

NEW PATENTS

CHEMICAL COMPOUNDS

Oxygen Centred Ruthenium Acetate

JOHNSON, MATTHEY & CO. LTD.

British Patent 1,405,592

A compound cation or anion has the general formula— $M^1M^2M^3XAn_6L^1L^2L^3$ in which $M^1M^2M^3$ are the same or different metals selected from the Pt group excluding Os; X is oxygen, and An is an anionic radical in the form of an acyloxy group (OCOR) when R is alkyl or aryl and L^1, L^2 or L^3 are neutral or anionic ligands.

New Palladium Compound

SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.

British Patent 1,409,994

$HPd(CN)_3$ is prepared by reacting $(Pd(CN)_2)$ with a 1–10% aqueous hydrogen cyanide solution at 70–90°C for 0.5–5 h. The $HPd(CN)_3$ is used in the preparation of high molecular weight copolymers of CO with ethylenically unsaturated compounds. A further method of producing the $HPd(CN)_3$ includes reacting an aqueous solution of the salt of the acid $H_2P(CN)$ with a cation exchange resin in the acid form.

ELECTROCHEMISTRY

Electrodes with a Delafossite Surface

P.P.G. INDUSTRIES INC. *British Patent 1,400,948*

Electrodes for electrochemical reactions are provided with an electrocatalytic layer having the delafossite structure (similar to that of $CuFeO_2$): some specific delafossites claimed contain Pt/Co, Pd/Co, Pd/Cr, Pd/Rh, Pd/Ru, Pd/Pb, Pd/Y, Pd/lanthanide, Ag/Co, Ag/Gd and Ag/Sc.

Electrolytically Etching Thin Films

WESTERN ELECTRIC CO. INC.

British Patent 1,408,352

A thin film containing Au, Pt and/or Rh is treated by immersing it together with an auxiliary electrode and a reference electrode in an electrolyte and applying a potential, which varies periodically between 1600mV and –60mV with respect to the reference electrode, between the film and the auxiliary electrode. The potentials are measured on the H scale and their upper values are 900–1100mV for etching Rh with respect to Pt and Au.

ELECTRODEPOSITION AND SURFACE COATINGS

Bright Rhodium Electroplating

DEUTSCHE GOLD- & SILBER-SCHIEDANSTALT

British Patent 1,402,521

Bright plated coatings are deposited from a Rh

sulphate or phosphate bath containing free acid and 50 mg/l–10 g/l of chloride in the form of one or more Group IA, IIA, Al and/or Cr chlorides. In an example 1g/l chloride, as Mg chloride is added to a bath containing 40g free H_2SO_4 and 2g Rh sulphate.

Electroplating Rhodium-Rhenium Alloys

OXY METAL INDUSTRIES CORP.

U.S. Patent 3,890,210

Brighter coatings are obtained by plating from an electroplating bath containing Rh and Re compounds in the ratio of 4 to 1 than if the Re is omitted. Suitable compounds for use in the bath are Rh sulphate, sulphamate or phosphate and perrhenic acid or its alkali metal or ammonium salts.

Electrodepositing Rhodium-Ruthenium Alloys

OXY METAL INDUSTRIES CORP.

U.S. Patent 3,892,638

Deposition obtained from electroplating baths containing Rh and Ru in proportions of 10 to 200 to 1 shows improved brightness and reduced stress cracking as compared to similar deposits from Rh-Pt baths. In an example a plating bath contains 100g sulphamic acid, 25g sulphonic acid, 2g Rh as sulphate and 0.05g Au as $K_3N[RuCl_4H_2O]_2$ in each litre of H_2O .

LABORATORY APPARATUS AND TECHNIQUE

Flame Ionisation Detector

THE FOXBORO CO.

British Patent 1,406,572

A flame-proof corrosion-free flame ionisation detector with a collector electrode, a burner electrode, an air intake port and an exhaust port, has an ignitor constructed of Pt.

