

## Hydrogen-permeable Electrodes of Pd-Ag-Au Alloy

T. SHIROGAMI, *Denki Kagaku*, 1972, 40, (8), 605-610

The ternary alloy 66.6 wt.% Pd-13.4 wt.% Ag-20 wt.% Au combines good polarisation characteristics with excellent mechanical properties for use as a H-permeable membrane electrode with a high resistance to pinholing. The lattice parameter and electrode potential as a function of dissolved H were measured and the diffusion coefficient of H through the membrane was determined.

## Preparation of Highly Dispersed Platinum on Carbon

K. F. BLURTON, *Carbon*, 1972, 10, (3), 305-315

The preparation, characterisation and properties of Pt-doped C for fuel cell electrodes are described. A high degree of dispersion of Pt (crystallites  $<15\text{\AA}$ ) was achieved only by pyrolysis at 500-800°C of the  $\text{Ca}^{2+}$  form of Amberlite IRC50 and CG50 resins on which Pt ions had been localised by exchange. The mechanism and influence of the pyrolysis are discussed.

## TEMPERATURE MEASUREMENT

### Resistance Thermometry in Magnetic Fields. I. Thermistors and Platinum Thermometers at 77K

J. E. VEVAI, D. G. ELLIOT and W. I. HONEYWELL, *Cryogenics*, 1972, 12, (3), 192-195

At 77K, in magnetic fields up to 16 kG, both negative temperature coefficient thermistors and Pt resistance thermometers show a virtual rise in

temperature due to the field. Pt thermometers seem more desirable for this application.

### The Calibration of Resistance Thermometers at Low Temperatures

R. L. RUSBY, M. V. CHATTLE and D. M. GILHEN, *J. Phys. E, Sci. Instrum.*, 1972, 5, (11), 1102-1105

Details are given of an apparatus for comparing resistance thermometers at 4-90K and for the routine calibration of Pt resistance thermometers in accordance with IPTS-68.

### The Automatic Calibration of Platinum-Platinum, Rhodium Thermocouples in the Temperature Range 0 to 1100°C

T. P. JONES, *Aus. J. Instrum. Control*, 1972, 28, (4), 91-96

Equipment for the automatic calibration of Pt : Rh-Pt thermocouples from 0-1100°C is described. The uncertainty of calibration is only  $\pm 0.3^\circ\text{C}$  and the time for calibration is 1 h compared to 46 h for the fixed-point method.

### A Centralised Temperature Control System for Diffusion Furnaces

G. J. FULLIN and N. BAHNCK, *Solid State Technol.*, 1972, 15, (11), 40-43, 48

The installation of a centralised temperature control system at the Allentown Works of Western Electric Co., Inc., has led to increased yields and significant savings in the manufacture of diffused-junction npn transistors. The system uses three Pt : 10% Rh-Pt in each of 35 diffusion furnaces. Automatic, continuous temperature measurement gives close control over quality, enabling a sampling method of testing to be established.

## NEW PATENTS

### METALS AND ALLOYS

#### Tarnish Resistant Alloys

PENNWALT CORP. *British Patent* 1,296,879

An alloy which resists tarnishing contains 39-47% Au, 9-12% Pd and the balance Ag and Cu in a 1:1-1.5:1 ratio. The alloy can be used for jewellery, dental work and electrical contacts.

#### Dental Gold Alloy

L. HIRSCHBORN *U.S. Patent* 3,679,402

A gold alloy for bonding to dental porcelain for capping teeth contains 67.7 wt.% Au, 16.7% Pd, 11.6% Pt, 1.3% Ru, 2.0% Ag, 0.6% Sn, 0.1% Cu.

#### Degassed Platinum Powders

E. I. DU PONT DE NEMOURS & CO.

*U.S. Patent* 3,674,515

Degassed Pt powders are prepared by mixing

finely divided Pt with at least an equal volume of a diluent metal oxide powder, heating the mixture to dissipate all gases from the Pt powder, cooling the mixture and separating the Pt from the diluent. The Pt powders are suitable for application to "green" ceramic sheets used to produce monolithic multi-layer ceramic circuit components.

