NEW PATENTS

METALS AND ALLOYS

Platinum-Based Precious Metal Compositions

IMPLICO B.V. *World Appl.* 97/15,694A

A decorative artefact is fabricated from a precious metal composition containing ≥ 55 wt.% of a Pt group metal, with a total precious metal content of ≥ 80 wt.%, together with one or more alloying elements. The composition includes intermetallic compounds and always has a Vickers Hardness of ≥ 600. These alloys are hard enough to be polished and/or faceted using techniques commonly used for gemstones and the precious metal content conforms to hallmarking standards.

Decorative Platinum Alloy for Jewellery

KUWAYAMA KIKINZOKU K.K.

Japanese Appl. 8/337,830

A Pt alloy mainly contains Pt and 0.001–0.5 wt.% of B. It has improved workability, strength and casting properties and is used in the production of jewellery accessories, such as rings, necklaces, etc.

Super-Elastic Palladium Alloy

FURUKAWA ELECTRIC CO. LTD.

Japanese Appl. 9/78,165

An alloy comprises (in at.%) 34–49 Ni, 48–52 Ti and 3–14 Pd. Stress hysteresis in a stress-stain curve, at the application and releasing of a load, at a temperature from A_f to A_f + 5°C, is 50–150 MPa. The alloy is effectively used as a wire for the correction of irregularities in teeth.

ELECTROCHEMISTRY

Cogenerating Electrochemical Cell

HURON TECH. CORP. *World Appl.* 97/16,584A

An electrochemical cell which cogenerates an ammonium peroxide compound and H_2O_2 consists of an anolyte compartment where the ammonium compound is generated at a discontinuous Pt group metal coated onto a valve metal anode, separated by a cation exchange permselective membrane from a catholyte compartment where alkaline H_2O_2 is cogenerated at a C black coated graphite chip cathode. The process operates as a closed loop with the ratio of alkali metal hydroxide:H_2O_2 controlled by NH_3 recovery from the catholyte.

Insoluble Electrode

NIPPON STEEL CORP. *Japanese Appl.* 9/53,200

An insoluble electrode is made of an electroconductive metal and a porous insulator oxide film, which is formed onto the electrode material. The pores of the insulator oxide film are filled with the electrode material, and a further porous layer is filled with IrO_2, which is covered, followed by coating and baking. The insoluble electrode gives long service life.

Electrode for Electrolysis

ISHIFUKU KINZOKU KOGYO K.K.

Japanese Appl. 9/87,896

An electrode for electrolysis consists of an alloy containing at least one 50–96 wt.% metal selected from Ti, Ta, Nb, Zr and W, and at least one 50–4 wt.% metal selected from Ir, Ru and Zn. Production involves forming an alloy layer on a Ti base, coating with Ir and Ta compounds and oxidising to form a coating layer of Ir and Ta oxide. Superior adhesion of the coating layers is achieved. The electrode has long term durability under the base electric potential environment and is used as an anode to surface-treat metals and in the production and recovery of metal foil.

Electrode Base for Anode

PERMELEC ELECTRODE LTD.

Japanese Appl. 9/125,292

An electrode base for an anode comprises a layer formed by thermally spraying a Pt-based metal or its compound onto the surface of TiO_2 particles, which are on the surface of a Ti base. The electrode base has high resistance to corrosion and is used as an anode for electrolysis at high current density in a strong acid bath, such as in high speed Zn plating or electrolytic Cu foil production.

ELECTRODEPOSITION AND SURFACE COATINGS

Palladium Plating

S. S. MOON *British Appl.* 2,305,188A

Plating Pd or a Pd alloy onto Fe-Ni alloy semiconductor lead frames involves plating a metal selected from Cu, Sn, Ni-Sn alloy and Cu-Sn alloy onto the substrate to form a first primer layer followed by Ni or a Au alloy to form a second primer layer followed by plating with a Pd or Pd alloy layer. These plated layers have good adhesiveness to the substrate, resulting in good corrosion resistance and solderability.

Metal Plating on Carbon

FUJI SEIKO HONSHA K.K. *Japanese Appl.* 8/319,575

Fine C particles consisting of mesophase spherical crystals are treated by oxidation and impregnated with $Pd(NH_3)_4Cl_2$ to form a Pd film by electroless plating. Using this method, uniform Pd metal film is formed on fine C particles.

