X-ray diffraction studies carried out on thick polycrystalline RuO_2 films, obtained by decomposition of $RuCl_3$, show that below 700°C the conductivity and lattice constant depend on Cl content but above 800°C the conductivity depends only on temperature and has a positive coefficient. The films are shown to be Cl-doped oxide.

TEMPERATURE MEASUREMENT

The Movable-junction Stationary-lead Thermocouple

E. G. MURDOCK and E. H. MCLAREN, *Rev. Sci. Instrum.*, 1972, **43**, (5), 787–790

Two types of movable-junction Pt : 10%Rh-Pt research thermocouples have been developed, one to measure temperature and low gradients accurately from 0–1100°C and the other to determine the immersion characteristics of each thermoelement of a couple.

A Method for the Control and Measurement of Wire Temperature in Preparatory Anneals on Standard Pt/Pt-10Rh Thermocouples

E. H. MCLAREN, E. G. MURDOCK and C. G. M. KIRBY, *Rev. Sci. Instrum.*, 1972, **45**, (5), 827–828

A method is described for annealing Pt : 10% Rh-Pt thermocouples at 0–1450°C (particularly at 450°C) by means of a 60Hz heating current and simultaneously measuring and controlling the temperature to ±10°C using the d.c. thermal e.m.f.

NEW PATENTS

METALS AND ALLOYS

Lead Alloys

BADISCHE ANILIN- & SODA-FABRIK A.G.
British Patent 1,293,031

The corrosion resistance of Pb alloys is improved by adding 0.05–0.2% Pd.

Nitrogen-free Platinum Powders

E. I. DU PONT DE NEMOURS & CO.
U.S. Patent 3,667,935

N_2-free Pt powders are prepared by precipitation from an aqueous $PtCl_2$ solution with Zn and HCl. This N_2-free Pt powder is relatively coarse and can be used in the production of various electrical circuit structures.

Dental Alloy

AURIUM RESEARCH CORP. *U.S. Patent* 3,667,936

An alloy for dental frames which are to carry ceramic coverings contains 8–50% Pd, 3–12% In and the remainder mostly Au or Au and Ag.

CHEMICAL COMPOUNDS

Production of Platinum and Palladium Complexes

PHILLIPS PETROLEUM CO. *U.S. Patent* 3,671,560

Elementary Pd or Pt is reacted directly with a trisubstituted phosphine to give a zerovalent complex with 4 phosphine groups, e.g. $Pd(PPh_3)_4$.

Rhodium-Tellurium Oxide

SOLVAY & CIE. *French Appl.* 2,099,648

A new compound of Rh and Te has the formula Rh_2TeO_6. It crystallises as a trirutile tetragonal system. It can be used as a semiconductor, catalyst, electrode material etc. The tungsten analogue Rh_2WO_6 has similar properties (*French Appl.* 2,099,649). *French Appl.* 2,099,647 is more general and covers the A_2BO_6 compounds where A is Co, Cr, Fe, Mn, Al, Ga, Ir, Rh or V and B is Te, W, Mo, Re. Pt group metal–Te oxides as electrochemical electrodes are covered by *French Appl.* 2,099,650.

ELECTROCHEMISTRY

MATSUSHITA ELECTRIC INDUSTRIAL CO. LTD.
British Patent 1,284,279

The catalyst for an electrode of an electrochemical cell is made by reducing a mixed solution of a U compound and an active catalyst metal compound of a Pt group metal to produce a U-containing active catalyst metal.

Electrolysis Electrode Coating

P.P.G. INDUSTRIES INC. *U.S. Patent* 3,663,414

An anode for the electrolysis of an aqueous solution includes an electroconductive base member, typically Ti, and an electroconductive coating or surface including an inner layer of a Pt group metal and an outer layer of a Pt group metal oxide.