#### Platinum Group Metal Alloys

JOHNSON MATTHEY & CO. LTD.

*U.S. Patent* 3,676,114

Pt group metal alloys, especially 9-45 (preferably 20-40) wt.% Rh-Pt, are dispersion hardened by the presence of up to 1 wt.% of Ti, V, Zr, Nb, Hf and/or Ta.

#### Superconducting Alloy

M. WILHELM et al.

*U.S. Patent* 3,684,495

A superconducting alloy has the formula

$(Ce_{1-x}A_x)Ru_2$ , where A is Tb, Dy or Ho and x is 0.10–0.28, depending on the nature of A.

### Beryllium Alloy

SOC. TREFIMETAUX G.P. *U.S. Patent 3,685,988*

A Be alloy contains 0.05–3% Ca and 0.15–3% of at least one additional metal selected from Pd, Pt, Ir, Rh, Au and Fe.

### Sprayed Metal Articles

JOHNSON MATTHEY & CO. LTD.

*U.S. Patent 3,689,987*

Metal articles or ingots with a fine stable grain structure and superior properties may be made by arc, flame or plasma spraying the metal or alloy on to a cold target so that the droplets form a coherent deposit in which most retain their identity. The method is very suitable for Pt group metals, an alloy of 49 wt.% Pt, 50% Au and 1% Rh being used in one example.

### Dispersion Strengthened Metal

JOHNSON MATTHEY & CO. LTD.

*U.S. Patent 3,696,502*

A strengthened ingot, e.g. of Pt, is obtained by spraying a target with a molten metal and a reactive constituent (e.g. Pt and Zr). In its passage through the atmosphere the reactive constituent is converted to oxide, carbide, etc.

## CHEMICAL COMPOUNDS

### Platinum Group Metal Oxides

DIAMOND SHAMROCK CORP.

*U.S. Patent 3,677,975*

Solid solutions of Pt group metal oxides and valve metal oxides (Ti, Zr, Nb, Ta) are formed by flame spraying a solution of salts of the two classes of metal, e.g.  $RuCl_3$  and  $Ti(OBu)_4$ . The products are useful as solid electrolytes.

## ELECTROCHEMISTRY

### Electrolysis Electrodes

P.P.G. INDUSTRIES INC. *U.S. Patent 3,677,917*

Electrolysis electrodes are coated with a layer of PdO containing (a) a film-forming metal oxide (Al, Bi, Nb, Ta, Ti, etc.), (b) a second Pt group metal oxide, such as  $RuO_2$ , and (c) an Fe group oxide.

## ELECTRODEPOSITION AND SURFACE COATINGS

### Chemical Plating

FARBENFABRIKEN BAYER A.G.

*British Patent 1,299,102*

Ni-B coatings are deposited by chemical plating on to surfaces previously cleaned and dipped in acid  $PdCl_2$  solution.

### Noble Metal Alloy Chemical Plating

MOBIL OIL CORP.

*British Patent 1,299,413*

A mixture of metals, especially Au, Ag and Pt group metal alloys, are deposited chemically from a non-aqueous solution of the metals, at least one being in the form of a  $\pi$ -complex, and then the metal compounds on the surface are reduced. In one example a  $PdCl_2$ -cyclooctadiene complex is used with chloroauric acid in chloroform solution.

### Cementing Metal Powders to Metals

DR. W. KAMPSCHULTE & CIE.

*British Patent 1,303,712*

A metallic powder is deposited and adhered to an electrically conducting surface by electrophoretically depositing the metal powder and then electroplating the deposit and surface. Pt and Au alloys are among the metals described.

### Sensitising for Chemical Plating

ALLIED RESEARCH PRODUCTS INC.

*U.S. Patent 3,674,550*

Substrates are treated with a Pt group metal nitrite, ketocarboxylate or diglycollate and then with a reducing agent to produce a sensitising deposit. Pd, Rh and Pt are the preferred metals.

### Palladium-Nickel Coatings

K. YAMAMURA et al.

*U.S. Patent 3,677,909*

Pd-Ni coatings are electrodeposited from a Pd-Ni salt bath containing  $NH_3$  which is brightened with a sulphonamide.

