

# NEW PATENTS

## CHEMICAL COMPOUNDS

### Bis(alkylcyclopentadienyl)ruthenium

KOJUNDO KAGAKU KENKYUUSHO K.K.

*Japanese Appl.* 11/35,589

Bis(alkylcyclopentadienyl)Ru complex is produced by reacting Ru trichloride hydrate and ethyl cyclopentadiene or isopropyl cyclopentadiene with Zn powder in an alcohol solvent. Ru-containing thin films are prepared by chemical vapour deposition, by contacting a heated base with bis(ethylcyclopentadienyl)Ru (1) or bis(isopropylcyclopentadienyl)Ru (2). At 20°C, (1) and (2) are in the liquid state.

## ELECTRODEPOSITION AND SURFACE COATINGS

### Palladium Electrolytic Bath

AMI DODUCO G.M.B.H. *European Appl.* 916,747A

An electrolyte bath for the deposition of Pd and Pd alloys comprises an aqueous solution of 1–50 g l<sup>-1</sup> of Pd chloride, sulfate, nitrate or nitrite, a conductive salt, a brightening agent (preferably *N*-(3-sulfopropyl)pyridium betaine), a cross-linking agent and 0.01–3 g l<sup>-1</sup> sulfite and has a pH of 6–9.5. Thick Pd coatings (> 10 μm) have high ductility, fewer cracks and a shiny surface, and are used in jewellery and dentistry.

### Aqueous Palladium Electroplating Bath

LUCENT TECHNOLOGIES INC.

*European Appl.* 921,212A

An aqueous Pd alloy electroplating bath comprises: a Pd salt (1) and a first complex-forming ligand, an alloying metal salt (2) and a second complex-forming ligand which brings the electroplating reduction potentials of (1) and (2) closer. A bright, adherent, ductile and stable 10–95% Pd-Co alloy is obtained for electrical connector contacts, giving low resistance, improved corrosion and abrasion resistance.

### Platinum-Ruthenium Catalyst Coatings

DEGUSSA-HUELS A.G. *European Appl.* 924,784A

A Pt-Ru catalyst contains finely divided alloying particles (average crystal size of 0.5–2 nm) on a powdered electrically conducting carrier. The carrier material is suspended in a solvent and a preformed Pt-Ru alloy colloid is added at 20–110°C, followed by calcination at 200–400°C. The coating is used for the gas diffusion electrode on the anode side of a polymer electrolyte membrane fuel cell.

### Catalyst Liquid for Electroless Platings

EBARA UDYLLITE K.K. *Japanese Appl.* 11/124,680

A catalyst liquid for electroless platings of electronic components, contains an organic acid, such as malic acid, oxalic acid, citric acid or tartaric acid; a H<sub>2</sub>O soluble Pd salt and an ammonium compound. Malic acid is preferably used. Electroless plating without bridges between circuits is obtained.

## APPARATUS AND TECHNIQUE

### Exhaust Emission Control Device

SUMITOMO ELECTRIC IND. CO.

*European Appl.* 925,823A

A device with good exhaust emission control performance and high durability is contained in an intermediate part of an exhaust system. It comprises a heat resistant porous body (1), carrying a mixture of Al oxide and Cu oxide (grain size ~ 0.1–5 μm) and Pt on the surface and inside. It is produced by applying a slurry of Cu and Al oxides to (1) and baking, and then applying the H<sub>2</sub>O-soluble Pt compound and baking.

### Oxygen or Lambda Gas Sensor

HERAEUS ELECTRONITE INT N.V.

*World Appl.* 99/14,584A

A gas sensor, for simultaneous measurement of O<sub>2</sub> and/or the air:fuel lambda ratio and at least NO or hydrocarbons in gas mixtures, comprises a reference electrode, which represents a constant O<sub>2</sub> partial pressure; a solid electrolyte to conduct O ions; at least two measurement electrodes, one of them made of Pt or Pt alloy; and electrical connections for the measuring signals. The arrangement of the electrodes delivers at least two measuring signals simultaneously which enables several gaseous constituents to be detected with one sensor. It is used in automobile engine control systems or to measure waste gas.

### NOx Sensor Structure

ROBERT BOSCH G.M.B.H.

