

# NEW PATENTS

## METALS AND ALLOYS

### Metal Powder Production

OCCIDENTAL RES. CORP. *U.S. Patent* 4,655,825  
Metal and alloy powders and particulates, especially of Rh, Pt, Pd, Ag, Au and others, are produced by distilling Zn from an alloy of Zn with the required metal(s). The powders can be produced in very pure form and need no further size reduction.

## CHEMICAL COMPOUNDS

### Palladium Complexes

CIBA GEIGY A.G. *European Appl.* 214,097A  
A mixture containing one or more dibenzalacetone-Pd complexes and one or more olefinic compounds is useful for electroless metallisation of mouldings, self-supporting films, hardened products.

### Stable Organopolysiloxane Compositions

GENERAL ELECTRIC CO. *U.S. Patent* 4,645,815  
Compositions containing a cyclic Pt phosphite complex catalyst, an olefinically unsaturated organopolysiloxane and an organo hydrogen polysiloxane, provide inhibitor-free, one-package compositions with superior shelf life.

## ELECTROCHEMISTRY

### Photo-Electrolysis Apparatus

R. GORDON *U.S. Patent* 4,650,554  
A photo-electrolysis apparatus has a conductive porous barrier layer sandwiched between photovoltaic and catalyst layers. The apparatus is used for solar production of H<sub>2</sub> and O<sub>2</sub> from water, and has a layer of Ru oxide for O<sub>2</sub> evolution, and a transparent catalyst coating of Pt, Pd, Ir, Os, Rh, Ru or their alloys for H<sub>2</sub> evolution.

### Platinum Cathode for Electrolysis

MITSUBISHI HEAVY IND. K.K. *Japanese Publ. Appl.* 62/7,887  
A cathode consists of a Pt layer ion plated onto the surface of a cleaned Ni or Ni alloy substrate. It is suitable for use in the electrolysis of sea water.

### Ruthenium Complex Film for Water Photolysis

RIKAGAKU KENKYUSHO *Japanese Publ. Appl.* 62/56,588  
The surface of a visible range n-type semiconductor electrode is modified by coating with a complex polymer film containing tris(2, 2'-bipyridine)Ru(II) complex, or a Group VIII metal or its oxide. Simple photolysis of water to O<sub>2</sub> and H<sub>2</sub> is possible by visible irradiation of the electrode, in electrolytic solution.

## ELECTRODEPOSITION AND SURFACE COATINGS

### Aluminium Coated Carbon Fibres

NIPPON OIL K.K. *Japanese Publ. Appl.* 62/4,845  
Pd complex compounds are deposited on the surface of C-fibres, which deposit metallic Pd on heating, these are then covered with Al metal by contact with organic Al compounds, during or after heat treatment. A C-fibre reinforced Al composite is obtained having good adherence, high strength, and without producing Al carbide.

### Platinum-Containing Polishing Agent

SHINETSU CHEM. IND. K.K. *Japanese Publ. Appl.* 62/10,178  
A new solid silicone type polishing agent consists of an organosiloxane composition containing Pt or Pt compounds, a liquid diorganosiloxane, and an organic solvent. It is used for car polish; providing a transparent coated film with good glaze, water repellency and dirt repellency.

## LABORATORY APPARATUS AND TECHNIQUE

### Platinum Sensing Elements

HITACHI K.K. *European Appl.* 218,232A  
An exothermic resistor has a coiled Pt wire, coated with an inorganic glass material. Two such resistive sensing elements are included in a device located in an engine intake air by-pass duct, for air flow velocity and temperature measurements.

### Electrochemical Sensor with Rhodium Cathode

BECKMAN IND. CORP. *World Patent Appl.* 87/2,461A  
An electrochemical sensor for a fluid sample has a cathode formed of a Rh disc fused in a glass sheath, an anode, and a selective membrane. The cathode has high resistance to thermal shock and an extended life.

### Gas Sensor

NIPPON PIONIX K.K. *Japanese Publ. Appl.* 62/22,062  
A gas sensor is composed of a mixture of a Pd salt and a cupric salt of an inorganic or organic acid, usually impregnated into a support. The gas sensor has excellent sensitivity to harmful gases.

