

# NEW PATENTS

## ELECTROCHEMISTRY

### Thermoelectric Generator

FORD MOTOR CO. LTD., FORD-WERKE A.G. and FORD FRANCE S.A. *European Appl.* 163,391

A device for converting heat directly to electricity by expanding Na across a solid electrolyte incorporates a permeable electrode such as Pt.

### Photocatalytic Structure

FORD MOTOR CO. LTD. *European Appl.* 164,184

A planar photoelectrochemical structure consists of a film of catalyst material such as platinum deposited over a thin, porous layer of semiconductor powder such as  $\text{TiO}_2$  on a substrate. The structure decomposes water into  $\text{H}_2$  and  $\text{O}_2$ .

### Metal Recovery Electrodes

W. C. HERAEUS G.m.b.H. *European Appl.* 169,301

Electrodes particularly useful as O anodes in the electrolytic recovery of metals from aqueous solutions consist of an electrically conductive plastics support with particles of catalytic material embedded in the surface. The catalyst is Pt, Pd, Rh, Ru or Ir metal and/or oxide.

### Oxygen Evolving Anode

ELTECH SYSTEMS CORP.

*U.S. Patents* 4,543,174 and 4,543,348

Ru can be used as the catalyst in O evolving anodes in a very economical manner by applying to a Pb substrate particles of a Ti sponge which has been impregnated with oxides of (a) Ru and Mn or (b) a platinum group metal, preferably Ru, and Ti.

### Electrode

AKTIEBOLAGET ASEA-ATOM *German Offen.* 3,515,051

An electrode for making electrochemical measurements in aqueous media at elevated temperatures, such as in nuclear reactors, consists essentially of a Pt wire partially sheathed in an oxide ceramic such as alumina or zirconia.

## ELECTRODEPOSITION AND SURFACE COATINGS

### High Temperature Coatings

U.K. SECRETARY OF STATE FOR DEFENCE

*U.S. Patent* 4,530,885

Components of gas turbine engines are protected from oxidation or sulphidation at elevated temperature by a coating of Ni and/or Co alloy containing 30–40% Cr, 1–5% Ti and 2–10% Al, applied over an intermediate film, not more than 25  $\mu\text{m}$  thick, of Pt, Rh or Ni.

## LABORATORY APPARATUS AND TECHNIQUE

### pH Measurement Device

TERUMO CORP.

*European Appl.* 167,117

Pt electrodes are used in a new device for pH measurement instead of conventional glass electrodes so that the device can be miniaturised.

### Infrared Detector

U.S. SECRETARY OF THE AIR FORCE

*U.S. Patent* 4,533,933

A specified i.r.-detection device, incorporates a Schottky barrier of Ir silicide.

### Gas Detector

BACHARACH INSTRUMENT CO. *U.S. Patent* 4,541,988

A constant temperature instrument for measuring concentrations of an unknown gas incorporates a reference element and an active element both of which are formed from Pt or Pt-Ir alloy wire. The active element is coated with a catalyst such as  $\text{Pt/Al}_2\text{O}_3$ .

### Electrical Device

VARTA BATTERIE A.G.

*German Offen.* 3,414,664

A device for indicating the fully-charged state of a lead-acid accumulator determines the temperature of a recombination catalyst such as Pd/C on a resistance thermometer.

### Safety Device

GESELLSCHAFT FÜR GERÄTEBAU m.b.H.

*German Offen.* 3,513,033

A sensor for the catalytic combustion of  $\text{CH}_4$ , incorporates a catalyst which is a compound of Pt, Pd, Rh or Ir, heated by a metal resistance element, preferably of Pt or Au.

## JOINING

### Alloy Layer Formation on Metal Surfaces

DAIKI ENGINEERING CO. LTD. *European Appl.* 162,601

A metal surface is coated with one or more uniform metal layers and these are then melted by irradiation with a laser or other high energy beam to form a tightly adherent bond. In some examples Pd alloy layers are applied to Ni and Ti.

### Nitride Ceramic Metal Composite

TOSHIBA K.K.

*European Appl.* 162,700

A nitride ceramic is heated in a vacuum in contact with a metal (such as Pt) so that the ceramic surface dissociates and the nitride precursor (such as Si) is formed and bonds with the metal.

## Braze for Carbide Composites

GENERAL ELECTRIC CO. *European Appl.* 166,379

A carbide composite abrasive is bonded to a cemented carbide support using a brazing alloy containing 18–39.5% Au, 3.5–14.5% Ni, 2.5–10.5% Pd, 7.5–9.0% Mn and the balance Cu.

## Chemical Vapour Deposition

ADVANCED TECHNOLOGY INC. *U.S. Patent* 4,535,029

In a process for coating a refractory substrate with Sn, Pb, In and/or one of their alloys, the adhesion is improved by adding to the deposited metal composition about 2% of Pt and/or Pd.