*World Appl.* 99/19,721A

A NOx sensor structure comprises a selective O ion conductive layer and a gas permeable non-conductive layer of porous spinel structure or of porous Pt. The NOx sensor measuring arrangement comprises the above structure on a cathode. It is used for monitoring exhaust gases from lean-burn engines.

### Hydrogen Separation Membrane

MITSUBISHI JUKOGYO K.K. *Japanese Appl.* 11/99,323

A hydrogen separation membrane (1) consists of Pd-Ag alloy containing ≥ 3 at.% of rare earth element(s) selected from Y, Gd and Lu, such that  $36 \geq 3y + x \geq 24$ , where the rare earth content is (y) at.% and the Ag content is (x) at.%. (1) gives an excellent H permeation performance and high temperature strength.

### Sensor for Detection of Gas Concentrations

HERAEUS ELECTRONITE INT N.V.

*German Appl.* 1/97/44,224

A sensor for detecting the concentration of gases, such as automotive exhaust gases, comprises a ceramic tube closed at one end and partly covered by a solid electrolytic material. The tube's outer face incorporates sensor- and heater-contacts, and an actively heated surface. The sensor surface is preferably Pt or Zr oxide, and especially measures the presence of O<sub>2</sub>. The sensor responds rapidly and accurately during the warm-up phase, and remains accurate for a long service life.

## HETEROGENOUS CATALYSIS

### Abatement of Organic Compounds

K. PEDERSEN *European Appl.* 913,193A

A catalyst for abatement of organic compounds in H<sub>2</sub>O comprises Pt group metals, preferably Pt or Pd, and Fe, Co, Mn and Ni oxides supported on activated C carrier. The raw H<sub>2</sub>O is enriched in a first step with ozone/oxygen and in a subsequent step passed through the catalyst. The catalyst is useful for avoiding undesirable intermediate products from the ozone treatment. It is used for H<sub>2</sub>O purification from pesticides, phenols and noxious compounds.

### Colloidal Palladium for Hydrogenation

BASF A.G. *European Appl.* 920,912A

Colloidal Pd for hydrogenating olefins, acetylene, dienes and (un)saturated nitriles consists of Pd clusters with an average particle size of 0.2–2.0 nm. The colloid is produced by reacting a Pd salt with a reductant made of 4–30C alcohol, and a protective ligand of phosphane and/or aromatic N compound at 0–300°C, followed by precipitation, adding a hydrocarbon solvent and drying. Heterogeneous catalysts are formed by impregnating a carrier, such as Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, etc., with this colloidal Pd solution.

### Catalysts for I.C.E.

UNION CARBIDE CHEM. & PLASTICS TECHNOL. *U.S. Patent* 5,856,263

An exhaust gas catalyst for combusting CO and HCs, and for the reduction of NO<sub>x</sub> from I.C.E. comprises a porous, substantially pure  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> carrier, of porosity 0.2–0.6 cm<sup>3</sup> g<sup>-1</sup>, surface area 0.2–10 m<sup>2</sup> g<sup>-1</sup> and average pore size 0.1–100  $\mu$ m. Pt or Pd and a promoter, selected from Ce, Mo, Cr, Ti, La, Nb, Zr and the rare earth metals are included. The catalyst is not wash-coated and has improved stability over time, excellent high-temperature and thermal-shock-strength.

### Selective Oxidation Catalyst

UOP INC. *U.S. Patent* 5,864,051

A catalyst for the selective oxidation of alkanes and alkenes consists of a Pt group metal component, such as Pt, Pd, Rh, Ru, Ir or their mixtures, and a SbO<sub>3</sub> component, where  $x = 1.5$ – $2.5$ . The noble metal component is present as particles and ~1–30 mol% of the particles are in the form of a Pt group metal-Sb metal. Optionally, a modifier and/or a refractory inorganic oxide may also be added to the catalyst. The catalyst has high activity for the selective oxidation of both alkanes and alkenes to aldehydes and ketones.

### Hydrogenation of Unsaturated Hydrocarbons

PHILLIPS PETROLEUM CO. *U.S. Patent* 5,866,735

Highly unsaturated hydrocarbons (1) are contacted in the presence of H<sub>2</sub> and a catalyst comprising a Pd-containing material selected from Pd metal and/or Pd oxides, an alkali metal iodide and an inorganic support, under conditions that will convert saturated (1) into less saturated (1). The process provides enhanced selective hydrogenation of alkenes, alkynes and diolefins, with increased catalyst life and activity.

