ELECTRICAL AND ELECTRONIC ENGINEERING

Semiconductors Produced by Doping Oxide-glasses with Ir, Pd, Rh or Ru
C. C. SARTAIN, W. D. KYDEN and A. W. LAWSON,
Semiconductors were produced by diffusion doping oxide glasses with more than 1 wt.% of Ir, Pd, or Ru and by implanting 40 keV Ir ions into several oxide glasses. The properties and methods of conduction in the semiconductors is discussed.

TEMPERATURE MEASUREMENT

New Reference Tables for Platinum 10% Rhodium/Platinum and Platinum 13% Rhodium/Platinum Thermocouples - An Interim Report
Existing reference tables for Pt:10%,Rh-Pt and Pt:13%,Rh-Pt thermocouples are known to be partially inaccurate and are being revised jointly by the NBS, NPL and NRC (Canada). Details are given of the progress to date and some of the results are presented and discussed.

NEW PATENTS

METALS AND ALLOYS

Gold-based Spinnerette Alloy
JOHNSON, MATTHEY & CO. LTD.
U.S. Patent 3,529,959
A gold-based spinnerette alloy contains between 50% and 80% Au, between 0.04 and 0.5% Ir and the remaining part Pt, apart from the impurities. A method of making the alloy consists of induction melting the components, casting a sheet and homogenising.

CHEMICAL COMPOUNDS

Osmium Carbonyl
JOHNSON, MATTHEY & CO. LTD.
U.S. Patent 3,508,870
Method of preparing Os carbonyls is described. A solution of OsO₄ in an inert hydrocarbon solvent is heated to an elevated temperature under super-atmospheric pressure in the presence of CO. The product is primarily Os₆(CO)₁₂ with traces of Os₄O₄(CO)₁₂.

Selection of Thermocouples for Temperature Profiling of Semiconductor Diffusion Furnaces
Pt:13%,Rh-Pt thermocouples are discussed in terms of their best characteristics for temperature profiling. The criteria for selection, care of the thermocouples, evaluation of the materials and the calibration are all discussed.

Noncatalytic Coating for Platinum-Rhodium Thermocouples
A mixture of Y oxide and Be oxide gave a good noncatalytic coating for Pt-Rh thermocouples. A series of thin coats of a solution of 6-8% Be oxide in a solution of YCl in HCl was applied to give a coating ≈0.015 mm on 0.12 mm wire, after firing at 1600°C.

Measurement of Temperature in Corrosive Melts
A Pt-clad Rh-Pt thermocouple is superior to refractory-clad Rh-Pt thermocouples at 900-1400°C in BaO-B₂O₃ and PbO-PbF₃-B₂O₃ melts.

ELECTRODEPOSITION AND SURFACE COATINGS

Coating or Inlaying
JOHNSON, MATTHEY & CO. LTD.
British Patent 1,207,970
A Cu or Cu alloy is coated or inlaid with a thin layer of a noble metal such as Au, Ag, Pd or Pt or alloys thereof by interposing between the two a layer of Ni, Fe, Co, Mo, or V, and heating the three layers under pressure to bond them.

Reductive Vapour Deposition of Osmium
ENGLISH ELECTRIC VALVE CO. LTD.
British Patent 1,209,318
High purity Os deposits are obtained on a surface by vapour deposition from an OsO₄/H₂ mixture. OsO₄ is dissolved in water at room temperature and H₂ (or a gas containing H₂) bubbled through the solution. The resulting gas is mixed with another reducing gas to give a predetermined ratio of OsO₄ to reducing gas. In contact with a hot body this gas deposits metallic Os.
Electroless Noble Metal Plating

MOBIL OIL CORP. U.S. Patent 3,511,683

Pt and other noble metals are deposited on metal or mainly metal colloidal particles by displacement plating in non-aqueous solution. The particles must have an outer sheath of a reactive metal which is above the noble metal in the electrochemical series. In an example Sn-coated C black particles are coated from a solution of PtCl₄ in C₆H₆. The coated particles are used in fuel cell manufacture. Other compounds used for displacement plating are Au octadiene complex, Ag acetylide, Ir allyl and Ag perchlorate.

