NEW PATENTS

CHEMICAL COMPOUNDS

Platinum Complexes Containing Sulphur

DOW CORNING LTD. *British Patent* 1,385,041

New complexes for use in preparative organosilicon chemistry have the formula $PtX_2(SR'R'')_2$ where X is Cl, Br or I, R′ is the R_3SiQ-group, R is 1–18C alkyl, aryl, aralkyl or alkaryl or Me_3Si, Q is a 1–16C organic group and R″ is 1–18C alkyl, aryl, aralkyl or alkaryl and/or R SiQ–. For example $[(Me_3SiCH_2)_2S]_2PtCl_2$.

Olefin Metallorganic Complexes of Saline Type

SNAM PROGETTI S.p.A. *U.S. Patent* 3,857,867

Complexes have the formula $[Rh(L)_n(CH_3CN)_a]X$, where L is ethylene or cyclooctene and X is an anion BF_4–, PF_6–, ClO_4– and NO_3–, provided that when L is ethylene and n is 2 or 3, a is 2 and when L is cyclooctene and n is 1, a is 3 and when n is 2, a is 2 or 3. A typical complex of this salt type is $[Rh(C_2H_4)_3(MeCN)_2]BF_4$.

ELECTROCHEMISTRY

Electrolytic Electrodes

DIAMOND SHAMROCK CORP.
British Patent 1,384,836

A new cell uses a number of substantially parallel anodes and cathodes placed face-to-face without diaphragms. The anodes may be constructed from valve metals faced with Pt, Pt alloys and/or solid solutions of noble metal oxides.

Electrochemical Cells

NATIONAL RESEARCH DEVELOPMENT CORP.
British Patent 1,385,201

An electrochemical cell for monitoring purposes, has active working electrodes of Pt/Pd or Ru-Pt.

Electrolysis Electrode

ASAHI KASEI K. K. *British Patent* 1,386,090

An electrolysis electrode consists of a Ti base coated with a mixture of (*a*) crystalline Ru having a lattice constant which is at least 0.1% greater than the normal lattice constant when Ru is used alone, and (*b*) at least 3% of crystalline Pt or Rh which has a lattice constant at least 0.1% smaller than normal.

ELECTRODEPOSITION AND SURFACE COATINGS

Rhodium-Platinum Plating Bath

O.M.F. CALIFORNIA INC. *British Patent* 1,383,850

Rh sulphate, Pt "P" salt and sulphamic acid are used to give a brighter alloy electroplated deposit. In an example, the bath contains 2g/l Rh.

Process for Coating Refractory Oxides

GULF RESEARCH & DEVELOPMENT CO.
U.S. Patent 3,840,389

A refractory oxide having a surface area of about 10–500 m^2/g is coated with Ru and/or Rh alone or in combination with at least one of Pt, Pd, Os, or Ir by impregnating the oxide with a solution of a salt of at least one of the metals while maintaining the pH between about 0.7–2.2 and contacting with H_2S at a temperature of about 15–95°C to precipitate the metals as sulphides before drying.

Electrolytic Deposition of Platinum, Iridium and Their Alloys

RHONE-PROGIL *U.S. Patent* 3,841,980

Baths which are aqueous, acidic and substantially bromide-ion free for Pt and/or Ir electroplating are formed from compounds of Pt and/or Ir giving, in aqueous solution, primarily the bromoiridic and bromoplatinic anions, and at least one acid selected from NHO_3, H_2SO_4, $HClO_4$ and $HBrO_3$. The Pt and/or Ir concentrations are 0.1–60 g/l and the acid is present in an amount of between about 0.05–1 equiv./l.

Valve Metal Electrode

ELECTRONOR CORP. *U.S. Patent* 3,846,273

A valve metal Ti or Ta base is coated with a mixture in liquid form which on heating forms an oxide layer on the base consisting of 39.2–78% TiO_2, 6.4–47.5% of a Pt group metal oxide and 1–17.7% V, La and/or Co doping metal. Typically Ru and Ir are used as the Pt group metals.

Process Employing Catalyst-coated Yarn Processing Rolls

E. I. DU PONT DE NEMOURS & CO. INC.
U.S. Patent 3,849,177

In the hot processing of textile materials, the lubricating films are removed chemically, rather than physically, by the use of heated rolls coated with irregular, rounded surface nodules whose interstices contain finely divided Pt, Pd, etc.

