NEW PATENTS

METALS AND ALLOYS

Platinum Alloy Used for Jewellery Articles

NAGAHORI CORP. *British Appl.* 2,279,967A

A Pt alloy containing 10–100 ppm Ce is claimed as an article of jewellery and comprises the Pt alloy, preferably containing ≥ 99 wt.% Pt and 18, 34, 66 or 98 ppm Ce. The Pt alloy has a high degree of hardness despite its low Ce content, and still has adequate hardness even after casting. Therefore no secondary processing for increasing hardness is required.

Fine Palladium Alloy Wire

NIPPON STEEL CORP. *World Appl.* 94/21,833A

A fine Pd alloy wire for bonding semiconductor elements is produced from a Pd alloy with ≤ 0.0003 wt.% of each of Ca, Al, Cr and Si, 0.001–0.01 wt.% Ir, and if necessary at least either 0.001–2 wt.% Au of purity ≥ 99.99 % or 0.001–5.0 wt.% Ag of similar purity, the balance being Pd. The wire has secured junction reliability and its configuration is improved.

Nickel-Free White Gold Alloys for Jewellery

HANDY & HARMAN *U.S. Patent* 5,372,779

A white gold alloy composition for jewellery comprises in wt.%: 35–50 Au, 25–63 Ag, 0.1–7 Zn and/or Ge as whitener, and ≤ 5 Pd. The liquidus temperature is ≤ 1950°F. The alloys are substantially free of Ni, and thus non-allergenic. They display a favourable white hue, low casting temperature, good workability, sufficient hardness and tarnishing resistance.

Production of Superconductor

CHODENDO HATSUDEN KANREN KIKI ZAIRYO *Japanese Appl.* 6/251,649

A superconductor member is produced by forming an oxide superconductor layer onto a Ag-Pt substrate alloy containing 0.1–50 wt.% Pt group metal. The superconductor body may be $La_{2-x}AE_xCuO_4$, $REBa_2Cu_3O_{7-k}$, etc., AE is at least one of Ba, Sr, Ca, x = 0.02–0.08, RE is one of Y, Sc, La, etc., and the superconductor layer can be produced by sputtering or CVD. The superconductor has a high critical point, good heat stability and is highly reproducible.

CHEMICAL COMPOUNDS

Double Oxide Preparation

SANTOKU KINZOKU KOGYO K.K. *Japanese Appl.* 6/246,155

A new double oxide containing Ce oxide also contains 0.01–10.0 wt.% of Pt group metal, such as Pd, and/or 0.01–10.0 wt.% of transition metal oxide. A solution containing Ce ions, Pt group metal and/or transition metal is mixed with an aqueous solution containing NH_3, NH_4HCO_3 or oxalic acid, followed by firing the precipitates at > 250°C. The oxide can absorb and discharge ≥ 100 μmol/g O_2 below 300°C. The oxide can be used for a waste gas purification catalyst and in other ceramics.

Iridium Acetylacetonate Solution Preparation

SUMITOMO METAL MINING CO. *Japanese Appl.* 6/247,890

An aqueous mixture of Ir(IV) ion and/or Ir(IV) complex ion, a reductant such as hydrazine, sulphurous acid, or oxalic acid, etc., and alkali acetylacetonate is heated, followed by salting out Ir acetylacetonate and acetylacetone from the heated mixture. Ir acetylacetonate is used as a clarification catalyst for NOx and as an electronic material in organic metal ink, etc. The reaction is carried out at 70–140°C. The complex is stable in store, and is obtained in high yield.

ELECTROCHEMISTRY

Electrode for Alkali Ion Water Generator

MATSUSHITA DENKI SANGYO K.K. *Japanese Appl.* 6/228,783

The electrode has base metal coated with Al oxide or Ti oxide, and a Pt alloy film coated on the oxide film. The electrode is used for an alkali ion H_2O generator. It has a large surface area and good adhesiveness.

Electrode Coated with Iridium Oxide

NIPPON STEEL CORP. *Japanese Appl.* 6/235,097

The non-soluble electrode comprises a metal base optionally with a layer of valve metal, which includes Ti and Zr, an Ir oxide layer and a metallic Ir layer. The Ir oxide layer and the metallic Ir layer are formed in turn to obtain an uppermost layer of Ir oxide; each coating layer is ≤ 20 μm thick. The Ir oxide layer preferably accounts for 67–99% of the total film thickness, and the metallic Ir layer for 1–33% of the total film thickness. The film is deposited at ≤ 700°C. The coating layer adheres tightly to the metal base.

Electrodes for Water Generation

TOHO TECH. SERVICE CO. LTD. *Japanese Appl.* 6/254,564

Electrodes used in an electrolytic tank of an electrolytic H_2O generator comprise a thin plate of metal formed by applying Pt burning to a flat plate of Ti. The thin plate of metal is provided along the shape of the electrode-facing-surface of an insulating base. Pt is applied to the facing surface of each electrode along the surface of the cylindrical insulating base. There is no metal elution even if the polarity is inverted.

Electrolysis Cell Production

MITSUBISHI JUKOGYO K.K. *Japanese Appl.* 6/260,181

A cell is produced by applying a Pt paste onto both sides of a solid electrolyte layer to form an electrode, applying Pt wire nets onto the solid electrolyte layer, followed by heat treatment for sintering. The solid electrolyte layer is Y_2O_3-stabilised ZrO_2 and the Pt paste is 70% Pt and balance binder. The electrode has good electroconductivity and the solid electrolyte has good resistance to deterioration. The current density distribution in the solid electrolyte is uniform.

ELECTRODEPOSITION AND SURFACE COATINGS

Electrolytic Palladium Coating Solution

ATOTECH DEUT. G.m.b.H. *European Appl.* 619,386A

A Pd electroplating solution contains Pd sulphate and/or sulphamate, complexing agents and heterocyclics, such as 2,3-bis-(2-pyridyl)-pyrazine, etc., and is used for electroplating electrically conducting substrates with Pd or Pd alloy, in jewellery, watches and printed circuit boards. The addition of a heterocyclic compound allows the production of high-gloss, light Pd coatings which are very ductile and free from haze.