Oxygen Concentration Measuring Cell

PHILLIPS ELECTRONIC AND ASSOCIATED INDUSTRIES LTD.

British Patent 1,407,928

Rings in a measuring cell for determining O_2 concentrations in a gas mixture consist of a metal which is coated with Pt black or the rings may be made of Pt.

HETEROGENEOUS CATALYSIS

Platinum/Rhodium Supported Catalysts

JOHNSON, MATTHEY & CO. LTD.

British Patent 1,401,002

A catalyst for organic compound oxidation, NO_x reduction with a reducing fuel and CH_4 production by the steam reforming of naphtha consists of a cellular and/or macroporous inert support, coated with an intermediate layer of one or more

refractory oxides of Ti, Zr, Hf and Th and finally with an alloy or mixture of 1-50% Rh and 99-50% Pt. The alloy may also contain up to 25% Ag or a base metal or a metalloid.

Water Recombination Catalyst

ACCUMILATORENIVERK HOPPECKE CARL ZOELLNER & SOHN
British Patent 1,401,818

H and O recombination to form H₂O is catalysed by a cylindrical porous coherent carrier of high thermal conductivity supporting a Pt group metal. Typically the catalyst consists of Pd deposited on a Cu-filled hollow Al₂O₃ cylinder.

Oxidation of Sulphur Compound

BRITISH PETROLEUM CO. LTD.

British Patent 1,404,513

Dialkyl sulphide, aromatic S compounds and other compounds containing S are oxidised to sulphones and/or sulphoxides in the presence of a supported Ru catalyst or a solution of a compound of Ru, Au, Cu, Ir, Os, or Fe containing halide, diketone or acetate ions. Suitably 0.1-1.0% Ru is deposited on Al₂O₃.

Rh/Pt Stainless Steel Catalyst

JOHNSON, MATTHEY & CO. LTD.

British Patent 1,404,576

Catalytic gauzes, for catalysing a reaction between two or more gases passing through them, are arranged so that a first group of gauzes are made from a precious metal alloy, particularly an Rh-Pt alloy, and a second group of gauzes are disposed so that in use they are downstream of the first group and are made of e.g. stainless steel.

Neodymium Oxide Promoter

JOHNSON, MATTHEY & CO. LTD.

British Patent 1,405,405

A catalyst of particular value in the purification of exhaust gases consists of an inert material, an intermediate coating containing one or more oxides of Sc, Y or a lanthanide and a final coating of a mixture or alloy of Pt, Rh and optionally a base metal. Rh comprises 1-50% and the base metal 0.01-25% of the total metal content. The base metal may be 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 the actinides. The intermediate coating is preferably activated Al₂O₃ containing up to 50% of a zeolite converted to Nd form.

Platinum-Tin Reforming Catalyst

EXXON RESEARCH & ENGINEERING CO.

U.S. Patent 3,883,419

Supported hydrocarbon conversion catalysts containing a Pt group metal and Sn are prepared by impregnating the support with a solution of a Pt group halogen acid, drying, impregnating the composite with a solution of a divalent Sn compound in an atmosphere which is non-

reducing and non-oxidising and finally drying. H₂PtCl₆ and SnCl₂ are suitable compounds for use in impregnating an Al₂O₃ support.

Ruthenium Catalyst for Methane Production

INSTITUTE OF GAS TECHNOLOGY

U.S. Patent 3,884,838

The activity of Ru, used alone or up to 50% alloyed with Pt, in the conversion of CO and/or CO₂ plus H₂ to CH₄ is increased by the presence of reduced amorphous W oxide, preferably in an amount of 5-20%.

Three Metal Catalyst Preparation

CIE FRANÇAISE DE RAFFINAGE

U.S. Patent 3,886,061

Hydrorefining catalysts are prepared by using 0.02-2% Sn to modify the Al₂O₃ support before 0.02-2% each of Pt and Ir are deposited. The Sn is considered to make the support more accessible to the Pt.

