NEW PATENTS

CHEMICAL COMPOUNDS

Platinum or Palladium Porphyrins

NOVARTIS A.G. *World Appl.* 98/3,512A

New phosphorescent Pt(II) or Pd(II) porphyrins (1) are described. Also claimed is a composition containing (1), an O_2 permeable and membrane-forming polymer selected from polystyrene, copolymers of styrene, etc., and an organic solvent. Porphyrins (1) have a high quantum yield, a long life in the excited state and good light stability. They are used in the preparation of metal benzporphyrin compounds, which are phosphorescence indicators, and can be used as O_2 sensors in gases and liquids. Due to their long wave phosphorescence in the near IR range, measurements can be carried out in cloudy liquids or gases.

ELECTROCHEMISTRY

High Purity Oxygen Production

SHINKO PANTEC CO. LTD. *Japanese Appl.* 9/316,675

High purity O_2 is produced by an H_2-O_2 generator having O_2 and H_2 generating chambers separated by an electrolytic film with an electrically insulated Pt group metal arranged in and/or around the electrolytic film. The Pt group metal acts as a catalyst to remove H_2 gas contained in the O_2 gas. High purity O_2 is manufactured at low cost by the electrolysis of pure H_2O.

Electrolysis Vessel

PERMELEC ELECTRODE LTD. *Japanese Appl.* 10/1,794

An electrolysis vessel has anode and cathode chambers separated by a perfluorocarbon-based cation exchange membrane with an anode (1) and a cathode (2) catalyst on either surface of the membrane. (1) is selected from Pt group metals and their oxides and (2) uses a Pt and/or C porous sheet. Pure H_2O and/or HCl is supplied to the anode chamber. The membrane has high resistance, preventing uneven current distribution, thus reducing wastage of the electrode materials. The vessel is used for producing acid H_2O for cleaning electronic devices, including semiconductors and liquid crystals.

Electrolysis Tank

JOUNAN DENKI KOGYO K.K. *Japanese Appl.* 10/8,281

An electrode for a H_2O electrolysis tank is composed of a Ti substrate coated with a Pt plated layer and another noble metal layer, such as Ir. The tank is used for the electrolysis of H_2O to generate strongly acidic and alkaline H_2O. The tank can suppress ozone production while retaining sufficient sterilising ability.

Water Electrolysis

TECHNOVA K.K. *Japanese Appl.* 10/18,070

Water electrolysis is controlled at a constant voltage by a Pd cathode by measuring the resistance ratio $R:R_0$ (R_0 is the initial resistance) of the Pd electrode. Large amounts of H_2 are produced. The occluded H_2 in the Pd electrode is maintained stable for a long period.

Electrode for Electrochemical Cell

DORNIER G.m.b.H. *German Appl.* 1/96/40,926

An electrode for an electrochemical cell has an active layer made of a ternary mixed oxide having a crystal structure of perovskite-type $A(B_{1-x}C_x)O_3$, where x = 0–1, A = a Group IIA or lanthanide metal cation; B = a Pt metals cation; and C = a Group IVB, VB, VIB, VIIB, VIIIB or IIB metal cation. The electrode has high conductivity and is used in fuel cells, gas sensors and double layer capacitors.

ELECTRODEPOSITION AND SURFACE COATINGS

Platinum Aluminide Diffusion Coatings

HOWMET RES. CORP. *European Appl.* 821,075A

The oxidation resistance of a Pt modified diffusion coating for gas turbine engine parts is improved by electroplating the substrate with a Pt layer from an aqueous caustic solution followed by aluminising. The plating reduces the presence of harmful impurities such as P, S and Cl in the Pt deposits. The coating has excellent high temperature oxidation resistance.

Chemical Vapour Deposition of Platinum

ADVANCED TECHNOLOGY MATERIALS *World Appl.* 98/432A

A Pt source liquid solution for the chemical vapour deposition (CVD) of Pt comprises a Pt(IV) cyclopentadienyl trialkyl and/or a Pt(II) *bis*(β-diketonate) and a solvent. A random access memory (RAM) device comprising a ferroelectric thin film capacitor with Pt electrodes formed by CVD in the presence of an oxidising gas is also claimed. Higher mass transport (10–100 times greater) of the Pt source vapour can be achieved, giving faster Pt film growth and higher manufacturing throughput.

