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 O₂ 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 O₂ 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 O₂ is produced by an H₂O₂ generator having O₂ and H₂ 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 H₂ gas contained in the O₂ gas. High purity O₂ is manufactured at low cost by the electrolysis of pure H₂O.

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 H₂O 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 H₂O 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 H₂O 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 H₂O to generate strongly acidic and alkaline H₂O. The tank can suppress ozone production while retaining sufficient sterilising ability.

Water Electrolysis
TECHNOVAK K.K. Japanese Appl. 10/18,070
Water electrolysis is controlled at a constant voltage by a Pd cathode by measuring the resistance ratio R₀/R, (R₀ is the initial resistance) of the Pd electrode. Large amounts of H₂ are produced. The occluded H₂ 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(Bₓ₋₁Cₓ)O₃, where x = 0-1, A = a Group IIA or lanthanide metal cation; B = a Pt metal 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
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(P-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
MITSUBISHI MATERIALS CORP. 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.

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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 H2O comprises etching both sides by UV radiation, washing in SnCl2 and HCl, and immersing in a solution containing 0.05–2 g PdCl2, 0.5–2 ml HCl and pure H2O 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 chloroplatinate 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 lamina 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 O2 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 nitriles 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 N2 and/or NH3 to 1000–1350°C. The mouldings are used for the synthesis of hydrogen cyanide from hydrocarbons and NH3. 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 O2-rich exhaust gases comprises Ir, an alkali or alkaline earth metal, and an element of Group IIIIB or Group IVA (except C) or a Fe family element, on at least one Ti family oxide. (1) is highly durable in gases containing H2O vapour and SO2, 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 CO2; 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 H2-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, as an isomerisation catalyst involves blending Pt and/or Pd and/or Ni and an Al/Cl-containing compound with an AlCl-containing compound. This is treated with H2 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 H2O2 to steam and O2 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 H2O2 concentrations of ≥ 95%.

Exhaust Gas Purification Catalyst

NISSAN MOTOR CO. LTD. *Japanese Appl.* 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 Pt1 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 HNO3 (1) from waste H2O comprises heating the H2O to 50–100°C and adding a Pt/C catalyst to decompose the oxalic acid into CO2 and H2O. The H2O 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 H2 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 O2. 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 O2 in the presence of a catalyst. The catalyst contains Pd, Rh and/or Pt, and a Te compound on an inorganic porous support, preferably SiO2. 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 O2 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% O2 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 O2 or O3-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 H₂O-soluble bidentate bis(dil-substituted phosphino)methyl)-1,1′-binaphthalene ligand and a base in H₂O. 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 H₂O 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 H₂ 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 AG

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 H₂.

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 Appl. 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 compromises 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 AG

German Appl. 1/96/30,110

A structure has a buffer layer 10–120 nm thick of amorphous Al₂O₃, formed by sputtering at 100–300°C, on a substrate of silicon glass or Si wafer, etc., optionally with a SiO₈ or Si₃N₈ 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 reducing 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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