Palladium-Coated Copper-Based Lead Frames

HERAEUS G.m.b.H. *European Appl.* 621,633A

A lead frame for ICs comprises a metallic base with at least two coating layers, the outer being Pd and the inner layer Ni-P or Cu-Sn. The Pd layer is 0.01–5 μm, preferably 0.1 μm thick. Good solderability, both before and especially after ageing is obtained.

Electroless Metallisation of Optical Fibre

AMERICAN TELEPHONE & TELEGRAPH CO. *European Appl.* 623,565A

Optical fibres are electrolessly metallised by treating with an aqueous sensitising solution of SnF_2, then with an activating Pd(II) solution to deposit a catalytic layer on the sensitised surface, and finally depositing Ni by immersion. The process is reliable and achieves uniform reproducible Ni plating on SiO_2 fibres.

Coating Metal Surfaces with Palladium

ATOTECH DEUT G.m.b.H. *World Appl.* 94/26,954A

Layers of Pd are deposited on a metal surface from a formaldehyde-free chemical plating bath containing a Pd salt, N-containing complexing agents and formic acid or formic acid derivatives at pH > 4. The process allows the deposition of permanently glossy, bright, ductile layers of highly pure Pd on metal substrates, at ≤ 5 μm/h.

Electroless Deposition

MONSANTO CO. *U.S. Patent* 5,348,574

An electroless deposition-catalysing film-forming solution comprises: (a) 0.1–15 wt.% polyamic acid, (b) 0.1–15/100 pts. polyamic acid noble metal of Pt, Pd, Rh, Ir, Ru, Ag or Au, and (c) 60–95 wt.% aprotic solvent from acetone, etc., and mixtures with H_2O, and (d) 0–10 wt.% anionic or non-ionic surfactant. The solutions provide coherent polyamic acid films which can be imidised to provide tough and adhesive polyimide films for electroless deposition.

Thick Crack-Free Ruthenium Coating

JAPAN ENERGY K.K. *Japanese Appl.* 6/256,988

Coating with Ru comprises the use of a coating solution containing a complex of Ru with N and S acid and blowing an O_2-containing gas into the solution. The O_2 blow assures the formation of a crack-free thick Ru coating layer. A mixture of Ru chloride and sulphamic acid with H_2SO_4 acid and other additives was used to give crack-free 7.6 μm thick coatings.

Palladium Coating Solution

VICTORIA K.K. *Japanese Appl.* 6/264,281

Pd coating solution contains a primary Pd oxide compound at 5–30 g/l as Pd metal, and a weak organic acid as conductive salt at 30–500 g/l. An object is immersed into the Pd coating solution to acquire an electrocoating at 10–50°C and 0.1–3 A/dm^2. The plating solution contains Pd acetate 10 g/l as metallic Pd, oxalic acid 150 g/l and Na sulphite, and has pH 3. Plating is performed at 1.5 V, 0.5 A/dm^2 for 30 min. No coating separation was observed after bend tests.

Plated Ornament Component

NAU CHEM. YG. *Japanese Appl.* 6/264,282

An ornament component comprises a conductive substrate coated by a Au-Pt alloy layer containing 0.001–30 wt.% Pt and balance Au. In an example, the plating bath contained 10 g/l Au, 0.3 g/l Pt, citric acid and Na citrate, at pH 4.0. A brass sheet electrolysed in the bath at 1.0 A/dm^2 using a Pt counter electrode acquired a coating layer 7.2 μm thick of hardness Hv 132 with a mirror gloss face. The component does not harm skin and there was no discoloration after 6 days.

APPARATUS AND TECHNIQUE

Iridium Oxide Film Manufacture

NIPPON STEEL CORP. *Japanese Appl.* 6/235,065

Ir oxide film is manufactured by sputtering a target of Ir oxide disposed in a vessel with inert gas ions irradiated from an ion gun at a pressure of 1×10^{-1} to 1×10^{-3} Torr by an ion beam sputtering process. The technique is used to coat the surface of electrodes giving an insoluble anode for electroless plating; good coating adherence is obtained.

Hydrogen Separation Membrane Production

NOK CORP. *Japanese Appl.* 6/254,361

The membrane is prepared by coating porous hollow ceramic yarn with γ-Al_2O_3 by a sol-gel method, spraying with $Pd(NO_3)_2$-$AgNO_3$ mixed solution, which is thermally decomposed to form Pd-Ag alloy. The membrane is chemically and thermally resistant. In an example, porous hollow ceramic yarn Al_2O_3 is sprayed with a nitrate solution containing a Pd : Ag ratio of 60 : 40 and is thermally decomposed with H_2 to form a ceramic membrane for H_2 separation with permeation coefficient for $H_2 = 5 \times 10^{-7}$ mol/m^{2}s Pa.

HETEROGENEOUS CATALYSIS

Ether Alcohol Production

KAO CORP. *European Appl.* 616,994A

Ether alcohols, which are useful as perfumes or for perfume production, are produced by subjecting a cyclic ketal to hydrogenolysis in the presence of a catalyst containing 50–100 wt.% Pd based on the total active catalytic component present and further containing 0-50 wt.% metal(s) selected from Ru, Rh, Pt and/or Ni, supported on C, Al_2O_3, SiO_2 and zeolite. The ether alcohols can be produced easily at low cost and in high yield. The process does not require a diol solvent and is highly efficient.

Hydrogenation and Isomerisation of Amines

AIR PROD. & CHEM. INC. *European Appl.* 618,188A

The catalytic hydrogenation and isomerisation of aromatic amines to their ring hydrogenated counterparts is made with high selectivity at low pressure and with good reaction rates, by contacting the aromatic amine with H_2 in the presence of a catalyst comprising a mixture of Co and Rh, Ru, Pd and/or Pt. The process is useful for the production of 4,4′-methylene-di(cyclohexylamine), the *trans,trans*-isomer of which can be used to produce polyamine fibres and epoxy additives.

