

NEW PATENTS

METALS AND ALLOYS

Platinum-Aluminium-Copper Alloys for Jewellery

MINTEK

European Appl. 421,731A

The colour of intermetallic Pt-Al compounds is modified from yellow through orange to Cu red by the addition of Cu. The alloys consist of 50–81 wt.% Pt, 5–30 wt.% Al and 1–47.5 wt.% Cu, and may be formed by addition of Cu to the compound PtAl₃ or by melting individual components together in an inert atmosphere. The addition of Cu gives a range of aesthetically pleasing colours, and the alloys are used in the jewellery trade.

Palladium Based Alloys for Metal Powders

LEACH & GARNER

U.S. Patent 5,000,779

Metal powder alloys consist of at least one of Pd, Au and Ag; Cu; and 0.20–0.80 wt.% of at least one metalloid from B, P, Si and Li; with preparation including atomisation and rapid solidification. A preferred metal powder contains 40 wt.% Pd, 30 wt.% Ag, 30 wt.% Cu, 0.5 wt.% B and 0.5 wt.% P, and has particle size <100 μm and grain size <10 μm . The alloys have increased hardness, the supersolidus temperature is reduced, and the metal powders have optimum particle and grain size for supersolidus sintering.

High Brightness White Gold Alloy

NIPPON KIKINZOKU KO. *Japanese Appl.* 3/87,323

An alloy having high brightness contains 75 wt.% Au, 8–12 wt.% Pd, 7–5 wt.% Ag, 5–4 wt.% Ni and 5–4 wt.% Cu and/or Co in total. The alloy is an 18 carat Au (white Au), has high brightness similar to Pt, and has good physical, mechanical and chemical properties.

Platinum Alloy Material for Colouring Ornaments Black

AGENCY OF IND. SCI. TECH. *Japanese Appl.* 3/100,159

A Pt alloy material consists of 3–20 wt.% Pt and 3–20 wt.% of at least one of Cu, Fe, Co and Ti. The process includes heat treatment in a low oxidation atmosphere and cooling the material to room temperature with air, water or oil, and the material is used for black colouring of ornaments to give a lustre.

Silver-Palladium Alloy Powder Preparation

KOJUNDO KAGAKU KENK. *Japanese Appl.* 3/126,805

A Ag-Pd alloy for use in thick film pastes is prepared by dissolving a Ag-Pd alloy in HNO₃, and then adding a reducing agent to obtain a precipitate of the Ag-Pd alloy. The process is suitable for mass production, giving an alloy powder of uniform quality which is capable of providing good electric and soldering properties when used as pastes.

CHEMICAL COMPOUNDS

Preparation of Stable Platinum Compounds for Use in Platinum Pastes

TANAKA KIKINZOKU KOGYO

Japanese Appls. 3/99,087–89

Pt camphene mercaptate, Pt limonene mercaptate or Pt terpineol sulphide are useful materials for Pt pastes used to prepare Pt catalysts, electronic parts, corrosion-proofing layers or liquefied Pt film materials; and have good storage stability and are easily prepared. Preparation comprises reacting platinum acid salts with camphene mercaptan, limonene mercaptan or terpineol sulphide respectively, extracting with chloroform, washing, evaporating, and in the final step crystallising the products to give light yellow crystals.

ELECTROCHEMISTRY

New Electrode for Oxygen Generation Process

TDK CORP.

British Appl. 2,239,260A

A new electrode for O₂ generation has a metal substrate such as Ti coated with alternate layers of composite oxides containing (a) 40–79.9 mol% Ir oxide and 60–20.1 mol% Ta oxide, and (b) 80–99.9 mol% Ir oxide and 20–0.1 mol% Ta oxide. The electrode has good adhesion, long life at low cell voltage and current densities up to 100 A/dm², and low O₂ overvoltage and enhanced durability when used for O₂ generation by electrolysis of aqueous solutions.

Electrolytic Cell with Hollow Anodes Containing Platinum

PEROXID-CHEMIE G.m.b.H. *European Appl.* 428,171A

An electrolytic cell has alternating cathodes and anodes which are shaped hollow bodies, with the effective anode surface consisting of a valve Pt overlayer made by hot isostatic pressing a Pt foil onto a metal substrate. The cell blocks are useful electrochemical reactors for production of peroxo and perhalogenate compounds, have a long working life and high current density, and can be used together, with low energy consumption.

Production of High Purity Ammonium Paratungstate

GTE PRODUCTS CORP.

U.S. Patent 5,021,133

A cemented tungsten carbide-Pt anode is used in the electrolysis of an electrolyte consisting of ammonium hydroxide and an ammonium salt, where electro-dissolution decomposes the cemented tungsten carbide to form a solution of ammonium tungstate from which ammonium paratungstate is crystallised. A product of high purity is obtained without firing the starting material to tungstic oxide and without digestion in sodium hydroxide.

Electrochemical Oxygen Separator with Iridium Anode

JAPAN STORAGE BATTERY *Japanese Appl.* 3/94,086

An electrochemical separator has an integrated electrochemical cell consisting of a cathode for electrolytic reduction of O_2 , an ion-exchange membrane used as a solid electrolyte, and an Ir anode used for generating O_2 . The cell is used to separate O_2 from a gas mixture by supplying the mixed gas to the cathode, and collecting the O_2 from the anode. By using an Ir anode the cell operates under low voltage and at increased efficiency.

Electrolysis Electrodes with Porous Platinum Protective Coating

PERMELEC ELECTRODE LTD. *Japanese Appl.* 3/126,884

Electrodes are manufactured by electrodeposition of a PbO_2 coating layer on a metal or alloy base, followed by forming a porous Pt protective layer by electrodeposition or electroless plating. The electrode consists of multiple layers of PbO_2 and multiple porous Pt layers. An insoluble electrode is obtained.