Electrochemical Electrodes

SOLVAY & CIE. *U.S. Patent* 3,668,005

Electrochemical electrodes are made by coating a base with RuO_2. The base electrode, consisting of Ti, Ta, etc., is first etched and coated with an oxidisable substance, such as an oil, grease or hydrocarbon. The coated surface is then exposed to RuO_4 which oxidises the coating and deposits RuO_2.

Electrode for a Conducting Cell

E. SLEVOGT *German Offen.* 2,061,976

A cell for measuring electrical conductivity is provided with an electrode made with a Pd skeleton or of compressed Pd powder.

Electrolysis Electrodes

METALLGESELLSCHAFT A.G.

German Offen. 2,100,652

Electrolysis electrodes are made from a graphite body coated with a Pt group metal or metal oxide and fixed with a chemically resistant layer, e.g. TiO_2.

ELECTRODEPOSITION AND SURFACE COATINGS

Pt Thin-film Metallisation Method

TEXAS INSTRUMENTS INC. *U.S. Patent* 3,657,029

Pt thin-film metallisation layers are selectively etched with aqua regia using a Cr or Ti film as the mask. For example, an integrated circuit structure is metallised with successive layers of Ti, Pt, Au and a metal selected from Mo, W, Re and corrosion-resistant alloys.

Rhodium-Platinum Electroplating

SEL-REX CORP. *U.S. Patent* 3,671,408

A Rh-Pt alloy is electrodeposited from a bath containing, per litre, 0.1–15g Rh as sulphate, 0.04–24g Pt as the 'P salt', $Pt(NH_3)_2(NO_2)_2$, and at least 20g sulphamic acid.

Coated Electrodes

BADISCHE ANILIN- & SODA-FABRIK A.G.

U.S. Patent 3,672,990

Adherent coatings on electrodes are produced using a mixture of SiO_2, GeO_2 and/or SnO_2 and a Pt group metal or compound. The mixture is applied to the metal and fired. SiO_2 and ruthenium acetylacetonate can be used on Zr sheet.

Palladium Electroplating Bath

DEUTSCHE GOLD- & SILBER-SCHEIDEANSTALT

German Offen. 2,105,626

Bright, crack-free coatings are electrodeposited from a bath containing $Pd(NO_3)_2$, H_2SO_4 and $PdSO_3$.

HETEROGENEOUS CATALYSIS

Hydrosilane Preparation

DOW CORNING CORP. *British Patent* 1,285,167

Hydrosilanes are produced by the hydrogenation of disilanes in the presence of a 'transition metal catalyst'. This term is defined as Pd/C, Ru/C, Rh/C and complexes such as Pd and Pt chloride-phosphine complexes.

Allyl Carboxylate Production

FARBWERKE HOECHST A.G.

British Patent 1,286,443

In the production of allyl carboxylates propylene, O_2 and a carboxylic acid are reacted together in the presence of a supported mixture of Pd and Bi and optionally a Group I or II salt. Other Pt metals can be used with or instead of Pd.

Polymers Containing Phosphorus

BRITISH PETROLEUM CO. LTD.

British Patent 1,287,566

Vinyl phosphine monomers are used, e.g. with styrene, to produce polymers containing phosphine groups. These can complex Pd, Ir and other metals to give solid catalysts.

Semiconducting Films

T. YAMAZAKI *British Patent* 1,290,491

Surfaces are coated with semiconducting films of materials formed in the gas phase in the presence of catalysts. These include Pt, Pd and Pt-Si alloys. Pt gauze is used in the silane-NH_3 reaction to form a Si_3N_4 film.

Hydrocarbon Conversion

SHELL INTERNATIONALE RESEARCH MIJ. N.V.

British Patent 1,291,047

Cyclic hydrocarbons are converted to paraffins using a Rh and/or Ru catalyst supported on a refractory oxide and promoted with a halogen. Convenient catalysts may be produced by impregnating Al_2O_3 with Ru or Rh chloride solution and then drying and calcining.