Manufacture of Palladium Sulphate for Plating

TANAKA KIKINZOKU KOGYO K.K.

Japanese Appl. 9/86,935

$PdSO_4$ containing < 0.05% nitride and < 0.2% insoluble matter was produced by dissolving Pd in a mixture of H_2SO_4 and HNO_3, heating to 125°C to deposit $PdSO_4$, followed by washing in dilute H_2SO_4 and propanol-diethylether and diethylether. With $PdSO_4$, good plating can be achieved without the formation of any unevenness or grains.

APPARATUS AND TECHNIQUE

Removing Hydrogen from Water

SHINKO PANTEC CO. LTD. *Japanese Appl.* 8/311,676

H_2O containing dissolved H_2 generated in the cathode chamber of a H_2O electrolysis cell is contacted with Pd to occlude H_2 and remove it from the H_2O. H_2O free of dissolved H_2 gas is then returned to a tank to supply pure H_2O or H_2O containing ions to the anode chamber. The Pd is recycled by contacting with H_2O saturated with O_2 in the anode chamber, continuously or intermittently.

Absolute Gas Concentration Sensor

ITVI INT. TECHNO VENTURE INVEST. A.G. *German Appl.* 1/95/43,296

Equipment for measuring absolute gas concentrations is based on a sensor having a gas-sensitive layer, with an electric heater, which is preferably made of Pt with a high temperature coefficient of resistance. The temperature of the sensing element is raised and lowered by adjustable steps faster than it takes to attain 99% saturation. The sensor is used for monitoring air quality around vehicles or buildings.

NOx Sensor

HONDA GIKEN KOGYO K.K. *German Appl.* 1/95/49,090

A sensor for NOx in exhaust gases from motor vehicles has two interdigitated thin-film Pt electrodes arranged on a heated baseplate and covered with a mixture of sintered β-Nb_2O_5 as the primary constituent and 0.1–20 wt.% TiO_2 or 0.1–10 wt.% Ru. It has outstanding NOx absorption properties and high sensitivity. The quantities of NOx and O_2 decrease with the gas concentration, and the quantities adsorbed increase as the temperature falls.

HETEROGENEOUS CATALYSIS

Nitrogen Oxide Trap

FORD FRANCE S.A. *European Appl.* 764,459A

A NOx trap (1) for use with lean burn engines comprises a mixture of 0.1–5 wt.% Pt and 2–30 wt.% alkali metal or alkaline earth element loaded on separate porous γ-Al_2O_3 supports. (1) absorbs NOx under lean conditions and then releases it when the O_2 concentration is lowered and may be used with a three-way catalyst. The trap has improved NOx absorption efficiency compared with conventional traps where materials are loaded on the same support.

Selective Hydrogenation of Acetylene

BASF A.G. *European Appl.* 764,463A

A supported catalyst for the selective hydrogenation of C_2H_2 in hydrocarbon streams is prepared by impregnating SiO_2 with 0.001–1 wt.% Pd and 0.005–5 wt.% Group I and/or II metal(s) as promoter. The catalyst is used especially for streams of C_2H_4 and C_2H_6 containing 0.01–5 vol.% C_2H_2. Small amounts of C_2H_2 can be hydrogenated with high selectivity without the addition of CO. It is especially useful in steam crackers and in the production of polyethylene.

Selective Upgrading of Naphtha Feedstock

UOP *European Appl.* 770,666A

A process for selectively upgrading naphtha feedstocks (1) containing naphthalenes to obtain products with increased isoparaffin content involves contacting (1) and H_2 with a non-acidic ring-cleavage catalyst comprising at least one Pt group metal component and a non-acidic support at 100–500°C, 100 kPa–10 MPa and LHSV of 0.1–30 h^{-1} to produce a paraffinic intermediate. This is then catalytically isomerised at 40–250°C, 100 kPa–10 MPa and LHSV of 0.2–15 h^{-1} with a solid acid catalyst containing a Pt group metal. This gives high octane products useful as gasoline blending components for high-performance I.C.E.s.

Exhaust Gas Purification Catalyst

TOYOTA JIDOSHA K.K. *European Appl.* 773,057A

A catalyst for the purification of exhaust gas from an I.C.E. comprises a zeolite carrying Pt and Cu to simultaneously remove NOx and NH_3 in an oxidising atmosphere over a wide temperature range.

