NEW PATENTS

METALS AND ALLOYS

Amorphous Alloys

TOKYO SHIBAURA DENKI K.K. *U.S. Patent* 4,428,416

Multilayer amorphous alloys are made by rapidly cooling two layers of metal between high-speed rollers. Examples of the pairs of metals include $Fe_{75}Si_{10}B_{15}/Pd_{83.5}Si_{16.5}$ and $Fe_{55}Ni_{45}/Pd_{80}Si_{20}$.

Titanium Alloys

UNITED TECHNOLOGIES CORP. *U.S. Patent* 4,433,005

The fatigue resistance of Ti alloys is increased by ion implantation of a platinum group metal.

CHEMICAL COMPOUNDS

Bismuth Pyrochlores

E. I. DU PONT DE NEMOURS & CO. *U.S. Patent* 4,420,422

Pyrochlores of formula $Bi_{2-x}M_xM'_zO_{7-z}$ are made by firing a mixture of Bi oxycarbonate, M carbonate and $M'O_2$ and dissolving out any unreacted material with mineral acid. M is Cu, Cd, Pb, In, Gd and/or Ag, M' is Ru and/or Ir, x is 0–0.5 and z is 0–1. The finely divided products are useful as the conductive phase in screen printed thick film resistors.

ELECTROCHEMISTRY

Electrochemical Cell

ELECTRICITY COUNCIL *British Appl.* 2,127,856A

Electrochemical cells may have an anode of Ti coated with RuO_2, Pt or Pt and Ir. One such cell is used in the oxidation of cerous to ceric in aqueous H_2SO_4.

Flexible Electrode

GOULD INC. *British Appl.* 2,129,830A

The outer protective and electrically conductive sheath of an elongated dimensionally stable flexible electrode, for use in salt water environments, is preferably formed of RuO_2.

Supported-Membrane Diffusion Cell

JOHNSON MATTHEY P.L.C. *European Appl.* 106,523

In an apparatus for separating gases by means of a selectively permeable membrane, the membrane is reinforced with a perforated support. The support may be a perforated metal sheet or a sheet of woven metal gauze. The membrane is secured to the support close to each hole in the support. A foil of Ag-Pd is used as the membrane for H_2 diffusion.

Chlorine Dioxide Manufacture

DIAMOND SHAMROCK CORP. *U.S. Patent* 4,426,263

ClO_2 is produced by electrolysis of a Na chlorate-H_2SO_4 solution using a cathode coated with catalytic mixed oxides of Ru and Rh, Ru and Pd, Rh and Pd, Ir and Rh, Ir and Pt or, Ru, Rh, Pd.

Electrocatalysts

EXXON RESEARCH & ENGINEERING CO. *U.S. Patent* 4,434,031

In various organic electrocatalytic oxidation reactions the catalytic anode coating is a mixed oxide of pyrochlore structure and general formula $M_2(M'_{2-x}M''_x)O_{7-y}$ where x and y are each 0–1, M is Pb, Bi or Tl, M' is Pb, Bi, Tl or Sn and M'' is Rh, Ir, Ru or Os, such as $Pb_2Ru_2O_{6.5}$.

Hydrogenation Process

KERNFORSCHUNGSANLAGE JULICH G.m.b.H. *German Offen.* 3,235,578

Methanol is converted to CH_4 and O_2 by reaction with H_2 which is produced simultaneously by electrolysis of, for example a phosphoric acid solution. The anode is preferably made of Pt and the cathode is a foil of Pd through which the H_2 diffuses to contact the alcohol, the reverse side of the foil being coated with a Ru catalyst.

ELECTRODEPOSITION AND SURFACE COATINGS

High Temperature Coatings

AVCO CORP. *European Appl.* 107,508

Coatings for protecting components of turbine engines consist of MCrAl compositions containing 0.01–3% lanthanide metal(s) and optionally 0.1–10% noble metal, preferably Pt and/or 0.1–8% refractory metal. M is a solid solution of Mo, W or Nb in Ni and/or Co.