LABORATORY APPARATUS AND TECHNIQUE

Pulse-activated Polarographic Hydrogen Detector

NATIONAL AERONAUTICS & SPACE ADMINISTRATION U.S. Patent 3,599,034

A polarographic H₂ detector has three electrodes, a platinised anode, a Cu reference electrode and an auxiliary electrode, and a system for periodic reactivation of the platinised anode by means of potential pulsing.

HETEROGENEOUS CATALYSIS

Oxidation Catalyst

JOHNSON, MATTHEY & CO. LTD. British Patent 1,208,101

In a continuous process for the preparation of gluconic acid or glucosaccharic acid, an aqueous solution of glucose containing Na or K carbonate or bicarbonate is contacted in a trickle column with an O₂-containing gas and in the presence of a supported Pt group metal.

Oxidation Catalyst

ROHM & HAAS G.m.b.H. British Patent 1,214,958

Dicyanogen is obtained by the oxidation of gaseous HCN admixed with CO or steam in the presence of a Pt group metal, e.g. a Pt gauze.

Oxidation Catalyst

ZAKLADY AZOTOWE IM. P. FINDEVA British Patent 1,216,019

Oxidation of NH₃ to HNO₃ is catalysed by PtO₂.

Curing of Organosilicon Compositions

DOW CORNING CORP. British Patent 1,217,618

Si resin compositions are cured with 0.1 ppm of Pt and a tetramethyl guanidine carboxylate in an anhydrous medium.
amount representing 0.01-4 moles per g.atom of Pt.

**Hydrocracking Process**
TEXAS DEVELOPMENT CORP.  
*British Patent 1,217,815*

High octane fuels are produced by two stage hydrocracking. The first stage uses a base metal catalyst and the second stage a noble metal catalyst.

**Unsaturated Ester Production**
MITSUI PETROCHEMICAL INDUSTRIES LTD.  
*British Patent 1,219,510*

The reaction of an alcohol and/or aldehyde with O₂ to form an ester of an unsaturated carboxylic acid is catalysed by Ru, Rh, Pt, Pd or an oxide of one of these metals on a support.

**Aromatic Compound Production**
ASAHI KASEI K.K.  
*British Patent 1,219,704*

Aromatic compounds are produced from petroleum fractions by contacting them with H₂ at 400-650°C in the presence of a supported catalyst. The catalyst consists of Al₂O₃ or another support impregnated with 0.1-1% Pt, 0.1-1% Pd and 3-25% Cr oxide. The catalyst is treated with H₂ after impregnation with the active metals.

**Hydrogenation Catalyst**
SINCLAIR RESEARCH INC.  
*U.S. Patent 3,506,566*

Clarified or decant oil is converted to distillate fuel by a two-stage catalytic hydrocracking-hydroisomerisation process. The second-stage catalyst is a noble metal catalyst, e.g. Pt/Al₂O₃ or Pt/alumino-silicate.

**Catalytic Reforming Process**
CHEVRON RESEARCH CO.  
*U.S. Patent 3,507,780*

A reforming process using a catalyst containing 0.01-0.3% Pt, 0.01-0.3% Re, and 0.001-0.1% Ir associated with a porous solid carrier is started by contacting the naphtha with the catalyst in the presence of an inert gas, for example, N₂. The pressure in the reforming zone should be about 200 p.s.i.g. and the catalyst temperature about 650°F when the naphtha is first contacted with the catalyst at a space velocity of 1 v.v.h. The catalyst temperature is increased to 900°F over a 2-3 hour period while building up autogenous pressure of produced H₂. See also U.S. Patent 3,507,781.

**Catalytic Production of LPG**
UNIVERSAL OIL PRODUCTS CO.  
*U.S. Patent 3,511,773*

A hydrocarbon feedstock is converted to LPG and high octane reformate using a catalyst of a Pt group component and a halogen component combined with a carrier containing Al₂O₃ and about 1-10% of crystalline alumino-silicate. Pt is the preferred catalyst for the selective cracking of paraffins to C₃ and C₄ hydrocarbons and production of a high octane reformate.