Diesel Engine Exhaust Gas Purification

CATALER IND. CO. LTD. *European Appl.* 781,590A

A catalyst for the purification of diesel engine exhaust gases comprises: a support, a carrier layer which has an activated Al_2O_3 internal part within an amorphous clay mineral superficial part, and at least one catalyst ingredient of Pt, Pd and Rh loaded on the carrier layer. The catalyst can convert diesel hydrocarbon particulates, sulfates and CO with improved efficiency. It has enhanced carrier layer adhesion to the support.

Combustion of Alcohol Based Fuels

INST. KEMITEKNIK. KEMISK. TEKNOL. *World Appl.* 97/9,114A

A catalyst, for the combustion of alcohol based fuels, is produced by coating a carrier, which is distributed on a monolith, with a suspension of particles of two Pt group metals in a microemulsion or the active phase of two Pt group metals co-reduced in the microemulsion. The particles, such as Pt and Pd, form a monolayer on the carrier, which consists of Al_2O_3, TiO_2 or SiC. This catalyst may be used in energy recovering systems, such as industrial boilers, gas turbine burners and heat generating systems. It may also be used for the purification of effluent from diesel engines where ethanol is used as fuel, such in buses. It is efficient at low temperatures, such as when an engine is idling, in contrast to previous systems.

Hydrogenation Catalyst Production

BASF A.G. *World Appl.* 97/12,673A

A hydrogenation catalyst, used for preparing hydroxylammonium salts, is produced by reducing Pt(IV) to Pt(II) with a selective reducing agent in an acidic aqueous medium in the presence of a C-containing carrier. The Pt(II) is then partially poisoned with a S-containing selective reducing agent and reduced to metallic Pt. This catalyst has longer service life, high selectivity and high space-time yield, and only small amounts of by-products are produced.

Hydrocarbon Conversions

UOP *U.S. Patent* 5,614,454

A catalyst for the catalytic reforming of hydrocarbons, especially gasoline-range, and dehydrocyclisation of paraffins comprises a multi-gradient noble metal component comprising Pt and surface layer Ru, a non-acidic large pore molecular sieve or a non-acidic L-zeolite, and an inorganic oxide binder of SiO_2 or Al_2O_3. The Ru concentration in the 100 μm surface layer is ~ 2 or 3 times that of the metal in the central core of catalyst particles or, for a 50 μm surface layer, ~ 2 times higher. This catalyst has high activity and stability, and high selectivity to aromatics.

Heat-Proof Catalyst

BABCOCK-HITACHI K.K. *Japanese Appl.* 8/309,183

A heat-proof catalyst, used at > 100°C, consists of Pt, Pd or Rh or its oxide on a porous Al_2O_3 carrier and Si on the substrate covering the whole carrier. The catalyst maintains high catalytic activity over a long time at high temperature. It is used for the treatment of inflammable, harmful and odorous gas.

Combustion Catalyst

ZH. SEKIYU SANGYO KASSEIKA CENTER *Japanese Appl.* 8/309,184

A catalyst, used at 600–1000°C, comprises 5 mol% of reduction-retardant Pd oxide carried on a heat-proof inorganic carrier containing ZrO_2. The catalyst has less drop or fluctuation in oxidation activity at the above temperature. It is used in high temperature burners, such as gas turbines and boilers.

Platinum Catalyst

LION DENSHI K.K. *Japanese Appl.* 8/312,956

A Pt catalyst holding structure for a combustion device, such as a gas lighter, consists of a ring with grooves through which the terminations of a Pt coil are passed and bent along the periphery of the ring, thereby suspending the coil in the centre of the ring. This reduces the number of parts and simplifies fixation.

Dehydrogenation Catalyst

CHIYODA CORP. *Japanese Appls.* 9/70,535 and 9/70,544

A dehydrogenation catalyst for alkanes comprises γ-Al_2O_3, of a specific surface area and pore size, holding 5–50 wt.% Zn oxide. Onto this is supported 0.05–1.5 wt.% Pt and 0.5–10 wt.% Sn by immersing in chloroplatinic acid and reducing, using hydrazine or Na borohydride, followed by washing with hot H_2O and reducing the Sn. The catalyst has high activity and selectivity, and reduced deterioration rates.