Hydrogen Peroxide Production

MITSUBISHI GAS CHEM. CO. INC. *European Appl.* 621,235A

H_2O_2 is produced by reacting O_2 and H_2 in the presence of a Sn-modified Pt group metal catalyst on a carrier. The carrier, which has solid acidity, is ZrO_2 or Al_2O_3 supporting H_2SO_4 on a composite oxide of Mo and Zr or Sn and Si or a compound of Sn and Zr or the H^+ form of mordenite or MFI-type zeolites. The reaction medium is H_2O containing an H_2O_2 stabiliser, and the reaction conditions are 0–50°C and pressure 3–150 kg/cm^2. The reaction medium may be free of halogen ions and acid, thus alleviating dissolution of the catalyst metal and reactor corrosion.

Preparation of Diacetoxybutene

MITSUBISHI KASEI CORP. *European Appl.* 625,503A

Diacetoxybutene (1) is prepared by reacting butadiene, acetic acid and O_2 in the presence of Pd based catalyst, followed by continuous two-stage distillation in two distillation towers and by thin-film evaporation. (1) is recovered from the top of the second tower, and the material containing (1) from the bottom of the first tower is recycled into the second tower. The Pd based catalyst contains Pd metal or Pd salt singly or in combination with Bi, Se, Sb, Cu, etc., and is supported on SiO_2, Al_2O_3 or activated C. The process allows recovery of high purity diacetoxybutene in high yield. (1) is a raw material for the production of 1,4-butanediol and tetrahydrofuran, etc.

Treatment of Waste Water

SOLVAY DEUT G.m.b.H. *World Appl.* 94/20,423A

Waste H_2O containing organic and optionally inorganic compounds with adsorbable organo-halogen compounds, especially from epichlorohydrin production, is treated in the presence of H_2 by a supported Pt group metal catalyst, preferably Pd, Pt, Ir or Rh, supported on SiO_2, Al_2O_3, MgO, ZrO_2, etc., prepared by the sol/gel process. The waste H_2O, having pH 3–10 (4–6), is fed into a reactor containing the high activity catalyst, and treated at 5–80°C and 1–10 bars with H_2.

Removing Nitrogen Oxides from Exhaust Gas

NIPPON SHOKUBAI CO. LTD. *World Appl.* 94/25,143A

A method of removing NOx contained in an exhaust gas comprises contacting the gas in an oxidising atmosphere with a catalyst of 0.1–30 g/l-catalyst of at least one of Pt, Pd, Rh and Ru metals or their compounds, and 1–80 g/l-catalyst of Li, K, Na, Rb, Ce, Be, Mg, Ca, Sr, and Ba, on a refractory inorganic oxide.

Conversion of 1–4C Hydrocarbons to Olefins

KOREA RES. INST. CHEM. TECHNOL. *World Appl.* 94/27,722A

New supported Ru catalyst for the preparation of lower hydrocarbons containing a double bond and C_2 is produced by the conversion of 1–4C hydrocarbons or purified natural gas. The catalysts contain 0.25–5 wt.% metal in the catalyst of $RuCl_2(PPh_3)_3$, $RuCl_2(CO)_2(PPh_3)_2$, $Ru_3(CO)_{12}$, $RhCl(CO)(PPh_3)_2$, $IrCl(CO)(PPh_3)_2$, $Pd(PPh_3)_4$, $Pt(PPh_3)_4$, $RuCl_3.xH_2O$, $RhCl_3.xH_2O$, etc., supported on α- or γ-Al_2O_3, SiO_2 and SiO_2-Al_2O_3, Y zeolite, etc. The conversion is carried out at 500–980°C and at a pressure of 1–10 atm.

Dehydrogenation Catalyst

CHINA PETRO CHEM. CORP. *U.S. Patent* 5,358,920

A long-life supported catalyst for use in dehydrogenating saturated hydrocarbons comprises, in wt.%: (a) 0.01–2.0 Pt; (b) 0.01–5.0 Sn; (c) 0.01–5.0 Na; and (d) the remainder of large pore diameter τ-Al_2O_3 support having a dual pore diameter distribution such that at least 40% of the total pore volume has pores of diameter 1000–10,000 Å. The catalyst is used to dehydrogenate (6–16C) linear paraffins to prepare linear mono-olefins. The catalyst has a high stability and can be used under severe operating conditions, such as high temperature and low pressure and does not need sulphiding treatment before use.

Method of Controlling Hydrosilylation

DOW CORNING CORP. *U.S. Patent* 5,359,111

Hydrosilylation in a reaction mixture is controlled by adjusting the concentration of O_2 in solution, relative to any Pt catalyst in the reaction mixture, as Pt metal/support, Pt compound or complex. Hydrosilylation is also controlled by reacting a Si hydride with olefinically unsaturated alkenyl compounds selected from 4–8C cycloalkenyl compounds, linear 2–30C alkenyl compounds, and branched 4–30C alkenyl compounds in the presence of catalyst.

Tert. Butanol Production

TEXACO CHEM. CO. *U.S. Patent* 5,359,130

A solvent solution of a *tert*-butyl hydroperoxide (TBHP) charge stock is decomposed by a mixed Pd and Pt/Al_2O_3 hydroperoxide decomposition catalyst; *tert*-butanol is recovered from the products of the decomposition reaction. The reaction is performed at 25–250°C and 0–1000 psig and the catalyst contains 0.1–5 wt.% Pd and 0.1–5 wt.% Pt in ratio Pt:Pd of 0.1–10:1. The TBHP may be dissolved in an isobutane-*tert*-butanol mixture, at 0–10,000 psig. Conversion rates and selectivity for *tert*-butanol are high.