Single Crystal Diamond Thin Film

KOBE STEEL LTD. *Japanese Appl.* 10/7,492

A single crystal diamond thin film is formed on a Pt alloy substrate or film which has a (100) crystal plane and contains > 50 at.% Pt, by vapour synthesis under a plasma atmosphere. A large surface single-crystal diamond thin film is obtained without crystal defects at low cost by vapour phase synthesis.

High Purity Thin Platinum Films

MITSUBISHI MATERIALS CORP. *Japanese Appl.* 10/18,036

A high purity thin Pt film is formed at 100–150°C by CVD of an organometallic Pt compound dissolved in an organic solvent, preferably alkylamine or trimethylsilylolefin, quantitatively introduced into the vaporisation chamber. The generated vapour is introduced into the film-forming chamber along with a carrier gas. The organic compound has a stable vaporising rate at 50–100°C, which ensures that the film has uniform and fine crystal grains.

Palladium-Silver Plating Bath

NIPPON ELECTROPLATING ENGINEERS K.K. *Japanese Appl.* 10/18,077

A Pd-Ag plating bath for electronic goods, such as lead frames and connectors, comprises 1–30 g of Pd salt and 0.01–15 g of Ag salt with 1–300 g of amino polycarboxylic acid. The amino carboxylic acid is used as a complex forming agent. The bath is stable, providing adherent coatings of good surface quality.

Platinum Plating

SUGA SHIKENKI K.K. *Japanese Appl.* 10/30,187

Pt plating of an ion exchange membrane used in the electrolysis of H_2O comprises etching both sides by UV radiation, washing in $SnCl_2$ and HCl, and immersing in a solution containing 0.05–2 g $PdCl_2$, 0.5–2 ml HCl and pure H_2O and heating to 40°C for 1–3 minutes. This process is repeated, then followed by washing and finally heating to 50°C in a solution containing 2–8 g chloroplatinic acid. The plating efficiency is improved, giving a porous membrane.

APPARATUS AND TECHNIQUE

Gas Sensor for Detecting Carbon Monoxide

MATSUSHITA DENKI SANGYO K.K. *Japanese Appl.* 10/2,878

A sensor for detecting CO in air and exhaust gas has a pair of Pt electrodes formed on the surface of an O ion conductive solid electrolyte. An absorption layer (1) containing an alkali absorber (2), and ceramic fibre, are formed onto a lamination of (1), which contains a catalyst layer; (2) contains an oxidation catalyst. Ceramic fibre is formed on the Pt electrodes.

Oxygen Sensor

NGK SPARK PLUG CO. LTD. *Japanese Appl.* 10/26,603

An electrode for an O_2 sensor used to detect air:fuel ratios in I.C.E. consists of a raw material powder containing 100 wt. parts of Pt powder and 14–25 wt. parts of Zr powder which are baked at a predetermined temperature. The grain size and bulk specific gravity of the Pt powder are 2–20 μm and 2.5–4.2, respectively. The required properties of the electrode are stable over a long time.

HETEROGENEOUS CATALYSIS

Catalytically Active Coatings

DEGUSSA A.G. *European Appl.* 803,470A

Catalytically active coatings on ceramic mouldings are produced by wetting the mouldings with a coating dispersion containing a particulate (< 100 μm) Pt metal and a further coating component, such as particulate nitrides with Al, B, Ti, or Si as cations, in a carrier fluid. The coating is converted into a catalytically active state by heating in the presence of N_2 and/or NH_3 to 1000–1350°C. The mouldings are used for the synthesis of hydrogen cyanide from hydrocarbons and NH_3. They have higher catalytic activity and can be charged with the high output streams from the stationary operation in a very short time.

Ruthenium or Palladium Catalysts

BASF A.G. *European Appl.* 814,098A

A catalyst (1) contains 0.01–30 wt.% Ru or Pd as an active metal, optionally with Group I, VII or VIII transition metal(s), on a carrier in which 10–50% of the pore volume consists of macropores and 50–90% consists of mesopores. Also claimed is the hydrogenation, dehydrogenation, etc., of polymers having multiple C-C bonds. These reactions can be carried out with a high catalyst loading, giving a very high turnover and products in very high yields and purity, and almost complete conversion. Service life is long.

Exhaust Gas Purification

NE CHEMCAT CORP. *European Appl.* 822,005A

A catalyst (1) for purifying O_2-rich exhaust gases comprises Ir, an alkali or alkaline earth metal, and an element of Group IIIB or Group IVA (except C) or a Fe family element, on at least one Ti family oxide. (1) is highly durable in gases containing H_2O vapour and SO_2, and has increased activity after being aged. It is used for the removal of NOx from I.C.E., boilers, etc.

