

## Alkyrhodium Tetracarbonyl Derivatives as Catalytic Intermediates in Homogeneous Hydroformylation Reactions. An Infrared Spectroscopic Study

R. B. KING, A. D. KING and M. Z. IQBAL, *J. Am. Chem. Soc.*, 1979, **101**, (17), 4893-4896

The Rh-catalysed hydroformylation of  $C_2H_4$  in n-tetradecane solution was monitored by i.r. spectroscopy of the  $\nu(CO)$  region. Various Rh(I) carbonyl derivatives generate systems that catalyse the hydroformylation of  $C_2H_4$  at  $35^\circ C$  and 20-100 atm pressure. In each system absorption bands due to an unstable metal carbonyl derivative develop as the hydroformylation proceeds. These bands occur at  $\nu(CO)$  frequencies and are attributable to unstable Rh allyl,  $C_2H_5Rh(CO)_4$ . This is the first time evidence for a  $RRh(CO)_4$  derivative has been obtained.

## The Activity of Homogeneous and Heterogeneous Rh(I) Complexes in Hydrogenation of Alkenes

Z. KOZAK and M. ČAPKA, *Collect. Czech. Chem. Commun.*, 1979, **44**, (9), 2624-2632

Kinetics of liquid phase hydrogenation of alkenes catalysed by homogeneous Rh(I) complexes prepared in situ from  $[RhCl(C_6H_{14})_2]_2$  and (3-triethoxysilyl)propyldiphenylphosphine in toluene and by heterogeneous analogue catalyst on  $SiO_2$  was studied. The reaction was first order in  $H_2$ , alkene and catalyst. The activity of 0.3-0.6% Rh/ $SiO_2$  was not affected by pore size within the 4-10 mm region. The supported catalysts prepared by the saturation of the support followed by drying were more active and stable than their homogeneous counterparts.

# NEW PATENTS

## METALS AND ALLOYS

### Current Carrying Alloys of Titanium

JOHNSON MATTHEY & CO. LTD. *British Patent* 1,552,427

Ti alloys containing 6-40% Ir, Rh and/or Ru possess improved corrosion resistance compared with Ti metal, particularly when subjected to a.c. current at high densities, such as when used as water heater electrodes. Preferred alloys contain 94% Ti, 6% Ir and 88% Ti, 6% Pt, 6% Ir.

## ELECTROCHEMISTRY

### Composite Electrode

INTERNATIONAL NICKEL CO. INC.

*U.S. Patent* 4,157,943

A composite electro-winning electrode has a barrier layer of platinum group metal or Au on the substrate, a  $RuO_2$ -containing non-electro deposited surface layer and an intermediate layer of electroplated Ru-Ir in a partially oxidised state.

## ELECTRICAL AND ELECTRONIC ENGINEERING

### TiN as a Diffusion Barrier in the Ti-Pt-Au BEAM-Lead Metal System

W. J. GARCEAU, P. R. FOURNIER and G. K. HERB, *Thin Solid Films*, 1979, **60**, (2), 237-247

The Ti-Pt-Au beam-lead metallisation system has good reliability for connections on integrated circuits. Interdiffusion of the metal films (Ti and Pt) can sometimes result in the formation of unetchable intermetallic compounds that may impair device performance. This can be eliminated by the incorporation of a thin ( $\sim 150\text{\AA}$ ) TiN layer between the Ti and Pt films. Electron microprobe and secondary ion mass spectrometry analyses measured the effectiveness of TiN as a diffusion barrier.

### Anodic Iridium Oxide Films: A New Electrochromic

J. L. SHAY and G. BENI, *IEEE Trans. Electron Devices*, 1979, **ED-26**, (8), 1138-1143

The preparation and properties of electrochromic anodically grown Ir oxide film (AIROF) are reviewed. A heat process which improves the response time and improves stability of AIROF is discussed. Maximum coloration and speed of response were found to be independent of pH and a transmission device is described whereby the AIROF is grown on a semi-transparent conducting substrate. There are two distinct electrochromic processes with different isotherms which colour AIROFs. Both processes are dominated by internal entropy changes of non-interacting particles.

