NEW PATENTS

METALS AND ALLOYS

Amorphous Magnetic Alloy
READRITE CORP.

European Appl. 803,882A

An amorphous magnetic metal alloy comprising T,T,T_T, where T includes 75-98 at.% of Fe and/or Co; T includes 2-20 at.% of Rh; and T includes 2-15 at.% of Zr, has a saturation magnetic induction B of ≥ 1200 Gauss and a saturation magnetostriction constant α < 10 x 10^-6. Also claimed is a similar alloy which contains 2-15 at.% Rh and additionally 3-20 at.% of Pt and/or Pd. The alloys have a high corrosion resistance and are used in magnetic transducers or heads for use in magnetic recording devices.

ELECTROCHEMISTRY

Anode with Enhanced Durability
ELECTRICITE DE FRANCE

A photocatalyst for hydrogen production
MITSUBISHI MATERIALS K.K.

A thin Pt film, used in dielectric memory and in semiconductor devices, is formed on a substrate by organometallic chemical vapour deposition of an organic Pt compound by irradiation with light of wavelength ≥ 240 nm. This method forms a thin film of high-purity Pt at low reaction temperatures without deterioration of purity from decomposed ligands. Decreases in the film density by Pt coagulating into island shapes on the surface are also prevented.

Electrodes for Electrolysis
TDK CORP.

Japanese Appl. 9/279,381

An anode electrode for electrolytic O2 generation has a coating layer containing at least one Pt group metal or its oxide and has orthogonal grooves, which form quadrangular pyramid and/or quadrangular frustum pyramid convex parts. The electrode is stable for long periods, has a long life and good durability, even when used in electroplating baths containing additives to promote consumption of the electrode.

ELECTRODEPOSITION AND SURFACE COATINGS

Platinum-Iridium Alloy Plating
NIPPON ELECTROPLATING ENGINEERS K.K.

Japanese Appl. 9/256,189

A Pt-Ir alloy plating bath contains 1-30 g/l of an Ir(III) complex containing halogen and either an acid or a salt, and 0.1-15 g/1 of a Pt(II) complex containing nitrous ion. The Pt-Ir alloy plating bath gives good deposition.

High-Purity Platinum Thin Film
MITSUBISHI MATERIALS K.K.

Japanese Appl. 9/287,075

A high efficiency H2O electrolysis cell comprises a solid polymer electrolyte of a fluoro-resin ion exchange membrane, a catalytic anode and cathode, and feeders consisting of Pt plated sintered metal powder or sintered Pt plated metal powder. This cell can decrease the amount of catalyst on the electrodes, and can depress cell voltage to a low level.

Apparatus and Technique

Oxygen Sensor
TOYOTA JIDOSHA K.K.

Japanese Appl. 9/229,900

An oxygen sensor comprises a tube with inner and outer electrodes. A Pt coating layer is formed on the front face of a Si nitride heater, to deter Si sublimation from the heater at high temperature. The output characteristics of the sensor are maintained over a long time and the effective area of the electrode is maintained by the prevention of Si adhesion.
Sampling Uranium Oxide Fuel
MITSUBISHI JUKOGYO K.K.  Japanese Appl. 9/276,658
NOx gas treatment equipment for sampling U oxide fuel has a catalyst containing Pt and Rh, arranged in a catalytic reaction treater, which accepts exhaust gas from the upper gas space of a coolant chamber of a cooling treater. The equipment is compact in structure and easy to install in an airtight analysis box. It eliminates gas, such as NO.

HETEROGENEOUS CATALYSIS

Purification of Diesel Engine Exhaust Gases
DEGUSSA A.G.  European Appl. 800,856A
A catalyst for purifying diesel engine exhaust gases contains zeolites and a Pt group metal deposited on metal oxide(s) selected from AI silicate, Al2O3, and TiO2. The Al silicate has a weight ratio of SiO2:Al2O3 of 0.005–1. The catalyst can oxidise long chain heavy paraffins in the exhaust gas and simultaneously reduce the NOx despite the high O2 content of the diesel exhaust gas.

