NEW PATENTS

CHEMICAL COMPOUNDS

Rhodium and Ruthenium Compositions

INTERNATIONAL BUSINESS MACHINES CORP.
U.S. Patent 3,904,404

A composition of the formula Z_2TX, where Z is Rh or Ru, T is Fe, Co, Ni, V, Cr or Cu and X is Al, Ga, In, Tl, Ge, Sn or Sb, is a useful ferromagnetic material suitable for inductive magnetic recording devices. A typical composition is Rh_2FeSn.

Preparing Electrochemically Active Thallium Palladate

C. CONRADTY *French Appl.* 2,249,038

Thallium palladate ($TlPd_3O_4$) is obtained in a pure crystalline form, cardinal red in colour as a cube with an atom at the centre of each face, for use as an electrochemically active coating for metal anodes.

ELECTROCHEMISTRY

Corrosion Resistant and Dimensionally Stable Electrode for Electrochemical Processes

HOECHST A.G. *British Patent* 1,415,684

The electrode consists of at least one electrically conductive oxido compound of Ru and/or Ir with a metal selected from Ga, In, Cu, Zn, Co and Tl.

Electrolytic Production of Hypochlorite Compositions

DIAMOND SHAMROCK CORP.
British Patent 1,417,949

Hypochlorite is produced by electrolysing an aqueous alkali metal chloride solution. The anode consists of a conductive base carrying a coating formed of 30–90% SnO_2, 1.0–10% Sb_2O_3, 1.0–50% of at least one Pt group metal oxide, and 0.5–30% of a valve metal oxide, e.g. Ta_2O_5.

ELECTRODEPOSITION AND SURFACE COATINGS

Composite Structure

IMPERIAL METAL INDUSTRIES (KYNOCK) LTD.
British Patent 1,412,836

A composite structure consists of a precious metal, particularly Pt, Ir, Rh, Pd, Os, Ru and Au (alloys), bonded to a substrate of a film-forming metal, and is made by assembling a sheet of precious metal foil between a substrate of a film-forming metal having a higher electrical conductivity core and a protection, and a lubrication material.

Activation Method for Electroless Plating

BELL & HOWELL CO. *U.S. Patent* 3,900,320

A plastic or ceramic is coated with a 20–3000 Å film of a mixture of a Pd salt in a binder. A dry film of this thickness is produced from a solution of 0.05 parts $PdCl_2$ and 0.25 parts vinyl chloride copolymer in 100 parts MEK. The coated surface is heated to pyrolyse the binder and the residual metal to catalyse subsequent chemical plating.

Chemical Metal Plating

WESTERN ELECTRIC CO. INC.
U.S. Patent 3,900,614

$SnCl_2/PdCl_2$ sensitising solution is applied to a surface which has the required pattern delineated in reducing agent. Only these patterned areas acquire the required chemical plating nuclei.

LABORATORY APPARATUS AND TECHNIQUE

Catalytic Fluid Heater

INSTITUTE OF GAS TECHNOLOGY
U.S. Patent 3,910,255

The heater has a housing in which is contained a Cu tube formed into a series of concentric helical coils, and a number of perforated Al plates that are supported by the coils in various symmetric locations along the vertical axis of the Cu tube. The undersides of the plates are coated with a catalyst, e.g. of the Pt metal group, for combusting H_2, reformed natural gas or low CO-content manufactured gas. The fluid to be heated flows through the Cu tube.

Oxygen Detector Having a Platinum Electrode on a Zirconia Electrolyte

E. I. DU PONT DE NEMOURS & CO.
U.S. Patent 3,914,169

An O_2 detection device consists of a first electrode layer, an intermediate ZrO_2 layer and a second electrode layer consisting of 76–97.6% Pt and 1.2–12% Al_2O_3 and/or a lanthanide oxide.

HETEROGENEOUS CATALYSIS

Treatment of Platinum Group Metal Reforming Catalysts

THE BRITISH PETROLEUM CO. LTD.
British Patent 1,412,277

The activity of fresh reforming catalysts containing Pt group metal is improved by treatment at 400–550°C with a gas containing 0.5–20% free O_2, 5–500 p.p.m. Cl, HCl, Cl-containing compound, and 50–20,000 p.p.m. H_2O, then stopping the injection of Cl, but continuing the operation

at the same O_2 and H_2O concentrations and the same or reduced temperature and then reducing the catalyst at 350–550°C.

Petroleum Additives

JOHNSON, MATTHEY & CO. LTD.
British Patent 1,414,622

Supported catalysts for I.C.E. exhaust systems are activated or re-activated by supplying a suspension or solution in a hydrocarbon solvent of one or more metals or mixtures or alloys containing one or more metals or compounds selected from Ru, Rh, Pd, Ir, Pt, Ag and Au into the engine exhaust gas stream at a point upstream of the catalyst support, or (b) supplying to the engine a fuel and/or lubricant to which such a suspension or solution has been added.