Air Purifying Filter

AISIN AW CO. LTD. *European Appl.* 826,531A

An air purifying filter for vehicles contains a photo catalyst supporting a Pt group catalyst (1). CO in air is adsorbed on the surface of (1), decomposed and oxidised to CO_2; S compounds are oxidised to sulfate on the photocatalyst surface when it is irradiated. The air purifier also has a light source to irradiate the photocatalyst. There is less (1) on the photocatalyst in areas towards the light source. The air filter is smaller and has a long life. Pt is not poisoned by S compounds.

Nitrogen Oxide Trap

FORD GLOBAL TECHNOLOGIES INC. *World Appl.* 97/47,374A

A NOx trap for exhaust gases generated during the lean-burn operation of an I.C.E. comprises a porous support, and a catalyst containing ≥ 10 wt.% Li and 0.2–4 wt.% Pt loaded on the support. NOx is trapped with high efficiency and without forming sulfates.

Platinum Three-Way Catalyst

JOHNSON MATTHEY PLC *World Appl.* 98/3,251A

A Pt group metal three-way catalyst for treatment of engine exhaust contains high- (> 500°C) and low-temperature (200–400°C) components as separate discrete particles on the same washcoat. The Pt group metal(s) catalyst is impregnated onto the high- and low-temperature support materials. The catalyst has greatly improved three-way activity even after extended high temperature ageing.

Conversion of Aromatic Compounds

PHILLIPS PETROLEUM CO. *U.S. Patent* 5,698,757

The conversion and hydrodealkylation of aromatic compounds involves contacting with a H_2-containing fluid using a Pt/zeolite and a Ga/ZSM zeolite catalyst, preferably ZSM-5, to give 6–8C aromatics. The catalyst has a high hydrodealkylation activity, selectivity to xylenes and good stability.

Platinum Isomerisation Catalyst

PHILLIPS PETROLEUM CO. *U.S. Patents* 5,707,918 and 5,707,921

The preparation of a solid composition, containing a Group VIII metal and Cl_2, as an isomerisation catalyst involves blending Pt and/or Pd and/or Ni and an Al_2O_3 support together with an Al_2O_3-supported Al- and Cl-containing compound. This is treated with H_2 and chloroalkane. The catalyst has high activity, selectivity and effectiveness in the isomerisation of alkanes and cycloalkanes.

Catalytic Decomposition of Hydrogen Peroxide

SHELL OIL CO. *U.S. Patent* 5,711,146

A catalyst to decompose H_2O_2 to steam and O_2 is a (supported) mixture of 20–70 at.% Ru, balance Ir and/or Pt. It is used in monopropellant thruster chambers which provide position control in space or high altitude vehicles. The catalysts are superior to prior art Ag catalysts and maintain prolonged activity and strength even with H_2O_2 concentrations of ≥ 95%.

Exhaust Gas Purification Catalyst

NISSAN MOTOR CO. LTD. *Japanese Appls.* 10/5,588–89

A catalyst for I.C.E. comprises a honeycomb carrier with a coating of a fire-resistant inorganic acid compound carrying 4–15 wt.% Pd. The coating is provided so that the honeycomb carrier contains 3.5–18 g l^{-1} Pd. This catalyst reduces the discharge of hydrocarbon/nitrogen oxide and increases the speed of the catalytic reaction.

Zeolite Catalyst with Platinum

TANAKA KIKINZOKU KOGYO K.K. *Japanese Appl.* 10/15,391

A manufacturing method for a zeolite catalyst with Pt involves a pyrogenetic reaction of Pt chloride ammonium acid in surplus aqueous ammonia. Surplus ammonia is volatilised to obtain the ammine complex ion of Pt(IV). This method facilitates effective use of Pt to give a large reaction rate.

Oxalic Acid Elimination

SHINETSU CHEM. IND. CO. LTD. *Japanese Appl.* 10/24,284

Eliminating oxalic acid and collecting HNO_3 (1) from waste H_2O comprises heating the H_2O to 50–100°C and adding a Pt/C catalyst to decompose the oxalic acid into CO_2 and H_2O. The H_2O is then distilled or treated with an ion exchange membrane to collect (1).