ELECTRODEPOSITION AND SURFACE COATINGS

Metal Surface Substitution Using Palladium Plating Solution

ORIENT TOKEI K.K. *Japanese Appl.* 3/94,072

A process to effect metal surface substitution has as the first stage an etching process in a mixed solution of NaOH, KOH, KCN and NaCN at 5–35°C, and as second stage electroless plating using a 0.1–1.0 g/l solution of $PdCl_2$, $Pd(NO_3)_2$, $PdSO_4$, $Pd(COOH)_2$ or its salt, at pH 10–12, and at 5–35°C. The process is useful for plating onto thin metal foil or film of electronic devices, and for forming Al foil patterns.

Membrane Coating for Spinning Nozzle

TANAKA KIKINZOKU KOGYO

Japanese Appl. 3/104,909

A mixture consisting of chloroplatinic acid and Pt metal chlorides such as $PdCl_2$, $IrCl_3$ and $RuCl_3$ in an organic solvent is used to coat the spinning face of a spinning nozzle which consists of an alloy of Pt and Au, Ta and stainless steel. The coating is then dried and sintered to form a thin membrane having a micro structure of Pt and Pt group metal oxides which is very stable and has good anti-corrosion properties.

Palladium Deposition Bath Containing Ethylenediamine

OFF. NAT. AEROSPATIALE *French Appl.* 2,652,823

A basic aqueous bath for chemical deposition of Pd contains Pd chloride, hydrazine as reducing agent, ethylenediamine as the Pd ion complexing agent and a stabiliser. The complexing agent is present in sufficient amount to complex all of the Pd ions and the Cl ions near the plating surface, and the bath has an autocatalytic action.

Radionuclide Source Preparation

V.M. RADCHENKO *Russian Patent* 1,266,366

An increased power radionuclide source has a radionuclide oxide layer on a Pt wire, and is prepared by electromechanically coating a 0.3 mm Pt wire with the hydroxide of Cm-244 at 1200 $\mu\text{g}/\text{cm}^2$ of surface. The composition is then calcined at 800°C in air to obtain a Cm oxide layer of 0.5 mm thickness. Formation of the radionuclide source is thus simplified.

APPARATUS AND TECHNIQUE

Determination of Nitrous Oxide and Oxygen in Gas Mixtures

GTE LABS INC. *European Appl.* 432,649A

A sensor used in medical anaesthesia for determination of N_2O and O_2 concentrations in a N_2O , O_2 and N_2 mixture has Pt electrodes separated by a solid electrolyte wall, preferably of yttria stabilised ZrO_2 . A negative voltage is applied to the electrodes which are first exposed to a gas containing a known amount of O_2 , and then to the gas mixture for determination. Comparison of the current plateaux obtained gives the N_2O and O_2 concentrations.

Platinum Resistance Thermometer for Use in a Gas Detector

MICROSYSTEM DESIGN *World Appl.* 91/5,998A

A gas detector to monitor the concentration of a component of a gas mixture, for example O_3 or Cl dioxide, has a catalyst coated Pt resistance thermometer which effects an exothermic decomposition of the component and generates a signal indicating its concentration. A cheap, accurate and reliable sensor with no moving parts is obtained which is specific to the gas to be detected, and can detect a wide range of concentrations.

Platinum Cup for Pyrolysis of Pulp Samples

P. SHAKKOTAI

U.S. Patent 5,002,894

A Pt cup is used for pyrolysis of samples of paper making materials for measurement of the lignin content by mass spectrometry. The Pt cup is welded to a ribbon of poor heat conducting metal such as stainless steel, and is electrically pulsed for a short time for pyrolysis of the samples at 530–570°C. The method is used for quality control of pulp manufactured in a paper making mill.

Ruthenium Concentration Sensor for Atomic Fuel Reprocessing Plant

HITACHI K.K.

Japanese Appl. 3/48,748

A Ru concentration sensor for detecting RuO_4 concentration uses oscillators where an organic membrane is provided on the surface of an electrode. Ru concentration is measured by the difference in frequency change between oscillators in sample and reference environments. The sensor enables RuO_4 concentration to be detected on the spot with high sensitivity, and is useful in atomic fuel reprocessing.

Durable Gas Sensor Element

KURABE K.K. *Japanese Appl. 3/59,450*

A gas sensor element consists of an insulating base plate such as Al_2O_3 or SiO_2 , a pair of comb shaped Pt or Au electrodes, a SnO_2 or ZnO gas sensor, a Pt and/or Pd catalyst layer up to 5 nm thick, and a heater. The gas sensor is kept at 150°C and is used for reducing gases such as CO and H_2 . The sensor has a simple structure, high sensitivity, good durability and is stable over a long period of time.

Enzyme Electrode with Conductive Platinum Base Body

KANZAKI PAPER MFG. K.K. *Japanese Appl. 3/59,453*

An enzyme electrode consists of a conductive base body of Pt, Au or C, having its surrounding part covered with a hydrophobic insulator such as polyethylene, and the section covered with an immobilised enzyme film such as glucose oxidase through a permselective membrane. The electrode can be assembled simply, and has good durability.

Heat Resistant Humidity Sensing Element

SHINETSU CHEM. IND. K.K. *Japanese Appl. 3/72,253*

A humidity sensing element consists of an insulating base plate, a pair of Ag-Pd, Ru oxide or Au electrodes on the base plate, and a polysiloxane film. The sensor can be used at $<100^\circ\text{C}$, and has high heat resistance, high response speed, and low hysteresis.

Small Heat Generating Device

T. MOTOE *Japanese Appl. 3/86,233*

A vaporised industrial alcohol such as CH_3OH is passed through a porous body, and then through a Pt honeycomb catalyst where the alcohol decomposes to CO_2 and H_2O , generating heat which is collected in the Pt honeycomb. The heat can be used in the form of hot air or by contacting a conductor with the hot Pt honeycomb. Heat can be generated safely and easily with this small apparatus.