Synthesis of Methyl Tert.-Butyl Ether

TEXACO CHEM. CO. *U.S. Patent* 5,364,981

One-step synthesis of an alkyl *tert*-alkyl ether comprises reacting a 1–6C primary alcohol with a 4–10C tertiary alcohol at molar ratio 10:1–1:10 in the presence of a β-zeolite modified with metals from Group VIII, also containing a halogen or Group IB metal, at 20–250°C and 1000 psi pressure. The catalyst is reduced in a stream of H_2 at 100–600°C. The Pt-Pd-modified zeolite catalyst exhibits high activity.

Two Stage Reforming of Naphtha

EXXON RES. & ENG. CO. *U.S. Patent* 5,368,720

A two-stage process for improving the octane quality of a naphtha feedstock containing a mixture of paraffins, aromatics and naphthenes involves a reforming first stage of fixed-bed reforming zones containing a catalyst of 0.1–0.7 wt.% Pt, 0.1–0.7 wt.% Ir and 0.02–0.4 wt.% Sn on an inorganic oxide support, and a second stage of moving-bed reforming zones with a Pt containing catalyst. The catalyst is continuously regenerated and recycled. Catalysts have high activity and produce high yields of 5C+ reformate.

Diesel Exhaust Purification Catalyst

TOYOTA JIDOSHA K.K. *Japanese Appl.* 6/182,204

An exhaust gas purification catalyst for diesel engines comprises a honeycomb support having axially parallel paths and a core section, and plugged-in chequers-like patterns at the outlet and inlet. A Pd catalyst is supported on the cross flow section while a Pt catalyst is supported on the straight flow section. The catalyst is used for a diesel engine to burn HC, CO and soluble organic fraction contained in exhaust gas. The catalyst retains low pressure loss and reduces the release of particulates over a large temperature range.

Catalyst for Purifying Exhaust Gas

NISSAN MOTOR CO. LTD.

Japanese Appls. 6/182,213 and 6/182,215

Catalysts for purifying exhaust gas from cars comprise a honeycomb support, and either a first layer of Al_2O_3 containing Pt, Pd and/or Rh and a second layer of zeolite containing Cu, Co, Ni, etc.; or a first layer of Al_2O_3 with Pd or Rh, a second layer comprising metal oxide supporting Pt and a third layer of zeolite. The catalysts efficiently purify HC, CO or NOx from car I.C.E; they have high NOx activity at low temperatures from the theoretical air:fuel ratio to the lean region, and good fuel consumption.

Alicyclic Diol Preparation

NEW JAPAN CHEM. CO. LTD. *Japanese Appl.* 6/184,032

Alicyclic diols (1) are prepared in high purity and yield by the catalytic hydrogenation of aromatic diols in the presence of a catalyst comprising one or more Ru, Pd and Rh on carriers, such as oxides of Ca, Mg, Al, Si, Ti, Cr or/and Zr. In an example, the catalyst is Ru or Pd supported on Al_2O_3 or SiO_2 preferably in the ratio of metal:carrier of 0.5–5 wt.%. The hydrogenation is performed at 60–170°C for Ru or Rh, or at 120–220°C for Pd under 30–200 kg/cm^2 for 1–7 h.

Preparation of Hydrogen Peroxide

MITSUBISHI GAS CHEM. CO. INC.

Japanese Appl. 6/191,804

H_2O_2 is prepared in high concentration by reacting O_2 and H_2 catalytically in a reaction medium using a Pt group metal catalyst, such as Pt or Pd on an organic halogen compound (not a F containing compound) on a solid acid support with acidity function < –3 or a solid acid support with very strong acidity. The support preferably contains an insoluble heteropolyacid, of phospho-wolframic acid or tungstosilicic acid, cation exchanged with K or Cs.

Production of Dimethylol Alkanoic Acids

KOEI CHEM. IND. CO. LTD. *Japanese Appl.* 6/192,169

Dimethylol alkanoic acids (1) useful as raw materials for polyurethane and epoxy resin preparation, were prepared by oxidising trimethylol alkane with O_2-containing gas in aqueous solvent using Pd and/or Pt catalyst, such as 5 wt.% Pd/C, while keeping the system at pH 7–12. O_2-containing gas was bubbled through, at 0–100°C, preferably 20–70°C. (1) can be produced safely by a short process from easily available materials.

Purification of Exhaust Gas of Diesel Engine

CATALER IND. CO. LTD. *Japanese Appl.* 6/198,181

A catalytic system that purifies exhaust gas from diesel engines, consists of a base material carrying a catalyst layer on its surface, a chamber containing Pt/Al_2O_3 upstream in the exhaust gas flow and another chamber containing Pd/Al_2O_3-SiO_2 downstream. Altogether, three catalysts are installed. This method prevents sulphate discharge, generation of white smoke, and generation of NO_2, and decomposes NOx efficiently.

Decomposition of Nitrous Oxide

SAKAI KAGAKU KOGYO K.K. *Japanese Appl.* 6/198,187

An Al_2O_3 catalyst carrier has two catalytic metals one being at least one of Ru, Rh and Ir, and the other at least one of Cu, Co and Fe. The catalyst decomposes N_2O in NOx efficiently at low temperature and in the presence of H_2O vapour.

Exhaust Gas Denitration Process

SUMITOMO METAL MINING CO.

Japanese Appl. 6/210,137

Exhaust gas is firstly contacted with a catalyst, which is active at higher temperature, containing 0.01–5 wt.% Pt and 0.01–10 wt.% of at least one of Fe, Co, Cu and Mn, and secondly is contacted with 0.01–5 wt.% Pt catalyst which is active at lower temperature. The process operates over a wide temperature range.

Denitrification Catalyst for NOx Removal

SUMITOMO METAL MINING CO.

Japanese Appl. 6/210,171

NOx in exhaust gas is contacted with a denitrification catalyst containing 0.05–5% Pt on a support of specific surface area at least 200 m^2/g, containing B_2O_3, SiO_2 and Al_2O_3, for purification in the presence of hydrocarbons and oxidative atmospheres. NOx is removed efficiently, even under excessive O_2 atmospheres, using this catalyst.