### Simultaneous Dehydrogenation and Isomerisation of Paraffins

INTEVEP S.A. *U.S. Patent* 5,880,324

Simultaneous dehydrogenation and isomerisation of paraffins to isoparaffins and isoolefins is achieved by contacting a paraffin and H<sub>2</sub> with an activated 0.1–1.5 wt.% Pt/mordenite zeolite catalyst, at 250–800°C using a paraffin space velocity of 0.1–1000<sup>-1</sup> and H<sub>2</sub>:paraffin ratio of 0.1–30. The catalyst is promoted with 0.1–1.5 wt.% Zn, Sn and/or Cr. Side reactions are minimised. The hydrogenated and isomerised products are used in the manufacture of methyl tertiary butyl ether and isobutylenes.

### Catalytic Reforming of Hydrocarbon Feeds

UOP L.L.C. *U.S. Patent* 5,885,439

Three-step catalytic reforming of hydrocarbon feeds involves contact with a bifunctional catalyst comprising a Pt group metal, a metal promoter, a refractory inorganic oxide and a halogen component; contacting the resulting effluent with a zeolitic reforming catalyst and contacting the resulting aromatised effluent with a terminal bifunctional reforming catalyst. The use of bifunctional and reforming catalysts allows production of petroleum feed stocks with increased aromatics content in the production of gasoline.

### I.C.E. Purification Catalyst

NISSAN MOTOR CO. LTD. *Japanese Appl.* 11/47,596

A catalyst for purification of engine exhaust gas has a catalyst component layer containing an inorganic substance with 4–15 wt.% Pd. The Pd concentration is 100–500 g cf<sup>-1</sup> in the catalyst. The principal component of the hydrocarbon absorbent is  $\beta$ -zeolite. The concentration of the catalyst is maintained within predetermined limits. Hydrocarbons are purified efficiently and separated from an absorbent when the temperature of the exhaust gas rises.

### Nitrogen Oxides Decomposition Catalyst

TOYOTA JIDOSHA K.K. *Japanese Appl.* 11/57,473

A NO<sub>x</sub> decomposing catalyst for I.C.E. is manufactured by etching an alloy of quasi crystalline texture to expose Pd or Pt out of its surface. The general formula is Al<sub>100(a+b)</sub>X<sub>a</sub>Mn<sub>b</sub>, where X = Pd or Pt; 18 at.%  $\geq a \leq 22$  at.% and 6 at.%  $\leq b \leq 12$  at.%. Characteristics of the quasi-crystalline alloy as starting material were inherited into the catalyst to raise its catalytic activity and widen the temperature range in which it displays the activity.

### Ethylbenzene and *o*-Xylene

BASF A.G. *German Appl.* 1/97/27,021

Ethylbenzene (1) and *o*-xylene (2) production from 8C hydrocarbons comprises dehydrogenation (aromatization) of an olefinically unsaturated 8C hydrocarbon mixture, separation from a 4C hydrocarbon fraction by dimerisation at 300–800°C and ~50 bar on a Pt group metal catalyst supported on an amphoteric ceramic substrate. In contrast to all existing processes of this type, which give low yields of 8C aromatics, this process is claimed to give high yields and very high selectivity for (1) and (2).

## HOMOGENEOUS CATALYSIS

### Soluble Cyclopentadiene Homopolymer

BASF A.G. *European Appl.* 890,585A

Soluble cyclopentadiene homopolymers (CpP) are produced by polymerisation using a Pd complex catalyst containing an alkyl cyanide ligand and a stable anion. Also claimed are (i) CpP with a mol. wt. of  $10^4 - 10^6$  and  $< 35\%$  1,2-linkages, and (ii) the above Pd catalyst optionally combined with a Pd-co-ordinated olefin or diolefins. The process enables the production of CpP with a very low content of 1,2-linkages resulting in better solubility in many solvents.

### Hydroformylation of Ethylenically Unsaturated Compounds

SHELL INT. RES. MIJ. B.V. *European Appl.* 903,333A

Hydroformylation of ethylenically unsaturated compounds with CO and H<sub>2</sub> is performed in the presence of a catalyst system comprising: (a) Pd, Pt or Ni cations, (b) anions other than halide, (c) at least one bidentate ligand, and optionally (d) a promoter. The catalyst system has molar ratios (a):(b):(c) = 1:2:1, a solubility of  $10 \times 10^{-4}$  mole of the cation (a) per litre of the liquid mixture. The hydroformylation products are separated from the catalyst system in a solventless evaporative separator.

