

NEW PATENTS

ELECTROCHEMISTRY

Manufacturing Active-Hydrogen Water

SUN ENG. K.K. *Japanese Appl.* 2000/192,272

A method to manufacture active-hydrogen (AH) H_2O uses Pd or a Pd alloy as the cathode for H_2O electrolysis. H_2 (as AH) is occluded into the cathode. The cathode is then put into H_2O containing an alkali electrolyte. This releases the AH in the Pd which attaches to the alkali ions. The AH-alkali-ion H_2O obtained is stable and can be preserved for long periods by freezing. As the AH has high reactivity it may be used as a H source in liquid phase hydrogenation.

Cathode for Electrolysis

PERMELEC ELECTRODE LTD. *German Appl.* 1/00/06,449

A cathode (1) for electrolysis of a H-containing material consists of a first layer of Pd or Pd alloy (2) deposited on the reaction chamber side of a membrane and a second layer of Pt black or Pt-Au porous catalyst deposited on (2). An electrolysis cell is divided by (1) into a reaction chamber and an electrolysis chamber, and is used for reduction or hydration of a reactant in the reaction chamber. (1) also contains an ion exchange membrane or a porous membrane.

ELECTRODEPOSITION AND SURFACE COATINGS

Improving Performance of Electroplating Bath

SPECIALTY CHEM. SYSTEMS INC. *World Appl.* 00/56,952

The plating performance of aqueous sulfate (1), sulfonic acid, fluoroborate and halide electroplating baths is improved by the addition of an alkyl and/or alkanol sulfonic salt. (1) comprises: a source of sulfate ions; soluble Rh, Ru, Sn, Ni, Cu, Cr, Cd, Fe, Zn, Pb and/or In metal salts; and a salt of an alkyl and/or alkanol sulfonic acid. The additives give a wider range of useful current densities and improved appearance.

Metal Component for Turbine Blade

ISHIKAWAJIMA HARIMA HEAVY IND.

Japanese Appl. 2000/178,763

A metal component for a turbine blade used in a gas turbine engine of an aircraft, has an antioxidant film (1) comprising an upper Al coating layer, an intermediate Ir layer and a lower Pt layer formed on the surface of a base material. (1) has improved strength and oxidation resistant ability.

Electroless Rhodium Plating of Ceramics and Metals

ROBERT BOSCH G.M.B.H. *German Appl.* 1/99/09,678

A Rh plating bath comprises H_2O and a readily H_2O -soluble Rh compound selected from ammonium Rh(III) di(pyridine-2,6-dicarboxylate), Rh amine complexes: $RhCl_x(NH_3)_{6-x}$ where $x = 0-3$, Rh acetate and Rh chloride triethylenetetramine or diethylenetriamine complexes. Rh precipitation is minimal, so plating efficiencies of $\geq 90\%$ can be obtained.

APPARATUS AND TECHNIQUE

Tunable Optic Filter for Filtering Light

MCNC *World Appl.* 00/45,202

A tunable optic filter (1), for filtering UV light in windows, comprises sets of alternating layers of dielectric material with different refractive indexes separated by an intermediate layer (2), of PLZT, PZT, $BaTiO_3$, etc., the refractive index of which changes with the intensity of an applied electric field. Two further electrically conductive layers: of ITO, SnO_2 , In_2O_3 , ZnO and RuO_2 , provide an electric field across (2). (1) has faster reaction time, requires no motor-driven mechanism to tune it, and is adaptable to different shapes without any energy increase.

Detection of Methyl Methacrylate

OPI PROD. INC. *U.S. Patent* 6,100,097

Methyl methacrylate (1) is identified quickly from other methacrylates in a liquid monomer by the formation of a blue coloured methacrylate-Pd molybdate complex after Pd molybdate is added to the monomer, followed by other treatment. (1) is detected in the liquid part of liquid/powder systems used for forming artificial nails.

Limiting-Current Type Oxygen Sensor

HITACHI CHEM. CO. LTD. *Japanese Appl.* 2000/146,904

A limiting-current type O_2 sensor (1) comprises a solid electrolyte adhered to an inner wall of a ceramic columnar body by heat resistant material. The surface is permeable to air. Electrodes are formed on either side of the electrolyte. A Pt wire is fixed to the electrolyte. (1) is used in gas supply apparatus. It has excellent heat resistance, is dependable and can withstand heat shock. It can also be mass produced.

