

formance with olefin additives. Anode over-voltage decreased as the number of allylic H atoms increased. Gains in performance could be made by increasing cell operating temperature. Long-term performance was studied at 175°C. The effect of additives is not necessarily the same as in the short-term. When a certain total additive limit is exceeded, the decrease in anode performance can be severe over an extended period. Cycling characteristics associated with direct electrochemical oxidation of hydrocarbons are described in terms of distinct modes of performance fluctuation prior to establishment of steady-state conditions.

CHEMICAL TECHNOLOGY

High Current Density Chlorate Cell Using Platinised Anodes

J. R. NEWBERRY, W. C. GARDINER, A. J. HOLMES and R. F. FOGLE, *J. Electrochem. Soc.*, 1969, **116**, (1), 114-118

NaClO₃ was produced in a monopolar cell with platinised Ti anodes and steel cathodes. The 144A cell was tested continuously for 31 days and energy requirements were 6300 KWh d.c./ton NaClO₃. Replacement Pt was 5.3 g/ton NaClO₃. The cell was operated at 1 A/in², 110°C, 3.7V, pH 6.7. The feed contained 190 g/l NaCl and 330 g/l NaClO₃. Cell effluent was 110 g/l NaCl and 580 g/l NaClO₃. 1/8 in. electrode spacing was preferred with electrodes 3 ft high. The process is the subject of *U.S. Patent* 3,043,757.

ELECTRICAL AND ELECTRONIC ENGINEERING

Emission-Adsorption Properties of Films of Barium Oxide and of Barium Oxide Activated by Barium on Platinum Group Metals

V. V. NIKULOV and G. A. KUDINTSEVA, *Radiotekhn. Elektron.*, 1969, **14**, (3), 516-521

The emission properties of Pt, Ir and Os were

determined from their work functions by measuring their various contact potentials. BaO dust or BaO activated by Ba reduce the work functions. The high temperature stability of these films is good. The work functions of Pt and Ir can be reduced to ~1.4 eV at room temperature by this method.

The Reliability of Palladium-Silver Thick Film Resistors

R. C. HEADLEY, *NTZ*, 1969, **22**, (1), 53-56

Reliability testing of Pd-Ag thick film resistors enabled the optimum firing conditions to be established. Change of unloaded resistances after 1000 h was 0.1-1%. Drift values of loaded resistances were essentially lower.

TEMPERATURE MEASUREMENT

Stability and Calibration of Miniature Platinum Resistance Thermometers

W. V. JOHNSTON and G. W. LINDBERG, *Rev. sci. Instrum.*, 1968, **39**, (12), 1925-1928

Miniature Pt resistance thermometers weighing ~1g were evaluated as substitutes for capsule-type instruments. They were calibrated between 12 and 373K at fixed points and by comparison with a NBS standard instrument. Above 90K IPTS requirements were met but below 90K $R_T/R_{273.15}$ drops slower than for capsule-type thermometers, perhaps due to geometric strains in the Pt element. Interpolation allowed a table to be plotted with a smooth curve through the data to better than 0.002 deg K. R_0 for these thermometers over 12 months was reproducible to 10 ppm.

Precious-metal Thermocouples

D. W. RHYS, *Metals Mater.*, 1969, (Mar.), 47-60

A review of the development and applications of precious-metal thermocouples. A short appendix modifies the article in the light of the IPTS-68.

NEW PATENTS

METALS AND ALLOYS

Metallising Compositions

E. I. DU PONT DE NEMOURS & CO.

British Patent 1,144,930

A noble metal alloy metallising composition comprises a Pd-Au, Pt-Au, Ag-Au, Ag-Pt or Pd-Pt alloy in powder form (average particle size not greater than 40 μ). The alloy powder is dispersed in an organic vehicle (which may con-

tain a vitreous binder) and constitutes 10-70 wt% of the metallising composition.

Finely Divided Metals of the Platinum Group

MONSANTO CO.