Catalyst Layer for Denitrification

NE CHEMCAT K.K. *Japanese Appl.* 9/70,538

A catalyst layer for denitrification contains a first catalyst of activated Al_2O_3 with Ag, Zn and P, and a second catalyst of activated Al_2O_3 containing at least one element selected from Pt, Pd, Rh, and Ce. The first catalyst is arranged at the front of a flow path of waste gas and the second catalyst at the rear. NOx in waste gas is removed under wide atmospheric conditions.

Dechlorination of Aromatic Chloride

AGENCY OF IND. SCI. & TECHNOLOGY *Japanese Appl.* 9/75,473

A method for dechlorinating aromatic chlorides involves contact with a dispersion of 100–200 mg of 5–10% Pd/C catalyst and K or ammonium formate in a hydrocarbon solvent, to form a biphasic solution. Tetra-*n*-butylammonium bromide or phenyltrimethylammonium chloride is added as a phase-transfer catalyst, followed by stirring and heating at 50–60°C for 1–3 h. Difficult dechlorinations of environmentally harmful aromatic chlorides, such as PCB, can be performed using this method under milder conditions.

Hydrogenation of Vegetable Oils

AS USSR CHEM. PHYS. INST. *Russian Patent* 1,321,052

A catalyst for hydrogenating vegetable oils and fats contains Pd/Al_2O_3 and B, which improves its activity. The component ratios are (in wt.%) Pd 5×10^{-3}–2.0, B 10^{-6}–10^{-4} and the balance is Al_2O_3. This catalyst increases the hydrogenation productivity by 1.5–3 times and improves the quality of the hydrogenated oils and fats produced.

HOMOGENEOUS CATALYSIS

Acetic Acid Production

BP CHEM. LTD. *European Appl.* 769,486A

Acetic acid is produced by reacting CO with a possibly-carbonylated reactant containing > 10 wt.% dimethylether. The reaction takes place at elevated temperature in a liquid phase containing a Group VIII noble metal catalyst, MeI promoter, an optional co-promoter and 0.1–10 wt.% H_2O. The rate of carbonylation for dimethyl ether is higher than that of methyl acetate and/or methanol.

Palladium Catalyst for Cross-Coupling

HOECHST A.G. *World Appl.* 97/5,151A

A catalyst system for cross-coupling reactions contains a Pd(II) compound, such as a Pd(II) salt, Pd tetrachloroacid or one of its salts, a H_2O-soluble phosphane ligand, and either a sulfoxide or water soluble polyhydric alcohol. H_2O and a solubility aid for the Pd compound, especially Na acetate, are added to the reaction mixture. This method works with the cheaper chloroaromatics and can be used to prepare compounds used as liquid-crystal materials or intermediates in the preparation of pharmaceuticals, cosmetics, fungicides, dyes, etc.

Hydroformylation Process

DSM N.V. *World Appl.* 97/8,127A

A hydroformylation process to prepare 5-formyl-valeric acid (ester) or 5-formyl-valeronitrile involves contacting a compound selected from 2-, or 3-pentenoic acid (ester) and 2-, or 3-pentenenitrile, with H_2 and CO in an organic solvent containing a dissolved catalyst. The catalyst is a Pt compound free of anionic halide, containing a bidentate diaryl phosphine ligand and an acid promoter. Internally unsaturated compounds are converted to linear products.

Hydrosilation Process

DOW CORNING CORP. *U.S. Patent* 5,616,763

A hydrosilation process for compounds having internal unsaturation involves the reaction with a Si hydride in the presence of a Pt catalyst and an aldehyde accelerator. This process is used for cyclic compounds, such as cyclopentene and cyclohexene.

Trans-Rose Oxide Preparation

TAKASAGO PERFUMERY CO. LTD. *Japanese Appl.* 9/71,579

The preparation of *trans*-rose oxide involves cyclising 3,7-dimethyl-5,7-octadiene-1-ol or 3,7-dimethyl-5,6-octadiene-1-ol, both optically active, in the presence of a Pd(0)/optically active phosphine complex (1). Preferably, (1) is a Pd(0)/(*S*)- or (*R*)-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP). Rose oxide containing ≥ 40% *trans*-isomer is prepared in yields ≥ 70%.