Purification Catalyst for Exhaust Gas

DAIHATSU MOTOR CO. LTD.

Japanese Appls. 6/210,174–75

A Pt group metal solution containing Pt, Pd, Rh, Ir or Ru at pH 4–10 is impregnated or adsorbed on perovskite oxide of $Ln_{1-x}A_xMO_3$ where Ln is a rare earth metal, A = alkali earth metal or Ce, M = transition metal, x = 0–1, and a thermal resistance oxide of composition $Ce_{1-y}Si_yO_2$, y = 0–1, dried and burned to give an exhaust gas purification catalyst. With this catalyst, HC, CO and NOx in exhaust gas is removed efficiently even at > 900°C.

Cleaning of Exhaust Gas Containing NO

SAKAI KAGAKU KOGYO K.K.

Japanese Appls. 6/218,232–33

Cleaning exhaust gas containing NO comprises contacting gas by a catalyst supporting Pt, Pd, Rh, Os, Ir, Ru or Re, and additionally Cu, Co, Fe, etc., in the presence of a reducing gas at 200–400°C and space velocity of 500–100,000. The carrier is treated with F by dipping zeolite, SiO_2, Al_2O_3, into aqueous HF, K ammonium fluoride, etc., washing with H_2O and calcining at 300–600°C. This method is useful for furnaces which burn city garbage and mud from treating sewage, by catalytic decomposition of NO-containing gas in high efficiency, even at low temperature.

Removing NOx from Exhaust Gas

AGENCY OF IND. SCI. & TECH.

Japanese Appl. 6/218,236

Removing NOx in exhaust gas containing an excess amount of O_2 comprises contacting exhaust gas with a catalyst of main component Pt in the presence of a cyclic HC having a C=C bond, such as cyclopentane, MCP, benzene, toluene, etc. The catalyst is prepared by dipping a carrier, such SiO_2, Al_2O_3, Y-zeolite, etc., into an aqueous solution of H_2PtCl_5, $Pt(NO_2)_2(NH_3)_2$, etc. The gas is contacted at 150–300°C and space velocity 1000–7000/h. The process removes NOx from gasoline or diesel-engine vehicles, at low temperature.

Treatment of Exhaust Gas

MITSUBISHI JUKOGYO K.K. *Japanese Appl.* 6/226,053

CO, HC and NOx are removed from exhaust gas by a Rh-containing catalyst and a Pt-containing catalyst arranged in series at the inlet and outlet sides, respectively. NOx, CO and HC are removed, even in excess O_2 at 300–700°C. In an example, gas containing 400 ppm NO, 1000 ppm CO, 1000 ppm C_2H_4, 340 ppm C_3H_6, 8% O_2, 10% H_2O and 10% CO_2 was contacted with Rh/Al_2O_3 and Pt/Al_2O_3 arranged in series at 350°C. 100% HC and 45% NOx were removed.

Catalyst for High Temperature Combustion

KOBE STEEL LTD. *Japanese Appl.* 6/226,099

A composite catalyst for high temperature combustion includes a Pd-based catalyst supported on a heat-resistant honeycomb base at the air-fuel mixture inlet. A second Pt-based catalyst is downstream and a Mn-based catalyst is further downstream. The catalyst is used in equipment for catalytic combustion of fuel gas-air mixtures at high temperatures. The first catalyst has highest activity for CH_4; the second catalyst depresses excess reaction and the third catalyst has high temperature heat resistance.

Catalyst for Purifying Exhaust Gas

MATSUDA K.K. *Japanese Appl.* 6/226,104

An Ir-containing noble metal active seed is supported on a metal-containing silicate in a catalyst, and is prepared from Ir salt, noble metal salt and organic binder. The boiling point of the Ir salt solvent is similar to the boiling point of H_2O. The metals are simultaneously deposited on the silicate and provide a uniform and dispersibility-enriched active seed-supporting state, enhancing NOx purification and heat resistance.

Catalyst for Exhaust Clean-up

NIPPON GLASS CO. LTD. *Japanese Appl.* 6/233,918

Highly durable catalyst is prepared by coating a monolith carrier with a catalyst layer that reduces CO, HC and NOx. The catalyst layer contains particulates formed by carrying Pt, Pd and Rh on a heat resistant inorganic oxide, as a whole layer, and 2–10 wt.% Pd in a depth less than half the thickness of the catalyst layer. Catalyst particulates carrying Rh are exposed on the surface of the catalyst layer.

Catalysts for NOx Decomposition

MATSUDA K.K. *Japanese Appl.* 6/238,170

A catalyst carrier is coated with a silicate-containing catalyst of Pt group metal such as Pt, Ir and Rh, by a wash coating method, followed by drying, sintering and thermally treating in inert gas at 500°C. The catalysts decompose NOx in the exhaust gas of lean burn engines. Pt group metal catalysts supported on zeolite have high NOx reduction capacity.

Preparation of 1,4-Butanediol

MITSUBISHI KASEI CORP. *Japanese Appl.* 6/239,778

1,4-butanediol is prepared in high selectivity by the catalytic hydrogenation of maleic anhydride, maleic acid, succinic anhydride, etc., in the presence of a supported Pt group metal and Sn catalyst, and an alkali (earth) metal compound or a N base compound. The method gives little tetrahydrofuran by-product.

Converter for Gas Engine Exhaust Purification

OSAKA GAS CO. LTD. *Japanese Appl.* 6/246,159

Pt, Rh, Pd and Ce are contained in a wash coated layer coated on a honeycomb support. The wash coat contains Pt ≥ 1 g/l, Rh ≥ 0.2 g/l, Pd ≥ 2 g/l, and Ce ≥ 5 g/l. A gas engine uses CH_4 as fuel and has a γ-detection system for the air:fuel ratio, mounted upstream of the Rh catalytic converter to apply feedback control to the engine intake or the fuel supply.

Preparation of Platinum Alloy Catalyst

TANAKA KIKINZOKU KOGYO K.K.