### Preparation of Formylimidazole Derivatives

LONZA A.G. *European Appl.* 913,394A

The preparation of 4-halo-5-formyl-(or 4-formyl-5-halo)imidazole derivatives (1) comprises catalytically oxidising the corresponding hydroxymethyl-imidazole compounds in the presence of Pt/Bi or Pt/Pb catalyst and H<sub>2</sub>O<sub>2</sub>. (1) are useful intermediates in the preparation of pharmaceuticals such as diuretics and antihypertensives. The process avoids the formation of byproducts and reduces reaction times.

## FUEL CELLS

### Electrode Catalyst Powder

MATSUSHITA ELECTRIC IND. CO. LTD. *European Appl.* 898,318A

An electrode catalyst powder is produced by oxidising a Pt complex compound to form a colloidal solution of an oxide of the Pt complex, adjusting the pH of the solution to  $\geq 6$ , and depositing the colloidal particles onto an electrically conductive C powder. Also claimed is the above method wherein a solution of RuCl<sub>2</sub> is added after adjusting the pH to form colloidal Ru particles. The powder is used for fuel cells.

### Fuel Battery

JAPAN STORAGE BATTERY CO. LTD. *Japanese Appl.* 11/16,587

A DMFC electrode consists of a solid polymer electrolyte film to which a cathode catalyst layer containing Pt and Ru is attached by electroless plating. Pt- and Ru-layers are formed on the surface of the electrolyte film. CO is removed from the Pt surface by the Ru, thus maintaining constant catalytic activity for the Pt.

## ELECTRICAL AND ELECTRONIC ENGINEERING

### Metallised Material Production

FUJI PHOTO FILM CO. LTD. *European Appl.* 892,089A  
A metallised material, used to make flexible printed wiring boards, is formed by first applying a polymeric primer layer to the substrate, and then brought into contact with a Pd-containing solution to make it electrically conductive. Finally, a metal layer (film) is provided by electroplating onto the electrically conductive layer, resulting in easy electroplating.

### Thick Film Conductor-Resistor Composition

NAT. STARCH. & CHEM. INVEST. HOLDING CORP. *European Appl.* 910,232A

A thick film conductor or resistor composition comprises in wt. %: 2-17 of a glass frit binder, 74-90 of a mixed Pd-Ag powder, Pd:Ag is 55-63:45-37, and balance an organic vehicle. The glass frit comprises oxides of Li, B, Si and other metals. The composition has a sheet resistivity of  $< 62 \text{ m}\Omega/\text{square}$  and a low temperature coefficient of resistance,  $< 100 \text{ ppm}/^\circ\text{C}$ . It is used for thick film resistors/conductors for lightning surge protection, sense resistors, heating elements and terminations for Ru-based resistors.

### Photosensitive Conductive Paste

TORAY IND. INC. *Japanese Appl.* 11/31,416

Photosensitive conductive paste used in forming a conductor pattern on a ceramic circuit substrate contains at least one conductive powder selected from Pt, Pd, Au and Ag; an acryl-based copolymer with an acid value of 40-200; a photoreactive compound; and a photopolymerisation initiator. The paste forms a fine pattern, gives low wiring resistance and reduces transmission loss at high frequency in a transmitter.

### Internal Electrode Composition

HITACHI LTD. *Japanese Appl.* 11/121,820

An internal electrode of a laminated piezoelectric actuator includes ceramic material added to a Ag-Pd alloy consisting of 70-50 wt. % Ag and 30-50 wt. % Pd. The laminated type piezoelectric actuator has a high productivity and product reliability without any melting of the internal electrode part.

## TEMPERATURE MEASUREMENT

### High Temperature Sensor

MURATA MFG. CO. LTD. *German Appl.* 1/98/30,821

A temperature sensor for automobile exhaust pipe and/or catalyst, has an insulating substrate, a metal film with a resistor structure, Pt connection electrodes and Pt-Rh alloy wire leads connected to the connection electrodes. The sensor element can be used up to 1000°C and has a high mechanical strength in its connection section.

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