Combustion of Methane Fuel

DENRYOKU CHUO KENKYUSHO *Japanese Appl.* 10/28,863

A catalyst for the combustion of methane includes Rh particles and Pt-Pd alloy particles on the surface of a carrier. The Pt-Pd alloy is chosen from a Pt-PdO alloy, mixed Pt and Pd or mixed Pt and PdO. The Rh particles and the Pt-Pd alloy particles are separately configured onto the support. The Pd carrying catalyst maintains high activity by controlling self excited vibration phenomenon. This prolongs the life of the catalyst.

Palladium/Phosphorus Supported Catalyst

ASAHI KASEI KOGYO K.K. *Japanese Appl.* 10/28,865

A Pd/P supported catalyst for carboxylic ester production is made by reducing a catalyst precursor, with a Pd:P atomic ratio of 3:0–1:1.3, with formalin, formic acid, hydrazine or H_2 in an aqueous solution or methanol. This gives a Pd/P supported catalyst containing Pd/P at an atomic ratio of 3:0.7–3:1.3. With this catalyst, carboxylic ester can be produced by reacting an aldehyde and an alcohol in the presence of O_2. Yields, based on aldehyde and on alcohol, can be simultaneously improved by increasing the aldehyde concentration and raising the reaction temperature.

Diesel Engine Exhaust Catalyst

ICT K.K. *Japanese Appl.* 10/33,985

A catalyst for diesel engine exhaust gas purification includes a Pt group metal selected from Pt, Pd and Rh combined with a super strong acid. The catalyst allows the efficient removal of fine particles from the exhaust gas.

Unsaturated Glycol Diesters

MITSUBISHI CHEM. CORP. *Japanese Appl.* 10/36,315

Unsaturated glycol diester compounds are prepared by reacting a conjugated diene, such as butadiene, with a carboxylic acid, such as acetic acid, and O_2 in the presence of a catalyst. The catalyst contains Pd, Rh and/or Pt, and a Te compound on an inorganic porous support, preferably SiO_2. The active component is preferably Pd/Te or Rh/Te. High activity and selectivity are achieved with minimised Rh elution.

Catalytic Combustion Device

MITSUBISHI JUKOGYO K.K. *Japanese Appl.* 10/47,610

A catalytic combustion device for gas turbines has a catalyst with a magnetic cutting-tool structure. A catalyst layer contains Pd in the gas entrance side and Mn in the outlet side. The device reduces discharge of NOx and allows long term usage of the catalyst.

Lean-Burn Engine

RHONE-POULENC CHIM. *French Appl.* 2,750,058

A process for the reduction of NOx from exhaust gases from lean-burn engines or petrol engines containing a stoichiometric excess of O_2, uses a catalyst with a Pt-containing active phase deposited, in the form of a sol, on a support. The gases for treatment may contain 5–20% O_2 and optionally hydrocarbons and/or oxygenated organic compounds.

HOMOGENEOUS CATALYSIS

3-Hydroxypropionic Acid Preparation

DEGUSSA A.G. *European Appl.* 819,670A

The preparation of 3-hydroxypropionic acid (1) or its salts involves the catalytic oxidation of 3-hydroxypropionaldehyde (2) with O_2 or O_2-containing gas in the presence of 10% of a platinum group metal as a catalyst in an aqueous phase, then isolation of (1) or its salts. (1) has higher yields than from acrylic acid hydration, without using any toxic starting materials.

Telomerisation of Dienes

HOECHST RES. & TECHNOL. DEUT. G.m.b.H. & CO. *World Appl.* 98/8,794A

The telomerisation of dienes, useful in the production of di-*n*-octylphthalate from butadiene, with an active H-containing compound, uses a Pd compound, a H_2O-soluble bidentate *bis*(di-substituted phosphinomethyl)-1,1'-binaphthalene ligand and a base in H_2O. The process gives good yields of the dimers with high selectivity and purity, making isolation simple. None of the usual organic ancillaries and organic solvents are required if H_2O is used as the active H compound.

Carbonylation Catalyst

SHELL OIL CO. *U.S. Patent* 5,719,313

A carbonylation catalyst for acetylenically unsaturated compounds, especially containing minor amounts of 1,2-alkadiene compounds, comprises a source of cations of Group VIII metals, a halogenated phosphine and a source of protons. The catalyst is stable at 70–100°C.