Japanese Appl. 6/246,161

The preparation comprises supporting Pt and an alloy containing metals except Pt on a C support. The Pt and metals are alloyed at a high temperature, cooled, stood in an atmosphere containing 0.01–5 wt.% O_2, followed by removal of the Pt and metals from the N_2 atmosphere to the air. The Pt alloy catalyst has high activity, a high surface area and gradually generates an oxidation reaction to burn a non-C support.

Denitration Apparatus for Reducing NOx

SUZUKI KINZOKU KOGYO K.K.

Japanese Appl. 6/254,349

A denitration apparatus comprises a wire net of heat resisting metal wire plated with Pt placed on piping through which gas is exhausted from combustion apparatus, I.C.E., gas turbines, etc. It is arranged vertically or in parallel. The wire may be steel, Ni, Cu, Ti, etc. It is plated with Pd, Pt-Pd, Pt-Rh or Pt-Pd-Rh alloys. The N-compound content in the combustion gas is reduced. The apparatus has thermal resistance and durability, regardless of the O_2 content.

Catalyst for Removing Organic Halogen

SUMITOMO METAL MINING CO. *Japanese Appl.* 6/254,399

A decomposition catalyser which contains 0.1–5 wt.% Pt or Pt-oxide is supported on a 0.5–5 wt.% H_3PO_4-containing ZrO_2 carrier. Organic halogen compounds are removed from H_2O and air by contact with this catalyser. The catalyst is stable to HCl and HF which are generated by the decomposition of organic halogen compounds, even in high concentration.

Hydroxylation of Aromatic Compounds

TOSOH CORP. *Japanese Appls.* 6/256,241–42

Hydroxylated aromatic compounds (1), especially phenols, are prepared by reacting aromatic compounds with a mixture of O_2 and H_2 in the presence of a V-P complex oxide, such as vanadyl phosphate or divanadyl pyrophosphate, etc., and a catalyst of Pt, Pd, Rh, or Ru, preferably Pd and Pt, used in a ratio of 0.01–20 wt.% (calculated as metal) to total catalyst weight, on a carrier. The reaction is at normal temperature to ~ 200°C and normal to 200 kg/cm^2 pressure. (1) are useful intermediates of aniline, bisphenols, alkylphenols and phenol resin.

Platinum Loaded Catalyst for Hydrosilylation

TANAKA KIKINZOKU KOGYO K.K. *Japanese Appl.* 6/262,076

A new Pt-loaded catalyst used for hydrosilylation of olefins comprises an Al_2O_3 support of 0.1–10 m^2/g specific surface area loaded with 0.1–10 wt.% Pt. The catalyst is used to produce silicone resin or in the cross-linking reaction of silicone rubber. The catalyst is easy to contact with the highly viscous reaction mixture and provides a higher catalytic activity.

Heat Resistant Catalyst for Combustion

TONEN K.K. *Japanese Appl.* 6/262,077

A heat resistant inorganic support containing 2.5–25% SiO_2, Al_2O_3, etc., of specific surface area after burning at 1200°C in air of 50 m^2/g, is coated with 0.1–5% Pd or Pd/Ti, Mg or Mn (0.08–1%, Ti/Pd = 5–30 wt.%) to form a catalyst for combustion. A thermally resistant and highly active catalyst is obtained.

Catalyst for Purifying Exhaust Gas

NISSAN MOTOR CO. LTD. *Japanese Appl.* 6/262,088

Catalyst for purifying exhaust gas containing excess O_2 has a honeycomb first layer based on active Al_2O_3 containing a Pt group metal such as Pt, Pd and Rh, a second layer of Al_2O_3 without noble metals, and a third layer on top made of Cu or Co ion exchanged zeolite. This three-layered catalyst shows high cleaning capacity for the exhaust gas of lean burn engines.

Oxidising and Decomposing Waste Liquid

DAIDO TOKUSHUKO K.K. *Japanese Appl.* 6/269,671

A catalyst is prepared by forming a Au plating layer onto the surface of a stainless steel net and laminating a Pd layer onto the Au by semi-lustre Pd plating or Pd black plating. The catalyst is used to treat waste liquid and particularly H_2O containing hydrazine. It is catalytically stable, has good adhesion to the substrate and high corrosion resistance to chemicals.

Dechlorination of Chlorinated Polycyclic Aromatic Compounds

BAYER A.G. *German Appl.* 4,310,704

Chlorinated, optionally O-containing polycyclic aromatic compounds are dechlorinated in a continuous reaction with H_2 at 270–450°C in the spray phase using a fixed-bed Pd/spinel catalyst. The process gives quantitative conversion and disposes of polychlorobiphenyls. The catalyst has good selectivity and can be applied to a wide range of different starting materials.

Aromatic Amine and Diazonium Salt Preparation

HOECHST A.G. *German Appl.* 4,316,923

Aromatic amines (1) are prepared by reducing the corresponding nitro compound with phosphorus acid, which is a by-product of organic acid chloride preparation from organic acids and PCl_3, in the presence of a heterogeneous Pd catalyst. Halogenated aromatic diazonium salts (2) are also prepared by reacting the solution obtained with excess acid and aqueous $NaNO_2$ solution at –10 to 15°C. (1) and/or (2) are useful as diazo copying precursors and/or intermediates in the preparation of active substances, polymers and/or dyestuffs. The process is selective and gives high yields. It also has ecological advantages, since it removes the need for energy-intensive purification.

Catalyst for Removing Particulates from Diesel Exhaust Gases

YUKONG LTD. *German Appl.* 4,410,353

A catalyst for the removal of particulates from diesel engine exhaust gases is produced by impregnating the supported coated filter with a colloidal Pt group metal solution followed by heating the product at high temperature. The colloidal Pt group metal solution is prepared by treating a Pt group metal salt with an aqueous polymer solution and a reducing agent. The catalysts promote combustion of particulates at lower temperature so reducing SO_3 formation.