Filter for Removal of Tobacco Odour

KOBE STEEL LTD. *Japanese Appl.* 2000/210,373

A deodorant placed in a deodorising filter, for efficient removal of tobacco odour, has a porous support containing 0.1–10 wt.% Pd and Cl with Pd:Cl molar ratio ≥ 2.5 . The deodorant can also efficiently remove chemical agents such as alkali and acid and other odorous components.

Spin Valve Magnetoresistive Sensor

RIDORAITO SMI K.K. *Japanese Appls.* 2000/251,225–256

A spin valve type magnetoresistive sensor (1) for a magnetic recording device, includes an antiferromagnetic alloy layer containing either (in at.%): 45–55 Cr, 2–10 Mn and remainder Pt; or (in wt.%): 2–10 Pd, 45–55 Mn, 20–35 Cr and remainder Pt. The alloy layer is heat treated at 250–300°C. (1) suppresses rotation of the thin magnetic layer by the bias magnetic field of the magnetic head, hence improving the thermal magnetic stability. A high magnetoresistive variation rate and high linear response result in a high recording density and a reliable magnetic head.

HETEROGENEOUS CATALYSIS

Hydrogenation of Epoxidised Cyclohydrocarbons

UBE IND. LTD. *European Appl.* 1,018,498

Epoxidised 6C–12C cyclohydrocarbons are efficiently hydrogenated in a single-step process by contacting the hydrocarbons with H₂ at a pressure of 0.1–5.4 MPa and a temperature of 100–280°C in the presence of Ru, Rh, Pd, Os, Ir and/or Pt catalysts supported on activated C, Al₂O₃, SiO₂, SiO₂-Al₂O₃, TiO₂, zeolites and spinel. Total yields of cycloalkane and cycloalkanol of ≤ 93% were obtained. These are intermediates for the production of lactams, lactones, etc., for use in synthetic resins and fibres.

Hydrodesulfurisation-Isomerisation Catalyst

COSMO OIL CO. LTD. *World Appl.* 00/35,581

A catalyst for simultaneous hydrodesulfurisation and isomerisation of light hydrocarbons comprises a support of Zr oxide or Zr hydroxide and a sulfate radical, impregnated with (in mass%) either: 0.05–10 Pd; 0.05–10 Pd and 0.05–10 Pt; or 0.05–10 Ni. After heat stabilisation at 550–800°C the specific surface area is 50–150 m² g⁻¹. Manufacture of the catalyst is also claimed. The catalyst has high activity, high S resistance, and reduced running costs.

Production of Alkylhydrogenohalosilanes

RHODIA CHIM. *World Appl.* 00/39,132

Alkylhydrogenohalosilanes (1) are produced by the catalytic hydrogenation of alkylhalosilanes (2) using a bimetallic Ru-Sn catalyst. The process is especially useful for vaporising excess (2), especially MeSiCl₃, formed as byproduct during the Rochow-Müller synthesis (direct reaction of metallic Si with CH₃Cl). This reaction gives monomers used to produce silicone resins. Under industrial conditions in the presence of the Ru-Sn catalyst, (2) can be easily converted into (1) with a high degree of specificity.

Steam Reforming Hydrocarbons

IMPERIAL CHEM. IND. PLC *World Appl.* 00/43,121

A catalyst to steam reform hydrocarbons, such as CH₄, naphtha, LPG, etc., and to treat coal gasification gases comprises 0.1–2.5 wt.% Ru and/or Ru oxide, impregnated on a preformed porous carrier with oxides of Ni, La and Al. Hydrocarbon feedstock and steam are passed over the cylindrical catalyst heated at 600–850°C. Ru and/or Ru oxide improve resistance to C deposition and give high catalytic activity.

Catalyst for Vinyl Acetate Synthesis

CELANESE CHEM. EURO. G.m.b.H. *World Appl.* 00/44,496

A catalyst for gas-phase production of vinyl acetate from ethylene, acetic acid and O₂, contains Pd, Cd and/or their compounds and alkali metal(s) on a moulded porous support. The support is based on pyrogenic SiO₂ and contains Mg. It has a hollow cylindrical configuration with facet edges. Activity and selectivity are increased by using this support, which gives a totally impregnated or shell catalyst.

Removal of Methanol from Off-Gases

GENERAL ELECTRIC CO. *World Appl.* 00/47,309

MeOH impurities in off-gases generated during isopropylbenzene oxidation are oxidised to CO₂ and H₂O at low temperature by contacting the off-gases with a Pt/zeolite catalyst. Granulated HZSM-5 zeolite is impregnated with H₂PtCl₆ solution, followed by drying and calcining to decompose the acid to give ≥ 0.1% Pt content. The resulting discharge stream contains MeOH at concentrations of ≤ 20 ppm.