Hydrocarbon Conversion Catalyst

UNIVERSAL OIL PRODUCTS CO.

British Patent 1,293,247

A hydrocarbon conversion catalyst consists of a porous Al_2O_3 support carrying 0.01–1% Pt, 0.01–5%Sn, 0.1–1.5%halogen and 0.05–0.5%S.

Exhaust Gas Purification

UNIVERSAL OIL PRODUCTS CO.

U.S. Patent 3,657,892

Exhaust gas purification catalysts containing Pt, for example, are protected from poisoning by a bed of C.

Process for the Production of Hydrocyanic Acid

DEUTSCHE GOLD- & SILBER-SCHEIDEANSTALT

U.S. Patent 3,658,471

Hydrogen cyanide and hydrogen are prepared from acetonitrile and NH_3 using a Pt group metal catalyst at 1100–1400°C, quenching to below 500°C.

Cyclic Hydrogenation-Reforming

CHEVRON RESEARCH CO. *U.S. Patent* 3,660,275

Gasoline and jet fuel are produced in a cyclic hydrogenation-reforming process using a Pt/Al_2O_3 catalyst.

Hydrocarbon Conversion Catalyst

UNIVERSAL OIL PRODUCTS CO.

U.S. Patent 3,660,309

A more resistant hydrocarbon conversion catalyst consists of a Pt group metal and Ge on a mixture of Al_2O_3 and aluminosilicate. Pt itself is the preferred metal of the group.

Bimetallic Reforming Catalyst

MOBIL OIL CORP. *U.S. Patent* 3,661,768

An improved start-up procedure for a bimetallic reforming catalyst containing Pt involves reducing the catalyst, previously purged of O_2, with moisture-saturated H_2 gas until a temperature of 485°C is reached, then sulphiding the reduced catalyst and charging naphtha in contact with it.

Exhaust Gas Oxidation

W. R. GRACE & CO. *U.S. Patent* 3,661,806

The exhaust gas oxidation catalyst, which may be a Pt group metal, is dispersed on an inorganic matrix of specified pore size and distribution.

Paraffin Dehydrogenation

SHELL OIL CO. *U.S. Patent* 3,662,019

Paraffins are dehydrogenated to olefins over a Pt group metal catalyst containing at least one Group IIB and VIIB metal, e.g. Pt with Cd, Zn, or Re.

Platinum Catalyst

FARBENFABRIKEN BAYER A.G.
U.S. Patent 3,663,166

A catalyst for hydroxylamine production is prepared by hydrolysing a Pt compound, such as K_2PtCl_4, at pH 4.5–9.0 so that hydrated Pt oxide is deposited on a support such as graphite.

Ethylene Hydrogenation Catalysts

E. I. DU PONT DE NEMOURS & CO.
U.S. Patent 3,663,181

Orthorhombic Pt metal oxides of the type Pt_3MO_6, where M is Mn, Fe, Co, Ni, Cu, Zn, Mg or Cd, are catalysts for the hydrogenation of C_2H_4.

Ethylene Oxide Production

STA. ITALIANA RESINE S.p.A.
U.S. Patent 3,663,455

C_2H_4 is oxidised to ethylene oxide in the presence of a catalyst containing 7–30% Ag and 0.01–1% Pt, Pd or Au (based on the weight of Ag).

Hydrogenation of Arylaldehydes

UNIVERSAL OIL PRODUCTS CO.
U.S. Patent 3,663,626

A continuous process for the hydrogenation of aryl aldehydes to the corresponding alcohols is effected in contact with a catalyst composite of Pt and an alkali metal component.

Multireaction Reforming

STANDARD OIL CO. *U.S. Patent* 3,664,949

Petroleum feedstocks are reformed in several reactors each containing a Pt group metal, such as Pt, on a mordenite support.

Light Alkane Disproportionation

CHEVRON RESEARCH CO. *U.S. Patent* 3,668,268

Light alkanes are disproportionated to produce higher hydrocarbons by heating in the presence of a molecular sieve carrying a Group VIII noble metal, e.g. Pd/mordenite.