### Alkaloid Analysis

SHIMADZU SEISAKUSHO K.K. *Japanese Publ. Appl.* 62/25,261  
A heated metal solid composed of Pt, Ir, Re or Mo, their oxides, or a mixture of these, is contacted with separated alkaloid gases, and the ionisation current of the decomposed gases is measured. Stable, quick and accurate analysis can be achieved.

## Protein or Nucleic Acid Detection

KONISHIROKU PHOTO K.K.

*Japanese Publ. Appl.* 62/35,262

Metal staining with Pt, Pd, Ir, Ag or Au is used to dye protein or nucleic acids in a carrier, after separation by electrophoresis. The resulting metal nuclei are treated with an intensifier and a dye-forming compound. In this way, proteins or nucleic acids are detected with high sensitivity by adding the simple operation of dye formation to metal staining.

## Gas Detecting Element

NOHMI BOSAI KOGYO K.K.

*Japanese Publ. Appl.* 62/67,437

A gas detecting element consists of a Pt and Pd catalyst, a metal oxide semiconductor mainly consisting of stannic oxide, an Sb compound as stabiliser, and a means of heating the semiconductor. The element selectively detects gas such as silane with high response speed, exhibits high S/N ratio, and can detect low gas concentrations.

## Extensometer Strip with Platinum Alloy Layer

DEGUSSA A.G.

*German Offen.* 3,532,328

An extensometer strip has a resistance layer of a binary Pt alloy containing Ir or Ru, on an electrically insulating carrier. It is used for measuring mechanical deformation by changes in electrical resistance of the alloy layer. An advantage is that the resistance layer contains no Pd.

## Pressure-Force Measurement Sensor

DEGUSSA A.G.

*German Offen.* 3,532,333

An electrical sensor has a circular elastic membrane with a circular array of extensometer strips, preferably made of a Pt-Ru alloy or a binary Ir alloy containing Pt, Ru, Re, Mo, W or Cr. The sensor is used for pressure and force measurement, and has extremely low temperature sensitivity without needing separate temperature sensors.

## Ionic Activity Measuring Device

UNIVERSITY PATENTS INC. *Canadian Patent* 1,219,632

A device for measuring ionic activity especially H ion concentration, has an electrode of an amorphous oxide of a platinum or rhenium group metal, preferably sputtered Ir oxide, and a means for measuring the potential developed in use. The electrode has excellent stability, low impedance, good response and may be very small.

## Heated Platinum Filament for Polymer Molecular Weight Determinations

O.V. SIGOV

*Russian Patent* 1,242,799

Testing the characteristics of liquid media involves using an electrically heated Pt filament and measuring the imbalance of a measuring bridge containing sample and comparison cells. Using this method, quicker thermophysical determination of polymer mean molecular mass is achieved.

## Measuring Organic Impurities in Water

ELECTROCHEM. INST.

*Russian Patent* 1,250,928

A dynamic potential method for the determination of organic impurities in water involves using an electrochemical cell containing a sensing Pt electrode fed with square and sawtooth pulses of controlled duration. The method lowers the detection limit to 0.05 mg/l which is less than other known methods.

## JOINING

### Brazing Alloy for Abrasive Tool

GENERAL ELECTRIC CO.

*European Appl.* 213,300A

An alloy of Pd, Cr, B and Ni is used for brazing an abrasive compact support to a substrate. The brazed bond has high strength, heat resistance, reliability and reproducibility. The implement is used as a drilling or cutting tool, for oil exploration.

### Effective Bonding to Platinum Metals

NIPPON ABIONICS K.K.

*Japanese Publ. Appl.* 62/22,878

A metal workpiece of Pt, Pd, Rh, Os, Au, Ag or other metals can be bonded to another metal or non-metal workpiece by base metal electrodeposition on the metal body, expelling H<sub>2</sub> from the deposited layer, and coating both workpieces with an adhesive. This is especially effective for Pd, and degradation of the adhesive is eliminated.