### Metal Patterns on Insulators

WESTERN ELECTRIC CO. INC.

*U.S. Patent 3,679,472*

$Al_2O_3$  or another insulator substrate is sensitised, Pd catalyst is deposited and then a continuous Au film is formed. The Au/Pd film is shaped to make patterns.

### Noble Metal Sensitising Solutions

KOLLMORGEN CORP.

*U.S. Patent 3,682,671*

Surfaces are sensitised for subsequent chemical plating by treatment with a solution containing a Pt group metal, Au or Ag and a Group IV metal stabilised with a polyol. Pd and Sn are suitable components.

### Metallisation Compositions

E. I. DU PONT DE NEMOURS & CO.

*U.S. Patent 3,684,536*

Metallisation compositions for screen printing circuits on substrates contain noble metal powders in 3–15% of bismuthate glass-ceramic precursors. These give better adhesion of the composition.

### Metallised Fibres

ASAHI KOGYO K.K.

*U.S. Patent 3,686,019*

Nylon and other fibres are given a metal coating

to improve their antistatic properties. Metallisation involves the deposition of a noble metal catalyst (e.g. Pd) on the fibres, processing of the fibres by the usual textile treatments and the subsequent deposition of Pd, Au, Co, Ag, Cu, Ni, etc.

### Heater Coating

G.T.E. SYLVANIA INC. *U.S. Patent 3,691,421*

A double layer coating on a wire support consists of a layer of  $Al_2O_3$  and a layer of  $Al_2O_3$  mixed with  $ZrO_2$  or  $BeO$ . This layer is coated with Pt, Ir, etc., to prevent the oxidation of W.

### Protection of Cobalt-Based Alloys

DEUTSCHE EDELSTAHLWERKE A.G.

*U.S. Patent 3,692,554*

Co-based alloys are protected by diffusing into their surfaces a mixture of Ni, Pt (or other Pt group metal) or Al.

### Ruthenium Alloy Plating

SEL-REX CORP.

*U.S. Patent 3,692,641*

Thick electroplated coatings of low stress are obtained by plating from an ammonium ruthenate bath containing a Group IIIA metal (In, Ga or Tl) and optionally another Pt group metal.

### Osmium Electroplating

INTERNATIONAL NICKEL CO. INC.

*U.S. Patent 3,692,642*

Os is electroplated from a bath containing diammonium hexachloroosmate acidified with  $H_2SO_4$  or  $HSO_3NH_2$ .

### Platinum Chemical Plating

F. H. LEAMAN

*U.S. Patent 3,698,939*

Metallic and non-metallic surfaces are chemically plated using an ammoniacal chloroplatinate solution mixed with hydrazine or a hydrazine derivative.

### Transparent Conductive Coating

HUGHES AIRCRAFT CO.

*U.S. Patent 3,698,946*

Transparent coatings able to conduct electricity are produced by the vacuum deposition of thin consecutive layers of  $TiO$ , noble metal such as Au or Pd, and  $TiO$ .

## LABORATORY APPARATUS AND TECHNIQUE

### Detecting Reducing Vapours

T.R.W. INC.

*U.S. Patent 3,676,188*

Reducing vapours are detected by the change in resistance of a noble metal strip applied to a non-corrodible backing and coated with a reducible metal salt. The strip can consist of Pt, Rh, Au, Ag, etc. Suitable reducible salts contain Au or Ag, e.g.  $AuI/KI$ .

## JOINING

### Solderable Stainless Steel

P. R. MALLORY & CO. INC.

*U.S. Patent 3,698,880*

Stainless steel is rendered solderable by applying a barrier layer of Ni, Co or Cr and covering it with a layer of Ag alloyed with Au, Pt, Pd, Re or Os.

## HETEROGENEOUS CATALYSIS

### Unsaturated Aldehyde Hydrogenation

UNIVERSAL OIL PRODUCTS CO.

*British Patent 1,296,448*

Anisaldehyde is hydrogenated continuously to anisyl alcohol in the presence of a Pt/alkali metal catalyst. A preferred catalyst contains Pt and  $Li_2O$  on an  $Al_2O_3$  support.