British Patent 1,146,530

A salt of a Pt metal is reduced in the presence of an alcohol, acetal, ketone, ether, carboxylic acid ester or olefine which complexes the metal formed. The complex is then decomposed.

Noble Metal Alloy for Porcelain Cladding

DEUTSCHE GOLD- & SILBER-SCHNEIDANSTALT

U.S. Patent 3,413,723

A dental alloy adapted for fixing on porcelain coverings consists essentially of 80-90% Au, 5-15% Pt, 0.1-2% In, 0.1-2% Sn and 0.05-1% Re. Other compositions with the same components are specified.

Production of Alloys of Platinum Metals

JOHNSON MATTHEY & CO. LTD

Dutch Patent 68.09,169

Thermal sensitivity in Pt metal alloys is reduced by introducing a maximum of 20 at.% of one or more of Se, Ti, V, Y, Zr, Nb, Hf and the lanthanides.

Improved Method of Coating and Inlaying

JOHNSON MATTHEY & CO. LTD

Italian Patent 822,094

Phosphor bronze strip inlaid with Pd may be produced by means of rolling processes including an intermediate layer of Ni, Fe, Co, Mo, or V.

ELECTRODEPOSITION AND SURFACE COATINGS

Palladium-Nickel Alloy Plating Bath

KABUSHIKI KAISHA SUWA SEIKOSHA NISSHIN KASEI K.K.

British Patent 1,143,178

A plating bath for electrodeposition of a Pd-Ni alloy comprises an aqueous solution of Pd and Ni amines at specified critical concentrations. The relative proportions of Pd and Ni are such as to deposit an alloy with a Pd content of 30-90%. An example bath contains Pd(NH₃)Cl₂ and NiSO₄·7H₂O. Optional additives are a soluble salt of a naphthalene sulphonic acid and *p*-toluenesulphonamide.

Deposition of Platinum Group Metals

NATIONAL RESEARCH DEVELOPMENT CORP.

British Patent 1,145,285

Pt or Rh is deposited on a Ni- or Ni/Fe alloy surface by (a) subjecting the latter to a charging treatment, (b) introducing H₂ and (c) bringing the treated surface into contact with a solution of a reducible Pt- or Rh-compound. The latter is reduced to metal by the H₂. The surface is charged by cathodic treatment in an electrolytic bath.

Porous Cathode Body Coated with Osmium

PHILIPS ELECTRONIC & ASSOCIATED INDUSTRIES LTD

British Patent 1,145,967

A porous W cathode body, containing Ba compounds in its interior, is coated with Os by heating the body to an elevated temperature in an atmosphere of H₂. The Os coating is formed by the reduction of OsO₄. The heated body may be brought into contact with OsO₄ vapour or immersed in a solution of OsO₄.

Platinum Coatings

JOHNSON MATTHEY & CO. LTD

British Patent 1,147,563

A Pt-containing dispersion, which forms adherent coatings on the substrates to which it is applied, is prepared by reducing PtO₂ and/or a mixture of PtO₂ with at least one oxide of the metals Rh, Ru, Ir and Pd. The Pt content should be at least 50% of the metal content of the mixture.

Iridium Coated Graphite Articles

UNION CARBIDE CORP.

British Patent 1,149,625

A graphite substrate, resistant to oxidation at temperatures up to 2,000°C, bears an adherent, substantially pore-free coating of Ir consisting of an inner layer adjacent to the graphite substrate. This inner layer is formed of sintered finely divided particles of Ir. An intermediate layer is vapour-plated before the electroplating of an outer Ir layer.

Coating Catalyst for Chemical Plating

SPERRY RAND LTD

U.S. Patent 3,414,427

The surface to be plated is treated with a solution of PdCl₂ in an organic solvent in the presence of HCl or HF as complexing agent.