Polyhydroxyxcarboxylic Acids
AKZO NOBEL N.V.  World Appl. 97/34,861A
Polyhydroxyxcarboxylic acids are prepared by oxidation of di-, tri-, oligo- and polysaccharides in an alkaline medium with an oxygenous gas using Pd/carrier as a catalyst and Bi as promoter. The Pd concentration is ≥ 40 mg l−1 and the molar ratio Pd:Bi is 1:5–1:40. Towards the end of the reaction, when the O2 concentration in the liquid phase greatly increases, the O2 supply is reduced to ≤ 20 ppm. This process gives higher conversions and minimises catalyst deactivation and product contamination by Pd.

Vinyl Ester Production
HOECHST CELANESE CORP.  World Appl. 97/36,679A
A catalyst for producing vinyl esters, especially vinyl acetate, comprises a honeycomb carrier with SiO2 coated cells extending the entire length of the carrier, and Pd and Au metals distributed throughout the SiO2 coat. The catalyst has high activity and selectivity, long life and lower pressure drop across the catalyst. Heat distribution is improved. The SiO2 coated honeycomb carriers eliminate problems with cracking and brittleness which could occur with honeycombs containing only SiO2 or Al2O3.

Three-Way Catalyst
ARD CO. PTE. LTD.  World Appl. 97/40,923A
An exhaust gas purification catalyst comprises a carrier; a first catalyst layer made from magnetite, Ce oxide and Re which provides an O2 reservoir during catalysis; and a second layer comprising fine Ni needles distributed over the catalyst surface and a Pt group metal, preferably Pt. The three-way conversion catalyst is manufactured by applying a first catalyst layer to the carrier; immersing in a Ni2+ solution to form a Ni washcoat; autoclaving to form Ni needles then adding a coating of a Pt group metal. The catalyst has good stability at high temperature.

Palladium-Gold Catalyst
HOECHST CELANESE CORP.  World Appl. 97/44,130A
A bimetallic Pd-Au catalyst for the production of vinyl acetate from ethylene, acetic acid and O2 is prepared by the dispersion coating of colloidal Au on a shell dispersion coating of colloidal Pd on a porous support. The catalyst has high Au retention and is durable with long term selectivity and activity. The Pd and Au can both be deposited from organic solvent.

Benzene Saturation
UOP  U.S. Patent 5,663,466
A process for the saturation of benzene involves passing a feedstream of 5C and/or 6C paraffinic hydrocarbons and benzene through a guard bed to remove S, admixing with a H2-containing stream, contacting the feed with 0.1–1 wt.% Pt/Al2O3 catalyst and heating to 480–600°F. Controlled H2 addition improves the efficiency and cost-effectiveness. It is used in the production of high octane gasolines.

Naphtha Reforming
UOP  U.S. Patent 5,665,223
A catalytic composite comprises a combination of a refractory inorganic oxide support with 0.01–5 wt.% of a Group IVA metal, 0.01–2 wt.% Pt group metal and 0.05–5 wt.% Eu, with > 50% of the Eu being the oxide and the atomic ratio of Eu:Pd being > 1:3. The catalyst has improved selectivity for hydrocarbon conversion, especially for gasoline or aromatics.

Alkane Isomerisation Catalyst
PHILLIPS PETROLEUM CO.  U.S. Patent 5,668,074
A catalyst used in alkane and/or cycloalkane isomerisation is prepared by reducing compounds of Pt and/or Pd on an Al2O3 support at 300–600°C, incorporating Nb and/or Ta, heating in non-reducing gas at 300–500°C and treating with halocarbon compounds selected from fluoroalkanes and chlorofluoroalkanes at 200–500°C. The catalyst has high activity and selectivity for (cyclo)alkane isomerisation.

Three-Way Catalyst for I.C.E.
ASEC MFG.  U.S. Patent 5,672,557
A catalyst for reducing the amount of CO, hydrocarbons and NOx in exhaust gases of I.C.E. comprises Al2O3, CeO2 and/or lanthana, and optionally 5–20 wt.% of a promoter, with 0.05–5 wt.% Pd. The amount of Ce and La metals in the support is 80–300 g/1’ at a ratio of Ce:La of ≥ 3.5:1 and the wt. ratio of Ce + La/Al2O3 in the support is > 3. This Pd-only catalyst has reduced levels of Al2O3 (< 50%) in the support and improved durability and activity.