Paraffin Disproportionation

ATLANTIC RICHFIELD CO. *U.S. Patent* 3,668,269

Paraffins are disproportionated to yield higher and lower hydrocarbons in the presence of a Pt group metal deposited on an acidic mixture of aluminosilicate and inorganic oxide. In an example Pt is deposited on a faujasite-SiO_2-Al_2O_3 mixture.

Cobalt Particles

BELL TELEPHONE LABORATORIES INC.
U.S. Patent 3,669,643

Fine hexagonal particles are produced by precipitation using a strong reducing agent in the presence of Pt or other metal ions.

Alcohol Dehydrogenation

TEXACO INC. *U.S. Patent* 3,671,591

Ketones are produced by dehydrogenating alcohols over a Pt catalyst deposited on pyrolysed polyacrylonitrile.

Hydroxyaldehyde Production

TENNECO CHEMICALS INC. *U.S. Patent* 3,673,257

The oxidation of hydroxybenzyl alcohols to salicylaldehydes is catalysed by Pt and promoted by Cd, Ce, In or La.

Exhaust Gas Combustion Catalyst

H. BERGER *German Offen.* 2,058,264

An active ICE exhaust gas catalyst consists of a finely divided carrier impregnated with catalyst and then shaped, fired, etc. The fine state of division is produced by colloid milling. Pt metals on Mg-Al silicates form suitable compositions.

HOMOGENEOUS CATALYSIS

Acetic Acid Production

AJINOMOTO CO. INC. *British Patent* 1,286,224

CH_3COOH is produced by heating methyl formate and CO in the presence of a Rh catalyst and a halogen promoter. A wide variety of inorganic and organic Rh salts can be used.

Cyano-substituted Silicon Compounds

UNION CARBIDE CORP. *British Patent* 1,290,549

HCN adds on to unsaturated groups in siloxanes in the presence of Ni, Pd or Pt zerovalent complexes [e.g. $Pd(PPh_3)_4$] to form cyano-substituted Si compounds.

Organic Isocyanate Production

OLIN MATHIESON CHEMICAL CORP.
U.S. Patent 3,657,308

The production of isocyanates by the reduction of organic nitro compounds is catalysed by a Pt group metal complex of a Lewis base, such as

pyridine or isoquinoline, in the presence of an organic carbonate.

Hydrosilation Catalysts

TORAY INDUSTRIES INC. *U.S. Patent* 3,658,866

Hydrosilation reactions are catalysed by zero-valent Pd complexes of P, As or Sb ligands, e.g. triphenyl phosphine or trimethyl arsine.

Aldehyde Production

UNION OIL CO. OF CALIFORNIA

U.S. Patent 3,660,441

Higher aldehydes are produced from lower aldehydes and acids in the presence of Pt group metal complexes, e.g. an $Ir(PPh_3)_3$ complex.

Isocyanate Production

OLIN MATHIESON CHEMICAL CORP.

U.S. Patent 3,660,458

Organic isocyanates are produced by reacting an organic azo and/or azoxy compound with CO in the presence of a p.g.m. catalyst, e.g. $PdCl_2$.

Hydroformylation Catalyst

BRITISH PETROLEUM CO. LTD.

U.S. Patent 3,660,493

Hydroformylation reactions are catalysed by a complex of Rh(I) carboxylate, e.g. a Rh acetate-PPh_3 complex.

Cyclic Hydrocarboxylation Process

UNION OIL CO. OF CALIFORNIA

U.S. Patent 3,668,249

Straight chain acids, anhydrides or esters are produced by the hydrocarboxylation of olefins over Pt group metal catalyst, e.g. a Pd-P complex.

Vinyl Chloride Production

ESSO RESEARCH & ENGINEERING CO.

