTARIO CANCER INST. *European Appl. 467,366A*

A plasma membrane antigen is correlated with resistance to Pt-containing anti-neoplastic agents such as *cis*-diaminedichloro Pt(II), carboplatin, tetraplatin or iproplatin. The plasma membrane antigen is used to obtain antibodies and nucleotide sequences for detection and diagnosis of cells resistant to Pt-containing anti-neoplastic agents.

New Platinum Complexes for Diagnosing Infections

STICHT KLINISCHE RE. *World Appl. 92/1,699A*

New square planar Pt(2+) complexes and octahedral Pt(4+) complexes have optionally interconnected ligands, where at least one is a labile ligand such as Me₂SO, Cl or H₂O, and at least one is a detectable marker ligand, such as a fluorescent ligand derived from tetramethyl rhodamine. The new Pt complexes are useful for labelling nucleic acids, especially for production of labelled hybridisation probes for detection of viruses, bacteria, parasites, genetic deviations or gene expression.

Palladium Alloy for Use as a Medical Implant

TOYAMA KIKINZOKU K.K. *Japanese Appl. 4/342*

An alloy consisting of 45–60 mol% Ti and 40–55 mol% Pd+Co, with up to 30 mol% Co, is held at 500–1000°C, and then quenched to prepare an alloy used as an implant, artificial coxae, bone setting plate, and as artificial bones. The alloy has high mechanical strength, excellent corrosion resistance and biocompatibility.

Titanium-Palladium Alloy for Corrective Dentistry

TOKIN CORP. *Japanese Appl. 4/38,948*

A TiPd alloy containing 45.0–51.0 at.% Pd, and Ti, has at least one of Fe, Cu and W substituted for at least 30 at.% of the TiPd alloy. The alloy is not biotoxic and is used for corrective dentistry.

Platinum Co-ordination Compound

ZENT INST. KREBSFORSCH *East German Patent 295,987*

An agent used for treating retroviral infections, especially HIV infections contains, as the active ingredient, a Pt co-ordination compound including, as ligands, an amine, diisopropylamine or diaminocyclohexane, an acid anion, and optionally an OH group. The Pt compound is highly effective, has good bio-availability, tolerable specific toxicity, and has a good long term effect even with low doses. It reduces the virus content in the blood and limits the denaturing of normal tissue.

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