Stable Catalyst Filter for Particle Removal from Diesel Engine Exhaust Gas

YUKONG LTD. *German Appl.* 4,414,625

Catalyst for removing particles from diesel vehicle exhaust gas has a support of Al phosphate or P-doped Al_2O_3, which is on the surface of a heat-resistant filter and is impregnated with Pt, Pd and/or Rh. The catalyst is stable at high temperature, is effective for long periods and is not deactivated by SO_3. The supports also reduce the regeneration temperature.

HOMOGENEOUS CATALYSIS

Hydrogenation Catalyst

BASF A.G. *European Appl.* 620,042A

An hydrogenation catalyst, useful for the preparation of hydroxyl-ammonium salt from NO with H_2, is prepared by treating Pt metal salt with finely-divided S followed by reduction to metallic Pt. The production is simplified, the amount of waste product is reduced and the use of easily decomposed and toxic substances which cause partial poisoning is avoided.

Asymmetric Hydrogenation of Furoimidazole Derivatives

LONZA LTD. *World Appl.* 94/24,137A

Asymmetric hydrogenation of furoimidazole derivatives to the corresponding diastereomeric dihydrofuroimidazole derivatives (1), is carried out by reaction with H_2 in the presence of a homogeneous catalyst obtained by reaction of a Rh complex with a chiral ferrocenylphosphine ligand. Derivatives (1) are intermediates used in the preparation of the vitamin (+)-biotin, which is used for treating dermatosis, or as an animal feed additive. The process has very good diastereo-selectivity with good yield.

Synthesis of Aromatic Diamino-Diols

DOW CHEM. CO. *U.S. Patent* 5,360,932

Synthesis of aromatic diamino-diols (1) comprises contacting an aromatic halo-dinitrodiol compound (2) with excess H_2 in the presence of a noble metal hydrogenation catalyst, preferably containing Pd, an aqueous solvent, 2 moles of H halide/mole of (2) and an additional amount sufficient to provide a 0.75–4 molar solution in the aqueous solvent. (1) are useful as intermediates in the synthesis of dyes or pharmaceuticals, or as photographic developers, etc. The process eliminates or minimises organic solvents and produces an aqueous waste stream containing only hydrogen halide ions.

Aromatic Carbonate Manufacture

IDEMITSU KOSAN CO. LTD. *Japanese Appl.* 6/211,750

The manufacture of an aromatic carbonate comprises reacting an aromatic hydroxyl compound, CO and O_2 in the presence of a Pd compound catalyst, such as $PdCl_2$, $Pd(OAc)_2$ and $Pd(NO_3)_2$, a mono- or divalent Cu compound and an NH_4 halide compound. This one-step manufacture method gives aromatic carbonates in high yield at a high conversion rate without using halogen-containing solvents.

Production of Alkadienols

MITSUBISHI KASEI CORP. *German Appl.* 4,410,746

Alkadienols, used to prepare octanol and its esters, are produced from conjugated alkadienes and H_2O in the presence of CO_2 using a Pd compound and a free phosphine compound, such as triarylphosphine, with at least one aryl group having a substituent in an ortho position, in the reaction solution, as catalyst. The reaction is performed at room temperature to 180°C, and a pressure of 200 kg/cm^2. Octa-2,7-dien-1-ol is produced in improved yield and selectivity.

FUEL CELLS

Phosphoric Acid Fuel Battery Stack

FUJI ELECTRIC CO. LTD. *Japanese Appl.* 6/260,207

A phosphoric acid fuel battery stack incorporates Pt in the stack top and bottom layers so that CO present in fuel is absorbed by Pt. The primarily Pt content of the catalyser layers is increased to allow H reduction. CO in the fuel is absorbed by the Pt alloy catalyser, so preventing poisoning of the battery contents. Output is increased without increasing the cost.

Hydrogen and Deuterium Occlusion by Hydrogen Storage Metal

TECHNOVA K.K. *Japanese Appl.* 6/287,786

The process involves using a closed type electrolytic apparatus with a gas diffusion electrode, such as a Pd anode used in a fuel cell. The electrolytic apparatus contains porous film, an anode of H_2 storage metal, a Pt cathode and an electrolyte of 1 M LiOH containing thiourea, etc. A high occlusion gas:metal atomic ratio of > 0.97 for H_2, and > 0.9 for D_2 are obtained and this process is expected to be used as a fuel cell.

Electrode for Solid Electrolyte Fuel Cells

JAPAN STORAGE BATTERY CO. LTD. *Japanese Appl.* 6/290,789

The electrode comprises an Ir electrode formed on an O-ion contactive solid electrolyte base by the metal organic chemical vapour deposition method. Ir acetyl acetonate may be used as a starting material. The electrode is used for solid electrolyte fuel cells.

CHEMICAL TECHNOLOGY

Hydrogen Storage Material

NIPPON TELEGRAPH & TELEPHONE CORP. *Japanese Appl.* 6/256,986

Production of H_2 storing material for inducing nuclear fusion uses a solution containing H ions or heavy H ions, and Pd ions; imposing a H generating voltage on the anode and cathode to deposit Pd and occluding H or heavy H on the cathode. By this method, a nuclear fusion reaction is induced between H isomers. Since Pd is deposited in a solution rich in H ions, the H occlusion is carried out during the Pd deposition and growth period, which allows H diffusion from the surface layer.

ELECTRICAL AND ELECTRONIC ENGINEERING

Thick Film Resistor Using Ruthenium Oxide

E. I. DU PONT DE NEMOURS & CO. *European Appl.* 628,974A

Thick film resistor composition comprises, by wt.%, 5–25 of divided solids of Ru oxide as a conducting component and 30–70 of glass as an inorganic binder, where the divided solids of Ru oxide have average specific surface areas of ≥ 30 m^2/g and average crystallite size of ≥ 160 Å, or 18–30 m^2/g and 220 Å. The thick resistor is particularly used for vehicles, particularly in ignition equipment. The high voltage endurance characteristics obtained, were typified by ESD and controllable values of resistance and TCR.