U.S. Patent 3,670,037

Monohalogenated olefins such as vinyl chloride are produced from an olefin, hydrogen halide and source of O_2 in the presence of a Pd halide, a ferric halide and an alkali metal halide.

Rhodium Complexes

JOHNSON MATTHEY & CO. LTD.

French Appl. 2,104,793

Rh(I) compounds for catalytic use have the formula $RhA(CO)_xL_y$, where A is a non-halide anion, L is a ligand, x is 0 or 1 and y is 2 or 3, e.g. L is phosphine and A is nitrate or $SnCl_3^-$.

Catalytic Hydrogenation or Hydroformylation

JOHNSON MATTHEY & CO. LTD.

German Offen. 1,518,236

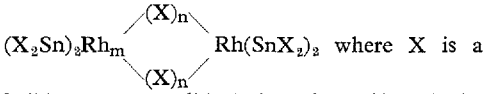
Unsaturated aliphatic hydrocarbons are hydrogenated with H_2 or hydroformylated with H_2 and CO in the presence of a complex compound of a Pt group metal halide and a ligand containing a Group VB or VIB element.

Rhodium Complexes

JOHNSON MATTHEY & CO. LTD.

German Offen. 1,793,616

Catalysts for hydrogenation, hydroformylation, and/or carbonylation reactions are Rh complexes or complex anions of formula $RhX(YR_3)_3$ or



where X is a halide or pseudohalide, Y is P, As or Sb, R is the same or different hydrocarbon groups and n = m = 1 or 3.

FUEL CELLS

Fuel Cell Catalysts

ROBERT BOSCH G.m.b.H. *British Patent* 1,285,861

A new catalyst for fuel cells is a mixture of Pt or Pt alloy and at least one metal sulphide in an electrically conducting matrix. In one example Pt, Ag_2S and an Au powder matrix are used.

Fuel Cells

MATSUSHITA ELECTRIC INDUSTRIAL CO. LTD.

British Patent 1,288,986

A fuel cell electrode consists of a mixture of Ni, Sb and a Pt group metal, e.g. Pd.

Fuel Cell Electrodes

ROBERT BOSCH G.m.b.H. *British Patent* 1,292,791

A fuel cell electrode has a skeletal structure supporting a mixed catalyst containing P, S, Se or Te and Pt or one of its alloys, e.g. Pt and P.

CATHODIC PROTECTION

Electrodes for Electrolytic or Cathodic Anti-corrosion Protection

SOCIÉTÉ D'ÉTUDES CONTRE LA CORROSION

British Patent 1,284,198

A robust electrode for anti-corrosion protection of marine structures and craft comprises one or more tubes of Ta or Ti with a Pt or Rh coating. The electrode is held in grooves of an insulating base by a sealant which penetrates perforations in the metal.

CHEMICAL TECHNOLOGY

Iridium in Uranium Dioxide

U.K. ATOMIC ENERGY AUTHORITY

British Patent 1,283,608

A fine, uniform dispersion of a refractory metal in UO_2 fuel inhibits grain growth and release of fission gases. An Ir compound in an HNO_3 solution of uranyl nitrate is decomposed to metal; NH_4^+ ions are added to precipitate ammonium diuranate. This is then calcined and reduced to UO_2 containing finely dispersed Ir.

Noble Metal Photographic Nuclei

EASTMAN KODAK CO. *British Patent* 1,290,618

Nuclei for reduction centres in Ag emulsions are produced by reducing a Pt, Pd, Au, Rh and/or Ru salt with a borohydride.

Hydrogen Separation

JOHNSON MATTHEY & CO. LTD.
British Patent 1,292,025

H_2 is separated from other gases by passage through a discontinuous and/or porous Pd or Pd alloy film deposited on an imperforate tube or membrane substrate made of Ni, Fe, V, Ta or Nb or their alloys.