### Production of Biphenyls

ASAHI KASEI K.K.K.

*British Patent 1,296,721*

Benzenes are converted to biphenyls by oxidation in the presence of Pd or a Pd compound and  $H_2SO_4$ .

### Jet Fuels

SHELL INTERNATIONALE RESEARCH MIJ. N.V.

*British Patent 1,296,772*

Jet fuels are obtained by hydrogenating kerosene fractions over a catalyst consisting of at least 1% Pt or other Pt group metal and at least 0.5% F on an  $Al_2O_3$  support.

### ICE Exhaust Gas Treatment

UNIVERSAL OIL PRODUCTS CO.

*British Patent 1,296,874*

ICE exhaust gases are treated in two catalyst beds, the first containing 0.01-1% Pt/oxide catalyst while the second contains a refractory oxide supporting 1-20% CaO, SrO or BaO and 0.01-1% Pt.

### Selective Hydrogenation

INSTITUT FRANCAIS DU PETROLE, DES CARBURANTS ET LUBRIFIANTS

*British Patent 1,296,943*

Unsaturated byproducts are removed from 3-10°C hydrocarbons by selective hydrogenation, e.g. over a Pd catalyst.

### Reduction Catalyst Alloy

BUSH BOAKE ALLEN LTD.

*British Patent 1,301,300*

Reduction processes with organic compounds are catalysed by a crystalline alloy of Sn with Pt and/or Pd, preferably on a support. A typical catalyst contains 3% of a 1:1 mixture of Pt and Sn on  $SiO_2$  gel support.

### Unsaturated Carboxylic Esters

TORAY INDUSTRIES INC. *British Patent 1,301,465*

Unsaturated esters are obtained when a con-

jugated diene and a carboxylic acid are reacted in the presence of Pd and an alkali metal carboxylate.

### Steam Reforming

IMPERIAL CHEMICAL INDUSTRIES LTD.

*British Patent* 1,301,836

"Reduced carbon lay-down" in the steam reforming of hydrocarbons is achieved using a Ru metal catalyst deposited on a refractory oxide support, optionally together with CaO, SrO and/or BaO. In an example 0.08% Ru and 0.55% CaO are deposited on Al<sub>2</sub>O<sub>3</sub> pellets.

### Hydrogenation Catalyst

PRODUITS CHIMIQUES PECHINEY-ST. GOBAIN

*British Patent* 1,302,269

Dienes and other impurities in olefins are selectively hydrogenated in the presence of a catalyst containing 100–800 p.p.m. Pd promoted by 50–1000 p.p.m. V, supported on Al<sub>2</sub>O<sub>3</sub> or Al<sub>2</sub>O<sub>3</sub> plus SiO<sub>2</sub> having a surface area of up to 150 m<sup>2</sup>/g. Au, Ag, Rh, etc., may be present as additional selectivity promoters.

### Dehydrogenation Catalyst

INSTITUT FRANCAIS DU PETROLE, DES CARBURANTS ET LUBRIFIANTS

*British Patent* 1,302,737

Straight chain paraffins and other saturated hydrocarbons are dehydrogenated over a catalyst based on Al<sub>2</sub>O<sub>3</sub> of 1–100 m<sup>2</sup>/g surface area carrying 0.05–0.7% Pt and Ir and/or Ru in an amount 0.05–0.3 times the amount of Pt. An alkali or alkaline earth metal is also present.

### Alkyl Aromatic Compound Isomerisation

ASHLAND OIL INC.

*U.S. Patent* 3,679,769

Alkyl transfer in alkyl aromatic compounds is catalysed by Pt, Pd, Rh, Ru, etc., on a zeolite support. *U.S. Patent* 3,679,773 uses the same catalyst for dehydrogenation reactions.

### Serial Reforming

J. H. SINFELT

*U.S. Patent* 3,684,693

Serial reforming of hydrocarbons uses Pt/Al<sub>2</sub>O<sub>3</sub> as a catalyst in the first zone(s) and Ir/Al<sub>2</sub>O<sub>3</sub> in the tail zone(s).