Manufacture of Acetic Acid

SHOWA DENKO K.K. *World Appl.* 00/51,725

A catalyst for the manufacture of acetic acid by reacting ethylene and O₂ in the gas phase, comprises Pd metal, Au metal and heteropoly acids and/or their salts on a support. The Pd:Au weight ratio is 1:0.1–5.0. The manufacture of the catalyst is claimed. Space-time yield, compared to prior art is high, and selectivity to CO₂ is low. Catalyst deterioration is low while acetic acid production is high.

Purification of Gas for High Purity Uses

AIR PROD. & CHEM. INC. *U.S. Patent* 6,093,379

Purified gas is produced by removal of CO₂, H₂O, CO and H₂ from a gas stream by adsorbing H₂O and CO₂ on a solid adsorbent, such as Al₂O₃ or zeolite, and oxidising CO to CO₂ over a Pt group metal catalyst on a support which has zpc (zero point charge) of > 8.0. The CO₂ formed is adsorbed, and any H₂ is chemisorbed on the catalyst, such as Pd/Al₂O₃. This method can purify air by removing CO and H₂ before or after cryogenic distillation for generation of N₂ and/or O₂ for electronic and high purity applications. Enhanced efficiency, simple energy-efficient regeneration for continuous use and reduction of costs are obtained.

Fischer-Tropsch Synthesis

ENERGY INT. CORP. *U.S. Patent* 6,100,304

Pd-promoted Co/γ-Al₂O₃ catalysts provide significantly enhanced activity for Fischer-Tropsch synthesis in a continuous reaction system, particularly in a slurry bubble column reactor. The catalyst contains (parts by weight): 10–65 Co and 0.25–7 Pd per 100 of γ-Al₂O₃ support. The catalyst is formed by total aqueous co-impregnation so that the Co and Pd form a dispersed catalytic phase and are in intimate contact. The process is rate and cost efficient, has higher selectivity, and is environmentally friendly.

Treating Diesel Engine Exhaust Gases

FORD GLOBAL TECHNOL. INC. *U.S. Patent* 6,103,207

A catalyst for treating diesel engine exhaust gases contains a mixture of 25–65 wt.% particles of a Mn and Zr bimetallic oxide and a supported Pt group metal, for example 0.25 wt.% Pt/Al₂O₃. The atomic ratio of Mn:Zr is 3:1–1:3. The catalyst reduces NO_x in an oxidising atmosphere during diesel engine operation. A wider NO_x conversion window in the low temperature region is obtained.

Manufacture of Polyalkylene Glycol 1-Alkenyl Ethers

SHOWA DENKO K.K. *Japanese Appl.* 2000/143,567

Highly pure polyalkylene glycol 1-alkenyl ethers are manufactured at a high selection rate and in high yield by inhibiting the formation of byproduct. The reaction comprises isomerisation at 30–200°C of a polyalkylene glycol 2-alkenyl ether using at least one type of a catalyst carrying 0.05–10 wt.% of a noble metal(s), such as Pd/carrier. The product ethers are useful as resin materials and reaction diluents.

Production of High Purity Sugar Alcohols

ROQUETTE FRERES S.A. *French Appl.* 2,789,683

Production of sugar alcohols comprises hydrogenating the corresponding sugar in a series of trickle-flow reactors comprising a first reactor containing a fixed bed of a Ru catalyst and a second reactor containing a fixed bed of a promoted Ru catalyst. The process can convert D-glucose into high purity sorbitol ($\geq 98.5\%$ for sorbitol) at high conversions ($\geq 99.85\%$) and with high selectivities ($\geq 99\%$).

Epoxidised Olefin Production

BAYER A.G. *German Appl.* 1/98/57,137

Epoxidised olefins (1) are produced by reacting olefins with H_2O_2 solution in the presence of a synthetic Ti-containing zeolite, followed by separation of (1) and recycling the H_2O_2 solution. The H_2O_2 solution, which is dilute alcoholic or aqueous-alcoholic, optionally contains a stabiliser and is prepared by continuous reaction of H_2 and O_2 on a Group VIII metal catalyst. The process gives high selectivities ($> 85\%$ for propylene oxide) despite using the dilute H_2O_2 solution directly, without any intermediate purification.

HOMOGENEOUS CATALYSIS

Production of Oligocarbonates

BAYER A.G. *European Appl.* 1,013,634

Oligocarbonates are produced by reacting an aromatic dihydroxy compound with CO and O_2 in the presence of a Pt metal catalyst, a cocatalyst, a base, an inert organic solvent and, optionally, a quaternary salt. The solvent forms an azeotrope with the H_2O byproduct and is removed from the reaction mixture. The catalytic system has increased activity. The oligocarbonates have low residual H_2O content.