High Sensitivity Gas Sensor Element

SUMITOMO CHEM. IND. K.K. *Japanese Appl. 3/89,156*

A gas sensor element consists of polyaniline between more than two conductive electrodes of Pt, Au, Ag, graphite, Sn or In oxide and Si. The electrodes can be clad, deposited or sputtered on the polyaniline film to form the element. Various gases such as NH_3 , CH_4 , H_2O , H_2S , NO and others can be detected.

Material for Detecting Combustible Gas

AGENCY OF IND. SCI. TECH. *Japanese Appl. 3/89,162*

A combustible gas detecting material consists of at least one of Pt, Pd, Rh, Ir, Au or Ag supported in fine granular form on metal oxide(s) of at least one of Ru, Cr, Mn, Fe, Co or Ni, present as a thin film on a transparent base plate. The material is used for detection of combustible gas by light signals, and can be assembled in a light control system. The gas detection device has excellent explosion-proof properties, and is hardly affected by electromagnetic interference.

Gas Sensor with Long Term Stability at Low Temperatures

FUJI ELECTRIC MFG. K.K. *Japanese Appl. 3/90,848*

A gas sensor consists of a base plate made of an insulator material, a gas sensitive layer containing 0.1–1 wt.% (total) of Pt and Pd in the proportion 1–3, and an *n*-type oxide semiconductor coating layer carrying 2–10 wt.% of a noble metal, for example Sn oxide carrying 3 wt.% Pt. The catalytic activity of the gas sensitive layer is stable over a long period, even at low temperatures.

Gas Sensor for Detecting Oxygen and Ozone

OAK SEISAKUSHO K.K. *Japanese Appl. 3/95,452*

A gas sensor consists of a semiconductor base plate such as a *p*-type silicon wafer, an insulating layer, a La fluoride layer having La:F atomic ratio 1:2–1:3, and a 100–500 Å laminated Pt electrode having properties intermediate between those of Pt and Pt black. The gas sensor is useful for detecting O_2 and O_3 at normal temperatures, and functions by absorbing the gas on the electrode and detecting the change in properties.

Platinum-Rhodium Melt Crucible with Longer Operational Life

BENCKISER-KNAPSACK *German Appl. 4,001,430*

Alkali metal monofluorophosphates are produced using a cylindrical Pt/Rh melt crucible 80 cm high and 8.0 cm in diameter which is heated to $800\text{--}1200^\circ\text{C}$. A direct potential is applied between the cooling aggregate (cathode) and the crucible (anode). The crucible has a longer operating life than other known crucibles, making the process more economical.

JOINING

Platinum Bonding Layer for X-Ray Target

GENERAL ELECTRIC CO. *U.S. Patent 5,008,918*

A composite structure for use as an X-ray tube target consists of a refractory metal portion bonded to a graphite substrate via a Pt bonding layer containing a bonding agent of W, Ni, Mo, V or Ti. The bonding alloy can be Pt containing at least 0.8 wt.% W to give a pull strength of at least 2600 psi. The product has thermal stability at 1350°C , and a brazed bond having superior strength and heat transfer is provided.

High Strength Palladium Solder Alloy

TANAKA KIKINZOKU KOGYO *Japanese Appl. 3/60,893*

A Pd based solder alloy contains 20–40 wt.% Pd, 50–70 wt.% Cu and 5–15 wt.% of at least one of Fe, Ni and Co. The alloy is used for soldering Ti or Ti alloy members with sufficiently high tensile strength, and is suitable for producing thin walled Ti parts and joint type Ti members, used for example in aeroplanes and so on.

HETEROGENEOUS CATALYSIS

Production of Amines for Polyurethane Foam

BAYER A.G. *European Appl.* 424,764A
Bis- and tris(3-dimethylaminopropyl)amine compounds are produced by hydrogenation of 3-dimethylaminopropionitrile using a catalyst consisting of 0.1–10 wt.% Pd on an Al_2O_3 or spinel support. Selectivity to the bis product is increased by using an Al_2O_3 support, and to the tris product by using a spinel, preferably LiAl spinel. The products are obtained with high yield and are useful for polyurethane foam production.

Platinum or Palladium Catalyst for Preparation of N-Alkylaminophenols

SUMITOMO CHEM. IND. K.K. *European Appl.* 427,572A
N-alkylaminophenols are prepared by reductive alkylation of an aminophenol with an aldehyde or ketone, in an organic solvent, and in the presence of H_2 and a catalyst consisting of Pt or Pd with at least one metal from Groups IB, IIB, IVB, VB and VIB on an activated C support. Side reactions are suppressed, and the catalyst can be used repeatedly with a high yield of desired products, which are used as intermediates for various dyes.

Rhodium Catalyst System for Preparation of Perfumery Intermediate

FIRMENICH S.A. *European Appl.* 427,965A
4-Tertiary-butyl-cyclohexanol can be prepared mainly in its isomeric cis form by hydrogenation of 4-tertiary-butyl-phenol or 4-tertiary-butyl-cyclohexanone in the presence of Rh supported on Al_2O_3 , charcoal or others, in combination with HBF_4 or a substituted BF_3 compound. The catalyst system can be recycled, has long service life, and gives high selectivity.

Platinum-Zeolite Exhaust Purification Catalyst

TOYOTA JIDOSHA K.K. *European Appl.* 427,970A
A catalyst for purification of exhaust gases from internal combustion engines consists of a zeolite layer or a support (metal or zeolite) loaded with at least 1.3 parts wt. Pt, or at least 0.8 parts wt. Pd, or at least 0.7 parts wt. Rh. The catalysts have better high temperature durability and conversion of NO_x .

Three-Way Catalyst with Enhanced High Temperature Activity

FORD MOTOR CO. LTD. *European Appls.* 430,435A and 430,437A
A three-way catalyst for vehicle emission control consists of a carrier such as cordierite coated with an Al_2O_3 support, optionally having 2–30 wt.% La_2O_3 discontinuously deposited on it, then 0.05–5 wt.% of deposited Pd and up to 8 wt.% of a discontinuous TiO_2 phase adjacent to or deposited on the Pd component. The catalyst reduces light-off temperatures by 20–100°C. It may also include Pt.