### Hydrogen Cascade Process

UNIVERSAL OIL PRODUCTS CO.

*U.S. Patent* 3,691,059

An economical H<sub>2</sub> cascade process uses Pt group metal catalysts in multiple stages with the hydrocarbon feedstock being treated in aliquot portions in each stage.

### Hydrocracking Catalyst

UNIVERSAL OIL PRODUCTS CO.

*U.S. Patent* 3,692,666

A hydrocracking catalyst for a low pressure process consists of a Pt group metal and Ni on a reaction product of Al<sub>2</sub>O<sub>3</sub> and a sublimed Friedel-Crafts halide, e.g. Pt-Ni/Al<sub>2</sub>O<sub>3</sub>-AlCl<sub>3</sub>.

### Olefin-Alkyl Iodide Exchange

SHELL OIL CO.

*U.S. Patent* 3,697,611

Higher olefins are produced by exchange between a lower olefin and a higher alkyl iodide in the presence of supported Pt, chloroplatinic acid, Pt trisphosphine or Ru bisphosphine carbonyl.

### Fuels from Cellulosic Wastes

JOHNSON MATTHEY & CO. LTD.

*German Offen.* 2,211,295

Organic fuel oils are produced by reduction of cellulose-based materials, chiefly waste products, at elevated temperature and pressure using at least one Group VIII metal and/or Cu as catalyst. The preferred catalyst is Ru and its compounds.

### Reduction and Oxidation Catalyst

JOHNSON MATTHEY & CO. LTD.

*German Offen.* 2,212,616

*Dutch Appl.* 72.03388

Oxidation of organic compounds with O<sub>2</sub> or NO reduction in the presence of a gaseous reducing fuel takes place at low temperatures in contact with an alloy or mixture of 1–50 wt. % Rh, 0.01–25 wt. % base metal and remainder Pt on an inert support, preferably a ceramic honeycomb optionally coated with a refractory oxide.

### Heat Exchanger Catalyst

JOHNSON MATTHEY & CO. LTD.

*German Offen.* 2,213,935

*Dutch Appl.* 72.03790

A catalyst support contains a thermally conductive base metal in the form of a metal strip, honeycomb or the fluid conducting conduit of a heat exchanger such that it can conduct heat away in a controlled manner. The catalytic metal is preferably a Pt group metal, Au, Ni, Cr or alloys thereof and the base metal is preferably Cu or stainless steel.

## HOMOGENEOUS CATALYSIS

### Hydroformylation Catalysts

JOHNSON MATTHEY & CO. LTD.

*British Patent* 1,298,331

The hydroformylation of olefins is catalysed by a Rh carbonyl hydride complexed with two or three mols of a tertiary phosphine, arsine or stibine, e.g. RhH(CO)(PPh<sub>3</sub>)<sub>2</sub> or <sub>3</sub> in the presence of an aldehyde (or alcohol corresponding thereto) which is a product of the reaction and excess of free trisubstituted phosphine, arsine or stibine.

### Ruthenium Carboxylate Catalysts

JOHNSON MATTHEY & CO. LTD.

*British Patent* 1,301,739

Ru(II) carboxylates, Ru<sub>2</sub>(OCOR)<sub>4</sub>, especially the acetates, may be prepared by heating together soluble Ru and carboxylate salts and the carboxylic acid. Its adducts with stabilising ligands,

e.g. pyridine or a trisubstituted phosphine, arsine or stibine, are also claimed. The compounds are useful as catalysts and catalyst precursors.

### Olefin Oxidation

UNION OIL CO.

*U.S. Patent 3,686,287*

Olefins are oxidised to unsaturated esters, including vinyl esters, by vapour phase oxidation in the presence of a heterogeneous catalyst containing a Group VIII noble metal, a nitrogen oxide as the oxidant and an aliphatic carboxylic acid. The metal is preferably in the form of a Pt, Pd, or Rh complex.