Preparation of Mono- and Di-arylphosphines

CYTEC TECHNOLOGY CORP. *World Appl.* 00/32,613

Mono- (1) and di-arylphosphines (2) are prepared by reacting an aryl compound with phosphine in the presence of a Group VIII metal catalyst, for example, an adduct of a Pd(II) compound and a triaryl phosphine. The aryl compound has a leaving group attached to a C atom of the aromatic ring. The process avoids or alleviates corrosion and can be carried out on a large scale. (1) and (2) are obtained in good yield along with relatively small amounts of tertiary phosphine.

Production of Aldehydes

MITSUBISHI CHEM. CORP. *Japanese Appl.* 2000/159,719

An aldehyde is produced by reacting an olefinic compound, such as propylene or 1-butene, with H_2 and CO in a solution containing a Rh complex catalyst which has an organophosphite ligand, such as diphenyl(2,4-ditertiary butylphenyl)phosphite, at 15–150°C and pressures of atmospheric to 200 kg cm^{-2} . Ni ($1-10^3$ ppm) is added to the solution to reduce catalyst decomposition and inhibit deactivation, so that the catalyst can be circulated and reused.

Biphenyl Tetracarboxylic Acid Ester

UBE IND. LTD. *Japanese Appl.* 2000/186,063

Manufacture of 3,3',4,4'-biphenyl tetracarboxylic acid ester involves the dimerisation of *o*-phthalic acid diester in the presence of sequentially added catalyst (powdered Pd salt of specific surface area ≥ 0.5 m^2 g^{-1}) and a basic bidentate ligand. The adherence of Pd metal precipitate to the reaction vessel is inhibited.

Preparation of Benzoic Amides

CENTRAL GLASS CO. LTD. *Japanese Appl.* 2000/191,612

Benzoic amides (1) are prepared in a single step by reacting aromatic compounds, Ar-X (Ar = optionally substituted aromatic group, X = halogen, trifluoromethanesulfonate, 1-4C alkylsulfonate, etc.), CO and NH_3 in the presence of a catalyst of Pd and phosphines. Benzoic acid is produced which is separated from the reaction system. The recovered Pd-phosphine complex is then used as a catalyst. (1) are useful intermediates for pharmaceuticals and agrochemicals.

Production of Alkyl 3-Alkenoates

BASF A.G. *German Appl.* 1/99/04,200

Alkyl 3-alkenoates are produced by adding formates to dienes in the presence of CO (at a partial pressure ≥ 1 MPa) and a catalyst containing a Pd compound and metal chloride(s) MCl_n (M is an alkaline earth metal when $n = 2$, or a metal ion of sub-Group IV when $n = 4$, or a metal ion of sub-Group VI when $n = 3, 5$ or 6). Organic base containing P or N is not present. The process is more selective and operates at lower pressures than existing processes. It can be carried out without solvent or with the educts as solvent, so HCl acid need not be added.

FUEL CELLS

Electrode Structure for Fuel Cells

JOHNSON MATTHEY PLC *World Appl.* 00/35,037

A piston-tolerant anode structure, for use in membrane electrode assemblies and PEMFCs, has two catalytic components. The first is Pt-Y, where Y is a bronze forming element, (Ti, V, Nb, Ta, etc.) with an optional third metal X (X = Ru, Rh, Ti, Cr, Mn, Fe, Co, Ni, Cu, Ga, Zr, Hf or Sn, especially Ru, Rh, Mn, Co and Ni). The second catalyst is Pt-M (M = one of the above metals, especially Ru or Rh). The anode has improved tolerance to CO and CO_2 poisons while maintaining high activity.

Catalyst Ink and MEAs for Fuel Cells

CALIFORNIA INST. OF TECHNOLOGY

World Appl. 00/45,448

A catalyst ink for DMFCs comprises catalytic material, such as Pt or Pt and Ru, and poly(vinylidene fluoride). The catalyst ink improves interfacial bonding characteristics between deposited electrocatalytic layers and the proton conducting moieties of MEA structures. Electrical performance is improved and impedance reduced. MeOH crossover in a fuel cell stack is reduced.