LABORATORY APPARATUS AND TECHNIQUE

Laser Materials

MINISTER OF TECHNOLOGY

British Patent 1,142,321

In the production of single crystal calcium aluminate, CaCO₂ and Al₂O₃ powders are melted in an Ir crucible in an Ar atmosphere. Single crystals are grown on the end of an Ir rod inserted into a crucible with a Pt heat shield.

JOINING

Welding Iridium and Ruthenium or Their Alloys to Silver

INTERNATIONAL NICKEL LTD

British Patent 1,145,971

Ag is welded to an Ir or to a Ru body (or an alloy of either) by interposing a bonding agent consisting of a Pd-Ag alloy containing 1-30% Pd (preferred 5%). The invention relates to Ir tips welded to Ag rods in sparking plugs.

Brazing Alloy Compositions

NORTH AMERICAN ROCKWELL CORP.

U.S. Patent 3,411,900

An alloy with brazing characteristics equivalent to a Au-Ni braze contains 80-95 wt% Ag, 1-10 wt% Pd, 1-7.5 wt% Cu and 0.5-3.5 wt% Ni with the usual impurities. A preferred composition, in wt% contains 89.5-90.5 Ag, 4.5-5.25 Pd, 3.95-4.5 Cu and 0.90-1.25 Ni.

Brazing Alloy

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
U.S. Patent 3,413,115

A ductile joint is obtained using an alloy of 80–83% Pd, 13.5–16.5% Ag and the remainder Si. A preferred alloy contains 81.5% Pd, 15.0% Ag and 3.5% Si.

HETEROGENEOUS CATALYSIS

Improvements in or Relating to the Production of Acetic Acid

B.P. CHEMICALS (U.K.) LTD
British Patent 1,142,897

C_2H_4 , steam and a gas containing O_2 are reacted in the vapour phase at temperatures of 50–350°C over a supported catalyst comprising Pd metal together with a transition metal (Fe, Ni, Mo, Ce, Cu, Cr, Mn or Co) oxide or salt, or mixtures of oxides, or salts of the same or of different transition metals, e.g. Pd/ Al_2O_3 impregnated with Cr acetate.

Improvements in and Relating to the Oxidation of Ferrous Compounds and to the Reduction of Ferric Compounds

JOHNSON MATTHEY & CO. LTD
British Patent 1,143,139

A feedstock containing Fe^{2+} or Fe^{3+} is reacted with O_2 or H_2 respectively in an acid solution in the presence of a catalyst comprising at least one Pt-group metal (Pt, Pd, or an alloy of Pt-Pd) on an inert support (charcoal) in a trickle column reactor. The feedstock may be obtained from a steel-pickling liquor or by extracting Fe ore with H_2SO_4 or HCl.

Dehydrocyclisation of Paraffins

SHELL INTERNATIONALE RESEARCH MIJ. N.V.
British Patent 1,143,147

A paraffin with 6–20 C per molecule is contacted at elevated temperatures (482–593°C) with a sulphided catalyst containing at least one noble metal from Group VIII (e.g. a sulphided Ir, Pd or Pt). The catalyst comprises 0.01–5% of the noble metal carried on silica in the presence of 500–10,000 p.p.m. S. The catalyst is prepared by impregnating SiO_2 with an aqueous solution of, for example, $RhCl_3$, $Pd(NH_3)_2Cl_2$, $H_2IrCl_6 \cdot 6H_2O$, $H_2PtCl_6 \cdot 6H_2O$ and dried finally at 371°C before being sulphided with *n*-hexane containing 1,000 p.p.m. S as dimethylsulphide.

Process and Apparatus for the Manufacture of Nitric Acid

HUMPHREYS & GLASGOW LTD
British Patent 1,143,946

A process for the manufacture of HNO_3 by the catalytic Pt oxidation of NH_3 is performed at a gas-turbine operating pressure. The hot gases from the oxidation stage are expanded in a gas turbine to recover energy.