Palladium Electroplating Bath

FA. DR. TH. WIELAND *German Offen.* 2,328,243

Better hardness, gloss and corrosion resistance are obtained with Pd films deposited from a bath containing Ni as well as Pd; preferably there are ten parts Pd to each part Ni.

Brazing of Titanium, etc.

DEUTSCHE GOLD- & SILBER-SCHEIDEANSTALT
German Offen. 2,329,613

Group IV–VII metals and alloys, especially Ti, Zr and their alloys, are brazed using molten salt baths to deposit electrolytically a Pt group metal which assists in bonding. The metal is especially Ir, Rh and/or Ru.

LABORATORY APPARATUS AND TECHNIQUE

Air Fuel Ratio Sensor

GENERAL MOTORS CORP. *U.S. Patent* 3,844,920

O_2 in an exhaust gas stream is sensed by a sensor having a hollow ZrO_2 body with Pt elements.

Method of Oxygen Detection and Removal

U.S. ATOMIC ENERGY COMMISSION
U.S. Patent 3,849,539

A gas with an O_2 content of less than 1% is dried over a zeolite or Mg perchlorate before passage through a Pd tube coil surrounded by a pure H_2 atmosphere. The O_2 combines with H_2 diffusing through the tube and the water that forms is detected. The tubing is Ag-Pd alloy.

HETEROGENEOUS CATALYSIS

Noble/Base Metal on Torvex Catalyst

JOHNSON MATTHEY & CO. LTD.
British Patent 1,390,182

A catalyst for oxidation, reduction, steam reforming, etc., consists of an inert material coated or impregnated with a metallic mixture or alloy of Pt, Rh and one or more base metals selected from Al, Mg, Cr, Mo, W, Mn, Fe, Co, Ni, Ti, V, Th, U, Cu, Ag, Zn, Cd, Hg, In, Tl, Bi, Sn, Pb, Sb, the lanthanides and actinides; 1–50% Rh and 0.01–25% base metal are present, supported on a porous refractory monolith. In an example, an I.C.E. exhaust gas catalyst consists of 20% Ni, 6% Rh and 74% Pt deposited on "Torvex".

Oil Production from Garbage

JOHNSON MATTHEY & CO. LTD.
British Patent 1,390,356

Agricultural, domestic or industrial waste containing cellulose material is reacted with one or more reducing gases at elevated temperature and pressure in the presence of a Cu, Ru, Rh, Pd, Ir, Os and/or Pt catalyst to give an organic oil suitable for use as a fuel oil.

Hydrocarbon Conversion Catalyst

STE. FRANCAISE DES PRODUITS POUR CATALYSE
British Patent 1,390,625

A long life catalyst for conversion reactions consists of an Al_2O_3 support carrying 0.005–1% Pt, 0.005–1% Ir and 0.005–5% of one or more of the lanthanide metals. A typical catalyst contains 0.2% Pt, 0.05% Ir and 0.5% La.

High Purity Hydrogen Production

UNIVERSAL OIL PRODUCTS CO.
British Patent 1,391,004

A process is described for the recovery of H_2 in high purity from a liquid petroleum reforming process using Pt/Al_2O_3 catalyst.

NO_x Removal from Exhaust Gases

FORD MOTOR CO. LTD. *British Patent* 1,391,509

The amount of NO_x in I.C.E. exhaust gases is reduced by operating the engine to give gases which have chemically reducing properties and passing the gases over finely divided Ru or Os catalysts, preferably Ru on a cordierite support.

Nitroso-modified Polymers

SNAM PROGETTI S.p.A. *British Patent* 1,391,846

Modified polymers are obtained by reacting a diene polymer or another unsaturated polymer with gaseous NO in the presence of a catalyst which may be a Pt group metal complex, e.g., $RhCl(PPh_3)_3$.

Hydrocarbon Conversion

UNIVERSAL OIL PRODUCTS CO.
U.S. Patent 3,839,192

A gasoline fraction is reformed by contacting it and H_2 with a Pt-free catalytic composite containing 0.01–2% Pd, 0.01–2% Ir and 0.1–3.5% halogen, the Pd and Ir components being present in an atomic ratio of 0.5:1 to 1.5:1.