**Paraffin Conversion Catalyst**
SHELL OIL CO.  
*U.S. Patent 3,514,888*

A new catalyst for paraffin dehydrogenation and dehydrocyclisation consists of 0.01-5% Pt and/or Pd modified with Sn or Bi on inert SiO₂.

**Purifying Hydrogen Separated from a Catalytic Reforming Effluent**
UNIVERSAL OIL PRODUCTS CO.  
*U.S. Patent 3,520,799*

A process is described for the catalytic reforming of hydrocarbons in the presence of H₂ to produce high quality gasoline boiling range products. Relatively impure hydrogen for recycle purposes and other uses is provided by compressing and contacting this hydrogen with a portion of the liquid reformed product. Catalysts are e.g. Pt/Al₂O₃. U.S. Patent 3,520,800 is similar.

**Hydrocarbon Conversion Process**
UNIVERSAL OIL PRODUCTS CO.  
*U.S. Patent 3,523,914*

A hydrocarbon conversion catalyst consists of a Pt group metal and a Re component combined with a carrier material containing Al₂O₃ and a finely divided crystalline alumino-silicate. In one example it contains 0.05-1.0% Pt and 0.05-1.0% Re, combined with γ-Al₂O₃ carrier material having 0.5-20% of the H₂ form of mordenite uniformly distributed.

**Hydrogenation Catalyst**
UNIVERSAL OIL PRODUCTS CO.  
*U.S. Patent 3,529,029*

Aromatic hydrocarbons are hydrogenated to cycloparaffins in the presence of a catalyst which contains 0.01-2.0 wt.% Pt or Pd, 0.01-2.0 wt.% Re and 0.01-1.5 wt.% of an alkali metal, preferably Li.

**Catalytic Dehydrogenation of Cyclohexanol and/or Cyclohexanone**
INSTITUT FRANÇAIS DE PÉTROLE, DES CARBURANTS ET LUBRIFIANTS  
*U.S. Patent 3,534,110*

Phenol is made by the catalytic dehydrogenation of cyclohexanol or cyclohexanone where the catalyst contains Pt and preferably also Ir on a SiO₂ carrier of 100-300 m²/g specific surface and 0.7-1.1 cm³/g porous volume.

**Dehydrogenation over Platinum-Rhenium Catalyst**
CHEVRON RESEARCH CO.  
*U.S. Patent 3,535,402*

Paraffins with 3-5 C atoms are dehydrogenated by contacting the paraffins with the catalyst containing 0.1-3% Pt and 0.1-5% Re associated with a non-acidic porous solid carrier. De-
hydrogenation conditions include a temperature of 900-1100 °C and a pressure of 3-100 psig.

**Catalytic Hydrogenation of Nitrobenzene**

**INTERNATIONAL NICKEL LTD.**

French Patent 1,587,963

An aqueous solution of nitrobenzene is hydrogenated to aminophenol in the presence of a Pt-Ru catalyst, e.g. Pt-Ru/C.

**Hydrogenation of Unsaturated Aldehydes**

**JOHNSON, MATTHEY & CO. LTD.**

German Appl. 1,568,861

Unsaturated aldehydes are reacted with H₂ in the presence of a catalyst containing Pt activated by an alcoholic alkali metal hydroxide or oxide solution.

**Improved Selective Catalyst Reduction**

**JOHNSON, MATTHEY & CO. LTD.**

German Appl. 1,568,894

A new process is intended to increase the selectivity and thus the yield of alcohol in the reduction of an aromatic aldehyde or ketone. For the process a known Pd catalyst, e.g. palladised wood charcoal, is used in the presence of an amine, especially an aromatic amine.

**Catalyst**

**W. R. GRACE & CO.**

German Appl. 1,933,240

HCN is produced by the gas-phase reaction of a hydro-carbon (e.g. CH₄) with NH₃ in the presence of a catalyst of 0.1-0.6 wt. % Pt on mullite.

**Dewaxing Catalyst**

**CHEVRON RESEARCH CO.**

German Appl. 1,954,368

Hydrocarbons are dewaxed by reaction with H₂ in the presence of a catalyst which consists of 0.01-3 wt. % Pt and 0.01 to 5 wt. % Re on a porous solid support.