Iridium Catalyst for Preparation of Chlorofluoroethanes

ATOCHEM. *European Appl.* 435,705A
Chlorofluoroethanes are prepared by hydrogenation of a perhalogenoethane at 50–300°C and 1–20 bar using a catalyst consisting of 0.1–10 wt.% Ir on a support of Al_2O_3 , AlF_3 or active charcoal. Use of the Ir catalyst improves selectivity so that only one Cl atom is eliminated from the starting material.

Platinum Catalyst for Isomerisation of Alkanes

UOP *U.S. Patents* 5,004,859 and 5,017,541
Isomerisable hydrocarbons are isomerised by contact with a bed of catalyst particles consisting of an Al_2O_3 support, 1–15 wt.% of a Friedel-Crafts metal halide, preferably Al chloride, and 0.01–2 wt.% of a surface-layer Pt group metal component, preferably Pt. Isomerisation is at 40–250°C and 1–100 atm pressure, and an organic promoter such as CCl_4 is optionally present in the feed or catalyst. The method is used for isomerisation of 4–7C alkanes, giving increased octane numbers for a 5–6C naphtha stream.

New Noble Metal Catalytic Composites with Long Life

UOP *U.S. Patent* 5,013,703
New catalytic composites of silicalite impregnated with at least 8 wt.% of Pt, Pd, Rh, Ir, Os, Ru, Au and/or Re have > 60% dispersion of the noble metal resulting from base pretreatment and double impregnation stages in the preparation. The composites have hydrophobic molecular sieve properties, long life, and are not combustible or pyrophoric. The Pt composite can be dispersed in a PTFE matrix and used to catalyse isotopic exchange between H_2 and H_2O vapour.

Molybdenum Promoted Catalyst for Production of Lower Alcohols

TEXACO INC. *U.S. Patent* 5,013,764
Lower aliphatic alcohols are prepared from the reaction of CO and H_2 in the presence of a catalyst composition consisting of 0.5–6.0 wt.% Pd, 2.0–15.0 wt.% of one or more of Cs, K, Na and/or Rb, and 1.0–10 wt.% Mo as a promoter, on a support which is especially Al_2O_3 . The catalyst is devoid of Cu and Th, and is useful for production of alcohol mixtures containing a substantial amount of 2–7C alcohols, used for example as fuel extenders or gasoline substitutes.

Platinum Wire Catalyst for Use in a Carbon Dioxide Laser

HUGHES AIRCRAFT CO. *U.S. Patent* 5,020,069
A catalyst for use in a laser consists of a Pt wire coated with a layer of Pt black and is preferably carried on an insulating support. The wire is heated by passing a current through it, and is used in a CO_2 laser for re-converting CO and O_2 lasing by-products to form CO_2 at 150–300°C. The low temperature catalyst has prolonged activity.

New Poison Resistant Three-Way Catalyst with Silica and Alumina Layers

TOYOTA JIDOSHA K.K. *Japanese Appl.* 3/68,448

A new catalyst for removal of hydrocarbons, CO and NO_x from car exhaust consists of a support, a SiO₂ layer loaded with Pd, and an Al₂O₃ layer loaded with Pt and/or Rh. The new catalyst is resistant to poisoning, and operates over a long time without degradation. In an example the catalyst consisted of a monolithic support, a SiO₂ layer impregnated with 0.5 g/l Pd, and an Al₂O₃ layer containing La and Ce, impregnated with 0.5 g/l Pt and 0.1 g/l Rh.

Differentially Charged Impregnation of Exhaust Purification Catalysts

TOYO KOGYO K.K. *Japanese Appl.* 3/72,948

An exhaust gas purification catalyst consists of a support with an Al₂O₃ coating layer supporting metals such as Pt and Rh. Preparation is characterised by differentiating the charged states of the noble metal ions and the Al₂O₃ layer during impregnation, equalising those of the second noble metal ions and the Al₂O₃ layer. Thermal deterioration of the catalyst can be prevented.

Exhaust Purification Catalysts for Alcohol Fuelled Engines

NIPPON SHOKUBAI KAGAKU
Japanese Appls. 3/72,949–50

Catalysts for purifying exhaust gas from internal combustion engines using alcohol as a fuel consist of a 3-dimensional structure coated with a catalyst composition containing: (a) 0.5–4.0 g of Pt, Pd or Rh and 1.0–20 g of Ag on stable Ce oxide (50–200 g) containing at least Mg, Ba, Ca, Sr or Y; or (b) 0.5–1.5 g/l Pd and 5–10 g/l Ag on Al₂O₃ (80–150 g/l) containing at least one oxide of Ti, Si and Zr. The catalysts decompose CO, CH₃OH and HCHO in the exhaust gas at low temperature, and catalyst (a) shows improved heat stability of the Ce oxide.

Palladium Catalyst for Preparation of Intermediates for Amino Acids

DAICEL CHEM. IND. K.K. *Japanese Appl.* 3/74,346

2-Oxo-4-phenylbutanoic acid derivatives are prepared by reduction of 2-oxo-4-phenyl-3-butenic acid derivatives in solution, at pH 6–10.5, in the presence of a Pd catalyst. Reaction can take place in a solution or a slurry, with water as the most appropriate solvent. The products can be formed selectively in excellent yield, and are useful intermediates.

Catalytic Converter with Different Inflow and Outflow Catalysts

NIPPON SHOKUBAI KAGAKU *Japanese Appl.* 3/77,625

A catalytic converter contains exhaust gas purification catalysts in a converter unit, with the catalyst on the exhaust gas inflow side containing Pd and Rh, and that on the outflow side containing Pt, Rh and optionally Pd. The volumetric ratio of inflow to outflow catalysts is 1:8 to 3:1. The catalyst converter has improved hydrocarbon purification.