## Sputtering Target

GTE PRODUCTS CORP. *U.S. Patent* 4,544,091

In a process for bonding a sputtering target such as  $Y_2O_3$  to a heat-conductive backing plate such as Cu, a bonding layer (preferably of Pt) is applied to the back of the target to provide an oxide-free layer to which an In/Pb solder will adhere.

## HETEROGENEOUS CATALYSIS

### Purification of Gases

BOC GROUP P.L.C. *British Appl.* 2,160,439A

A Pt hydrogenation catalyst is used in a method of removing an O impurity from a pressurised stream of gaseous  $N_2$  or noble gas other than He.

### Alkanoic Anhydride Production

BP CHEMICALS LTD. *British Appl.* 2,161,810A

A process for the production of acetic anhydride or other alkanoic anhydride from 2–6C alkene, CO and either methanol or acetic acid includes a carbonylation step at elevated pressure and temperature in the presence of a platinum group metal (preferably Rh or Ir or a compound thereof) and an iodide promoter.

### Hydrocarbon Production from Synthesis Gas

BRITISH PETROLEUM CO. P.L.C. *European Appl.* 162,554

A new catalyst for syngas conversion consists of a Group IVA and/or Group VIII metal, such as Ru, deposited on an amorphous framework matrix derived from a hydrolysable compound of Si, Al, Ga, Mg, Ca, P, Ti, Be, V, La or Ce. Preferably the Ru is also activated with Fe and K.

### Hydrogen Transfer Reaction Apparatus

ENERGY CONVERSION DEVICES INC. *European Appl.* 164,035

A specified reactor is provided with a transverse membrane of a H pump material such as Pd, Ti or Ni. This membrane is coated on one side with a H evolution catalyst such as Pt, Pd, Au or Ag, among others, and on the other side with a hydrogenation catalyst such as Pt, Pd, Ru or Os, among others.

## Catalysts

GOODYEAR TIRE & RUBBER CO. *European Appl.* 169,161

Improved Fischer-Tropsch catalysts consist of (a) a styrene-divinylbenzene copolymer functionalised with a pyridine derivative, complexed with (b) a Group VIII metal carbonyl derivative such as  $H_2FeOs(CO)_{13}$ ,  $Ru_3(CO)_{12}$  or  $MnCo(CO)_5$ .

## Removal of Nitrogen Oxides from Waste Gases

SUD-CHEMIE A.G. *European Appl.* 169,939

Waste gases from I.C. engines, boiler plant, etc., contain NOx as well as SOx. A new catalyst which resists S poisoning has a platinum group metal layer supported on or in a layer of  $Al_2O_3$ ,  $SiO_2$  and/or Al silicate on a substrate. The intermediate layer may also contain one or more lanthanide oxides. The new catalyst has good low temperature selectivity.

## Hydrocarbon Production Process

IMPERIAL CHEMICAL INDUSTRIES P.L.C. *European Appl.* 171,206

Hydrocarbons and oxygenated hydrocarbons are produced by reacting  $CO$ ,  $H_2$  and  $O_2$  in the presence of a Group VII or VIII catalyst, the  $O_2$  content of the mixture not exceeding 10% of the volume of  $H_2$ . Typically a Rh on Mg stannate catalyst is used for ethanol production.

## Gas Turbine Catalytic Combustion

GENERAL ELECTRIC CO. *U.S. Patent* 4,534,165

Fuel in a gas turbine is burnt in individual combustion sections containing a solid oxidation catalyst such as a platinum metal, as before, but now the fuel supply is staged at each section to optimise combustion and to reduce NOx emissions.

## Isotope Exchange Catalyst

ATOMIC ENERGY OF CANADA LTD. *U.S. Patent* 4,536,488

A catalyst for the exchange of H isotopes between liquid water and gaseous  $H_2$ , for example, is made by impregnating a high-surface crystalline silica with  $Pt(NH_3)_4Cl_2$ , drying, reducing with  $H_2$  and coating with PTFE.

## Alloy Catalyst

STANDARD OIL CO. *U.S. Patent* 4,536,585

The formation of acetals and acetal ethers from alcohols and aldehydes, such as 3-methoxypropionaldehyde dimethyl acetal from methanol and acrolein, is catalysed by finely divided  $PtTi_{0.7}$ .

## Hydrocarbon Reforming Catalyst

NIPPON OIL CO. LTD. *U.S. Patent* 4,537,872

An improved catalyst for naphtha reforming consists of an inorganic carrier impregnated with 0.01–5% of a platinum group cluster anion complex salt, such as  $(NEt_3)_2Pt_3(CO)_8$ , Re and halogen. After impregnation the catalyst is oxidised and reduced.