## ELECTRODEPOSITION AND SURFACE COATINGS

### Brush Electroplating

WELDEX A.G.

*European Appl.* 3,680

An improved electrode for brush electroplating is a stylus fabricated for instance from Pt, adapted to hold plating solution, and having its tip surrounded by an absorbent abrasive material made from synthetic fibres, such as a polypropylene/nylon felt bonded with acrylic resin.

### Electroless Plating on Non-Conductive Surfaces

HONEYWELL INC.

*U.S. Patent* 4,154,869

Pinhole-free and crack-free electroless coatings can be obtained on Pd-Sn activated non-conductive surfaces by using a two-stage plating process. The plated surface is removed from the bath when a visible plating has been formed and is reactivated before being returned to the electroless plating bath.

### Dot Printing Wire

PILOT MAN-NEN-HITSU K.K. *U. S. Patent 4,155,660*  
The tip of a dot printing wire is provided with a wear-resistant coating which can be an alloy of platinum group metals (Ir-Os) or a platinum group metal alloyed with another transition metal and/or B, such as Os-Re, Co-Ru-W or Re-Ru-Ta-B alloys.

## LABORATORY APPARATUS AND TECHNIQUE

### Fail-Safe Gas Detector

ELECTRICAL REMOTE CONTROL CO. LTD.  
*British Patent 1,550,615*

To reduce the risk of failure due to catalyst poisoning, a detector for combustible gases has two adjacent transducers, one of which is energised continuously and the other intermittently, and the outputs are compared when both are energised. The transducers ("pellistors") are preferably a pair of matched active Pt resistances.

### Determination of Total Nitrogen Content of Aqueous Solutions

SUMITOMO CHEMICAL CO. LTD.  
*British Appl. 2,012,953A*

The total N<sub>2</sub> content of an aqueous sample is determined by passing a N<sub>2</sub>-free, CO-free inert gas through a reaction tube packed with a Pt or Pd catalyst, maintained at 700–1200°C, then through a condenser and a moisture absorbing tube, injecting the test sample into the reaction tube and passing gaseous products emerging from the moisture absorbing tube to a spectrometer to determine N<sub>2</sub>.

### Determination of the Flow Velocity of Gases

DEUTSCHE GOLD- UND SILBER-SCHNEIDANSTALT  
*British Appl. 2,013,898A*

Drift in readings given by a hot-wire anemometer for measuring the flow velocity of the intake air of an I.C.E. is reduced if the temperature-sensitive resistors are formed from a thin layer of Pt, Cu or Ni deposited onto an insulating substrate, such as Al<sub>2</sub>O<sub>3</sub>.

### Nitrido-Bridged Staining Agents

JOHNSON MATTHEY & CO. LTD.  
*British Appl. 2,014,553A*

The staining of cells, particularly to detect DNA and polysaccharides, is achieved with an aqueous solution of a N<sub>2</sub>-bridged ammine complex of formula [M<sub>2</sub>N(NH<sub>3</sub>)<sub>8-2x</sub>X<sub>5-y</sub>.xH<sub>2</sub>O]Y<sub>y</sub> where M is Ru or Os, X and Y are nitrate, halide or pseudohalide anions, x is 0 or 1 and y is 2 or 3.

### Detector for Combustible Gases

JOHNSON MATTHEY & CO. LTD.  
*British Appl. 2,015,175A*

A detector is in the form of a quasibrige circuit which includes resistance thermometer elements one of which has a catalytic coating of a platinum group metal connected to a negative feedback amplifier

such that the impedance between the amplifier output and the earth is zero. The thermometer elements are preferably formed from fired frits containing Au, Ag and/or platinum group metal conductive particles.

### Solid Electrolyte Gas Sensor

BENDIX AUTOLITE CORP. *British Appl. 2,016,702A*  
A high voltage output and lower internal resistance of a solid electrolyte oxygen sensor is produced by chemically activating the inner Pt electrode with an inorganic acid or an acid salt, such as with H<sub>2</sub>PtCl<sub>6</sub>, HCl, H<sub>2</sub>SO<sub>4</sub> or HNO<sub>3</sub>. A faster switching response can also be obtained by subjecting the outer electrode to d.c. activation under a reducing atmosphere.