Palladium Catalyst for Preparation of Bisnaphthalic Acid

NIPPON STEEL CHEM. K.K. *Japanese Appl.* 3/77,844

Bisnaphthalic acid, its alkyl derivatives or salts are prepared by dimerisation of 4-halonaphthalic acids or their alkyl derivatives at 90–120°C in the presence of a Pd/C catalyst, in an aqueous alkaline medium containing bases, formic acid and lower alcohols. The products are prepared in 60–84% yield, and are used for polyimide resins or pigments.

Preparation of Malonic Acid Esters in High Yield

NIPPON KOKAN K.K. *Japanese Appl.* 3/77,847

Malonic acid esters are prepared from reaction of dibromomethane, an alcohol and CO in the liquid phase, in the presence of a catalyst consisting of Pd, Rh and/or Co or a compound supported on a C carrier of activated charcoal, C black or graphite. Malonic acid esters can be prepared in high yield, and are useful for pharmaceutical intermediates.

Exhaust Gas Purification Catalysts with Ultrafine Platinum and Rhodium

TODA KOGYO K.K. *Japanese Appl.* 3/86,240

Catalysts for exhaust gas purification are prepared by coating the surface of a ceramic catalyst support, preferably a honeycomb support, with a mixture of Pt and Rh organosols in an organic solvent, and then vaporising the solvent. The method provides ultrafine Pt and Rh particles uniformly dispersed on the support, without heating in H₂, and then air. The catalysts are used for removal of CO, hydrocarbons and NO_x contained in exhaust gases.

Selective Low Temperature Removal of Carbon Monoxide from Hydrogen

ASAHI CHEMICAL IND. K.K. *Japanese Appl.* 3/93,602

CO is selectively removed from H₂ gas by contacting with a supported Ru catalyst at 100–200°C. In an example the catalyst consisted of 1 wt.% Ru on γ -Al₂O₃, and after treatment in N₂/H₂ was used to purify H₂ gas containing 60 ppm CO. As CO can be removed at low temperature, inexpensive heating media can be used.

Waste Gas Purification Catalysts with Improved Heat Resistance

TOYOTA JIDOSHA K.K.
Japanese Appls. 3/94,830 and 3/98,644

Waste gas purification catalysts are produced by immersing an inorganic support in (a) a solution containing Pt and/or Rh, Ir and/or Ru, and citric acid, or (b) an aqueous Pd solution, drying, then immersing in a solution containing Rh, Ir and/or Ru salts and citric acid; then drying, calcining and reducing. Citric acid promotes inter-diffusion of the Pt group metals, and prevents grain growth and evaporation of Ir or Ru. The catalysts are used to remove hydrocarbons, CO and NO_x from car exhaust, and have improved activity, heat resistance and durability.

Platinum-Zinc Oxide Whisker Catalyst for High Temperature Oxidation

MATSUSHITA ELEC. IND. K.K.

Japanese Appl. 3/101,835

An oxidation catalyst for gas or liquid phase reactions consists of a tetrapod shaped whisker of ZnO optionally coated with porous SiO₂ or Al₂O₃, and supporting 0.5–1.0% Pt on its surface. The whisker of ZnO has a core with needle crystals projecting in 4 directions from the core centre. The catalyst has superior properties, giving high speed reaction, and is used for high temperature oxidation, for example cleaning waste gas from combustion devices.

Ruthenium Catalysts for Ammonia Production

SHIN NENSHO SYST. KE. *Japanese Appl.* 3/106,445

Catalysts for NH₃ production are obtained by supporting a Cl-free Ru compound – such as a carbonyl complex or nitrate – on a reduction resistant oxide, evacuating and/or reducing in a H₂ stream to obtain a metallic Ru catalyst, and supporting a Sm, La or Ce compound on the catalyst. The catalysts have high activities for the synthesis of NH₃ from N₂ and H₂, particularly when the support is Al₂O₃; and have water and heat resistance.

Exhaust Purification Catalyst with High Activity

NIPPON SHOKUBAI KAGAKU *Japanese Appl.* 3/114,539

A catalyst with high activity for purification of exhaust gases consists of a tungstate; Pt, Pd or Rh as the metal and/or oxide; and Ba or La molybdates supported on a moulded inorganic pellet or a gas filtering refractory three-dimensional material, and is preferably treated at 700–1000°C in air. In an example, a catalyst containing Pt, Rh, BaWO₄, BaMoO₄, Al₂O₃ and a cogelite support was prepared.

High Temperature Combustion Catalyst

UBE INDUSTRIES K.K. *Japanese Appl.* 3/118,835

A new high temperature combustion catalyst for complete burning of a fuel gas and O₂ containing gas to give only CO₂, H₂O and heat energy consists of Pt group elements and high purity magnesia single crystal fine powder 0.01–0.2 μm in diameter. The catalyst has higher heat resistance and is not sintered even at 1250°C, and is used for body warmers, kerosene stoves or boilers, or for car exhaust purification or deodorising apparatus.

Platinum-Carbon Catalyst with Ultrafine Particles

FUJI ELECTRIC MFG. K.K. *Japanese Appl.* 3/127,458

A Pt catalyst is prepared by depositing Pt on C by immersing a C powder support in a mixed solution containing H₂PtCl₆, a colloid coagulation protector and a reducing agent with an aldehyde group. The C powder support has had hydrophilic treatment and can be, for example, acetylene black. Ultra pure water is used as the solvent and for washing, giving a catalyst with ultra fine Pt particles dispersed on C.

Lanthanum-Aluminium-Platinum Waste Gas Purification Catalyst

BABCOCK-HITACHI K.K. *Japanese Appl.* 3/131,342

A catalyst for purifying waste combustion gas contains a double oxide of formula LaAl_{1-x}B_xO₃, where x is 0.01–1, and B is Pt or Pd. In an example a honeycomb body was coated with a mixture of the double oxide and Al₂O₃. The precious metals are highly dispersed over the catalyst which is resistant to high temperatures (>800°C) even in an oxidising atmosphere, and is used to purify waste gas.