### Barium Stabilised Lead Tolerant Catalyst

JOHNSON MATTHEY P.L.C. *U.S. Patent 4,539,311*  
A Pb resistant catalyst for the purification of I.C. engine exhaust gases is made by impregnating an  $Al_2O_3$  carrier preferably containing Ce oxide with Ba compound and calcining at not less than 400°C prior to impregnating with Pt, Pd and/or Rh.

### Catalyst for Urea Production

AT & T BELL LABORATORIES *U.S. Patent 4,542,006*  
Urea or ammonium cyanate can be obtained from a mixture of CO, N monoxide and  $H_2$  at moderate temperature and pressure in the presence of a hydrogenation catalyst such as spongy Pt or Pd.

### Photocatalyst

FORD MOTOR CO. *U.S. Patent 4,544,470*  
A catalyst for the production of  $CO_2$  and  $H_2$  by the u.v. irradiation of formic acid consists of a substrate coated with a sputtered layer of Pt and then with a porous layer of n-type  $TiO_2$ .

### Hydrocarbon Removal from Exhaust Gases

UHDE G.m.b.H. *German Offen. 3,405,649*  
Power stations operating on fossil fuels generate waste gases containing aromatic H. These are now removed by adjusting the O content of the waste gases to 0.1–5 vol.% and passing them over a catalyst containing 0.1–2% noble metal, such as Pt.

### Wires for Catalytic Gauzes

V.E.B. MANSFELD-KOMBINAT WILHELM PIECK  
*East German Patent 225,137*  
Wires for catalytic gauzes, consisting of a base or precious metal core and a sheath of Pd-Pt-Rh alloy, are made by a specified procedure.

## HOMOGENEOUS CATALYSIS

### Hydrocarbon Synthesis Catalysts

BRITISH PETROLEUM CO. P.L.C. *European Appl. 169,743*  
The conversion of synthesis gas to hydrocarbons is catalysed by mixed oxides  $Ru_aK_bCeO_x$ .

### Ethylene Glycol Production

BASF A.G. *European Appl. 171,632*  
Ethylene glycol is obtained from synthesis gas at elevated temperatures and pressures in the presence of Rh and Co compounds, such as carbonyls, in a ratio of 20:1 to 60:1.

### Surgical Silicone Products

INNOVATIVE SURGICAL PRODUCTS INC.  
*U.S. Patent 4,537,943*  
A lens is formed in vivo in an eye from a viscous siloxane polymer which is cured using a Pt catalyst, such as chloroplatinic acid complexed with a siloxane.

### Amination Catalyst

TEXACO INC. *U.S. Patent 4,543,411*  
The production of secondary or tertiary amines by reaction of olefins with primary or secondary amines and synthesis gas is preferably catalysed by  $Ru_3(CO)_{12}$  in molten tetrabutyl phosphonium bromide.

### Platinum and Palladium Siloxane Hydrosilylation and Hydrogenation Catalysts

DEGUSSA A.G. *German Offens. 3,404,702/03*  
New catalysts for addition reactions are haloplatinates and halopalladates attached to a polymeric siloxane quaternary ammonium cation, such as  $[MeN(CH_2CH_2SiO)_3]PtCl_4$ . The same catalyst is used in *German Offen. 3,404,703* for chloropropyl trichlorosilane production.

## FUEL CELLS

### Cathode Electrocatalysts

GINER INC. *European Appl. 165,024*  
The cathodes for phosphoric acid fuel cells are made of new ternary alloys of Pt with less noble elements, such as Cr and Ce, which have greater stability and/or activity in the hot acid.

### Catalytic Electrode

ELECTROCHEMISCHE ENERGIECONVERSIE N.V.  
*U.S. Patent 4,536,272*  
A porous electrode for use in fuel cells is coated with a catalytic layer made of 3–30% mouldable polymeric binder, 3–47% hard hydrophobic polymer particles and 50–94% C particles supporting the active catalyst, such as Pt and/or Pd.

## CHEMICAL TECHNOLOGY

### Diffusion Membrane

PHILLIPS PETROLEUM CO. *U.S. Patent 4,536,196*  
In a process for the dehydrogenation of hydrocarbons, the  $H_2$  liberated is continuously removed through a selectively permeable membrane. The resistance to poisoning of the membrane, which is preferably fabricated from Pd-Ag alloy, is improved by coating its surface with a metal, preferably Ti.

## GLASS TECHNOLOGY

### Toric Contact Lens

ČESKOSLOVENSKA AKADEMIE V.E.D.  
*British Appl. 2,160,677A*  
A toric contact lens has its centre of gravity displaced towards its edge by a one-sided thickening of the lens which may include at least one metallic corpuscle, preferably of a platinum group metal, Au or Ag.