One-Stage Alkane Conversion
AMOCO CORP.  U.S. Patent 5,672,796
A one-stage process for the conversion of 3–6C alkanes to a low CH3-containing hydrocarbon product rich in aromatics involves contacting a feed comprising the alkanes with a catalyst of a H-form, partially sulfided Pt-Re-loaded aluminosilicate molecular sieve. The catalyst is used for hydrocarbon aromatisation and gives high conversions and selectivity.

Platinum Metals Rev., 1998, 42, (2)
**Unsaturated Ester Production**

**HORCHST CELANENE CORP.**  
*U.S. Patent 5,691,267*

A catalyst for the synthesis of unsaturated esters is prepared by impregnating a carrier with H₂O-soluble Au and Pd compounds, fixing them to the carrier as H₂O-insoluble Au and Pd compounds, and reducing them to Au and Pd metal. The catalyst gives improved space time yield and, in the production of vinyl acetate, reduced selectivity to CO₂, ethyl acetate and heavy end products.

**Fuel Additive**

**PLATINUM PLUS INC.**  
*U.S. Patent 5,693,106*

A fuel additive composition for an I.C.E. comprises a Pt group metal compound sufficient to give 0.05–2 mg Pt/l fuel and a H₂O-functional lipophilic emulsifier and, or, lipophilic organic compound in which H₂O is miscible. Degradation of catalyst activity is minimised by preventing the separation of H₂O from the fuel and maintaining the catalyst in the fuel.

**Removing Non-Methane Hydrocarbons**

**FARMTEC K.K.**  
*Japanese Appl. 9/113,486*

Non-CH₄ hydrocarbons are removed from exhaust gas by flowing the sample gas containing hydrocarbons and O₂ through a discharge tube with an applied A.C. voltage of 10–20 kV, 50–100 Hz, and feeding to a tube containing a Pt oxidation catalyst at 100–150°C to burn the hydrocarbons, except CH₄. Non-CH₄ hydrocarbon is almost completely oxidised and removed by suppressing the oxidation rate of CH₄.

**Waste Gas Purifier**

**HINO MOTORS LTD.**  
*Japanese Appl. 9/271,639*

A waste gas purifier for diesel engines comprises a first Pt/Al₂O₃ catalyst, a second Rh/CeO₂ catalyst and a third catalyst comprising Al₂O₃ carrier carrying Pt, Pd or a mixture of these, arranged by the exhaust-tube path, one-by-one from the upstream side of the waste gas circulation direction. Hydrocarbon gas flow is controlled by a rate-of-flow controller. NOX is converted into N₂ and nitrous oxide in atmospheric air is significantly reduced without releasing hydrocarbon gas to the atmosphere.

**Purification Catalyst for Exhaust Gas**

**TOYOTA JIDOSHA K.K.**  
*Japanese Appl. 9/271,665*

A catalyst for the purification of exhaust gas is composed of a spinel type composite oxide AB₂O₄ (A = Pt, Fe, Co, Ni, Cu, Zn, Cd or Hg; B = Ce). This catalyst allows the soot in diesel engine exhaust gases to be combusted efficiently at low temperature.

**Silica Gel Catalyst with Platinum**

**TANAKA KIKINZOKU KOGYO K.K.**  
*Japanese Appl. 9/276,698*

A manufacturing method involves adding to a SiO₂ gel a complex Pt cation produced by the pyrogenetic reaction of Pt chloride ammonium acid with surplus aqueous NH₃, which is removed by volatilisation to give a tetravalent Pt amine complex ion. This Pt/SiO₂ hydrocarbon hydrogenation catalyst uses less Pt but retains the same catalytic properties.

**Exhaust Gas Purifier**

**NISSAN MOTOR CO. LTD.**  
*Japanese Appl. 9/287,438*

A purifier for an I.C.E. consists of a three-way component catalyst carrying Pd and an absorption catalyst carrying a zeolite, both on a heat resistant inorganic carrier, arranged upstream and downstream, respectively, of the exhaust gas flow to form a catalytic converter. This tandem arrangement gives the catalyst superior purification activity. It absorbs and separates hydrocarbons by self purification even when the exhaust gas temperature is low at engine start-up.