Palladium Catalyst for Vinyl Acetate Preparation

HOECHST A.G. *German Appl.* 3,940,125

A catalyst for gas phase preparation of vinyl acetate from ethylene, acetic acid and O₂ consists of Pd and/or its compounds, optionally Au and/or its compounds, alkali compounds, and optionally Cd compounds as activators, on a SiO₂ or SiO₂/Al₂O₃ carrier having specified surface characteristics, and using a binder such as a Mg carboxylate for the carrier particles. The selectivity and space/time yield of the catalyst are raised, and side reactions are reduced.

New Platinum-Tin Reforming Catalysts

INST. MEXICANO DEL. P. *German Appl.* 4,006,884

New catalysts are prepared by a two-stage impregnation process in which an inorganic oxide support is first impregnated with a solution of a Sn salt, a halogen compound and an organic acid, and then with a solution of a Pt compound and a halogen compound; finally activating in a reducing atmosphere.

Three-Stage Removal of Oxygen and Hydrogen from Inert Gas

ELECTROTHERM. EQUIP. R. *Russian Patent* 1,604,440

O₂ and H₂ are removed from inert gases by first passing over a catalyst of 48–51% Ni and 26–28% Cr at 180–250°C to remove O₂, then over a catalyst of 0.45–0.55% Pd/Al₂O₃ where H₂ reacts with residual O₂ to produce H₂O, and finally over the Ni catalyst where residual H₂ reacts with NiO to produce H₂O and regenerate Ni. Lower O₂ and H₂ contents in the inert gases are obtained using this method.

HOMOGENEOUS CATALYSIS

Rhodium Catalyst for Preparation of Difunctional Monomers

DU PONT DE NEMOURS CO. *European Appl.* 428,979A

3-Pentenoic acid and carboxylic acid anhydride derivatives are prepared by carbonylation of allylic butenols and allylic butenol esters. The allylic compound is reacted with CO at 10–250°C in the presence of 0.005–0.50 wt.% of a Rh catalyst and a HBr or HI promoter, with a promoter:Rh molar ratio of 1:1. The products are useful as difunctional monomers and intermediates in the synthesis of adipic acid, and can be prepared selectively.

Palladium Catalyst for Preparation of Adipic Acid Precursors

RHONE-POULENC CHIM.

European Appls. 433,189A and 433,191A

A Pd catalyst, especially Pd chloride, and metal halides are used in the preparation of (a) 1,6-hexenedioic acid from the reaction of CO with a butenediol, or (b) hex-3-ene dioic diesters from the reaction of diacryloxy-substituted butene, an alcohol and CO. The reactions take place in a basic, aprotic, polar solvent, at 50–150°C, at 10–250 bar pressure, and with 0.001–1 mol/l Pd. Both products are precursors for adipic acid, and can be produced with high selectivity using a metal halide.

Rhodium Catalyst System for Production of Moist-Grain Preservatives

CHEVRON RESEARCH CO. *U.S. Patent* 5,008,451

Carboxylic acid anhydrides are produced by reacting a carboxylic ester and CO at 50–300°C and an initial pressure of 1–100 atm, under anhydrous conditions, in the liquid phase, and in the presence of a catalyst system consisting of a Rh compound, an iodide promoter, and a proton donor. The process can be used to produce methylene and oxymethylene bis-esters.

Platinum Catalyst for Deblocking N-Formyl Protected Compounds

W.R. GRACE & CO-CONN. *U.S. Patent* 5,017,690

The formyl groups are removed from the N atom of an N-formyl aspartame compound by heating at 70–75°C using a catalyst consisting of 5% Pt on C or Pt chloride, with P present at 0.1–5 wt.% of the aspartame compound, and in the presence of a promoting amount of aniline or methylene dianiline. The method is used to deblock N-formyl protected amino acids, peptides and polypeptides, and minimises formation of the diketopiperazine by-product.

Ruthenium Catalyst for Lactone Preparation

MITSUBISHI KASEI CORP.

Japanese Appls. 3/74,377 and 3/83,974

Lactones are prepared by liquid phase hydrogenation of dicarboxylic acids, dicarboxylic anhydrides and/or dicarboxylic acid esters at Ru 50–250°C, under 0.1–100 kg/cm² H₂, and in the presence of a catalyst. The yield and selectivity to lactones can be improved markedly if the concentration of diols in the reaction zone is controlled below 5 wt.%, or catalyst deterioration can be prevented if the concentration of dicarboxylic anhydrides is kept below 3 wt.%.

Ruthenium Catalyst for Selective Production of Cycloolefins

ASAHI CHEMICAL IND. K.K. *Japanese Appl.* 3/115,233

Cycloolefins are produced by partial hydrogenation of monocyclic aromatic hydrocarbons in the presence of a Ru catalyst, and by dispersing at least one dissolved Zn oxide or hydroxide into the reaction system, with water or alcohol as solvent. Cycloolefins are produced with a high invert ratio and high selectivity.

Rhodium Hydrocarbonylation Catalyst for Ethylidene Diacetate Production

WACKER CHEMIE G.M.B.H. *German Appl.* 3,934,860

Ethylidene diacetate is prepared by reaction of methyl acetate with CO and H₂ at 180–220°C and 50–250 bar absolute, using a catalyst consisting of 0.05–0.50 mol % of a Rh compound, 0.04–0.50 mol % of a Pd or Ru compound, an ether-phosphane ligand to give a 1:1–2 Rh:ligand mol ratio, and 3–15 mol % of an alkali(ne earth) iodide. High conversions with high selectivity to the product can be obtained.

Preparation of Symmetrical Diarylacetylene Compounds

BAYER A.G. *German Appl.* 3,936,297

Symmetrical diarylacetylenes are prepared by reaction of an aryl halide with acetylene in the presence of a Pd catalyst and a base. The acetylene is fed into the liquid reaction mixture using an intensive gasifier, and the aryl halide is a stable, cheap, easily prepared bromide. The products are obtained from one reaction stage, with high yield and selectivity, at high space/time yields, and are used as intermediates for diaryl olefins.