Hydrocarbon Conversion with a Trimetallic Catalytic Composite

UNIVERSAL OIL PRODUCTS CO.
U.S. Patent 3,839,193

A hydrocarbon is converted by contacting it with a porous carrier material containing 0.01–2% Pt or Pd, 0.01–2% Ir, 0.01–5% Ge and 0.1–3.5% halogen; the Pt or Pd, Ir and Ge are uniformly dispersed throughout the porous carrier material and substantially all the Pt, Pd and Ir are present in the metallic state and the Ge is present in an oxidation state above that of the elemental metal.

High Severity Reforming Process with a Platinum-Iridium Catalyst

ESSO RESEARCH & ENGINEERING CO.
U.S. Patent 3,839,194

In a naphtha reforming process a naphtha feed stock and H_2 are contacted with a catalyst containing Al_2O_3 in association with 0.15–0.75% Pt, 0.15–0.45% Ir and 0.3–2.0% Cl, each based on total anhydrous catalyst. The surface area of the Pt and Ir/Al_2O_3 is at least about 200 m^2/g Pt and Ir.

Gasoline Reforming with a Platinum-Lead Catalyst

UNIVERSAL OIL PRODUCTS CO.
U.S. Patent 3,839,195

A gasoline fraction is contacted with a catalyst containing a porous carrier material containing 0.01–2% Pt group metal, 0.1–3.5% halogen and Pb in an amount sufficient to result in an atomic ratio of Pb to Pt group metal of 0.05:1 to 0.9:1. The Pt group metal, preferably Pt itself, is uniformly dispersed throughout the porous carrier material as metal.

Catalyst Comprising an Intermediate Coating of an Oxide of Scandium Yttrium or the Lanthanides and a Platinum Rhodium Top Coating

JOHNSON MATTHEY & CO. LTD.
U.S. Patent 3,839,225

A catalyst consists essentially of an inert material, an intermediate coating containing at least one of the Sc, Y or La oxides and a catalytically active surface coating of an alloy selected from: (1) 1–50% Rh-Pt alloys; (2) 1–50% Rh-Pt-base metal, the base metal from 0.01–25%.

Platinum-Rhodium-Base Metal Catalyst

JOHNSON MATTHEY & CO. LTD.
U.S. Patent 3,840,471

A catalyst consists essentially of an inert material impregnated or coated with an alloy of Pt, Rh and a base metal, the base metal being Ni, Co,Fe, Cu, Nd, In, Sn, Zn, Ag and/or Cr.

Bimetallic Catalyst Preparation

MOBIL OIL CORP. *U.S. Patent* 3,840,475

A supported bimetallic catalyst containing a Pt group metal, which is active in hydroprocessing reactions, is produced by intimately associating a porous Al_2O_3 with a compound capable of furnishing a complex ion containing both the Pt group metal and Sn, for instance ($PtCl_5SnCl_3$) cations.

Isomerisation Catalyst Activation Process

SHELL OIL CO. *U.S. Patent* 3,842,114

A process for activating a catalyst containing one or more Pt group metals supported on H-mordenite, for isomerising aliphatic saturated 4–6C hydrocarbons at temperatures between 200–300°C, e.g. Pt/H-mordenite, consists of dehydration at a specified rate.

Multicomponent Dehydrogenation Catalyst

UNIVERSAL OIL PRODUCTS CO.
U.S. Patent 3,843,560

A catalytic composite is a combination of Pt metal, Ir metal, an alkali or alkaline earth metal oxide and 0.05–0.5% S with a porous carrier material. The Pt and Ir are uniformly dispersed in the carrier material, in amounts giving an atomic ratio of Ir to Pt of about 0.5:1 to about 1.5:1.

Platinum-Magnesium Reforming Catalyst

EXXON RESEARCH & ENGINEERING CO.
U.S. Patent 3,846,281

The octane quality of naphthas is improved by contacting the naphtha in reforming conditions with a porous inorganic oxide support carrying 0.3–3% halogen and 0.01–5% of a hydrogenation-dehydrogenation component which contains a Group VIII noble metal and 0.1–5% of a Group IIA metal halide.