**Hydrocracking Catalyst**

**CHEVRON RESEARCH CO.**

German Appl. 1,956,715

A hydrocracking catalyst consists of a layered crystalline alumino-silicate on which is deposited 0.01-2 % of Pt, Pd, Ir or their compounds and 0.01-2 % of Re on a Re or a Re compound.

**Hydrocracking Catalyst**

**CHEVRON RESEARCH CO.**

Dutch Appl. 70.02,354

A hydrocracking catalyst consists of a hydrogenating metal deposited on an amorphous aluminosilicate carrying 0.05-5.0 wt. % F or fluoride. The Al₂O₃/SiO₂ ratio is 70:30 to 5:95. The catalytic metal is 0.005-2.0 % of Pt, Pd, Ir and or their compounds and 0.005-2.0 % of Re and or Re compounds.

**Dehydrogenation Catalyst**

**INSTITUT FRANÇAIS DE PÉTROLE, DES CARBURANTS ET LUBRIFIANTS**

Dutch Appl. 70.04,779

A new catalyst for the dehydrogenation of saturated hydrocarbons consists of Al₂O₃ sup-

**HOMOGENEOUS CATALYSIS**

**New Platinum Catalysts**

**GENERAL ELECTRIC CO.**

British Patent 1,211,699

Significantly improved hydrosilation of aliphatic unsaturated materials can be obtained by using as catalyst a Pt-siloxane complex, e.g. Pt complexed with 1,3-divinyl-tetramethyldisiloxane or 1,3-divinyltetraphenyldisiloxane.

**Catalyst**

**FARBERFAHRRIKEN BAYER A.G.**

British Patent 1,213,779

Organic-silicon compounds are obtained by the addition of a silane or siloxane to an olefinically unsaturated organic compound in the presence of Me₃PyPtI.

**Production of Hydroquinone**

**LONZA LTD.**

British Patent 1,215,568

C₆H₆ and H₂ are combined at increased temperature and pressure in the presence of Ru(CO)₃I₉₃.

**Catalytic Hydrogenation or Hydroformylation**

**JOHNSON, MATTHEY & CO. LTD.**

British Patent 1,219,763

A hydrogenation or hydroformylation process is catalysed in the presence of a base by a Pt metal hydride, halide or pseudohalide complexed by an organic isocyanide or a Group VB or VIH compound. For Rh and Ir halides a Sn or Cc dihalide may also serve as the complexing agent. Particular catalysts are (PPh₃)₂RuCl₂ and RhI(CO)(PPh₃)₂.

**Platinum Complexes**

**RHÔNE-POULENC S.A.**

U.S. Patent 3,522,327

New complexes of PtCl₂ with triaminophosphincs are useful catalysts for curing organopolysiloxane resins. They have the general formula: PtCl₂2P(NR'R")₃ and are formed by simple addition.

**Homogeneous Dehydrogenation of Paraffins**

**ETHYL CORP.**

U.S. Patent 3,524,898

6-20 C paraffins are dehydrogenated by contacting them with a carbonyl halide Group VIII metal catalyst complex, such as IrCl(CO)(PR₃)₃ at 300-425 °C, optionally in the presence of a H acceptor.

**Hydrogenation Catalysts**

**IMPERIAL CHEMICAL INDUSTRIES LTD.**

U.S. Patent 3,524,899

Catalysts for the hydrogenation of ethylenic or acetylenic compounds are the reaction products.
of a Ru compound in which the metal has a valency of two or more and a simple or complex halide of an element of Group IA, IIA or IIIA. Examples are RuCl₃(II, O)₂, RuCl₂(SEt)₂, RuCl₂(PPh₃)₂ and RuCl₂(AsEt₃)₂.

Hydrocarboxylation of Olefins

Union Oil Co. U.S. Patent 3,530,155

Olefins are hydrocarboxylated by contacting the olefin under liquid phase conditions with a catalyst which consists of a Pt or Pd complex with an aromatic phosphine, H₂O and CO. High reactivity and high yields of the normal acid are obtained by incorporating an anionic or nonionic surface active agent in the reaction medium.