## CHEMICAL TECHNOLOGY

### Nuclear Fuel Elements

U.K. ATOMIC ENERGY AUTHORITY

*British Patent 1,295,251*

The nuclear fuel element is enclosed in a sheet coated with Rh, Ir, Ru, Au, Cu, Ag and/or Re.

### Separating Hydrogen from Water

NATIONAL AERONAUTICS & SPACE ADMINISTRATION

*U.S. Patent 3,678,654*

Dissolved  $H_2$  in  $H_2O$  is removed by contact with a thin metallic film of Pd or Pd-Ag alloy coated with Pd black, preferably by rubbing with  $PdCl_2$  powder and reducing. There is a reduced pressure on the opposite side of the film.

### Diffusion Unit

JOHNSON MATTHEY & CO. LTD.

*German Offen. 2,213,599*

A diffusion unit of two superimposed metal foils, e.g. Ag/Pt, is described in which at least one foil, preferably both, is corrugated. A wire helix, e.g. of stainless steel, is situated in each corrugation trough to prevent collapse under high pressures and facilitate diffusion and collection of  $H_2$ .

## ELECTRICAL AND ELECTRONIC ENGINEERING

### Pyrochlore Conducting Oxides

E. I. DU PONT DE NEMOURS & CO.

*British Patent 1,295,517*

Electrically conducting, pyrochlore-type oxides have the formula  $(M_xBi_{2-x})(M'_yM''_{2-z})O_{7-z}$  where M is Y, Tl, In, Cd, Pb or a lanthanide, M' is Pt, Ti, Cr, Rh, Sb, Sn or Ge, M'' is Ru or Ir, x is 0-1, y is 0-0.5 and z is 0-1. y is 0-1 when M' is Rh or more than one metal. These oxides, e.g.  $Bi_2Ir_2O_7$ , are used in ceramic film resistances.

### Electrodes on Piezoelectric Ceramics

PLESSEY CO. LTD.

*British Patent 1,299,616*

Pt foil may be used to produce electrodes on Li niobate piezoelectric ceramics.

### Glass-covered Gold Pattern

BELL TELEPHONE LABORATORIES INC.

*U.S. Patent 3,676,087*

A Au conductor pattern on a substrate is more easily wetted by glass when it is covered with a thin film of Rh.

### Oxide Resistors

INTERNATIONAL NICKEL CO. INC.

*U.S. Patent 3,679,607*

Resistors are made from  $RuO_2$  and/or  $IrO_2$  of fine crystallite size.

### Solar Cell with Metal Layered Contact

TELEFUNKEN PATENTVERWERTUNGS A.G.

*U.S. Patent 3,686,036*

A solar cell consists of a semiconductor body having one or both contacts of three-layer construction comprising Ag/Ti, Cr, Mo or Ta/noble metal, e.g. Pt or Pd. A method of contacting a solar cell by vapour deposition is also included.

### Uranium Oxide Electrode

INTERNATIONAL BUSINESS MACHINES CORP.

*U.S. Patent 3,689,378*

A high impedance voltmeter has a standard reference electrode and a low impedance electrode consisting of Ir or another noble metal wire coated with a thin smooth layer of uranium oxide.

### Dispenser Cathode

SIEMENS A.G.

*U.S. Patent 3,692,575*

A W dispenser cathode is coated with Os, Ir or another Pt metal by displacement from solution, heating and reduction.

## TEMPERATURE MEASUREMENT

### Thermistor Compositions

E. I. DU PONT DE NEMOURS & CO.

*U.S. Patent 3,679,606*

A ceramic support is glazed with a mixture of 20-50% noble metal powder and 50-80% frit. The noble metal powder contains 15-85 wt.% Pd and/or Ru, 15-85% Rh and 0-12% Ag and/or Au.

### Thermocouple Compensating Leads

JOHNSON MATTHEY & CO. LTD.

*German Offen. 2,204,613*

A compensating apparatus for a thermocouple, preferably Pt:13% Rh-Pt, comprises two compensating leads, one of which includes at least two insulated conductor limbs, of which one limb is formed from material having thermoelectric properties different from any other conductor limb. The thermoelectric e.m.f. of the combined thermocouple and compensating leads is adjustable.