Dimethyl 4,4'-dicyclohexanedicarboxylate

TEIJIN LTD. *Japanese Appl.* 10/36,320

Dimethyl 4,4'-dicyclohexanedicarboxylate (1) is prepared by reacting dimethyl 4,4'-diphenyldicarboxylate with H_2 at 80–200°C under normal pressure to 50 kg cm^{-2} in the presence of at least one catalyst of Ru, Pd and Rh and alcohol and/or fatty acid ester, as solvent. (1) is prepared with high selectivity under low pressure.

Production of *N*-Acyl-glycine Derivatives

HOECHST A.G. *German Appl.* 1/96/29,717

The preparation of *N*-acyl-glycine derivatives involves the carbonylation of amide and aldehyde compounds at 20–200°C under CO at 0.1–15 MPa in the presence of a solvent, a Pd compound, an ionic halide and an acid as catalyst. The process is simple and gives high yields and good selectivity at relatively low temperatures and pressures without the addition of H_2.

FUEL CELLS

Small Scale Fuel Cell

UNIV. KEELE *World Appl.* 97/48,144A

A small scale fuel cell power generation system comprises a ceramic plug containing Pt to heat the fuel:air mixture before it enters a ceramic fuel cell. The system is powered by LPG or LNG and is suitable for replacing batteries as an electrical power source in electronic sensors, communications equipment, small motors and lights.

Phosphoric Acid Fuel Battery

FUJI ELECTRIC CO. LTD. *Japanese Appls.* 10/32,009–10

Phosphoric acid/solid state polyelectrolyte fuel batteries are manufactured by adding Ru to a fuel electrode which has a catalyst layer made from Pt. The fuel battery has a fuel pole containing a catalyst layer of a Pt-Co-Fe alloy. The batteries have longer life.

ELECTRICAL AND ELECTRONIC ENGINEERING

Preparation of Electronic Parts

MURATA MFG. CO. LTD. *Japanese Appl.* 9/306,239

A conductive paste comprises a metallic constituent of Cu powder and organic Pd resinate, and a glass frit, dispersed in an organic vehicle. Thick film conductors, with improved solder-wetting and sufficient bonding force with ceramic substrates, can be formed with this conductive paste.

Electrically Conductive Films

ASAHI GLASS CO. LTD. *Japanese Appl.* 10/1,777

A coating liquid for electrically conductive film formation (1) on glass CRT panels consists of a solution of fine metallic particles of one or more elements selected from Pt, Pd, Rh, Ir, Os, Ru, Ag, Re, Ni, Co, Sn, Cr, Au and In included in a dispersion. The resulting superior, low reflective and electrically conductive films are composed of metallic fine particles. They aid shielding against electromagnetic waves.

Structure with Amorphous Buffer Layer

SIEMENS A.G. *German Appl.* 1/96/30,110

A structure has a buffer layer 10–120 nm thick of amorphous Al_2O_3, formed by sputtering at 100–300°C, on a substrate of silicate glass or Si wafer, etc., optionally with a SiO_2 or Si_3N_4 surface layer. A 0.1–0.5 μm thick Pt layer is then applied by sputtering, followed by a ferroelectric PZT coat. Good substrate adhesion is produced. This is used for ferroelectric capacitors, pyroelectric detector arrays, piezo-actuators, etc.

Uniform Adherent Palladium

ATOTECH. DEUT. G.m.b.H. *German Appl.* 1/96/31,565

The electroless deposition of uniformly thick adherent Pd contact bumps (preferably ≥ 2 μm high) on the Al conductor structures of a semiconductor circuit involves treatment with an acidic Pd ion activating solution and electroless Pd deposition from a bath of pH 4–7 containing Pd ions, formic acid as a reductant and a N complex. The bumps have high adhesion and do not form surface oxide films on storage in air. Semiconductor chips can thus be contacted with hybrid circuit carriers by the flip-chip technique.

MEDICAL USES

Dental Alloy

PROSOR LLC *World Appl.* 98/3,688A

A matrix alloy for mixing with Au to form dental alloys comprises (in wt.%): 0–16 Pd, 20-41 Cu, 35–60 Ag and 0-1.5 Ir. Preferably, the matrix alloy can also contain: 8 Pt, 5 Au, 2 Ge, 4 Zn, 1.5 Fe, 1.5 Mn, 2.5 Ga, 3.5 In and 3.5 Sn. The balance may be made up by Ru, Rh, Re and other impurities. A single matrix alloy is used to form a range of dental alloys. The alloy retains very high mechanical strength.

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