Platinum Group Metal-Quinone Complexes

FUJI PHOTO FILM CO. LTD. *U.S. Patent* 3,656,961

A direct positive, photographic Ag halide emulsion contains a soluble salt or a condensed polycyclic quinone complex of a Group VIII metal. The metal is especially Rh, Ir, Ru, Pd, Os, Co or Pt; phenanthraquinone is a suitable quinone.

GLASS TECHNOLOGY

Optical Coatings for Glass

CARL-ZEISS-STIFTUNG *British Patent* 1,289,498

An approximately frequency-independent inhibition of radiation is achieved with coatings on glass. These consist of finely divided Pd or PdO in an oxide matrix. TiO_2 containing 18.1% Pd is one example of the coating.

Pt-Rh-Au Alloy

JOHNSON MATTHEY & CO. LTD.
U.S. Patent 3,672,880

Because of their low wettability by glass, corrosion resistance and high temperature strength, alloys comprising 72–90 wt.%Pt, 9–25%Rh and 1–3% Au are suitable for use as containers with perforated bushing plates for glass fibre manufacture.

Glass Industry Equipment

JOHNSON MATTHEY & CO. LTD.
U.S. Patent 3,657,784

Stirrers, crucibles, spinning dies and related glass industry equipment made from a refractory metal are flame-sprayed with an O_2 getter and a MgO barrier layer before cladding with an outer layer of a Pt group metal alloy. The volume between the barrier layer and the outer cladding is evacuated. A suitable getter is Zr metal.

ELECTRICAL AND ELECTRONIC ENGINEERING

Schottky Barrier Diodes

WESTERN ELECTRIC CO. *British Patent* 1,286,307

Schottky barrier diodes are formed using a metal silicide on Si, e.g. Rh, Pt or Pd silicide.

Contacts on Semiconductors

GENERAL ELECTRIC CO. *British Patent* 1,286,834

Contacts on semiconductors are made from layers of (*a*) Ti, V, Cr or Al, (*b*) Pd, (*c*) Ni and (*d*) Au, Ag, Sn and/or Pd.

Field Effect Transistors

TEXAS INSTRUMENTS LTD. *British Patent* 1,290,419

Gate electrodes and conductors on field effect transistors are made from Pt (Si semiconductor) or Au (GaAs semiconductor).

Platinum Alloy Semiconductor Electrodes

NIPPON ELECTRIC CO. LTD. *U.S. Patent* 3,658,489

The use of pure Pt for semiconductor electrodes leads to difficulties in the masking and etching stages. An alloy that is easier to etch contains Pt with 1–20 at.% Ni.

Low Current Electrical Contact

W. C. HERAEUS G.m.b.H. *U.S. Patent* 3,672,850

Ru is vapour deposited in a vacuum directly on to a springy magnetic contact carrier made of Fe-Ni alloy. It forms crystal columns.

TEMPERATURE MEASUREMENT

Marking Metallic Materials

JOHNSON MATTHEY & CO. LTD.
British Patent 1,280,454

Metal strip, rod or wire, especially Pt alloy thermocouple wire, is coded at intervals by a system of depressions or projections on the surface, including one larger 'marker' to show the direction the code should be read. The marks are inconspicuous but cannot be removed without damaging the wire.

Sheathed Thermocouple

JOHNSON MATTHEY & CO. LTD.
British Patent 1,280,674

Changes in Pt alloy thermoelectric properties due to the migration of a constituent of one limb to the other limb, especially in the form of the volatile oxide, are minimised by sheathing a thermocouple in a material containing none or less of that constituent than either limb contains and by maintaining a low oxidising potential by including a 'getter', e.g. Ti, Zr or Ta and/or by filling the sheath with an inert gas.

Platinum Coatings

JOHNSON MATTHEY & CO. LTD.
French Patent 2,084,651

Articles for use at high temperatures consist of a refractory metal core (Nb, Ta, Cr, etc.) coated with a MgO barrier layer and then a Pt group metal or alloy. The articles may be used in thermocouple assemblies.