Hydrogenation Reactions and Catalyst

LAPORTE CHEMICALS LTD *British Patent 1,146,437*
A hydrogenation catalyst consists of one or more Pt metals deposited on a macroreticular ion exchange resin (e.g. Amberlyst XN-1005) having a surface area of at least $5 m^2/g$.

Esters of Unsaturated Alcohols

B.P. CHEMICALS (U.K.) LTD
British Patent 1,148,583

The catalyst for the vapour phase reaction of C_2H_4 , air and CH_3COOH to give vinyl acetate is periodically reactivated by heating the catalyst/support mixture in a liquid alkaline medium. The catalyst comprises a Pt-group metal (Pd) deposited on Al_2O_3 , aluminosilicates, heavy metal oxides, metal oxide/ Al_2O_3 complexes, C or pumice (preferably Al_2O_3).

Catalytic Reforming

UNIVERSAL OIL PRODUCTS CO.
U.S. Patent 3,413,213

A catalyst for reforming gasoline feedstocks is prepared from purified Al_2O_3 by introducing 50–5,000 p.p.m. of an Fe compound and then impregnating with H_2PtCl_6 and calcining, the calcined product being sulphided.

Isomerisation of Saturated Hydrocarbons

UNIVERSAL OIL PRODUCTS CO.
U.S. Patent 3,413,369

The isomerisation catalyst is a Group VIII metal, such as Pt, deposited on a refractory support such as Al_2O_3 which has been treated with AlF or SiF_2 vapour at 650–1,200°C. See also 3,413,370–1.

Platinum-Rhenium Naphtha Reforming Catalyst

CHEVRON RESEARCH CO. *U.S. Patent 3,415,737*
Naphtha free from S may be reformed using a catalyst consisting of 0.1–3 wt% Pt and 0.01–5 wt% Re on a porous solid support.

Gas Purification by Hydrogenation

CATALYSTS AND CHEMICALS INC.
U.S. Patent 3,420,618

O_2 , C_2H_4 and C_2H_2 are removed from a H/CO feedstock by selective hydrogenation using a Pd/ Al_2O_3 catalyst where the Pd content varies with the gas to be removed.

Sulphided Platinum Metal Catalyst

SINCLAIR RESEARCH INC.
U.S. Patent 3,422,002

Hydrocarbons, (e.g. those boiling above 450°F), which contain N impurities are hydrofined using a catalyst consisting essentially of about 0.5–5 wt% of a Pt metal and about 4–30 wt% of MoO on Al_2O_3 . The catalyst is presulphided. Hydrofining conditions include a temperature of about 400–800°F. When using Ru and Ir, temperatures of at least about 635°F are employed.

HOMOGENEOUS CATALYSIS

Hydrogenation Process

IMPERIAL CHEMICAL INDUSTRIES LTD

British Patent 1,141,817

An organic substrate containing two or more sites of unsaturation is selectively homogeneously hydrogenated by contacting substrate with H_2 in the presence of a solution containing as catalyst a divalent Ru compound (e.g. $RuCl_2(PPh_3)_3$, $RuHCl(PPh_3)_3$ or $RuCl_2(AsEt_2Ph)_3$) and arresting the reaction when the substrate has reached the required degree of hydrogenation. The catalyst may also contain a hydride e.g. $LiAlH_4$.

Curable Organopolysiloxane Compositions

DOW CORNING CORP. *British Patent 1,141,868*

Organopolysiloxane compositions curable in the presence of Pt compounds (e.g. the reaction product of H_2PtCl_6 and a vinylated organopolysiloxane) are treated with an inhibitor (e.g. an acetylenic compound) so that the composition may be stored in the presence of the curing agent for considerable length of time without being cured.

Improvements in and Relating to the Production of Organic Isocyanates

IMPERIAL CHEMICAL INDUSTRIES LTD

British Patent 1,142,991

An aliphatic or cycloaliphatic hydrocarbon or substituted hydrocarbon containing at least one $-C=CH-$ group is reacted with isocyanate ions under substantially anhydrous conditions in the presence of a salt or co-ordinated compound of Pd (chloride). The inert solvent may be sulpholane or methylacetamide and there may be a redox system ($CuCl_2$ or an Fe salt) present which is reoxidised by O_2 . In an example, $KCNO + PdCl_2$ are heated to $90^\circ C$ in sulpholane and octene -1 added. Metallic Pd is precipitated during the reaction.