Trimetallic Catalytic Composite

UNIVERSAL OIL PRODUCTS CO.
U.S. Patent 3,846,282

A gasoline fraction is reformed by contacting the gasoline fraction, at a temperature of 800–1100°F, a pressure of 0–1000 p.s.i.g., a liquid hourly space velocity of 0.1–10/hr, and a mole ratio of H_2 to hydrocarbon of 1:1–20:1, with a catalytic composite of 0.1–3.5% halogen, 0.01–2% Pt or Pd, 0.01–2% Ir and 0.01–5% Ni.

Hydrocracking Process for the Production of L.P.G.

UNIVERSAL OIL PRODUCTS CO.
U.S. Patent 3,847,796

A Group VIII metal, especially Pt or Pd, is deposited on a combined support of Al_2O_3 and mordenite to act as a hydrocracking catalyst.

Sulphur-free Reforming with a Platinum-Tin Catalyst

UNIVERSAL OIL PRODUCTS CO.
U.S. Patent 3,847,794

A process for catalytically reforming a substantially S-free gasoline fraction contacts a gasoline fraction and a H_2 stream in reforming conditions with a substantially S-free catalyst combination of 0.01–2% Pt group metal, e.g. Pt or Pd, 0.01–5% Sn and 0.1–3.5% halogen. Sn component is uniformly dispersed throughout the porous carrier material in a particle size which is less than 100 Å in maximum dimension.

Hydroformylation Process and Catalyst

PHILLIPS PETROLEUM CO. *U.S. Patent* 3,847,997

In a hydroformylation process in which an olefin is reacted with CO and H_2, the catalyst is produced by contacting a solid P-containing polymer of at least one vinyl phosphine with at least one Co, Rh, Ru, Pt, and/or Pd carbonyl, the metal being present in an amount of 0.2–20 mmoles of metal per 5g of polymer support.

Hydrocracking Process

UNION OIL CO. *U.S. Patent* 3,849,293

A feedstock is hydrocracked to produce lower boiling hydrocarbons using a Pt group metal catalyst deposited on a siliceous zeolite carrier. When the catalyst is spent it is regenerated using hydrothermal treatment with a 0.1–30% aqueous NH_3 solution. A typical catalyst consists of 0.47% Pd/Y molecular sieve support of the cracking catalyst type.

Hydrogenation of Aromatic Hydrocarbons

TEXACO INC. *U.S. Patent* 3,851,001

In a process for the production of cyclohexane having a purity of at least 99.5%, a mixture consisting essentially of benzene and cyclohexane is passed in the presence of added H_2 into contact with a supported Pt catalyst promoted with 0.01–5% Tl. The catalysts of two examples contain 0.75% Pt and 0.5% Tl/Al_2O_3.

Dehydrogenation Method and Multicomponent Catalytic Composite

UNIVERSAL OIL PRODUCTS CO.
U.S. Patent 3,851,003

A catalyst for dehydrogenating a 2–30C normal paraffin hydrocarbon, alkylaromatic hydrocarbons and naphthenes is a composite consisting of an Sn component and a Pt component on a carrier material which is prepared by impregnating a high surface area, porous carrier material with a solution of a complex chlorostannate(II)-chloroplatinate anionic species. Typically Al_2O_3 is impregnated with 0.6% Pt, 0.5% Sn, 1.5% K and less than 0.2% chloride.

Reforming with Platinum on a New Alumina Support

CHEVRON RESEARCH CO. *U.S. Patent* 3,852,190

A naphtha feedstock is reformed in contact with a catalyst containing 0.01–5% Pt/Al_2O_3 which is obtained by removing water from Al hydroxide produced as a by-product from a Ziegler higher alcohol synthesis reaction and calcined at 1150–1350°F to have a surface area of 165–215 m^2/g.

Reforming Process Catalyst

PHILLIPS PETROLEUM CO. *U.S. Patent* 3,856,660

A process for the catalytic reforming of hydrocarbons consists of contacting at reforming conditions naphtha and H_2 with a catalyst having increased activity and selectivity which is a refractory support promoted with 0.01–5% of Pt, Ir and Ga respectively.