Palladium-Silver Electroplating Baths

LEARONAL INC. *European Appl.* 112,561

An excess of strong acid added to the plating bath brings the plating potentials of Pd and Ag closer together so that they may be deposited simultaneously. In one example methane sulphonic acid is used with Pd diaminodinitrite and $AgNO_3$.

Platinum Electroplating

BELL TELEPHONE LABORATORIES INC. *U.S. Patent* 4,427,502

Films of improved properties are obtained by electrodeposition of Pt and its alloys from baths containing a 3–20C polyamine such as 1,3-diaminopropane or diethylenetriamine.

Palladium Alloy Electroplating

K.K. SUWA SEIKOSKA AND NISSHIN KASEI K.K. *U.S. Patent* 4,428,802

An improved Pd-Ni alloy plating solution which can be replenished by the addition of a solid Pd complex contains 5–30g/l Pd, added as $[Pd(NH_3)_4Cl_2.H_2O]$, and 5–30g/l Ni, added as Ni acetate or $[Ni(NH_4)_2(SO_4)_2.6H_2O]$.

Electrodeposited Palladium Alloys

LANGBEIN-PFANHAUSER WERKE A.G. *U.S. Patent* 4,430,172

The corrosion resistance of a Ni-Pd alloy coating containing 30–90wt.% Pd, formed by electrodeposition from a bath containing 5–30g/l Pd and 5–30g/l Ni, is improved by including a benzene sulphonyl urea in the bath.

LABORATORY APPARATUS AND TECHNIQUE

Hydrogen Concentration Meter

NATIONAL RESEARCH DEVELOPMENT CORP. *British Appl.* 2,128,751A

A H_2 concentration meter includes a conductive component, such as Pd or a Pd alloy, in which H_2 is soluble and mobile, a reference electrode which can reversibly accept H_2 and which may include anodised Ir, and a solid state electrolyte such as partially hydrated zirconia.

Catalytic Combustible Gas Detectors

ENGLISH ELECTRIC VALVE CO. LTD. *British Appl.* 2,129,134A

A combustible gas detector element includes a heatable wire filament made of Pt or one of its alloys, embedded in a pellet of an oxidation Pd or Pt catalyst and a carrier therefor.

Pressure Sensor

M. A. BROOKS AND J. MILER *U.S. Patent* 4,426,406

A pressure sensor, particularly for use in an I.C.E., includes a quartz plate provided with electrode(s) by printing with an electrically conductive metal ink, such as an ink containing 15% Au, 2% Pt and 0.066% Rh.

Gas Sensor

WESTINGHOUSE ELECTRIC CORP. *U.S. Patent* 4,428,817

A thin film solid-electrolyte sensor for the low-temperature measurement of O_2 and combustible gases in the presence of each other includes a catalytic electrode chosen from platinum group metals and porous Au or Ag containing perovskite-type oxide impregnations and a non-catalytic electrode which may be a poisoned platinum group metal, Au, Ag or a lanthanide metal chromite among others.

JOINING

Ductile Brazing Alloys

G.T.E. PRODUCTS CORP. *European Appl.* 110,418

Ductile alloys which contain a reactive metal but still can be rolled down to a foil contain 0.1–4% Ti, Zr and/or V and only one metal selected from Pd, Au, Ag, Fe, Ni, Cu and Al. A typical alloy contains 3% Ti and 97% Pd and is used to bond Mo.

Silver Solder

DEGUSSA A.G. *German Offen.* 3,235,574

An alloy for soldering an oxide-containing Ag contact material to a substrate consists of Ag with 20–35% Cu and 0.1–5% Pd.

HETEROGENEOUS CATALYSIS

Internal Combustion Engines

BL CARS LTD. *British Appl.* 2,129,489A

Projections or depressions arranged in the combustion chamber of an I.C.E., of the liquid fuel injection compression ignition type, are coated with a catalytic film of a platinum group metal or a platinum group metal compound.