Oligomerisation Process

GEIGY (U.K.) LTD *British Patent 1,143,065*

Butadiene oligomers are produced by heating butadiene in the presence of a catalyst consisting of $RhCl_3$ reduced by reaction with a mixture of C_2H_5OH and acrylonitrile.

Preparation of Vinyl Esters of Carboxylic Acids

DENKI KAGAKU K.K.K. *British Patent 1,146,791*

The olefine-carboxylic acid reaction in the presence of O_2 takes place using a liquid phase containing Pt metal or a Pt compound promoted with a vanadyl salt.

Oxidation of Aromatic Compounds

IMPERIAL CHEMICAL INDUSTRIES LTD

British Patent 1,147,793

Phenols are produced by bringing into contact a

liquid aromatic hydrocarbon or phenol with H_2 and O_2 in the presence of a redox system and a compound of a Group VIII metal (Pd, Ru, Rh, or Pt). The redox system may be an Fe carboxylate (acetate). In examples platinumous chloride is the preferred noble metal compound.

Preparation of Aroyl Halides

NATIONAL DISTILLERS AND CHEMICAL CORP.

British Patent 1,149,359

An aroyl halide (benzoyl bromide or chloride) is prepared from an arylhalide containing at least one active H by reacting the latter with CO in the presence of a Pt- or Pd-triad catalyst. The catalyst may be palladous or platinumous chloride or bromide.

Butadiene Chloride Copolymerisation Catalyst

P.P.G. INDUSTRIES INC. *U.S. Patent 3,418,298*

Copolymerisation of dichlorobutadiene is catalysed by active Ir, Rh or Ru compounds, such as a cyclooctadiene complex of Rh dichloride.

Platinum Metal Azo Complexes

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

U.S. Patent 3,424,739

Organometallic complexes useful as catalysts for the polymerisation of olefines are formed by reacting a Pt or Pd salt with an aromatic azo compound.

FUEL CELLS

Catalyst for a Fuel Cell Electrode

AMERICAN CYANAMID CO. *British Patent 1,144,824*

A catalyst for a fuel electrode (H_2 , CO) of a fuel cell comprises Rh, an amorphous W oxide (valency of W less than 6), Pt, and Mo oxide in specified proportions. It is produced by coprecipitation, from aqueous solution, to form an intimate mixture of an alkali metal borohydride, a Rh salt, a metatungstate, H_2PtCl_6 and a molybdate.

Catalytic Fuel Cell Electrodes

ALLIS-CHALMERS MFG CO.

U.S. Patent 3,411,953

A catalytic electrode is produced by precipitation, using alkali metal hypophosphite, a flocculant Ni-Pd alloy from an aqueous ammonium solution, the alloy being shaped and made into the electrode in the usual way.

CHEMICAL TECHNOLOGY

Separation of Hydrogen from Other Gases

INTERNATIONAL NICKEL LTD

British Patent 1,147,010

H_2 is separated from other gases by bringing the

mixture into contact with a Pd sponge or the powder of a Pd-Ag-alloy consisting of at least 70% Pd and specified amounts of Au, Ag, B, Cu, Ni, Ru, Pt and/or Rh. Alternatively inert particles coated with Pd or with such an alloy may be used.

GLASS TECHNOLOGY

Apparatus for the Production of Glass Filaments

OWENS-CORNING FIBERGLASS CORP.

British Patent 1,143,725

In the formation of glass filaments, molten glass is drawn from Pt or Pt-alloy orifices and cooled by means of Cu or Ag fin shields. The fin shields are plated with Ni so that contact of the fin shield with the hot Pt orifice does not cause contamination of the latter.