**Purification of Exhaust Gases**

**NE CHEMOCAT K.K.**  
*Japanese Appl. 9/290,156*

A catalyst for purifying the exhaust gas from an I.C.E., gas turbine or boiler consists of Pd, Ag and Zn on Al₂O₃ carrier. The catalyst purifies NOx in an O₂ rich environment and completely oxidises the reducing hydrocarbons. It is extremely efficient at purification, as it maintains high denitration even when the exhaust gas flows at a high velocity.

**Hydrogenation of Butylenediol**

**LINDE A.G.**  
*German Appl. 1/96/25,189*

A two-stage process is claimed for the catalytic hydrogenation of butylenediol (1) to butanediol (2). Stage I is carried out in a stirred reactor with a suspended, Pd-Ag/Al₂O₃ catalyst giving complete conversion of (1) into butenediol (3) and 50–85% hydrogenation of (3) to (2). Stage II takes place in a solid-bed reactor. The process gives (2) in high yield with high purity.

**Palladium Exhaust Gas Purification Catalyst**

**MAZDA MOTOR CORP.**  
*German Appl. 1/97/13,103*

A Pd-carrying exhaust gas purification catalyst comprises CeO₂ and a mixed oxide of Ce and Pr. The catalyst is produced by mixing a porous base material with CeO₂ to form a carrier for the Pd; the Pd and carrier is then made into a slurry with a mixed oxide of Ce and Pr as solid components, followed by calcining. The catalyst has high heat resistance.

**HOMOGENEOUS CATALYSIS**

**Preparation of Aldehydes and Ketones**

**ZENECA LTD.**  
*British Appl. 2,312,209A*

Aldehyde or ketone derivatives (1) are prepared by oxidising an alcohol with O₃ in the presence of a catalytic amount of a tetra-alkylammonium Ru species under anhydrous conditions. (1) are useful as intermediates and products in the chemical industry.

**Diaryl Carbonate Production**

**BAYER A.G.**  
*European Appl. 794,168A*

A diaryl carbonate is produced by reacting the corresponding aromatic hydroxyl compound with CO and O₂ in the presence of a Pt metal catalyst, a cocatalyst, a quaternary salt and a base. Also claimed is the production of polycarbonates. The energy-coupled process with a closed material cycle avoids the use of phosgene and solvent, is easy to operate and gives pure products with a selectivity of > 99%.
Hydrogen Peroxide Production

ENICHEM S.P.A. *European Appl. 808,796A*

H₂O₂ is obtained by reacting CO₂, O₂, and H₂O vapour in a H₂O immiscible organic solvent in the presence of a soluble catalyst formed from a Pd salt, a non-co-ordinating organic or inorganic acid, and a ligand comprising a mono or polydentate nitrogenated compound which binds to Pd. High H₂O₂ yields are obtained with lower amounts of ligand and acid. It is used as a bleaching agent in the textile and paper manufacturing industries; in oxidation processes in the chemical industry or as a biocide.

Ethylidene Diacetate Production

AIR PROD. & CHEM. INC. *European Appl. 808,820A*

Ethylidene diacetate (EDA) is produced by reacting acetic anhydride, H₂, CO and acetic acid in the presence of an alkyl iodide and a catalyst which is stable to hydrogenation. The catalyst is bifunctional and comprises an insoluble polymer with pendant quaternised heteroatoms, some of which are ionically bonded to anionic Group VIII metal complexes and the remainder to iodide. Accelerators, such as 3-picoline, are not required and leaching of metal from the catalyst is minimised by bonding to the Group VIII metal. The catalyst can be recycled and the process is fast and highly selective towards EDA.

Preparation of Pesticidal Fluoro-Olefins

AMERICAN CYANAMID CO. *European Appl. 811,596A*

Pesticidal fluoro-olefins (1) are prepared by reacting a 4-aryl-2-fluoro-2-butene-1-ol with a brominating agent to form a 4-aryl-1-bromo-2-fluoro-2-butene and reacting with a Pd catalyst, a base and a boronic acid, boronic anhydride or borate ester. This is an efficient and effective method for the preparation of pesticidal agents (1).