Olefin Hydroxylation

EXXON RESEARCH & ENGINEERING CO. *British Appl.* 2,129,800A

Olefins are hydroxylated using an Os oxide catalyst and NaOH co-catalyst in the molar ratio of Na:Os of 0.1:1 to 20:1.

Traction Drive Fluids

IDEMITSU KOSAN CO. LTD. *British Appl.* 2,130,600A

A base stock for a traction drive fluid is prepared by contacting naphthalene or tetralin or their alkyl derivatives with a Friedel-Crafts catalyst followed by hydrogenation using a hydrogenation catalyst containing Pt or Ru.

Reforming Catalysts

EXXON RESEARCH & ENGINEERING CO. *European Appl.* 107,389

Hydrocarbon reforming catalysts prepared by a specified procedure consist of zeolite L, ion exchanged with Group IA metal(s) and/or Ba and impregnated with 0.1–6% Pt, Pd and/or Ir.

Laser Catalyst

UNIVERSAL MATTHEY PRODUCTS LTD. *European Appl.* 107,471

A catalyst for the oxidation of CO in breathable gases to CO_2 consists of a stannic oxide carrier impregnated with 0.5–5% Pt and 0.1–25% Ni or Mn. The catalyst may by used to remove CO produced by a CO_2 gas laser.

Hydrocarbon Reforming Catalyst

EXXON RESEARCH & ENGINEERING CO. *European Appl.* 111,036

A high activity catalyst able to operate in severe conditions contains 0.1–2% Pt, 0.1–2% Ir, 0.01–0.1% Cu, 0.001–3% Se and 0.1–2.5% halogen (Cl_2) on Al_2O_3 or another oxidic support.

Multimetallic Hydrocarbon Conversion Catalyst

UOP INC. *European Appl.* 111,578

A conversion catalyst of exceptional selectivity and resistance to deactivation consists of Al_2O_3 or another

oxide carrier supporting 0.01–2% platinum group metals such as Pt, Pd, Ir or Rh, 0.05–5% Co, 0.01–5% Sn, 0.01–5% P and 0.1–3.5% halogen.

Dehydrogenation Catalysts

UOP INC. *U.S. Patent* 4,420,649

Catalysts for the conversion of alkanes to olefins or ethylbenzene to styrene consist of a porous carrier such as Al_2O_3 impregnated with 0.01–2% Pt, 0.01–2% Ru and 0.01–5% Re formed by thermal decomposition of a carbonyl complex.

Reforming Catalyst

UOP INC. *U.S. Patent* 4,426,279

A hydrocarbon reforming catalyst preferably consists of a refractory carrier such as Al_2O_3 impregnated with about 0.4% Pt, 1% Cl and 0.5% P applied as a compound such as hypophosphorous acid.

Catalyst for I.C. Engine Exhausts

PROCATALYSE *U.S. Patent* 4,426,319

A catalyst for the purification of automobile exhaust gases consists of a particulate or monolithic carrier, preferably Al_2O_3, impregnated with Ce, Fe, Ga and/or Y, Pt, and/or Pd, and Ir and/or Rh.

Hydrocarbon Cracking Process

CHEVRON RESEARCH CO. *U.S. Patent* 4,427,536

In a process for cracking S-containing hydrocarbons, a sorbent for S oxides, such as finely divided Al_2O_3, is impregnated with a mixture of Pd, and Pt or Ir which catalyses the oxidation of SO_2 to SO_3 while minimising the formation of NO_x.

Hydrocarbon Conversion Catalyst

STANDARD OIL CO. (INDIANA) *U.S. Patent* 4,433,190

A catalyst for the dehydrogenation and/or isomerisation of normal alkanes, especially butane, consists of AMS-IB crystalline borosilicate molecular sieve ion exchanged with Pd or Pt and optionally also with La or another metal.