## HETEROGENEOUS CATALYSIS

### Ruthenium Fischer-Tropsch Catalysts

BRITISH PETROLEUM P.L.C. *British Appl.* 2,178,334A

Fischer-Tropsch catalyst precursors are prepared by impregnating CeO<sub>2</sub> with a non aqueous solution of a thermally decomposable Ru compound (other than a carbonyl). After reductive activation, the catalysts, optionally in combination with a zeolite, have high selectivity for production of gasoline range hydrocarbons from synthesis gas, especially at a temperature of 250–350°C and a pressure of 10–50 bar.

### Selective Diolefin Hydrogenation Catalyst

PHILLIPS PETROLEUM CO. *European Appl.* 211,381A

A supported catalyst containing a Group VIII metal, such as Pt, and Pb, Sn and/or Ge, is used for the selective hydrogenation of diolefin impurities in a hydrocarbon stream containing other unsaturated hydrocarbons, which are left unchanged.

### Alkane Dehydrogenation Catalyst

BRITISH PETROLEUM P.L.C. *European Appl.* 212,850A

The catalyst preferably contains Pt, Ru, Ir, Rh or Pd on a silicalite support, and is especially useful for dehydrogenation of 3–6C paraffins to the corresponding olefins. The catalyst has high activity and selectivity for dehydrogenation, and improved stability.

## Noble Metal Absorbent for SO<sub>2</sub> Removal

INST. FRANCAIS DU PETROLE

*European Appl.* 215,709A

SO<sub>2</sub> is removed from gases by contact with an Al<sub>2</sub>O<sub>3</sub> based absorbent, containing one or more Group VIII noble metals, preferably Pt and/or Pd, and MgO, in the presence of O<sub>2</sub>. The absorbent is then contacted with an H<sub>2</sub>S containing gas. Group VIII noble metals catalyse SO<sub>2</sub> fixation by conversion of MgSO<sub>4</sub>, and reduction of MgSO<sub>4</sub> to MgO by H<sub>2</sub>S.

## Hydrogen Production from Methanol

JOHNSON MATTHEY P.L.C. *European Appl.* 217,532A

A reactor having a downstream supported catalyst of Cu with Pt and/or Pd, and an upstream catalyst of supported Cu, is used for H<sub>2</sub> production by catalytic oxidation of CH<sub>3</sub>OH with O<sub>2</sub>. After initiation, oxidation moves away from the Cu-Pt-Pd catalyst zone which minimises catalyst loss and CO formation. The Pt-Pd catalyst converts unreacted O<sub>2</sub> to H<sub>2</sub>O.

## Hydride Storage Powder

MAX PLANCK GES. WISSENSCH.

*World Patent Appl.* 87/2,022A

A hydride storage powder contains a hydrogenation/dehydrogenation catalyst powder, preferably a platinum group metal but especially Pd and/or its oxides. The catalyst is in the form of a coated substrate, preferably Pd, Pd/Al<sub>2</sub>O<sub>3</sub> and/or Pd-coated Cu. The powder is used for H<sub>2</sub> storage, is easily produced, and is not contaminated/deactivated by air.

## Palladium, Platinum Catalyst Activation

NAT. AERO & SPACE ADMIN.

*U.S. Patent Appl.* 06/874,320

Pd and/or Pt on SnO<sub>2</sub> catalysts for recombining CO and O<sub>2</sub> in a closed-cycle, high-energy pulsed laser, can be activated simply and quickly by exposing to a reducing gas in an inert carrier, at a temperature above the operating temperature, followed by inert carrier alone, and cooling. Reactivation only requires the heating stage.

## Ruthenium Catalyst Pretreatment

EXXON RES. & ENG. CO. *U.S. Patent* 4,647,592

A Ru/TiO<sub>2</sub> catalyst useful for the production of hydrocarbons from synthesis gas is pretreated with a mixture of steam/carrier gas or steam/H<sub>2</sub> at about 200–550°C to produce larger Ru agglomerates. The increase in Ru particle size moderates the catalytic activity and reduces the CH<sub>4</sub> selectivity, in a much shorter time than previously.

## Lead-Tolerant Catalyst for Exhaust Gas Purification

ALLIED CORP. *U.S. Patent* 4,650,782

A Pb-tolerant catalytic composite comprises one of Ir, Rh, Pd, Ag, Au or especially Pt deposited on an inorganic refractory oxide support, with a protective coating of TiO<sub>2</sub> to enhance the Pb tolerance. It is used for treating automobile and other Pb-containing exhaust gases and can be used in the presence of SO<sub>2</sub>.