Dehydrogenation with a Nonacidic Multimetallic Catalyst

UNIVERSAL OIL PRODUCTS CO.
U.S. Patent 3,856,870

A method for dehydrogenating a hydrocarbon consists of contacting it with a nonacidic catalytic composite containing a porous carrier material, 0.01–2% Pt or Pd, 0.01–2% Ir, 0.01–5% Ge and 0.01–5% of an alkali or alkaline earth metal, where the Pt or Pd, Ir, Ge and alkali or alkaline earth metal components are uniformly dispersed throughout the porous carrier material.

Catalyst Cartridge

S.A.E.S. GETTERS S.p.A. *U.S. Patent* 3,857,680

Catalyst particles are embedded in thin green ceramic or metal foil sheets which are bent into an arcuate shape and fixed between a heat sink and/or an outer shell. The catalyst particles may consist of Pt group metals, Au and Ag (among others).

Exhaust Purification

KALI-CHEMIE A.G. *French Appl.* 2,216,438

The gas is contacted with a catalyst consisting of a calcined support containing at most 0.5% Pt in combination with 0.5% Ru, Rh or Re.

Dicyanogen Production

ROHM G.m.b.H. *German Offen.* 2,341,370

Dicyanogen is produced by the oxidation of HCN using a metallic Pt catalyst in which up to 50% of the Pt may be replaced by Re. Rh may also be present, e.g. a 90%Pt - 8%Rh - 2%Re alloy in the form of a gauze.

Exhaust Gas Treatment Catalyst

JOHNSON MATTHEY & CO. LTD.
German Offen. 2,431,768

A high stability catalyst for I.C.E. exhaust treatment consists of Ru or a Ru alloy and a metal oxide, especially a Group IIA oxide, able to form a stable mixed oxide or 'ruthenite' with RuO_2. Typically, Ba ruthenite for catalytic purposes is formed from Ba peroxide and Ru sponge.

HOMOGENEOUS CATALYSIS

Oxidising Epoxides to Acids

ATLANTIC RICHFIELD CO. *U.S. Patent* 3,839,376

In the production of carboxylic acids an epoxide of an α-olefin is contacted with a percarboxylic acid oxidising agent in the presence of a Ru containing catalyst selected from Ru metal, inorganic Ru salt and organic Ru salts and an inert paraffinic or halogenated hydrocarbon solvent at the reflux temperature of the solvent. Suitable catalysts are $Ru(CO)_3$, $Na_3[Ru(C_2O_4)_3]$ and Ru tris(ethylenediamine).

Preparation of Carbonyl Compounds

ATLANTIC RICHFIELD CO. *U.S. Patent* 3,847,996

Alcohols and ketones are prepared by reacting ethylene, propylene and/or butylene under effectively anhydrous conditions at 50–150°C with $PdCl_2$ and *t*-butyl alcohol to form alkanols, alkanones and isobutylene.

Hydroformylation Catalyst

MONSANTO CO. *U.S. Patent* 3,855,307

The hydroformylation of 2–6C unsaturated hydrocarbons in the presence of CO and H_2 is catalysed by a multiphase catalyst based on a porous, solid carrier having dispersed in it a liquid catalytic component including a solvent having a vapour pressure at 100°C of from 10^{-12} to 10 mm, and an aryl phosphine complex of Rh.

FUEL CELLS

Fuel Cell Electrode

U.S. SECRETARY OF THE ARMY
U.S. Patent 3,844,839

A hydrazine-air electrochemical cell in which the amount of NH_3 generated is reduced when the cell is operating has an approximate 60% porous Fe plaque anode impregnated with about 3 mg/sq^2 of Pd black, an air cathode and a solution of 2 molar hydrazine in 5 molar K hydroxide as electrolyte.

CATHODIC PROTECTION

Anode Containing Pin-type Inserts

ESSO PRODUCTION RESEARCH CO.
U.S. Patent 3,844,921

An anode for a cathodic protection system or similar electrolytic process has a lead metal anode body and pins extending into the body from the outer surface made from Ta, Ti, Nb, Zr, V and/or their alloys coated with a Pt group metal.