## Optical Glass Moulding

MATSUSHITA ELECTRIC INDUSTRIAL CO. LTD.  
*European Appl.* 164,930

Thermally softened optical glass is pressed into a mould coated with a thin film of noble metal alloy to give a lens, prism, etc., of high surface quality. A suitable alloy contains 99–30% Pt and the remainder of another platinum group metal.

## Glass Fibre Production

VITROFIL S.P.A. *European Appl.* 170,581

Pt-Rh alloy spinnerets are used to spin molten glass in a direction opposite to that of the force of gravity.

## Protection of Glass Spinning Bushings

OWENS-CORNING FIBERGLAS CORP.  
*U.S. Patent* 4,532,184

Bushings used in the production of fibreglass, and made of Pt, Ir and/or Rh, are protected from evaporation at elevated temperature by coating with a flame-sprayed layer of (a) a Ca aluminosilicate glass and (b) a refractory material such as a specified metal oxide, boride and/or silicide.

## ELECTRICAL AND ELECTRONIC ENGINEERING

### Tungsten Halogen Lamps

THORN EMI P.L.C. *European Appl.* 162,673

The darkening of a Mo filament shield in an incandescent lamp may be prevented by plating with Pt.

### Electric Connectors

INTERNATIONAL BUSINESS MACHINES CORP.  
*European Appl.* 163,050

A method for measuring the real contact area between a pin and a socket is provided. Both pin and socket are Au plated, then the pin is coated with Pt and mated with the socket. At points of contact the Pt is removed, and the area so affected is measured.

### Spark Plug Tip

NGK SPARK PLUG CO. LTD. *European Appl.* 171,994

A new energy saving spark plug has a noble metal tip in the centre electrode formed from a fine wire electrically welded to the leading end face of the main body. The protruding wire tip is forged to form a flange. The noble metal may be a Pt-Ir, Pt-Ni or another Pt alloy.

### Thick Film Resistor Composition

E. I. DU PONT DE NEMOURS & CO.  
*U.S. Patent* 4,539,223

A composition for making thick film resistors is a dispersion in a liquid organic medium of a finely divided mixture containing 4–75% of a Ru-based conductor such as  $\text{Bi}_2\text{Ru}_3\text{O}_7$ , 25–96% glass frit and 0.05–15%  $\text{Co}_2\text{RuO}_4$ .

## Glow Plug

ALLIED CORP. *U.S. Patent* 4,545,339

A heated glow plug for a diesel engine is designed for corrosion resistance, low power requirement and a reduced thermal response time. The heating element is a film of Pt, Pd, Ir or Rh.

## Thick Film Device

U.S. SECRETARY OF THE AIR FORCE  
*U.S. Patent* 4,546,283

A thick film conductor arrangement is suitable for making connections between a resiliently mounted element such as a surface acoustic delay line and adjacent thick film conductors. The conductors are preferably alloys of (a) Pd and Ag and (b) Pt and Au.

## MEDICAL USES

### Biodegradable Implants

ČESKOSLOVENSKA AKADEMIE V.E.D.  
*British Appl.* 2,160,422A

A biodegradable implant has a matrix of a starch gel containing NaCl and glycerol as plasticiser, in which is dispersed 1–15% of microcrystalline cisplatin (a cis-diamminedichloroplatinum addition compound).

### Antibody-Linkable Pt Compounds: Amine Functionality

JOHNSON MATTHEY P.L.C. *European Appl.* 167,310

New compounds for the treatment of cancer involve linkage to monoclonal antibodies. The Pt atom has at least one amine ligand which includes a functional group remotely bound to the amine group which can be used to attach the antibody. The compounds have the formula  $\text{YRNHR}'\text{Pt}(\text{NH}_2\text{R}'')\text{X}_2$ , where Y is the functional group, X is an anion or both X groups form a common anion and R, R' and R'' are organic groups. Typically a suitable compound is cis-amine sulphanyl amide Pt dichloride.

### Antibody-Linkable Pt Complexes: Leaving Group Functionality

JOHNSON MATTHEY P.L.C. *European Appl.* 169,645

Improved materials for the treatment of cancer are Pt complexes which are linkable to a monoclonal antibody; for example  $(\text{RNH}_2)_2\text{Pt}(\text{OOC})_2\text{CH}(\text{CH}_2)_n\text{COOH}$ . The complexes include an antibody-linkable functional group which stabilises the linked compound to in vivo hydrolysis.

### Blood Gas Sensors

DIAMOND SHAMROCK CHEMICALS CO.  
*U.S. Patent* 4,534,356

Transcutaneous solid sensors for measuring the  $\text{O}_2$  diffusing through the skin are made from a noble metal electrode (platinum group metal, Au, Ag, etc., in a thick film), a Ag/AgCl reference electrode and an O-permeable polymeric membrane electrolyte.