Ruthenium Promoter

JOHNSON, MATTHEY & CO. LTD.
British Patent 1,415,155

A process for reducing NO_x or oxidising CO and/or hydrocarbons uses a catalyst comprising a support of an inert material, preferably wash-coated and finally impregnated or coated with a metallic mixture or alloy which contains 5–75%, preferably 5–10% Ru; 5–30%, preferably 5–20% base metal chosen from Al, Mg, Cr, Mo, W, Mn, Fe, Co, Ni, Ti, V, Cu, Ag, Zn, Cd, Hg, In, Tl, Bi, Sn, Pb, Sb, the lanthanides and the actinides, and the balance Pt in an amount $\leq$ 5%.

Catalyst for Reducing Nitro-compounds

BAYER A.G. *British Patent* 1,416,612

A supported catalyst for the reduction of nitro-compounds consists of 0.1–10% Pd metal and 0.1–5% V (metal or compound) supported on an Al_2O_3 at least 20% of which has been converted into Li–Al spinel.

1–20% Rh/Pt Catalysts

JOHNSON, MATTHEY & CO. LTD.
British Patent 1,417,544

A catalyst of particular use in the catalytic vapour-phase oxidation of C-containing compounds, e.g. CO and the lower hydrocarbons, but also of use for the reduction of NO_x and the steam reforming of naphtha to produce methane, consists of a support of inert material, an intermediate layer of a refractory oxide, at least 5% of which is constituted by one or more oxides selected from Sc, Y and lanthanide oxides, and finally a layer of a mixture or alloy of Pt and Rh, the Rh being present in less than 20% of the total metal content of the mixture or alloy.

1–20% Rh/Pt Catalysts – Oxidation Process

JOHNSON, MATTHEY & CO. LTD.
British Patent 1,417,545

A process for the purification of a gas containing a C compound and O_2 comprises contacting the gas at an elevated temperature with an oxidation catalyst comprising an inert support carrying a layer of a mixture or alloy of Pt and Rh, the Rh constituting less than 20 wt.% of the total metal content of the mixture or alloy.

1–20% Rh/Pt Catalysts – Reduction Process

JOHNSON, MATTHEY & CO. LTD.
British Patent 1,417,546

A process for the purification of a gas containing an oxide of nitrogen comprises contacting the gas at an elevated temperature and together with a reducing fuel with a catalyst comprising an inert support carrying a layer of a mixture or alloy of Pt and Rh, the Rh constituting less than 20 wt.% of the total metal content of the mixture or alloy.

Regeneration of Damaged Zeolite-supported Metal Catalysts

UNION OIL CO. OF CALIFORNIA
U.S. Patent 3,899,441

Pd or Pt oxide catalysts finely divided on a zeolite support are regenerated by hydrating and ammoniating to produce, e.g. $Pt(NH_3)_4(OH)_2$ or $Pt(NH_3)_6(OH)_4$ which being stronger bases than NH_4OH will tend to combine with the original acid sites on the support. The catalyst is then dried and calcined in a dry, oxygen-containing gas stream at a controlled temperature between 500 and 1200°F.

Ruthenium-Zinc Oxide Catalyst for Steam Reforming

BRITISH GAS CORP. *U.S. Patent* 3,904,544

A catalyst composition for steam reforming hydrocarbons to produce gases containing a major proportion of methane, consists of 1–20% Ru, 30–50% Zn oxide and 65–35% of an Al_2O_3 carrier, the catalyst being prepared by co-precipitation from a solution of water soluble salts of Ru, Zn and Al.

Catalytic Ignition System

INSTITUTE OF GAS TECHNOLOGY
U.S. Patent 3,909,187

A supported Pt or Pd catalyst is used in a pilot ignition system for gas appliances which utilises a short-circuited, air-starved electrochemical cell or battery with an inert electrode and a metal electrode which will produce a small flow of pure H_2 gas which is ignited on the catalyst.

Refractory Metal Oxide Coated Ceramic Honeycombs as Catalyst Support

JOHNSON, MATTHEY & CO. LTD.
U.S. Patent 3,909,452

A catalyst for the oxidation of organic compounds which would otherwise cause atmospheric contamination consists of an inert rigid porous refractory ceramic honeycomb coated with a first adherent catalytically active refractory metal oxide coating containing at least 50% Al_2O_3 in which one or more of the oxides TiO_2, ZrO_2, HfO_2 and

ThO_2 constitute at least 50% of the refractory metal oxide and having a second coating of an alloy containing 1–50% Rh, 0.01–25% base metal selected from Cr, Fe, Co, Ni, Cu, Ag, Zn, In, Sn and Nd and balance Pt.