## Palladium Packaging Material

TORAY IND. INC. *Japanese Publ. Appl.* 61/293,846

A packaging material consists of a base, a thin layer of catalytic Pd formed on it by vacuum deposition, and a layer of a gas-selective permeable substance. It can prevent modification of packaged articles, and is useful for foodstuffs, drugs, electric contacts and precision or measuring devices. A gas(H) capable of reacting with an ambient harmful gas (O) is sealed in the packaging, and when H and O reach the Pd they react to form H<sub>2</sub>O.

## Ruthenium Catalyst for Hydrocarbon Production

KAIHATSU GIJUTSU K.K.

*Japanese Publ. Appl.* 62/1,783

A catalyst composition containing Ru, Mn oxide, an alkali metal, S, and a crystalline zeolite is used for hydrocarbon production from a mixture of CO and H<sub>2</sub>. A hydrocarbon usable as gasoline is produced in one stage from the synthesis gas, with high selectivity.

## Tertiary Amine Production

KAO CORP.

*Japanese Publ. Appl.* 62/10,047

A Pd or Pt catalyst supported on Al<sub>2</sub>O<sub>3</sub> or SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> is used in the preparation of tertiary amines, by reacting primary or secondary amines with formaldehyde and H<sub>2</sub>. High purity tertiary amines are obtained in high yield, and the catalyst can be easily recovered and used repeatedly.

## Catalyst for Fluorobenzene Production

ASAHI CHEMICAL IND. K.K.

*Japanese Publ. Appl.* 62/19,541

Fluorobenzene can be prepared in higher yield than by any other process by dehydration of 1-fluorocyclohexene over a supported platinum group metal catalyst, especially Pd, Pt or Ru. The reaction can be carried out in the vapour or liquid phase.

## Osmium Catalyst for Oxalic Acid Preparation

IDEMITSU KOSAN K.K.

*Japanese Publ. Appl.* 62/56,450

Oxalic acid is prepared by oxidation of propylene with O<sub>2</sub> over a supported OsO<sub>4</sub> or OsO<sub>4</sub>-Cu halide catalyst. High yield and selectivity are obtained in a single step reaction, with the Cu halide-containing catalyst giving superior results.

## Exhaust Catalyst with Separate Platinum Group Metal Layers

TOYOTA JIDOSHA K.K.

*Japanese Publ. Appl.* 62/57,651

A monolith catalyst with high activity for exhaust gas purification has three catalytic Al<sub>2</sub>O<sub>3</sub> layers: a lower layer of Pd with Nd or Sm, a middle layer of Rh with La, Y or Sc, and a top layer containing Pt and Ce. Separation of the platinum metals prevents alloy formation, thus catalyst deterioration is avoided.

## Absorbent for Waste Water Components

MITSUBISHI CHEM. IND. K.K.

*Japanese Publ. Appl.* 62/79,289

Sulphides of Ru, Rh, Pd, Pt, Au, Ag or other compounds, are supported on a spherical or granular carbonaceous mesophase material prepared from coal tar pitch, naphtha tar pitch or resin. The product is used to absorb trace amounts of radioactive constituents in waste water, such as I, and as a catalyst for various reactions.

## NO<sub>x</sub> Removal from Flue Gas

KRAFTWERK UNION A.G. *German Offen.* 3,534,845

A catalyst having one or more of Pt, Rh, CuO, CoO or V<sub>2</sub>O<sub>5</sub>, supported on SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and/or TiO<sub>2</sub>, is used for reduction of NO<sub>x</sub> in the flue gas stream of a steam generator fed with fossil fuel. Reaction is characterised by use of CO and/or H<sub>2</sub> as the reducing gas. The process is useful in power stations because the CO and H<sub>2</sub> can be produced on site.

## Catalysts for Phenol Hydrogenation

BAYER A.G.

*German Offen.* 3,538,129

Supported Pd catalysts useful in the hydrogenation of phenols to cyclohexanols are prepared from an inert support material, a Pd salt solution, and a base, in such a way that the base is retained after reduction. The catalysts have high long-term stability.