Multilayer Magneto-Optic Recording Media

EASTMAN KODAK CO. *European Appl.* 630,008A

A magneto-optic recording medium structure includes a substrate, an amorphous seed layer and a recording multilayer deposited on it as alternating layers of Co and Pt, or Co and Pt-Pd. The seed layer thickness of < 20 nm is selected to improve the coercivity and squareness of the Kerr hysteresis loop of the multilayer.

Metallisation for Hybrid Integrated Circuits

A. T. & T. BELL LAB. *U.S. Patent* 5,356,526

Interconnections between conductive elements on the major surface of an insulating substrate comprise successive deposits: Ti, Pd-Ti, Cu, Ni and Au. The use of a TiPd alloy avoids the occurrence of Pd residues remaining after the etching of the Ti layer.

Ruthenium Oxide Film for Integrated Circuits

NORTHERN TELECOM LTD. *U.S. Patent* 5,358,889

A conductive layer of RuO_2 for an IC comprises an IC substrate with a layer of H_2O soluble Ru(III) nitrosyl salt, a H_2O soluble viscosity modifier, and a volatile organic acid, which is heated to 150–200°C to form an amorphous phase of Ru oxide. The amorphous Ru oxide layer is then annealed at 300–700°C to induce crystallisation to form a tetragonal RuO_2 phase which is suitable for formation on a perovskite structure ferroelectric material. The chloride-free process is compatible with processing for submicron devices.

Integrated Circuit Package with Lead Frame

AMERICAN TELEPHONE & TELEGRAPH CO. *U.S. Patent* 5,360,991

The composite includes the following successive layers: Ni, Pd or soft Au strike, Pd-Ni, Pd and Au. The Pd acts primarily as a bonding layer between the Ni and Pd-Ni alloy layers and as a layer that enhances reduction in porosity of subsequent layers. The Pd-Ni alloy layer acts as a trap for base metal ions. The Pd layer acts as a trap for Ni ions from the Pd-Ni alloy layer, and the outer Au layer enhances the quality to the Pd layer. This composite can withstand the effects of the processing steps in the fabrication of encapsulated devices, while maintaining solderability.

Piezoelectric Ceramics for Resonator

SUMITOMO METAL IND. LTD. *Japanese Appls.* 6/206,767–68

The ceramics comprise Pd-Sn niobate, Y-Pb titanate and Pb zirconate, or Pd, Sn, Nb, Pb, Ti, ZrO_2, etc. The composition also includes 2.6–3.8 g atom Mn : 100 mol of the basic composition. The ceramics are used for a piezoelectric resonator or a filter and the composition prevents degradation.

Conductor Paste

MURATA MFG. CO. LTD. *Japanese Appl.* 6/260,016

Conductor paste is prepared by mixing metallic powders selected from Pd, Ag or Pd-Ag, with polymer binder, such as ethyl cellulose, and an additive. The metallic powder is kneaded with an organic binder, of ethyl cellulose and solvent of α-terpene oil. Delamination is controlled by making the resin less combustible.

Coating Structure of Wiring Electrode

EREKKU AZUMA K.K. *Japanese Appl.* 6/260,577

The coating structure of a wiring electrode comprises a conductor sheet member, a Cu film deposited on the outer surface, a Ni film deposited on the Cu film, a Pd film ≤ 0.5 μm thick applied on the Ni film and a Au film of 0.0025 μm applied on the Pd film. The coating is used for substrate wiring of lead frames and bump electrodes of semiconductor devices.

Multilayer Interconnection Substrate

HITACHI LTD. *Japanese Appl.* 6/260,762

A method to manufacture multilayer interconnection substrate involves building on a ceramic substrate, coating with a Cr thin film, coating with a Cu thin film, followed by another Cr film. Resist is applied. The upper Cr film is etched, then Cu plated and the resist is removed, leaving an exposed Cu pattern. A Pd catalyser is applied to the Cu surface, followed by Ni plating, and a final polyimide film. This method gives detailed wiring with a high aspect ratio. Wiring length is reduced by miniaturisation and the speed of operation is increased.

Magnetic Thin Film Material

TEIJIN LTD. *Japanese Appl.* 6/267,743

Magnetic thin film material for a magneto-optical recording medium includes a B8 type crystal structure having a unidirectional magnetic anisotropy and a Mn-Sb-Pt alloy. The alloy has a composition of formula $Mn_aSb_bPt_c$ (a = 40–60, b = 32–55, c = 1–20 and a+b+c = 100, by at.%), and a B8 type crystal structure in amount > 75 vol.%, is contained in the alloy. The film has good magnetic and optical properties.

Scratch Type Slide Brush

TANAKA KIKINZOKU KOGYO K.K. *Japanese Appl.* 6/275,356

A scratch type slide brush is provided with a bent L-shaped portion at one end which is coated with a layer of Rh. The end part may be made of precious metal. The life of scratch type slide brush is increased by greater wear resistance.

Manufacture of Semiconductor Devices

MITSUBISHI ELECTRIC CORP. *Japanese Appl.* 6/291,146

A manufacturing method for a semiconductor device, such as GaAs FET, involves formation of a gate electrode of Ti/Pt/Au on top of a WSi gate electrode on the first electric conduction type layer with high impurity density. The current concentration of the drain electrode and the short channel effect are controlled. The build-up of bottlenecks is prevented by spreading the surface depletion layer.

MEDICAL USES

New Tris Platinum Complexes

N. FARRELL *World Appl.* 94/27,595A

Tris (Pt) complexes contain neutral and/or anionic ligands, a di- or triamine bridging agent, a counter-ion optionally dependent on whether the 3 Pt co-ordination spheres have a net charge, and a net charge of the counter-ions such that the resultant tris(Pt) complex is neutral, etc. The complexes are pharmaceutical agents, for example for treating cancer, etc., and is administered orally or parenterally. Tris(Pt) complexes have enhanced DNA adduct formation compared to mono- or bis Pt complexes.

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