Fuel Cell Catalyst for PAFC and DMFC

SYMYX TECHNOLOGIES INC. *World Appl.* 00/54,346

A ternary Pt-Ru-Pd catalyst for use in electrochemical reactor devices, especially as fuel cell electrodes, comprises (in at.%): 20–60 Pt, 20–60 Ru and 5–45 Pd. The atomic ratio of Pt:Ru is 0.6–1.8. The fuel cells, for instance PAFCs or DMFCs, electrochemically convert a hydrocarbon-based fuel and O₂ to H₂O, CO₂ and electricity. The catalysts give improved fuel cell efficiency while allowing a decrease in the size of the cell and the costs.

Hydrogen Refiner for Fuel Batteries

MATSUSHITA DENKI SANGYO K.K.

Japanese Appl. 2000/178,007

A H₂ refiner which produces H₂ as a fuel for fuel batteries, comprises a feedzone for a modified gas and a reaction chamber downstream of the feedzone. The reaction chamber contains a catalyst which removes CO from the gas. The CO transforming catalyst is Pt, Ru, Rh and/or Pd. The gas may also contain H₂ and H₂O. The refiner has a shorter start-up time and problems caused by O₂ are prevented. The refiner operates stably for longer times.

ELECTRICAL AND ELECTRONIC ENGINEERING

Conductive Barrier Layers in Electronic Capacitors

SHARP K.K. *European Appls.* 1,035,588–89

A temperature stable conductive barrier layer, for IC ferroelectric capacitors used in FRAMs, comprises a first barrier layer containing Ta on a substrate, with a film of Ir or Ir-Ta-O. The film of Ir-Ta-O remains conductive after annealing at high temperature in an O₂ ambient atmosphere. Adhesion, conductance, hillock and peeling problems are minimised, as the Ir does not interact with the substrate.

Integrated Circuits

SYMETRIX CORP. *World Appl.* 00/49,660

An integrated circuit for non-ferroelectric or ferroelectric devices with high dielectric constant has a diffusion barrier layer of Ir oxide which is located between a thin film of layered superlattice material (1) and a local interconnect. The Ir oxide inhibits diffusion of chemical species from the local interconnect to (1) and is thus effective for preventing diffusion of metals, Si, and other chemical species.

Horizontal Magnetic Recording Medium

INT. BUSINESS MACHINES CORP. *U.S. Patent* 6,086,974

A horizontal magnetic recording medium (1) has a magnetic layer of granular film with grains of chemically ordered FePt or FePtX alloy (or CoPt or CoPtX) (X = Cr, Cu, Ag, Ta, etc.). It also has an etched seed layer of nonmagnetic Pt, Pd, Cr, CrV, etc., on a substrate. The magnetic properties are controlled by grain size and distribution, degree of chemical ordering, and the nonmagnetic materials. (1) has low-noise, high density and the high magnetic stability.

Ferroelectric-Based Capacitor

RADIANT TECHNOLOGIES INC. *U.S. Patent* 6,117,688

A ferroelectric-based capacitor used in memory systems has: a bottom electrode consisting of a Pt layer in contact with a layer of ohmic material; a dielectric of Pb-Zr titanate doped with an element having an oxidation state > +4; and a top electrode consisting of a second ohmic material layer in contact with a second Pt layer. The capacitor exhibits low fatigue, low imprint and is used in memory systems.

Production of Printed Circuit

SHINETSU CHEM. IND. CO. LTD.

Japanese Appl. 2000/138,442

Circuit board is produced by forming a thin film of a polysilane (1), containing a C functional silane, on a substrate and contacting it with a Pd salt to form a colloidal Pd layer. A photosensitive resin layer is placed on (1) and is then selectively irradiated with light to form a patterned groove. An electroless plating solution is applied to form a conductive metal layer in the groove. The circuit substrate has superior heat resistance and fineness of pattern.

Semiconductor Devices such as FRAM

FUJITSU LTD. *Japanese Appl.* 2000/156,471

A reliable semiconductor device, such as FRAM, with good fatigue resistant characteristics contains an electrode which carries a metal oxide (Pt, Ir, Ru, Ni, Ti, Zr and Ce) film on which a metal film is formed. A ferroelectric film (1) is formed on the electrode and on this is formed an electrode containing a perovskite. By repeated polarisation inversion, O vacancies in (1) are supplemented by O from the perovskite film. Capacitors which operate at low voltage can use the material.

Circuit Electrode of Laminate Structure

OCEAN K.K. *Japanese Appl.* 2000/160,348

A laminated electrode structure for use on a printed circuit board has a Pd corrosion-resistant film over a Ni plated film formed on the circuit pattern of the substrate. A Au film is formed on the Pd film surface. Contact adherence strength between each film layer in the laminate is improved as is surface flatness. Bonding and ball shear strength are also increased.

The New Patents abstracts have been prepared from material published by Derwent Information Limited.