Rhodium Catalyst System for Production of Aldehydes

HOECHST A.G.

German Appl. 3,942,954

Aldehydes are produced by reacting olefinically unsaturated compounds with CO and H₂ in a homogeneous phase at 20–150°C and 0.1–20 MPa in the presence of a catalyst system containing Rh and an ammonium salt of a sulphonated phosphite triester. The catalyst system is especially useful in hydroformylation of 4–20°C olefins with non-terminal unsaturation. Use of the organic P compound prevents side reactions and the catalyst retains its activity for very long periods.

FUEL CELLS

Platinum-Iridium-Iron Catalyst for Phosphoric Acid Fuel Cell Cathode

INT. FUEL CELLS CORP.

U.S. Patent 5,013,618

A catalyst for O₂ reduction in a phosphoric acid fuel cell consists of a ternary noble metal alloy of Pt, Ir and one of Ti, Mn, Ni, Co, V, Cr or Fe, preferably Cr or Fe. The catalyst is used on the cathode of a phosphoric acid fuel cell, and has high activity and stability, showing 50% less surface area loss in use than a conventional PtCrCo catalyst.

Platinum-Iron Alloy Catalyst for Phosphoric Acid Fuel Cell Electrode

FUJI ELECTRIC MFG. K.K.

Japanese Appl. 3/68,452

A Pt alloy catalyst is produced by depositing a Pt alloy on a C support, then depositing Fe, and heating in a controlled manner to 900–1000°C for 5–30 seconds to form a Pt-Fe alloy. The Pt alloy catalyst has smaller crystallite size, and is used for a phosphoric acid fuel cell electrode, giving a higher cell performance at a current >200 mA/cm².

ELECTRICAL AND ELECTRONIC ENGINEERING

Magneto-Optical Recording Element Containing Palladium

EASTMAN KODAK CO. *European Appl.* 428,454A

A magneto-optic recording element has a substrate and a recording layer containing a Tb, Fe and Co alloy with added Zr and Pd. The recording layer has improved corrosion and oxidation resistance without affecting the magneto-optic recording properties.

Multilayer Platinum-Cobalt Films for Magneto-Optical Recording

DU PONT DE NEMOURS CO. *World Appl.* 91/8,578A

Multilayer films no more than 75 nm thick consist of alternating layers of Pt and Co deposited by a sputtering process using Kr or Xe or a mixture as the sputter gas. All of the Co layers are a maximum of 1.2 nm thick, and all of the Pt layers are a maximum of 2.4 nm thick, with a Pt:Co layer thickness ratio of 1–5. The deposited films are used in magneto-optical recording, and have a higher coercivity than films sputtered in Ar.

High Coercivity Thin Film Magnetic Recording Medium

HMT TECHN. CORP. *U.S. Patent* 5,004,652

A thin film magnetic recording medium has a substrate, a sputtered Cr underlayer 300–3000 Å thick, and a sputtered magnetic layer 200–1000 Å thick consisting of an alloy of 8–20 at.% Pt, 70–80 at.% Co, 10–20 at.% Cr and 2–10 at.% Ta. The magnetic recording medium has high coercivity, resolution, amplitude and loop squareness values, low bit shift, and is used for high recording density read/write memory devices in computers.

Silver-Palladium Alloy Sheath for High Temperature Superconductor

WESTINGHOUSE ELEC. CORP. *U.S. Patent* 5,017,553

A metallic sheath for a superconducting core is a layer of Ag-Pd alloy having 10–50 wt.% Pd and containing 5–45 wt.% of interdispersed particles of W, Mo or Ni or mixtures of these of 0.05–75 μm diameter; and may have an inner or outer wall of Ag. A superconductor having a high strength, thermally matched, high-temperature sheath is provided, which is useful for fine wires or magnet windings.

Ruthenium-Containing Screen Printing Ink for Forming Resistors

MATSUSHITA ELEC. IND. K.K. *Japanese Appl.* 3/40,402

A screen printing ink consists of a Ru compound optionally mixed with another metal compound, carboxylic acids of terpenoids or their esters as viscosity increasing agent, and an additive consisting of an aliphatic carboxylic acid. The ink is used to form a resistor for a thermosensitive printer head, electrode and resistors. A good quality thin resistor film can be prepared by screen printing and calcination.

Palladium-Silver Conductor Paste

NIPPON CHEMICON K.K. *Japanese Appl.* 3/49,106

A conductor paste consists of 5–30 parts wt. Pd powder, 70–95 parts wt. Ag powder, and 0.5–10 parts wt. glass frit to which 0.1–10 parts wt. metal iodide was added. The paste is used for forming conductor patterns and electrodes on Al nitride compacts.

Longer Life Soft Magnetic Thin Film

MATSUSHITA ELEC. IND. K.K. *Japanese Appl.* 3/54,705

A soft magnetic thin film has a laminated structure consisting of 2–100 nm Fe thin films and 1–50 nm films of at least one kind of metal or at least 2 kinds of alloy of Pt, Rh, Ir, Ru, Au, Ag, Re or Ta. The soft magnetic thin film can be used at least as part of the core of a magnetic head, which has longer life and is suitable for high density write/read information.

Vertically Magnetic Recording Medium

SONY CORP. *Japanese Appl.* 3/58,316

A magnetic recording medium consists of a non-magnetic substrate with a Co-Pt-B-O magnetic layer composed of 50–100 Å diameter acicular crystals having a face centred cubic lattice. The magnetic crystal form, size and orientation are controlled to give greatly enhanced coercivity in the vertical direction. In an example a magnetic recording medium had a polyamide film substrate with a Pt underlayer and a Co-Pt-B-O magnetic layer.