Layered Rhodium and Nickel Catalyst for NO_x Reduction

MONSANTO CO. *U.S. Patent* 3,914,376

I.C.E. exhaust gases are treated to remove NO_x in reducing conditions with a catalyst consisting of Ni fixed on an inert support and having Al_2O_3 deposited over the Ni and Rh dispersed on the Al_2O_3.

Rh/Pt – Stainless Steel Catalyst

JOHNSON, MATTHEY & CO. LTD.
U.S. Patent 3,915,898

In an arrangement for reacting at least two gases by passing them through a pack of catalytic gauzes, the pack consists of a first group of gauzes made of an alloy consisting essentially of Pt and Rh and a second group of gauzes disposed on the downstream side of the first group of gauzes for supporting the first group, the second group of gauzes being made of an alloy consisting essentially of Pt, Ni and Cr. The system is typically used in the oxidation of NH_3 gas to oxides of N and H_2O during the manufacture of HNO_3, and the second group of gauzes are made from an alloy containing 16% Pt, 67% Ni, balance Cr.

Paraffin Hydroisomerisation Process

W. R. GRACE & CO. *U.S. Patent* 3,917,739

A process for hydroisomerisation of 4–7C paraffins, at 400–650°F, 300–500 p.s.i.g. and H_2 to hydrocarbon mole ratio of 3–10 : 1 uses a catalyst consisting of 0.1–1.5% Pt and/or Pd and 0.1–5% CeO_2, the Pt or Pd homogenously dispersed as crystallites in the 5–30 Å size range, the metal being dispersed into H_2 form mordenite by contacting the base with a mixed solution of Pt or Pd nitrate and Ce nitrate followed by controlled calcination and reduction with H_2 at a temperature of 500–900°F.

Preparing Catalysts for Hydrocarbon Hydrotreatment

COMPAGNIE FRANCAISE DE RAFFINAGE
French Appl. 2,252,394

Hydrocarbon treatment catalyst consists of a refractory mineral oxide support which has acid sites and includes a halogenic element and the free or combined metals (a) 0.02–2% at least one Pt group metal, (b) 0.02–2% at least one of Zr, Ti and W, (c) optionally 0.05–1% Sn.

Metallic Substrate Catalysts

JOHNSON, MATTHEY & CO. LTD.
French Appl. 2,257,336

A catalyst consists of a drawn metal support constituted by an Fe alloy which is heat and oxidation resistant and which contains at least one of: 3–40% Cr, 1–10% Al, traces –5% Co, traces –72% Ni and traces –0.5% C, a first layer on the drawn metal support, consisting of an adherent coating containing O_2, e.g. as an oxide such as Al_2O_3, SiO_2, Ti, Zr, etc., oxides, and a second catalytic layer including a metal chosen from Ru, Rh, Pd, Pt, Ag, Au and Ir, an alloy containing at least one of three metals, and alloys containing at least 10% of one of these metals and a base metal. The catalysts are useful in, e.g. oxidation of NH_3 in the manufacture of HNO_3, oxidation of organic compounds, e.g. methane, and reduction of NO_x in I.C.E. exhausts.

HOMOGENEOUS CATALYSIS

Improving the Dispersibility of Small Metallic Magnetic Particles in Organic Resin Binders

INTERNATIONAL BUSINESS MACHINES CORP.
British Patent 1,416,127

0.1% $PdCl_2$ is used in a solution in which particles of Co-P are prepared by reacting a solution of a hypophosphite anion reducing agent and Co cations which are reducible to Co metal, the process including the step of reacting the Co-P particles with a H_2SO_4-containing solution to improve the dispersion characteristics of the particles in an organic resin.

Carbalkoxylation and Carboalkoxylation of Olefins

E. I. DU PONT DE NEMOURS & CO.
U.S. Patent 3,906,015

The carbalkoxylation or carboalkoxylation of olefins is catalysed by L_2MXY, where M is Pt or Pd, X and Y are halogen or pseudohalogen and L is a phosphine, phosphite or thiophosphite, e.g. dichlorobis (methyl diphenyl phosphinite) Pd(II) used in the conversion of hexene to methyl-*n*-hexanoate.

Oxo-reaction for Triethanolmethane and Methylpentanediol

CHEVRON RESEARCH CO. *U.S. Patent* 3,912,785

Triethanolmethane and 3-methyl-1, 5-pentanediol are produced by contacting a mixture of 3-methylene-1,5-pentanediol and 3-methyl-2-pentene-1, 5-diol with a rhodium carbonyl complex catalyst in homogeneous liquid phase with the mixture and in the presence of CO at a partial pressure of 25–5,000 p.s.i.g. and H_2 at a partial pressure of 50–10,000 p.s.i.g. and at a temperature of 75–250°C for a time sufficient to react at least 90% of the olefinic double bonds.