### Carbon Deposit Control

BETHLEHEM STEEL CORP. *British Appl. 2,017,932A*  
A wire probe which measures the resistance between two Pt wound electrodes monitors C build-up during the coking cycle in a coke oven. A plot obtained from the probe is used to adjust the temperature of the gas flowing through the oven and thus prevent excessive C deposit.

### Gas Sensor

BRITISH GAS CORP. *European Appl. 4,184*  
A pellistor bead for use in a portable combustible-gas sensor is obtained by coating a Pt wire with a porous layer of Al<sub>2</sub>O<sub>3</sub> which is then impregnated with Pd or Pt as catalyst

### Platinum Metal Shell for Crucible

PROLIZENZ A.G. *U.S. Patent 4,159,891*  
The crucible, for use in heating and retaining melts at 1800°C and above, has a coating of Ir and removable shell of a platinum group metal.

## JOINING

### Welding under Water

COMEX S.A. *British Patent 1,552,340*  
CO released by welding operations in pressurised chambers is converted into CO<sub>2</sub> by passage over a catalyst bed containing Pt and the CO<sub>2</sub> is removed by passage through a CO<sub>2</sub> absorber. The method enables the welder to operate without a respiratory mask, enabling him to have unrestricted movement.

### Thermoplastic Braze-Paste

JOHNSON MATTHEY & CO. LTD.  
*French Appl. 2,403,156*

The composition consists of a granulated brazing alloy and a thermoplastic material. The alloy may contain Pd, Au and/or Ag. The thermoplastic material may be a mixture of a wax and a resin.

### Soldering of Light Metals

DEUTSCHE GOLD- UND SILBER-SCHNEIDANSTALT  
*German Offen. 2,807,039*

Al, Ti, Mg and Be surfaces are prepared for soldering by sputtering with a Pd-Ni alloy with 20–70% Ni.

## HETEROGENEOUS CATALYSIS

### Light-Oil Hydrogenolysis

STE. NATIONALE ELF AQUITAINE

*British Patent 1,550,050*

Ethane and other 1-4C hydrocarbons are obtained by the hydrogenolysis of light petroleum stock over a catalyst which contains Ir and a second Group VIII metal, preferably Pt, supported on a refractory oxide carrier containing < 0.5% of sulphate ions.

### Hydrocarbon Conversion Catalyst

U.O.P. INC.

*British Patent 1,551,307*

The reforming of gasoline boiling range feedstocks using Pt-Sn and related catalysts is made more selective by using a catalyst in whose production a chelating agent has been employed to prevent hydrolysis. In an example,  $Al_2O_3$  is pretreated with EDTA before impregnation with stannic chloride and chloroplatinic acid solutions.

### Nuclear Hydrogenation of N-Aryl Carbamates

UNIROYAL INC.

*British Patent 1,551,832*

N-alicyclic carbamates, used as starting products for isocyanates which give non-yellowing polyurethanes, are produced by the nuclear hydrogenation of the N-aryl carbamates in the presence of a Group VIII metal catalyst which has been treated with acid. The platinum group metals, especially Rh, are preferred. The acid treatment increases its activity and permits repeated re-use.

### Modified Organopolysiloxane Elastomers

S.W.S. SILICONES CORP.

*British Patent 1,553,125*

In an improved method of manufacturing oil-resistant modified organopolysiloxane elastomers, the modified organopolysiloxane may be reacted with a cross-linking agent in the presence of a Pt catalyst.

### Platinum Group Metal Hydrogenation Catalyst

INSTITUT FRANCAIS DU PETROLE

*British Appl. 2,012,606A*

A catalyst with improved S resistance, for use in hydrogenating aromatic compounds, consists of a platinum group metal deposited on a halogenated carrier which has been treated at 100-600°C with an inert gas and then at 50-400°C with a hydrocarbon containing at least one S compound. In an example,  $Al_2O_3$  supporting 0.3% Pt, 0.6% Ir and 2% Cl is heated in  $N_2$  and then in a hydrocarbon-containing dibenzothiophene.