Isomerisation Catalyst

AKADEMIE DER WISSENSCHAFTEN DER D.D.R. *East German Patent* 206,489

A catalyst for the hydroisomerisation of n. paraffins consists of an Al_2O_3 carrier supporting 0.1–2% Pt, 0.1–2% Cr and 0.8–1.4% Cl. A typical catalyst contains 0.5% Pt, 0.35% Cr and 1.3% Cl and is used for hexane isomerisation.

HOMOGENEOUS CATALYSIS

Carbonylation Catalyst

SHELL INTERNATIONAL RESEARCH Mij. B.V. *European Appl.* 106,379

The formation of carboxylic acids or their anhydrides or esters by carbonylation of olefins in the presence of water, carboxylic acid or alcohol is preferably catalysed by a system consisting of $Pd(OAc)_2$, PPh_3 and p-toluene sulphonic acid.

Catalyst System

BP CHEMICALS LTD. *European Appl.* 106,656

Homologous carboxylic acids or esters are obtained by reacting an olefin with a formic acid or ester in the presence of Ir chloride promoted with CH_3I and p-toluene sulphonic acid.

Rhodium and Ruthenium Complex Catalysts

PENNWALT CORP. *European Appl.* 106,911

In a process for the production of amines by photo-activated reaction of olefins with NH_3 or a primary or secondary amine, the catalyst may be $Ru(PPh_3)_3Cl_2$ or $Rh(PPh_3)_3Cl$ among others.

Hydroformylation Catalyst

TEXACO DEVELOPMENT CORP. *European Appl.* 107,430

Aldehydes and alcohols are obtained by reacting olefins with CO and H_2 in the presence of Ru oxide dispersed in tetrabutylphosphonium bromide.

Alcohol Production from Synthesis Gas

TEXACO DEVELOPMENT CORP. *European Appl.* 108,848

Methanol and other alcohols may be obtained in a highly selective manner by using a catalyst consisting of a Ru compound, a Re or Mn compound and a quaternary ammonium or phosphonium compound. An inert oxygenated solvent and an optional Group VB donor ligand such as a phosphine are also present.

Continuous Hydrogen Peroxide Production

DEGUSSA A.G. *European Appl.* 111,133

The anthraquinone process is operated with a Pd black suspension in a new reactor in the form of a meander tube.

Rhodium Polymer Complex Catalysts

POLYMER SCIENCES CORP. *U.S. Patent* 4,424,312

Catalysts for the asymmetric hydrogenation of unsaturated N-acyl aminoacids are made by reacting a polymer from a pyrrolidine phosphine, a hydrophilic vinyl monomer and a divinyl monomer with a Rh-diene complex such as $[Rh(cod)]Cl_2$.

Oxidation Catalyst System

PHILLIPS PETROLEUM CO. *U.S. Patent* 4,434,082

A low-corrosion catalyst for use in the oxidation of olefins to ketones preferably consists of Pd chloride, a phosphomolybdovanadic acid and cetyltrimethyl ammonium chloride.

Catalyst System

TEXACO INC. *U.S. Patent* 4,434,246

A catalyst for the conversion of synthesis gas to ethylene glycol and lower alkanols is a dispersion of a Ru derivative such as RuO_2 and a substituted benzene in tetrabutylphosphonium bromide.

De-Emulsifier Production

TH. GOLDSCHMIDT A.G. *German Offen.* 3,312,576

A de-emulsifying agent for crude oil/water emulsions is made by reacting a silane with a diene polymer in the presence of a noble metal catalyst such as Pt ethylene pyridine dichloride.

FUEL CELLS

Fuel Cell Catalyst

INTERNATIONAL BUSINESS MACHINES CORP. *European Appl.* 106,197

A catalyst for use in fuel cells consists of a carrier such as C coated with thin, flat, isolated crystallites of Pd, Pt or Ag, formed by electrodeposition.

CORROSION PROTECTION

Resistant Alloy Structures

TURBINE METAL TECHNOLOGY INC. *European Appl.* 108,797

Fe, Co, Ni and their alloys are protected from corrosion, erosion and wear by a diffusion coating of Pt, Rh or Pt ternary or quaternary alloy filled with interdispersed refractory particles. A typical coating consists of Al_2O_3 particles in an alloy of Rh, Pt, Ni and Al.