## Carboxylic Acid Ester Preparation

BRITISH PETROLEUM P.L.C.

*Australian Appl.* 86/62,013

A Pd-Cu catalyst is used in the preparation of carboxylic acid esters, by reaction of an olefinic hydrocarbon with a formate ester and a CO/O<sub>2</sub> mixture, in the presence of H<sub>2</sub>O and H<sup>+</sup>. This catalyst together with a source of aqueous acid allows the use of much milder conditions, without the corrosion and separation problems of halide promoters.

## HOMOGENEOUS CATALYSIS

### Catalyst for Diester Preparation

SHELL INT. RES. Mij. B.V. *European Appl.* 212,729A

A noble metal catalyst, preferably Pd or a Pd compound, is combined with a cupric salt and used for the reaction of a dihydrocarbyl peroxide, CO and optionally an alpha-ethylenically unsaturated compound. This method of preparation of diesters of alkanedioic acids can be a batch, semi-continuous or continuous process.

### Rhodium Hydroformylation Catalyst

RUHRCHEMIE A.G.

*European Appl.* 216,315A

Aldehydes are produced by the reaction of olefins with CO and H<sub>2</sub> in the presence of a catalyst containing Rh and the amine salt of a sulphonated or carboxylated triarylphosphine. Hydroformylation of the olefin occurs in high yield, and the method allows separation of the catalyst for recycling.

## Carbonate Ester Preparation

BRITISH PETROLEUM P.L.C.

*European Appl.* 220,863A

A catalyst containing a platinum group metal and a Cu compound is used in the preparation of a carbonate ester from an alcohol and CO, in the presence of a dihydrocarbyl peroxide. The ester is obtained in high yield under mild conditions.

## Rhodium Dimerisation Catalyst

SHELL OIL CO.

*U.S. Patent* 5,638,084

A dimerisation catalyst is prepared by reacting chlorobis(ethylene)Rh(I) dimer with Ag tetrafluoroborate in the presence of an olefin. It is used for the dimerisation of alkyl acrylates or methacrylate, and the catalyst produces unbranched dimers with high selectivity.

## Self Emulsifying Silicon Composition

SHINETSU CHEM. IND. K.K.

*Japanese Publ. Appl.* 62/7,438

The composition consists of a Pt catalyst, methyl hydrodiene polysiloxane, an oxyalkylene compound, an unsaturated hydrocarbon having a vinyl group, and an antifoaming agent. This self-emulsifying Si composition has improved high temperature and mechanical stability.

## Palladium Catalyst for Cyclic Ketone Production

AGENCY OF IND. SCI. TECH.

*Japanese Publ. Appl.* 62/26,244

Cyclic ketones are prepared in the liquid phase from cyclic olefins by oxidation with molecular O<sub>2</sub> in the presence of a catalyst consisting of a Pd compound and an organic base. Cyclic ketones can be simply prepared in high yields with high selectivity.

## New Preparation of Aromatic Carboxylic Acids

ASAHI CHEMICAL IND. K.K.

*Japanese Publ. Appl.* 62/53,955

A catalyst having at least one platinum metal (preferably Pd and/or Rh) and at least one of Br or I, is used in the preparation of aromatic alkoxy-carbamoyl carboxylic acids. This new preparation is simple, gives high yield and selectivity by reaction of aromatic amino carboxylic acids with alcohol and CO, and does not use phosgene.

## CHEMICAL TECHNOLOGY

### Platinum Wires for Crystal Manufacture

AKAD. WISSENSCHAFT D.D.R.

*East German Patent* 240,821

Two platinum wires are tensioned slightly above the surface of a melt, and are used to form profiled crystals – specially rectangular crystal bands – from the liquid phase. This method creates a continuous process over a long period, at reduced cost.

## ELECTRICAL AND ELECTRONIC ENGINEERING

### Optical Fibre Fracture

TELEPHONE CABLES LTD. *British Appl.* 2,179,341A  
A hot Pt or Ir metal wire, heated to  $>1000^{\circ}\text{C}$  is used to sever optical fibres and strip off plastic coatings from optical fibre ribbon. The advantage of this method is that fibres are severed cleanly in the same transverse plane, to enable coupling to a second ribbon.