CHEMICAL TECHNOLOGY

Organopolysiloxane Compositions

DOW CORNING CORP. *British Patent* 1,384,008

A few p.p.m. of Pt are used to cure non-hazing siloxane resins for optical use.

Impregnation of Graphite with Ruthenium

JOHNSON MATTHEY & CO. LTD.
U.S. Patent 3,850,668

A method of treating a porous body of C or graphite with Ru consists of removing gaseous fluid from the body, contacting the body with a solution of Ru acetylacetonate, evaporating the solvent and heating to cause the Ru acetylacetonate within the pores of the body to decompose. Even impregnation is obtained as the acetylacetonate sublimes causing an atmosphere of Ru throughout the pores of the body, prior to decomposition.

Palladium (Alloy) Diaphragm

URALSKY ORDENA TRUDOVOGO KRASNOGO ZNAMENI POLITEKHNICHESKY INSTITUT IMENI S.M. KIROVA
French Appl. 2,217,267

Extremely pure H_2 is prepared by passing industrial H_2 or H_2 separated from a mixture of gases through a Pd (alloy) diaphragm at 1 atm and at 200–900°C. Steam is introduced into the gaseous stream before passing through the diaphragm until the partial pressure is 5mm Hg.

ELECTRICAL AND ELECTRONIC ENGINEERING

Electrical Switch Contact

FUJITSU LTD. *British Patent* 1,386,157

In an electrical switch contact, the contact material is an alloy consisting of 45 to 85 at.% of Pd and 55 to 15 at.% of Al, e.g. Pd_3Al or PdAl.

Thick Film Circuit Ink

JOSEPH LUCAS (INDUSTRIES) LTD.
British Patent 1,387,267

The problems of soldering noble metal printed circuits are overcome by diluting the Pd used in an ink with Pb in a 3:1 to 3:2 ratio. The ink also contains a glass frit and a liquid vehicle.

Metal Silicide-Silicon Schottky Barrier

R.C.A. CORP. *U.S. Patent* 3,841,904

A silicon body is cleaned with HF and contacted with a HF/HCl solution of an Os, Ir and/or Pt salt to form a metal silicide layer.

Process for Treating Thermopiles

NUCLEAR BATTERY CORP. *U.S. Patent* 3,842,489

Terminal wires made from Pd, Au, Ni, Au plated Ni or 92% Au–8% Pd alloy are applied to telluride and/or selenide elements under pressure and a capacitance discharge pulse applied to heal defects and irregularities in the elements.

Glass Ceramic Capacitors

E. I. DU PONT DE NEMOURS & CO.
U.S. Patent 3,845,365

Ternary electrodes consist of a metal film of noble metal powder dispersed in an inert vehicle, the powder consisting of 20–90% Au, 2–30% Pd and 3–70% Ag.

Electroconductive Paste Composition

OWENS ILLINOIS INC. *U.S. Patent* 3,846,345

An electroconductive body of material has a plurality of particulate bodies of less than about 10 μm in diameter embedded within a fused glassy matrix of dielectric material. The particulate bodies have a core of dielectric material selected from glass, Al_2O_3, Be or ceramic material and surrounded by material selected from Pd, Rh and/or their oxides and alloys.

Reed Switches with Oxidised Rhodium Contacts

O.K.I. ELECTRIC INDUSTRY CO. LTD.
U.S. Patent 3,857,175

A method of manufacturing a reed switch consists of forming Rh contacts on leads, oxidising the Rh contacts and sealing the leads with the oxidised Rh contacts in a sealed envelope.

Printed Circuit Board Material Incorporating Binary Alloys

THE MICA CORP. *U.S. Patent* 3,857,683

A printed circuit made has an insulating base coated with at least one electrical resistance layer and a highly conductive circuit. A number of binary alloys are suggested for the resistance layer, including alloys of Co with 16–94% Ru and of Pd with 9–40% Mo.

Conductive Ink Composition Containing Palladium and Lead Metal Powders

JOSEPH LUCAS (INDUSTRIES) LTD.
U.S. Patent 3,857,798

An ink for use in the manufacture of a thick film circuit contains Pd powder, Pb powder (the ratio of the weight of the Pd powder to the weight of the Pb powder being in the range of 3:1 to 3:2), an inorganic bonding material and a binder liquid.