Hydroformylation of Unsaturated Organic Compounds

UNION CARBIDE CORP. *U.S. Patent* 3,917,661

A hydroformylation catalyst to produce aldehydes is a complex of Rh, CO and a phosphine or

phosphite ligand. A claimed catalyst is used in the combination 84g (1.0 mole) hex-1-ene, 150g acetophenone, 25g tri-n-butylphosphine and 2.0g tris(triphenylphosphine) Rh carbonyl hydride, which upon charging with $CO+H_2$ synthesis gas and heating to 80°C, gave a product with 85% unreacted hex-1-ene and 15% aldehydes.

CHEMICAL TECHNOLOGY

Recovery of Platinum Group Metals

MATTHEY RUSTENBURG REFINERS (PROPRIETARY) LTD. *French Appl.* 2,254,648

Pt, Rh and Ir salts in aqueous solutions are separated and purified by (a) adjusting the pH of the solution, (b) contacting the acid solution with an oxidising agent to oxidise all the Ir present to Ir(IV), (c) contacting the oxidised solution with an organic compound including N_2 chosen from the group formed by secondary or tertiary amines, and quaternary ammonium compounds, and (d) withdrawing from the oxidised solution an organic phase including practically all the Pt and Ir present associated with the organic compound used in (c). The Ir is subsequently separated from the organic phase containing Pt by, (e) contacting the organic phase with an aqueous solution of a reducing agent.

Platinum Group Metals Separation using H_2SO_4

MATTHEY RUSTENBURG REFINERS (PROPRIETARY) LTD. *German Offen.* 2,512,559

A process for refining and separation of Pt group metals from mixtures also containing Ag and base metals comprises contacting a solid, particulate mixture, preferably a powder, of the metals or metal compounds with concentrated H_2SO_4 at a temperature sufficient to convert the base metals and Ag to H_2O-soluble sulphates and dissolving out these sulphates into dilute H_2SO_4 or H_2O to leave a residue rich in precious metals.

GLASS TECHNOLOGY

Transparent Glass or Plastic with a Heat Reflecting Metal Layer

W. C. HERAEUS, G.m.b.H.
British Patent 1,419,036

Transparent glass or plastics has an intermediate layer of a volatilisable metal compound deposited on one side of it, and on the compound is deposited a heat reflecting Ag alloy layer which consists of 80–95% Ag, and 5–20% of one or more of Pd, Ni, Cd, and Si. The alloy layer has a transmission of light in the visible spectrum of 35–60%.

Formation of Phosphate Glass

GELSENBERG A.G. *British Patent* 1,421,219

During formation of a phosphate glass from a solution or slurry of radioactive waste materials, the solution is denitrated because of the volatility of Ru at high temperature.

ELECTRICAL AND ELECTRONIC ENGINEERING

Metallising Compositions

E. I. DU PONT DE NEMOURS & CO.
British Patent 1,419,549

A metallising composition, especially useful for printing metals on to substrates prior to firing to make electrical, e.g. microcircuit elements consists of finely divided metal particles, e.g. Pd and/or Au and/or Ag and/or Pt, dispersed in a long-chain saturated polymer of castor oil.

Low Temperature Coefficient of Resistivity Cermet Resistors

GLOBE-UNION INC. *U.S. Patent* 3,899,449

A cermet resistor composition having a low temperature coefficient of resistivity for firing on a substrate composed of high temperature, electrically nonconductive material consists of a conductive phase of 1.00–10.00% V oxide and 1.00–30.00% RuO_2 and 50.00–98.00% of an interdispersed glass phase. The glass phase is composed of 35.00–45.00% Pb oxide, 15.00–25.00% B_2O_3 and 30.00–40.00% SiO_2.

TEMPERATURE MEASUREMENT

Thick Film Resistance Thermometer

JOHNSON, MATTHEY & CO. LTD.
British Patent 1,415,644

A temperature sensitive element for use as part of a resistance thermometer consists of a substrate of electrically non-conducting material, e.g. a wafer of Al_2O_3, carrying an electrically conducting tortile path consisting of fused vitreous material loaded with electrically conducting particles made from a metal chosen from the group Au, Ag and the Pt group metals.

MEDICAL USES

Pharmaceutical Platinum Compositions

RUSTENBURG PLATINUM MINES LTD.
U.S. Patent 3,904,663

A complex active against tumours in mice is a Pt(II) complex of an optionally substituted *o*-phenylenediamine, e.g. a $PtCl_2$-4,5-dimethyl-*o*-phenylenediamine complex.

Dental Gold Alloy

DEUTSCHE GOLD- & SILBER-SCHEIDEANSTALT
German Offen. 2,424,575

An alloy which adheres to porcelain contains 80–90% Au, 5–15% Pt, 0.1–2% In, 0–2% Sn, 0.05–0.5% Ir and 0.5–3% Rh.