Laminated Material for Equipment

W.C. HERAEUS G.m.b.H. *European Appl.* 108,860

Pipes, equipment, etc., liable to come into contact with corrosive atmospheres, especially chemical apparatus, are made from a laminate formed by explosion bonding a steel base to a thin layer of Pt, Pd, Ir, Ti, Nb, Ta, Zr, Ni, Mo, Au, Ag, and/or alloys.

CHEMICAL TECHNOLOGY

Colour Photographic Material

FUJI PHOTO FILM CO. LTD. *British Appl.* 2,132,370A

The Ag halide emulsion used in a colour photographic material having a polymeric cyan-forming coupler can be chemically sensitised by a Au compound such as a chloroaurate or Au trichloride, or by a salt of Pt, Pd, Ir, Rh or Ru.

ELECTRICAL AND ELECTRONIC ENGINEERING

Energy Control Window Films

OPTICAL COATING LABORATORY INC. *European Appl.* 106,223

An energy control window film is claimed which shows good performance and can be produced economically and efficiently in a high-rate roll-coating apparatus. The environmental stability and durability of the conventional thin film Ag layer are increased very considerably by alloying the Ag with a small amount of Pd or forming a composite of very thin flash layers of Pd on one or both sides of the thicker layer of Ag and/or coating the metal with a protective layer of mixed metal oxides, preferably including lanthanide metals.

Infrared Source

HEWLETT-PACKARD CO. *European Appl.* 106,431

A small, inexpensive i.r. source having near black-body emission at 2–20μm consists of a narrow ceramic tube heated with a wound coil of Pt, Rh and/or Ir wire.

Low Resistance Elastic Connector

TORAY INDUSTRIES INC. *European Appl.* 110,383

In a connector electro-conductive filaments isolated from each other are allowed to penetrate an electrically insulating elastomer across its thickness to reduce its resistance. The filaments may be stainless steel fibres activated with Pd and plated with Cu, Ni and Au.

Thin Film FET Device

MATSUSHITA ELECTRIC INDUSTRIAL CO. LTD. *European Appl.* 111,568

A thin film electric field light-emitting device has a thin fluorescent film, a thin dielectric film and electrodes made of Au for applying the voltage. The new dielectric which is superior to Y oxide is a compound of formula AB_2O_6 where A is Pd, Sn, Zn, etc., and B is Ta or Nb.

Thick Film Electrodes

E. I. DU PONT DE NEMOURS & CO. *U.S. Patent* 4,426,356

Capacitor electrodes are applied to the green substrate by printing, using an ink consisting of a liquid organic medium and a mixture of 70–95% Ag, Au, Pt and/or Pd with 0.5–30% specified metal oxide, fluoride, phosphate or glass, preferably GeO_2 or $Pb_5Ge_3O_{11}$.

Spark Plug Electrode

NGK SPARK PLUG CO. LTD. *U.S. Patent* 4,427,915

An improved central electrode for a sparking plug is obtained by sintering a mixture of Ti oxide, carbide or nitride, Pd and/or Pt, and Ag, Rh and/or Ru.

MEDICAL USES

Organic Platinum Complexes

G. E. ADAMS, I. J. STRATFORD AND I. AHMED *British Appl.* 2,131,020A

Novel bis(nitro-l-imidazolyl alkylamine) Pt complexes are useful in increasing the sensitivity of tumour cells to radiation in radiotherapy and in enhancing damage to tumours by chemotherapeutic agents.

Diplatinum Naphthazarinate Complexes

RESEARCH CORP. *European Appl.* 109,677

New anticancer agents are complexes of two atoms of Pt with halide, amine and other substituents with one molecule of naphthazarine, such as bis-diamino-bis-dichloro-μ-naphazarinato-diplatinum.