Copolymerisation Catalysts

Ceskoslovenska Akademie Ved. German Appl. 2,008,427

A siloxane is copolymerised with an unsaturated compound in the presence of a Group VIII metal complex, which may be, e.g. RhCl₂(PPh₃)₃, RuCl₂(H)(PPh₃)₂ or H₂CO₂Rh₂(PPh₃)₃.

FUEL CELLS

Three-layer Fuel Cell Electrode

Union Carbide Corp. British Patent 1,216,794

The fuel cell electrode structure consists of a fine-pored porous metal layer on the electrolyte side, a gas-permeable plastic-bonded catalyst layer and a coarse-pored porous metal layer. The plastic-bonded layer may contain a noble metal catalyst, e.g. Pt/C in p.t.f.e.

Gas Diffusion Electrodes

Robert Bosch G.m.b.h. British Patent 1,220,013

Gas diffusion electrodes for fuel cells are produced by coating a gas-permeable base with a varnish containing the catalyst metal. In one example Au and Pt dioxide dispersed in a cyclised rubber varnish are used to produce a catalyst layer on a p.t.f.e. plate.

Metal Boride Fuel Cell Catalyst

Leesona Corp. U.S. Patent 3,513,028

New catalysts for fuel cells are Group III-VIII transition metal borides. The preferred catalysts are Ni, Ru, Rh, Pd, Os, Ir and Pt borides. They may be produced by coating a porous substrate with a metal black and then treating the coating with an alkali metal borohydride.

Fuel Cell Electrode Production

Matsushita Electric Industrial Co. Ltd. German Appl. 1,964,568

A mixture of Ni and Sb is produced by reduction from a solution containing ions of both metals. This mixture is then added to a solution of a Pt group metal salt and the Pt ions reduced to Pt metal.

CHEMICAL TECHNOLOGY

Heating of Corrosive Vapours

Laporte Titanium Ltd. British Patent 1,219,573

TiCl₄ vapour is heated in a plurality of tubes having inlets and outlets made of Pt or an alloy of Pt with Rh, Ru or Ir.

Degassing Platinum Powders


A process for preparing degassed Pt powders consists of mixing finely divided Pt powder with at least an equal volume of a diluent metal oxide powder and heating the mixture until all gases have evolved. The powder mixture is cooled and the Pt powder separated from the diluent. The degassed powders are particularly suitable for application to "green" ceramic sheets used in the production of monolithic multi-layer ceramic circuit components.

Catalytic Igniter Members

Rolls-Royce Ltd. U.S. Patent 3,527,680

The activity of a Pt or Pt alloy catalytic igniter for a gas turbine engine is improved by etching the igniter to remove the initial surface layer, plating the member with a layer of Pt which supports catalytic ignition and heat treating.

Separation of Hydrogen from Gas Mixtures

Johnson, Matthey & Co. Ltd. German Appl. 1,567,601

A H₂ diffusion membrane consists of a Pd alloy containing 0.7–0.8% B and 4.5% Ag, or 4.3% Ag and 0.75% B.

Diffusion Device

Johnson, Matthey & Co. Ltd. German Appl. 2,005,494

A device for the separation of H₂ from gas mixtures consists of a stack of spaced Ag-Pd diffusion members.

Platinum Coating of Refractories

Corning Glass Works German Appl. 2,007,056

Refractory materials are coated with Pt or Pt alloys by flame spraying with a plasma flame at a rate of at least 30 m/sec. The powder is classified to 20–44 μ before spraying. The coating is heated to at least 1250°C.

GLASS TECHNOLOGY

Stirrer for Molten Glass

Pilkington Bros. Ltd. British Patent 1,211,797

A stirrer for molten glass consists of a Mo core coated with a refractory material (e.g. Al₂O₃) and sheathed with Pt or Pt alloy. The gas space between core and sheath is charged with inert gas.
ELECTRICAL AND ELECTRONIC ENGINEERING

Capacitor
ERIE TECHNOLOGICAL PRODUCTS INC.
British Patent 1,212,820
A capacitor consisting of a central ceramic layer sandwiched between two outer layers of the same ceramic has painted-on electrodes of Pt-Pd, for example, and electrode terminals of Ag paint.