### Optical Fibre Protection

CAVI PIRELLI S.P.A. *European Appl.* 217,066A  
An optical fibre telecommunication cable consists of at least one optical fibre embedded in a mixture of a Pd or Pt catalyst and Mo trioxide, enclosed by a sheath. The mixture protects the fibre from degradation by  $\text{H}_2$  over its useful life.

### Resistive Material for Semiconductor Chip Housing

MO VALVE CO. LTD. *World Patent Appl.* 87/1,240A  
Ru oxide may be used to coat the inner lid surface of a sealed housing for a semiconductor chip. It forms a layer of resistive material having a permittivity similar to that of free space, and prevents performance being disturbed by reflection of microwave energy from the housing lid.

### Electrochromic Display Element

ALPS ELECTRIC K.K. *Japanese Publ. Appl.* 62/30,184  
Ag and/or Ru or Os may be contained in a polynuclear transition metal cyanide used to prepare an electrochromic substance, which is coated on the display electrode of an electrochromic display element. The technique enables a better variety of colours to be displayed, and an element with a rapid response is obtained.

### Gel Composition for Optical Joint

TOSHIBA SILICONE K.K. *Japanese Publ. Appl.* 62/39,660  
A Pt, Pd or Rh catalyst with a polyorganosiloxane and a siloxane, forms a gel composition which has excellent adhesion, and does not discolour or change at high temperature. It is used for electric or electronic parts, especially for optical coupling pads, which need optical transparency, and in the manufacture of human body models.

### Conductive Organic Material

TORAY IND. INC. *Japanese Publ. Appl.* 62/58,508  
A conductive organic material contains conductive inorganic particles preferably of Pt, Pd, Au, Ag or others, physically or chemically adsorbed on the surface of spherical particles made from an organic polymer. The material is reliable, and is used for making conductive paste, conductive adhesives and pressure sensitive rubber.

## Platinum or Rhodium Layer for Gas Turbine Blades

BBC A.G. BROWN BOVERI CIE *Swiss Patent* 660,200  
An intermediate layer of Pt or Rh acts as a diffusion barrier between an Fe, Co or Ni superalloy base and its corrosion protection layer. Interdiffusion and building of brittle phases between the body and the corrosion protection layer are prevented, thereby avoiding flaking. This is useful for turbine blades.

## MEDICAL USES

### Catalyst for Eye Surgery Material

MOSC. EYE MICROSURGE *British Appl.* 2,179,667A  
A catalyst based on compounds of platinum group metals is used in the vulcanisation of a mixture of siloxane derivatives. The final cured composition is an elastic material of low density, good mechanical and high optical properties, and is biologically inert. It is especially used in eye surgery as part of, or in support of, prosthetic crystalline lenses or lenticuli.

### New Complexes for Imaging

HARVARD COLLEGE *European Appl.* 213,945A  
New co-ordination complexes consist of lower alkyl isonitrile ligands and a radioactive isotope of Ru, Pt, Re or others. The complexes are useful in imaging of body tissues, giving high liver and lung clearance, and high contrast.

### Anti-Tumour Platinum Compounds

JOHNSON MATTHEY P.L.C. *European Appl.* 222,522A  
New anti-tumour Pt complex compounds are claimed with amino containing dioxolane groups, useful for treating cancer in humans and animals. An intermediate based on an isopropylidene threitol compound is also new.

### Biomedical Iridium Isotope Generator

U.S. DEPT. OF ENERGY *U.S. Patent Appl.* 06/769,519  
An Os-191/Ir-191m isotope generator comprises an activated C adsorbent loaded with a compound containing Os-191, preferably K hexachloro-osmate(IV). Physiologically compatible saline is used to elute Ir-191m. The generator has good yield of Ir-191m, low breakthrough of Os-191 and is used for biomedical applications.

### Platinum Complexes for Inducing Cancer Regression

AMERICAN CYANAMID CO. *U.S. Patent* 4,665,210  
New Pt complexes with tricarboxylic acids are used for inducing the regression and/or palliation of leukaemia and related cancers. The dose is preferably  $1-50 \text{ mg/m}^2$  of body surface area.

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