Plasma Deposited Magnetic Recording Medium

MATSUSHITA ELEC. IND. K.K. *Japanese Appl.* 3/78,114

A magnetic recording medium has a substrate with a γ-type Fe oxide magnetic layer including one of Pd, Rh, Os, Ru, Co, Cu, Ti, V or Nb, where the magnetic layer is deposited in a plasma state generated by electron cyclotron resonance (ECR). The magnetic properties and recording fidelity of the medium are improved by utilising the activity of the ECR plasma.

Manufacture of a Superconductor Wire with a Platinum Core

NICHIDEN ANERUBA K.K. *Japanese Appl.* 3/79,766

A superconductor wire consisting of a superficial oxide superconductor film formed on a continuous fine wire of Pt or ceramic is manufactured by shifting the fine wire continuously, while sputtering the thin superconductor film onto it, and then heating in an O₂ atmosphere to effect crystal growth of the film.

Magnetic Alloy Memory with Thermal Hysteresis of Magnetisation

TOSHIBA K.K. *German Appl.* 4,030,476

A magnetic alloy has as the main phase an isomolar compound phase of formula Pt(Fe_{1-x}Mn_x)Sn, in which x=0–1 exclusive. The magnetic alloy exhibits significant thermal hysteresis of magnetisation, and allows production of magnetic memories of simple structure and operation for recording systems.

Thermosensitive Circuit Breakers for Automatic Fire Alarms

M. A. AKIMOV

Russian Patent 1,238,610

A thermosensitive circuit breaker has an insulating substrate with sprung contact plates, and a Pt, Pd or Mo dispersing plate on these plates. The dispersion material acts as a catalyst for oxidising processes on its surface. The circuit breaker has reduced inertia, and is used in electrical engineering, for example in automatic fire signalling.

TEMPERATURE MEASUREMENT

Thermocouple-Type Temperature Sensor

ASAHI GLASS K.K.

World Appl. 91/7,643A

The Pt-Rh thermocouple of a thermoelectric temperature sensor has an insulating tube inserted in a metal-boride ceramic protective tube to prevent deterioration of the thermocouple by reducing gas at high temperatures. The tip of the insulating tube is covered with a cap made of a Pt group metal. The thermocouple has extended life, and is used to measure the temperature of hot metal and molten steel continuously, for extended periods of time.

Melt-Adhered Platinum-Rhodium Thermocouples for High Temperature Measurements

KOBE STEEL K.K.

Japanese Appl. 3/66,481

Pt-Rh thermocouples are melt-adhered on the surface of a Ti(alloy) material test piece by incorporating a thin Ta plate between the thermocouple and test specimen. Temperature measurements of Ti(alloy) materials can then be made at 1300°C or above which is requisite for recognising thermal properties of these materials for use in the space and aero industries.

MEDICAL USES

New Platinum Anti-Tumour Compounds

BRISTOL-MYERS SQUIB.

European Appl. 423,707A

New Pt(IV) complexes containing axial hydroxy or mono- or dicarboxylate groups are used as anti-tumour compounds, and have lower kidney and bone marrow toxicity than known Pt-containing anti-tumour compounds. Certain of the complexes are water soluble, while others are lipo-soluble and can therefore be used in liposomes, in oil-water emulsions, injected as oil solutions, or used topically.

Low Toxicity Platinum Anti-Tumour Complexes

TORAY IND. INC.

World Appl. 91/9,041A

New γ -butyrolactone Pt complexes have a cis, trans-1, or trans-d 1,2-diaminocyclohexane ring, and have high anti-tumour activity and low toxicity. In an example, one of the complexes was used to treat L1210 leukaemia in mice.

Low Toxicity Platinum Anti-Tumour Agents

TSUMURA & CO.

World Appl. 91/9,042A

New oxalate-diaminocyclooctane Pt(II) complexes and stereoisomers are prepared from dinitrato (diaminocyclooctane) Pt(II) and oxalic acid. The complexes are anti-tumour agents with low toxicity, used at a dosage of 5–600 mg/day.

Zirconium-Palladium-Ruthenium Alloy for Dental or Medical Use

AMER. DENTAL ASSOC. H.

U.S. Patent 5,019,337

An alloy composition for dental or medical use consists of 35–60 wt.% Zr, 1–60 wt.% Pd and 1–60 wt.% Ru, while another composition has Pt, Rh, Ir, Os, Ru, Al, Si or Co as the second element. The alloy has a cubic CsCl or B₂ type structure which can undergo stress-induced transformations at body temperature. The alloy is used for casting crowns, bridges, dental or medical implants or prosthetic devices, and has enhanced ductility, adequate strength, and biocompatibility.

Platinum Complex for Tumour Inhibition or Radio-Sensitisation

BRIT. COLUMBIA CANCER.

U.S. Patent 5,026,694

A composition for tumour inhibition or radio-sensitisation consists of a square planar Pt(II) complex of formula PtX_n(NR, H)L and an excipient; where n is 1 or 2, X is an anion, R is H or alkyl or NRR is piperidino or morpholino, and L is a radio-sensitising ligand. The complex is used at 0.1–5 mg/kg and can bind DNA, sensitise hypoxic cells to radiation and is directly toxic to tumours.

Laser Beam Reflectors Containing Ruthenium

TOSHIBA K.K.

Japanese Appl. 3/104,839

A laser beam reflector is prepared by laser beam irradiating a sintering of 5–60 wt.% Ru, 0.5–3 wt.% Zr and/or Ti, 0.001–0.1 wt.% C and balance Mo in vacuum or under an inert gas atmosphere, to densify the mixture. The method provides reflectors free from surface degradation due to oxidation or corrosion, for use in laser knives or other surgery devices, and used in place of conventional Cu reflectors.

New Platinum Complexes with Anti-Tumour or Anti-Microbial Activity

S. HANESSIAN

Canadian Patent 1,282,058

New Pt complexes are derived from vicinal diamines substituted by carboxy, hydroxy or alkoxy groups, for example diamino sugars, and are useful as anti-microbial or anti-tumour agents. Compared with known Pt complexes they have better water solubility, more rapid excretion, improved transport in the body, improved biocompatibility, and a more selective interaction with DNA receptors.

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