Field Effect Transistor
TELEFUNKEN PATENTVERWERTUNGS G.m.b.H.
British Patent 1,217,665
In a field effect transistor, metal electrodes are applied to its semiconductor body as a source and drain and, together with the body, for metal-semiconductor rectifying contacts. Au, Pt and Pd are suitable contacts.

Self-regulating Heating Elements
JOHNSON, MATTHEY & CO. LTD.
U.S. Patent 3,520,043
Self-regulating heating elements have first and second components connected in parallel so that the resistivity of the element increases with temperature. Preferably one component forms a sheath for a core made from the other component. Suitable materials for the sheath include Ni-Cr and Fe-Ni-Cr alloys; suitable materials for the core (apart from Fe, Fe alloys, Ni and Ni alloys) include Co, Mo, W, Pt, Pd and Ta.

Semiconductor Connections
HEWLETT-PACKARD CO.
U.S. Patent 3,521,134
A metallic contact pad is formed on stripped areas of a semiconductor to reduce the thermal and electrical resistance. Pt silicide covered with Au and Mo provides a suitable material for the pad.

Glass Electrode
BECKMAN INSTRUMENTS INC.
U.S. Patent 3,523,777
In a method of sealing an internal half-cell (Pt:Ag/AgCl) into a constricted portion of an inner glass tube, the constricted portion is painted with Ag paint and then sealed on to the Pt wire by induction heating.

Platinum Coated Electrode
MATTHEY BISHOP INC.
U.S. Patent 3,532,556
A process of coating substrates with Pt involves reacting a Pt-type oxide with a reducing and dispersing medium composed of a 2-5 C aliphatic alcohol. A water-soluble inorganic salt or acid is added and most of the dispersing medium is removed from the platinated substrate while retaining the Pt wet and oxidising residual adsorbed organic matter, and removing water.

The reducing and dispersing medium preferably also includes formaldehyde.

Electric Film Resistance
SIEMENS A.G.
German Appl. 1,480,606
An electric film resistance, applied to glass or ceramic, consists of 40-60% Au, 10-15% Pt, 25-30% Pd and 5-10% Rh or Rh₂O₃.

Printed Heater Elements
JOHNSON, MATTHEY & CO. LTD.
German Appl. 1,912,216
Resistor compositions for use as heating elements may be applied by screen or other printing techniques to various ceramic substrates. They consist of a mixture of 10-80 wt.% (especially 46-65 wt.%) of finely divided RuO₂ and balance glass. Alternative compositions include finely divided Ag and compositions of matter formed by heating RuO₂ with a Group V metal oxide, such as Nb₂O₅. See also German Appl. 1,640,561.

Anode for X-Ray Tubes
METALLWERKE PLANSEE A.G.
German Appl. 1,952,526
The anode is made from an alloy of W containing 0.05-5%, preferably 0.15-1.5%, Pt.

Brine Electrolysis Electrode
IMPERIAL METAL INDUSTRIES (KYNOC) LTD.
Dutch Appl. 70.06,285
An electrode is made with a surface of film-forming metal coated with Ru and/or RuO₂ mixed with a chemical compound containing the film-forming metal, Cl₂ and O₂. The film-forming metal may be Ti, Ta, Nb or their alloys. A suitable chemical compound is Ti oxychloride.

MECHANICAL ENGINEERING

Drawing Ruthenium and Alloys to Wire
INTERNATIONAL NICKEL CO.
U.S. Patent 3,528,862
Improved results in drawing Ru or Ru alloy wire are obtained with a new process involving special control of the die temperature at 1000-1300°C in a non-oxidising atmosphere. The metal is drawn through a wire drawing die at 900-1050°C.

TEMPERATURE MEASUREMENT

Thermocouple
GENERAL MOTORS CORP.
U.S. Patent 3,527,620
A high-temperature thermocouple system consists of a pair of interconnected thermoelectric elements, one an alloy containing 55 wt.% Pd, 31 wt.% Pt and 14 wt.% Au, and the other 65 wt.% Au and 35 wt.% Pd.