Production of Asymmetric Cyano-biphenyls

GREAT LAKES CHEM. KONSTANZ G.m.b.H. *German Appl.* 1/96/7,135

The production of asymmetrically substituted biphenyl nitriles (1) involves the Pd-catalysed coupling of an aryl Grignard compound (2) with a bromobenzonitrile at 10–100°C. The concentration of the Pd catalyst is 0.1–20 mol% and (2) is added slowly over a period of time of ≥ 30 min, to avoid the production of large quantities of by-products. (1) are useful as raw materials and intermediates for the production of biphenyls, which are structural components for angiotensin II inhibitors, and are also used for liquid crystals and for electro-optical materials.

FUEL CELLS

Catalyst Body for Use as Fuel Cell Anode

AISIN SEIKI K.K. *British Appl.* 2,307,651A

A composite catalytic moulding is obtained by applying a Pt chloride solution to a C support material, such as PTFE, followed by drying and reducing in H_2 to deposit metallic Pt on the surface of the conductive material. The same process is then repeated to deposit metallic Ru. The amounts of Pt and Ru deposited depend on the amounts of the respective solutions used. The catalytic component is of good quality with no dispersion in the composition ratio and is used for making the anode side of a fuel cell.

A Non-Acid Fuel Methanol Fuel Cell

CALIFORNIA INST. OF TECHNOL. *World Appl.* 97/21,256A

A non-acid fuel MeOH fuel cell for motor vehicles comprises a backing and a catalytic material which includes uniformly mixed and randomly spaced Pt-Ru bimetallic powder with distinct sites of Pt and Ru. The anode comprises a bimetallic powder of Pt and Ru and the cathode comprises Pt particles bonded to a solid polymer electrode. Improved electrode operation is achieved, especially the efficiency of MeOH production. Air at ambient temperature and pressure can be used as the reduction mechanism.

ELECTRICAL AND ELECTRONIC ENGINEERING

Metallised Ceramic Substrate

WESTAIM TECHNOL. INC. *European Appl.* 773,309A

A ceramic is metallised for electrical applications by cleaning, etc., sensitising for electroless deposition, forming Pd active sites on the surface, and electrolessly depositing Ni, Ag, Au, Co, Pd or Pt; optionally depositing an intermediate layer of the same metal, activating, etc., then electrodepositing a metal or alloy of Ni, Cu, Ag, Au, Co and Pt, or P, B, W or Mo alloys, to the desired thickness. The substrate has excellent metal-ceramic adhesion strength and a smooth surface, for use in high density AC/DC converters, etc.

Soldering System

NAT. STARCH. & CHEM. INVEST. HOLD. CORP. *European Appl.* 773,709A

A soldering system for making electronic circuit patterns, comprises two conductive thick film pastes, the first contains 70–75 wt.% Au, Pt and Pd conductive metal powder in ratio 100:23–27:5–7; 4–11 wt.% conventional glasses and oxides; 3–4 wt.% Cr_2O_3; optionally 4–6 wt.% Bi_2O_3 and balance organic vehicle which is deposited directly onto a substrate. The second conductive paste of Au, Pt and Pd in ratio 100:15–10:0–4; glasses and oxides; Cr_2O_3; Bi_2O_3 and balance organic vehicle is deposited onto the first.

Magnetic Recording Medium Alloy

TOSHIBA K.K. *Japanese Appl.* 9/81,927

A magnetic film on a non-magnetic base is composed of Co, 15–40 at.% Pt, 1–8 at.% of X (X is a metal, not from Groups Ia and IIa, with an ionisation potential lower than that of Co) and O and/or N. It has crystalline and non-crystalline areas, the latter containing more X than the former. This medium has reduced noise.

Semiconductor Device Manufacture

TOSHIBA K.K. *Japanese Appl.* 9/82,915

A semiconducting dielectric film, such as Ba titanate Sr film (1) is formed on a Ru film to give a first conductive material electrode, followed by heating in O_2 at a temperature higher than the crystallisation temperature of (1). A Ti nitride film is formed as a second conductive material. The device has reduced leakage current, increased dielectric constant, and is used for capacitor insulating films.

MEDICAL USES

Magnetic Dental Implant

DENKI JIKI ZAIRYO KENKYUSHO *Japanese Appl.* 9/84,807

A magnetic dental implant comprises a permanent magnet composed of 33–48% Pt and balance Fe, and an anti-degradable magnetic material. The implant can be moulded to fit the desired shape of the teeth.

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