Sulphided Bimetallic Catalytic Composite

UNIVERSAL OIL PRODUCTS CO.

U.S. Patent 3,888,763

Reforming a gasoline fraction to produce a high octane reformat is catalysed by a porous carrier material containing 0.01-2% Pt group metal, 0.05-1% S, 0.1-3.5% halogen and Bi in an amount giving an atomic ratio of Bi to Pt group metal of 0.1 : 1 to 1 : 1. The Pt group metal and Bi are uniformly dispersed throughout the porous carrier material and are present in the elemental metallic states.

ICE Exhaust Gas Oxidation

W. C. HERAEUS G.M.B.H. *U.S. Patent* 3,893,950

ICE exhaust gases are subjected to oxidative purification over a catalyst consisting of a Pt group metal deposited on a support coated with boehmite. For example a honeycomb tube may be coated with a suspension of boehmite in Al nitrate solution and heated at 250°C. After a second coating has been applied it may be impregnated with chloroplatinic acid solution.

Hydrogenation of Chloronitrobenzenes using Noble Metal Catalysts Treated with a Sulphoxide and a Hydrazine

DEUTSCHE GOLD- & SILBER-SCHNEIDANSTALT

U.S. Patent 3,897,499

A process of selectively hydrogenating chloronitrobenzene or chloronitrobenzene substituted on the benzene ring with lower alkyl to chloroaminobenzene or chloroaminobenzene similarly substituted on the ring uses as a catalyst Pt or Pd on activated C, the catalyst having been prepared by treating the noble metal on activated C with a sulphoxide of the formula RSOR' where R and R' are alkyl, aralkyl or aryl and then with a hydrazine material having the formula R''₃NHNH₂ where R'' is H, alkyl, aryl, aralkyl or alkenyl.

Hydrogenation Catalyst

ATLANTIC RICHFIELD CO. *U.S. Patent* 3,898,298

A butadiene stream contaminated with vinyl acetylene is hydrogenated to convert the vinyl acetylene only in presence of Pd on Al_2O_3 at about 45°C.

Ruthenium and Platinum Exhaust Gas Catalyst

JOHNSON, MATTHEY & CO. LTD.

French Appl. 2,241,339

A catalyst for the treatment of exhaust gases contains Ru or its alloy and a metal oxide which is capable of forming a stable mixed oxide with RuO_2 . The catalyst is preferably of formula $A_2B_2O_7$, ABO_3 , B_2O_3 or AB_2O_4 (A is Na, K, Ca, Sr, Ba, Ag, Cd, Hg, Pb, Bi, Y and the lanthanides; B is Ru and optionally cations of Li, Mg, Cr, Nb, Pd, As, Au, Ga, In, Rh, Sb, Si, Ti, Hf, Ir, Mo, Os, Pt, Re, Sn, Zr, W, Ta, Mn, Fe, V or Co).

NO_x Removal Catalyst

JOHNSON, MATTHEY & CO. LTD.

German Offen. 2,509,204

A NO_x removal catalyst is either a compound of formula A_xBO_y , where A is a Group IA, Group IIA or lanthanide metal, Ba, Pd, Tl, Cu, NH_4 , Ag, Ni or H, B is Pt, Ti, V, Nb, Mo, Ta, W and Re, x is 0-2 and y is 2-3, or a compound of formula $C_xD_3O_4$, where C is Na, Mg, Ca, Ni, Cd or Sr, D is Pd or Pt and x is 0-1.

HOMOGENEOUS CATALYSIS

Production of Carboxylic Acids

MONSANTO CO. *British Patent* 1,406,672

A carboxylic acid is produced by reacting an ethylenically unsaturated hydrocarbon having 2-30 C atoms with CO and H_2O at 50-300°C over an Ir or Rh compound or metal catalyst. A halogen-containing promoter (other than Ir or Rh halide), the ratio of atoms of halogen in the promoter to atoms of Ir or Rh in the compound being from 1:1 to 2500:1, and a trialkylphosphine oxide, triarylphosphine oxide, trialkylarsine oxide, trialkylamine oxide or a trialkylstibine oxide stabiliser are also present.