### Palladium Catalyst for Solar Energy Storage

R.C.A. CORP.

*U.S. Patent 4,150,816*

In a process for storing solar radiation, the radiation is converted into electrical current which is supplied to an electrochemical cell, with  $H_2O$  and gaseous  $CO_2$ , to give formic acid as the storage medium. This can be decomposed, for example, using a Pd catalyst, to give gaseous  $CO_2$  and  $H_2$ .

### Conversion of Synthesis Gas to Hydrocarbon Mixtures

MOBIL OIL CORP.

*U.S. Patent 4,157,338*

Heterogeneous catalysts consisting of a mixture of a Ru, Rh or Os co-reduction catalyst and a crystalline aluminosilicate, such as a ZSM-5 zeolite, are effective for converting synthesis gas into hydrocarbons suitable for use as petrol.

### Selective Hydrogenolysis of Light Gasoline Stocks

STE. NATIONALE ELF AQUITAINE

*U.S. Patent 4,157,949*

Light gasoline stocks are selectively hydrogenolysed in normal hydrogenolysis conditions using an Ir-Group VIII metal catalyst to yield an ethane-rich gaseous fraction and a high-octane gasoline fraction. A preferred catalyst is Ir-Pt supported on a high specific surface area porous refractory oxide.

### Platinum Metal Containing Cracking Catalyst

MOBIL OIL CORP.

*U.S. Patent 4,159,239*

The operation of a fluid catalytic cracking unit having a regenerator designed to completely burn CO to  $CO_2$  is improved by circulating a trace amount of one or more of the six platinum group metals and Re with the circulating solid acidic cracking catalyst.

## HOMOGENEOUS CATALYSIS

### Sulphur and/or Aromatic Compound Reduction

PROTEC PROCESSI & TECNOLOGIE S.p.A.

*British Patent 1,549,363*

In processes for reducing S in petroleum fractions and for reducing the aromatic content of paraffin cuts and waxes, the liquid compounds are treated with an oxidising agent, particularly  $H_2O_2$ , in the presence of  $RuO_2$  as an  $O_2$  carrier.

### Heat Curable Siloxane Foams

DOW CORNING CORP.

*British Patent 1,550,891*

Fire-retardant siloxane foams, for cushioning and seating, are prepared using Pt catalysts and specified catalyst inhibitors which increase the pot-life of the siloxane to more than 8 hours. A preferred Pt catalyst is Pt(II) diacetylacetonate.

### Platinum-Tin Hydroformylation Catalyst

CELANESE CORP.

*U.S. Patent 4,152,357*

An improved catalyst for the rapid conversion of olefins to aldehydes consists of an ionic combination of a quaternary ammonium component and a ligand stabilised complex of Pt dihalide and stannous halide.

### Silicone Rubber Compositions

TOSHIBA SILICONE CO. LTD.

*U.S. Patent 4,157,426*

Silicone rubber compositions contain a zerovalent Pt(III) phosphor complex which acts as a curing catalyst.  $(Ph_3P)_4Pt$ ,  $[(MeO)_3P]Pt$ ,  $[(PhO)_3P]_4Pt$  and  $(Bu_3P)_4Pt$  are used in examples.

## CHEMICAL TECHNOLOGY

### Improving the Light Fastness of Organic Materials

FUJI PHOTO FILM CO. LTD. *British Appl. 2,013,227A*  
Specified Pt, Pd, Ni, Cu and Co chelates are used to increase the sunlight stability of organic materials, particularly of dyes used in photographic materials.

### Platinum and Palladium Ethylene-thiolates

POLAROID CORP. *U.S. Patent 4,152,332*  
Plastics are modified to enable them to absorb the i.r. part of the spectrum by incorporating a Pt, Pd or Ni complex of two molecules of a dithiol of formula HS(R)C = C(R)SH where R is a substituted furan or pyrrole group.

### Room Temperature-Curing Silicone Rubber

TORAY SILICONE CO. LTD. *U.S. Patent 4,156,674*  
A flame resistant rubber composition vulcanising at room temperature has triazole compounds added to enhance its extinguishing properties. The azoles are added in addition to conventional Pt powder extinguishing additives.