Vitreous Ceramics

MATSUSHITA ELECTRICAL INDUSTRIAL CO.

U.S. Patent 3,421,916

Addition of 2-8 mol. % PtF_2 to a glass composition produces a glass composition of good sinterability.

ELECTRICAL AND ELECTRONIC ENGINEERING

Method of Producing Semiconductor Devices Having Connecting Leads Attached thereto

SYLVANIA ELECTRIC PRODUCTS INC.

British Patent 1,143,506

The body of a semiconductor material has conductive contacts (Pt silicide) in ohmic connection with its underlying portions. A first temporary layer of conducting material (e.g. Cu) leaves exposed areas on which the conducting leads are to be formed. Then a second layer (e.g. Ti and Pt) is laid over all and the first layer is etched away.

Cathodes for Electrical Discharge Vessels

SIEMENS A.G.

British Patent 1,143,865

The emissive substance carrier of a dispenser cathode is covered with a layer of at least one Pt metal, especially a metallic Os layer to reduce the escape energy of the cathode.

Electrodes for Electrolysis

H. B. BEER

British Patent 1,147,442

An electrode for an electrolytic process comprises a core of a film-forming metal (Ti, Ta, Zr, Nb and alloys) and a layer, the outside portion of which is resistant to electrolyte and electrolysis products and which consists of at least one oxide of a metal selected from Pt, Ir, Rh, Pd, Ru, Os and alloys formed between these metals. The entire layer may be formed of this material or only the outer portions of it.

Composition for Electrical Contacts

E. I. DU PONT DE NEMOURS & CO.

U.S. Patent 3,413,240

Fired on contacts for Pd-based electrical resistors are produced from (a) a finely divided Pd, Pd oxide or Pd-Ag alloy, (b) finely divided Ag and (c) finely divided ceramic binder.

Palladium Copper Contact

WESTERN ELECTRIC CO. *U.S. Patent 3,413,711*

A metallic lead is soldered to a base of a metal other than Cu but having an affinity with Cu (e.g. a thin film Ta nitride circuit path) by depositing on the lead a layer of Cu of specified thickness, depositing a Pd layer over the Cu layer, applying solder to the lead and the Pd layer to dissolve the Pd and form a bond with the underlying Cu layer.

Metallising Compositions for Conductors and Condenser Electrodes

E. I. DU PONT DE NEMOURS & CO.

French Patent 1,536,249

The metallising composition consists of 75-95% finely divided noble metal (100 parts Ag, 0-100 parts Pd and 5-40 parts Pt) and 25-5% of a mineral binder e.g. Bi_2O_3 as a Cd or Na borosilicate glass.

Resistance Film Composition

JOHNSON MATTHEY & CO. LTD

French Patent 1,541,456

A metallising composition is proposed which produces a film on a non-conducting base whose resistance does not vary firing temperature. It consists of finely divided Ru oxide (preferably 10-80 wt%) or a Ru oxide/Group V metal oxide composition and glass (preferably 90-20 wt%) with optionally up to 10 wt% of a Group I or II metal oxide.

TEMPERATURE MEASUREMENT

Thermocouples

JOHNSON MATTHEY & CO. LTD

British Patent 1,148,305

A thermocouple has a positive element of a binary Pd-Pt alloy and a negative element of a binary Au-Pd alloy. Both alloys are made by powder metallurgical methods. The percentage compositions of the alloys are within the ranges: positive element: Pd 80-90 wt%, Pt 10-20 wt%; negative element: Au 50-60 wt%, Pd 40-50 wt%.

Thermistor Manufacture

RESEARCH CORP.

U.S. Patent 3,414,861

A thermistor is constructed of a Pt-wire with an enlarged bulbous head. This bulb is covered with thermistor material ($\text{NiO}/\text{CuO}/\text{Mn}_2\text{O}_3$) and this in turn, by a conductive film (e.g. of Pt) deposited by a sputtering process.