Oxidation of Substituted Olefinic Compounds

SNAMPROGETTI S.p.A. *British Patent* 1,407,480

Oxidation of an olefinic compound substituted in the 1- or 2-position with respect to the double bond by an electron attracting atom or group, to yield a derivative of glycolaldehyde containing at least 2 ester groups, is carried out with a compound of Pd, Pt, Rh or Ru in the presence of ions of formula $R'O^-$ or $R''COO^-$ in which each of R' and R'' , which can be the same or different, is an alkyl or cycloalkyl radical having up to 8 C atoms. Chloride and vinyl acetate are reacted in the presence of acetic anhydride.

Hydrogenation Catalysts

DIAMOND SHAMROCK CORP.

U.S. Patent 3,890,329

The hydroxides of Group VIII metals such as Co, Ru, Pd, Rh and Ni are employed in an undried, unsupported state (e.g. a $Ru(OH)_3$ paste) as catalysts for hydrogenation of unsaturated cyclic compounds such as benzene, pyridine and substituted pyrroles and pyrrolines.

Rhodium Complex Catalysts

DOW CORNING *U.S. Patent* 3,890,359

Rh (III) complexes of general formula $RhX_3(SR'_2)_3$, where at least one R' represents R_3SiQ^- , are useful as catalysts for reactions between aliphatic unsaturated compounds and compounds containing Si-bonded H. Examples are $RhCl_3(EtSCH_2SiMe_2)_3$, or corresponding compounds containing a Bu or Ph instead of Et and $RhCl_3S[(CH_2SiMe_2)_2]_2$.

Olefin Carboxylation Catalyst

TEXACO INC. *U.S. Patent* 3,892,788

Olefins are carboxylated with CO and hydroxyl-containing reactants in presence of a three component catalyst consisting of a ligand stabilised PdK_2 and a Group IVB metal halide. In an example a $PtCl_2[AsPh_3]_2.SnCl_2$ catalyst is used.

Oxidative Coupling Process

UBE INDUSTRIES LTD. *U.S. Patent* 3,895,055

Aromatic compounds having at least two H atoms in the aromatic nucleus are coupled by reaction with O_2 in the presence of an organic Pd compound. For example bitolyl may be obtained from toluene in the presence of Pd benzoate.

CHEMICAL TECHNOLOGY

Metal Oxide Fibres

IMPERIAL CHEMICAL INDUSTRIES LTD.

British Patent 1,402,544

Mixed metal alkoxy are spun in a viscous state and then the fibres are heated to form metal spinels, among them Ru titanate and Ag molybdate and tungstate.

Rhodium in Photographic Emulsions

EASTMAN KODAK CO. *British Patent* 1,402,748

Photographic emulsions with good storage stability are obtained by precipitating Ag halide grains in the presence of a Rh salt and then adding a manganous salt, optionally together with Cd bromide. Rh chloride, trichloride and ammonium chloride are suitable H_2O soluble salts used in amounts of 0.01-0.25 mg per mole of Ag halide.

Rhodium-Platinum-Iridium Separation

MATTHEY RUSTENBURG REFINERS (PROPRIETARY)

LTD. *German Offen.* 2,459,098

A parent solution containing Rh, Pt, Ir and the

usual impurities is acidified and oxidised to form Ir(IV) which is removed with a secondary or tertiary amine or their ammonium salt which gives a complex with the Ir that may be extracted into an organic phase together with the Pt. Reduction of the organic phase releases the Ir which may be recovered. N-Dodecyl (trialkylmethyl)amines are one class suitable for extraction.