## GLASS TECHNOLOGY

### Alloys for Use in Glass Fibre Bushings

W. R. HERAEUS G.m.b.H. *U.S. Patent 4,155,730*  
Jets, nozzles and nipple plates of glass fibre bushings are made from an alloy containing 40-70% Pt, 20-50% Pd, 5-15% Rh and 0.5-4% Au. The alloys are resistant to attack by silicate-containing glass.

## ELECTRICAL AND ELECTRONIC ENGINEERING

### Integrated Circuit Devices

I.B.M. CORP. *British Patent 1,550,600*  
In an improved fabrication procedure, interconnected arrays of IGFET devices are produced using only two masking steps. The devices are provided with source and drain contacts of Pd or Pt silicide.

### Microcircuits

HUGHES AIRCRAFT CO. *British Patent 1,550,867*  
In an arrangement for fabricating microcircuit devices, semiconductor workpieces are provided with pairs of spaced alignment marks to facilitate their positioning. The substrates are preferably of GaAs, Ge or Si and the marks of Pt, Ir, Os, Ta, W, Re, Ti or Au. The most preferred combination is Ir and Si.

### Solid-Electrolyte Capacitors

MATSUSHITA ELECTRIC INDUSTRIAL CO. LTD. *British Patent 1,551,210*  
The  $\tan \delta$  loss of conventional MnO<sub>2</sub> capacitors is substantially reduced when the colloidal C cathode collector coating is replaced by a low-resistivity platinum group metal oxide. Ru oxide is preferred.

## Metallization Process

EUROGRAPHICS HOLDING N.V.

*British Appl. 2,017,577A*

An extremely thin (< 100Å) metal film is deposited on a transfer and a thin coat of varnish is applied to either the transfer or the substrate before laminating the substrate and transfer layer together. The metallic particles become absorbed into the varnish to provide the substrate with a highly polished specular metallic finish. Pt, Ag and Au finishes may thus be obtained.

## Electric Vehicle

FORD MOTOR CO. LTD.

*European Appl. 3,739*

An electric vehicle is driven by a unipolar dynamoelectric motor and preferably Na-S batteries. The motor stator includes a field coil surrounded by a conductive Cu jacket, Ni-plated and with a flash coating of Rh to minimise the resistance to current flow.

## High Temperature Electric Furnace

DAIDO STEEL CO. LTD.

*U.S. Patent 4,152,572*

An electric furnace which can be used in oxidising atmospheres, operating at 1800°C, has a shaped Zr oxide or La chromide heating element and annular Pt electrodes at each end of the tube.

## Noble Metal Contact for Solar Cells

ATLANTIC RICHFIELD CO.

*U.S. Patent 4,158,591*

Pt, Pd, Al, Au, Cu, Ni and/or glass frit are used as back contact materials for semiconductor wafers for use in solar cells.

## MEDICAL USES

### Prosthetic Device

BBC BROWN, BOVERI & CO. LTD.

*British Patent 1,550,219*

A device for implantation in living tissue, particularly eyelids, consists of two permanent magnets enclosed in a ductile, gas-tight tissue-compatible material. The magnets are of Co<sub>2</sub>Sm, and the envelope material is Pt, Rh, Ru, Pd, Au, Ag or an acceptable alloy thereof.

### Bonding a Bioglass to Metal

BOARD OF REGENTS OF THE UNIVERSITY OF FLORIDA

*British Patent 1,552,570*

In an improved method of bonding glass to a metal substrate, the heated metal is immersed in the molten bioglass, quickly withdrawn, rapidly cooled to about 800°C and then cooled more slowly in a furnace. The method is used for the construction of bone prostheses. Pt, Pt-Rh alloy and surgical stainless steel are suitable metal substrates.

### Noble Metal Coated Prosthesis

JOHNSON MATTHEY & CO. LTD. *French Appl. 2,392,661*

A metallic bone prosthesis is coated with Pt, Ru or Ir or an alloy containing at least one of these metals and also Pd, Rh, Au and/or a supporting metal.