Carboxylic Acid Production

RHÔNE-POULENC CHIM. *World Appl. 97/35,826A*

Carboxylic acids and/or their corresponding esters are prepared by the isomerisation of formic acid ester and an alcohol in the presence of H₂O, a solvent and an Ir-based catalyst with a halogen promoter, under partial CO pressure. With alcohols containing more than one OH, adipic acid (or esters) or terephthalic acid (or esters) can be produced. This process gives improved productivity without the addition of supplementary compounds such as strong acids.

Pentenoic Acid and Pentenoate Ester

F. P. W. AGTERBERG *U.S. Patent 5,672,732*

A pentenoic acid (1) or a pentenoate ester (2) is prepared with good selectivity and conversion by the carboxylation of butadiene or its derivatives in the presence of CO₂, an alcohol or H₂O and a catalyst system comprising Pd, a carboxylic acid and a monodentate phosphine ligand. (1) and (2) can be used as intermediates in the preparation of α-caprolactam and adipic acid, in nylon-6 and nylon-6,6 production, respectively. Good selectivity and conversions are achieved. The catalyst system is stable and may be reused several times without loss of activity.

Alkoxy-Silane Compounds

BASF A.G. *German Appl. 1/96/49,998*

The preparation of alkoxy-silane compounds containing vinyl ether groups comprises reacting divinyl ethers (1) with silanes (2) at 70–150°C in the presence of a homogeneous hydrosilation catalyst. The catalyst is a Pt or Rh compound and the amount of Rh or Pt is 0.05–10 ppm with respect to (1) and (2).

FUEL CELLS

Fuel Cell Electrode

S. SARANGAPANI *U.S. Patent 5,683,829*

A fuel cell electrode comprises an anode with a Pt electrocatalyst including a redox promoter composed of a Ru or Sn complex. The anode is resistant to poisoning, and low loadings of Pt are needed to give higher current densities. The electrode is used in the oxidation of MeOH or MeOH reformate in a fuel cell, and the fully assembled fuel cell may be of stack design.

Anode Catalyst

STONEHART ASSOC. INC. *Japanese Appl. 9/116,811*

An anode for high molecular electrolyte-type fuel cells comprises 84–99 at.% Pt and 1–16 at.% Fe held on a catalyst support. The anode catalyst has a long life, superior poisoning resistance and is free from elution.

Pt-Fe Alloy Fuel Cell Electrode

EQUOS RES. K.K. *Japanese Appl. 9/206,597*

An electrode catalyst for fuel cells or electrolysis cells contains a Pt-Fe alloy with a tetragonal crystal structure. The electrode catalyst reduces the concentration overvoltage, and allows higher utilisation of fuel and air electrodes, resulting in a higher output, even with lowered partial pressures of air or fuel gas.

Electrode Structure

MATSUEDA K.K. *Japanese Appl. 9/265,992*

The electrode structure of a solid state polymer fuel battery used for electric vehicles includes a set of catalytic electrodes with two catalyst layers between which a solid state polymer electrolyte film is sandwiched. The first catalyst layer consists of a polytetrafluoroethylene (1) dispersion solution mixed with C black containing 40% Pt, and the second layer consists of (1) mixed with C and 20% Pt. The electrode improves the electricity generation efficiency and reduces manufacturing costs.

Electrode Catalyst for Fuel Cells

TOSHIBA K.K. *Japanese Appl. 9/293,517*

An electrode catalyst layer for phosphoric acid fuel cells is manufactured by heat treating a mixture of C and fluoro resin, which has been uniformly applied to a support substrate. C is eliminated, giving a fluoro resin sheet onto which a catalyst layer is formed by impregnation with Pt and C. Reduction in surface area is prevented, and battery characteristics and the water proof nature of the catalyst layer are improved.
A zeolite based Pt catalyst is used in the catalytic reduction of CO from a starting mixture rich in H₂ and in the selective oxidation of CO from a MeOH reforming reactor. The catalyst is produced by dissolving Pt(NH₃)₄Cl₂ in distilled H₂O and adding a zeolite, stirring the suspension, filtering, washing, drying, heating, reducing the heated material by adding a forming gas, and finally cooling under N₂. The catalyst is used in H₂ processing for use in fuel cells for electrical vehicles.