Palladium Separation from Other Platinum Metals in Solution

MATTHEY RUSTENBURG REFINERS (PROPRIETARY) LTD. *German Offen.* 2,459,099

An aqueous solution containing Pt group metals is adjusted to an acidic pH value and contacted with an organic phase containing an oxime which extracts the Pd from the aqueous solution. The complexing agent is preferably a 1-hydroxyoxime of formula $RR'C(OH)-C(NOHR)R''$, where R, R' and R'' are hydrogen, alkyl, aryl, aralkyl, alkaryl, etc., and R and R' may together with the C atom form a benzene ring.

ELECTRICAL AND ELECTRONIC ENGINEERING

Thin Film Devices

MULTI-STATE DEVICES LTD.
British Patent 1,408,122

V oxide thin film devices having a low ohmic contact resistance consist of (a) a plate-like electrically insulating substrate, (b) spaced Pt contacts deposited on the substrate, and (c) a thin film of V oxide deposited on the substrate and bridging a portion of the spaced Pt contacts.

Dielectric Compositions

E. I. DU PONT DE NEMOURS & CO.
British Patent 1,408,256

A glass frit useful as a sintering or densification aid for Al_2O_3 and which can be co-fired with Pd metallisations, consists of 30-50% SiO_2 , 5-20% Al_2O_3 , 14-26% of one or more alkaline earth metal oxides, 1-15% TiO_2 , 1-10% ZnO and 1-10% PbO .

Platinum Contacts

MULTI-STATE DEVICES LTD.
U.S. Patent 3,886,578

An insulating substrate of a thin film device has Pt contacts partly covered with a thin film of V oxide as circuit elements. The remaining surface is covered with Au.

Ohmic Contact with a Semiconductor Substrate

NIPPON ELECTRIC CO. LTD.
U.S. Patent 3,887,993

W, Pt or Mo, which contains at least one kind of impurity, such as As, B, P or Sb is deposited on

a semiconductor substrate with a conductivity type opposite to the impurity contained in the metal. The metal layer is then heated to diffuse the impurity into the semiconductor to form the p-n junction. At the same time a compound is formed which serves as an ohmic contact with the semiconductor body at the region in which the impurity is diffused.

Ohmic Contacts to Silicon

BELL TELEPHONE LABORATORIES INC.
U.S. Patent 3,889,359

An ohmic contact on a relatively high resistivity n-type Si is made by forming a thin layer of Pt on the Si surface by means of chemical vapour deposition using a phosphorus compound of Pt such as liquid $Pt(PF_3)_4$.

Silicon Semiconductor Component Contact

LICENTIA-PATENT-VERWALTUNGS-G.m.b.H.
U.S. Patent 3,893,160

A resistive connecting contact suitable for high frequency transistors includes a Si semiconductor component on which are deposited successive layers of Pt silicide and Ti, Mo and Au metals by vacuum or by sputtering.

TEMPERATURE MEASUREMENT

Encapsulating Thermistors

STANDARD TELEPHONES & CABLES LTD.
British Patent 1,407,583

A thermistor bead for operating at high temperatures, e.g. 1000°C, has Pt leads welded to a Ni/Fe alloy hair pin.

MEDICAL USES

Electrodes for Implantation Battery

D. BURNEL ET AL. *British Patent* 1,405,185
A tubular Pt or iridised Pt cathode is used with a Mg or Mg alloy anode in an implantable heart pacemaker operating by bio-galvanic energy.

Muscle Stimulating Electrode

CORDIS CORP. *British Patent* 1,405,360
An electrode for muscle stimulation consists of a member made of Ti and having a portion adapted to make electrical contact with the stimulation site, and an element made of Pt and located in the contact-making portion of the Ti member.

Platinum Compositions

RUSTENBURG PLATINUM MINES LTD.
U.S. Patent 3,892,790

A composition active against tumours in mice comprises a *cis* coordination compound of Pt containing alicyclic amine groups such as $PtCl_2$ -bis-cyclopropylamine and $PtCl_2$ -bis-cyclopentylamine.