**Wireless Bonding of IC Chips**

TANAKA DENSHI KOGYO K.K.  
**European Appl. 810,293A**

A Au alloy wire containing 0.2-5 wt.% Pd and 1-100 ppm (by wt.%) Bi is manufactured from Au of purity ≥ 99.99 wt.%. A Au alloy bump is formed by bonding a ball at the end of an Au alloy wire passing through a capillary, bonding the ball to an electrode of an IC chip, and breaking the wire from the ball. The process is used for wireless bonding of IC chips.

**Semiconductor Chip Package**

MICRON TECHNOLOGY INC.  
**U.S. Patent 5,677,566**

A semiconductor chip package for connection to a lead frame has conductive leads connected to the chip and passing over the top, connected to bond pad areas on the chip via bond wires. The leads are coated with Pd/Ni, Au or Ag, and the chip and leads are encapsulated by a thermosetting epoxy resin. This package can be used with standard formats developed for larger chips without reconfiguration.

**Fluoro-Polymer Metallised Substrate**

GEO-CENTERS INC.  
**U.S. Patent 5,696,207**

A fluoropolymer substrate with a metallised surface is prepared by contacting a fluoropolymer substrate with an electroless metallisation catalyst, selected from Pd, Rh, Ir, Ni, Cu, Ag and Au, and then with an electroless metallisation solution. The metallised surface comprises a conductive layer of Ni, Cu, Au, Pt, Pd, Co, or an alloy, an intermediate layer of Ni and an outer layer of Pt, Au, Cu or alloys of Ni or Pt. The metallised surface exhibits good adhesion to the fluoropolymer substrate and may be patterned.

**Ferroelectric Element**

MATSUSHITA DENKI SANGYO K.K.  
**Japanese Appl. 9/280,947**

A ferroelectric element, for pyroelectric type infrared sensors, etc., has a contact layer made of a Ti film, which is arranged between a MgO single crystal substrate and a lower electrode made of Pt film. The element eliminates rupture and improves the yield in the manufacture of ferroelectric elements.

**Sintering Material Composition**

NIPPON STEEL CORP.  
**Japanese Appl. 9/275,119**

A sintering material composition for opto-magnetic recording medium manufacture comprises an alloy containing 38-55 Mn, 35-55 Sb and 1-15 Pt, all in at.%. The alloy is very strong, prevents crack generation during sputtering and has thermal shock resistance. High density recording media can be produced.

**Magnetic Recording Medium**

FUJITSU LTD.  
**Japanese Appl. 9/246,214**

A thin metal film type magnetic recording medium consists of a laminated structure of a non-magnetic substrate, a base layer (1-6 at.% W), a magnetic layer (8-16 Cr, 4-7 Ta and 3-6 Pt (all in at.%), and the balance Co) and an overcoat layer. The medium has improved coercive force and improved recording density. Sputtering film is easily formed.

**Ruthenium Thin Films**

TANAKA DENSHI KOGYO K.K.  
**Japanese Appl. 9/272,969**

Ru or Ru oxide thin films are prepared from Ru(DMHPD), (1), where DMHPD = 2,6-dimethyl-3,5-heptanedione, by chemical vapour deposition. Also claimed is the preparation of a semiconductor device using the above thin films. Due to a stable supply of (1), thin films of uniform quality are obtained. C impurities are reduced by the introduction of H₂.

**Semiconductor Chip Joining**

MITSUBISHI MATERIALS CORP.  
**Japanese Appl. 9/283,557**

A semiconductor chip joining method uses flip chip bonding, sequentially depositing a thin base layer of Pd-X alloy (X = Zn, Pb, etc.), a Ni layer and a metal layer, by non-electrolytic plating, on the surface of an input/output terminal. The chip improves the corrosion resistance of the input/output terminal and the junction reliability and allows high density mounting.

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