

TEMPERATURE MEASUREMENT

A Platinum Resistance Thermometer Calibration between 2 and 273.15°K

CHAN YET-CHONG and A. M. FORREST, *J. sci. Instrum., J. Phys. E.*, 1968, 1, (8), 839-842

Selected Pt resistance thermometers were calibrated approximately at 2-273.15°K using only the b.p. of He, the ice point, and temperatures at 2-4.2°K from He vapour pressure thermometer measurements. Interpolation for 4.2-273.15°K used a table of Z functions and for 2-16°K used a polynomial equation in T against R.

Comparison between Gas Thermometer, Acoustic, and Platinum Resistance Temperature Scales between 2 and 20°K

J. S. ROGERS, R. J. TAINSH, M. S. ANDERSON and C. A. SWENSON, *Metrologia*, 1968, 4, (2), 47-59

The NBS Pt resistance thermometer scale of 1955 at 2-16°K was used in determining the resistance versus temperature relation of Ge thermometers to ± 3 mdeg against a constant volume gas thermometer.

Temperature Measurements with Metal Ribbon High-temperature X-ray Furnaces

W. OSTERTAG and G. R. FISCHER, *Rev. sci. Instrum.*, 1968, 39, (6), 888-889

Thin Pt and Rh-Pt thermocouple wires were welded to the Pt ribbon of a high-temperature X-ray diffractometer attachment. The temperature profile of the specimen stage, determined as functions of temperature, heater position and heater shape, showed improved accuracy of temperature measurement.

Protective Devices for Thermocouples Used in Glass-melting Furnaces

V. M. OBUKHOV, *Steklo Keram.*, 1968, 25, (4), 12-14
Four types of protective casings for 6%Rh-Pt: 30% Rh-Pt thermocouples are described. Pro-

tection against flame above 1450°C is given by a three-layer cover of corundum, ZrO₂ and corundum. Protection against molten glass up to 1200°C may be afforded by corundum, or at temperatures $\pm 1200^\circ\text{C}$ by a three-layer cover of corundum, steel and corundum. Protection against molten glass above 1250°C consists of corundum sheathed with Pt. In each case the thermocouple itself is supported in a twin-bore corundum tube.

Determination of Temperature According to the Thickness of the Clinker Deposit

V. V. PUZANKOV, YU. P. SHCHUKIN and M. L. VISHNEVETSKII, *Stal'*, 1968, (4), 304-305

To eliminate errors of temperature measurement with Rh-Pt thermocouples due to clinker build-up on the sheath a probe has been developed at the Karaganda works which extends telescopically so that the hot junction projects beyond the point of clinker build-up.

Calibration and Stability of Miniature Resistance Thermometers

G. W. LINDBERG and W. V. JOHNSTON, *Abstr. Papers, 155th Mtg, Am. Chem. Soc.*, 1968, (Mar.), V9

Miniature Pt resistance thermometers 0.5 in. long, 0.156 in. diameter, weighing 1 g were calibrated at -182 to +100°C by comparison with capsule-type Pt resistance thermometers and at -262 to -182°C by interpolation data. The resistance at 0°C was reproducible to 10 ppm for six months.

The Accuracies of Calibration and Use of I.P.T.S. Thermocouples

T. P. JONES, *Metrologia*, 1968, 4, (2), 80-83

Uncertainty expressed as 99% confidence limits from precise calibration of Pt : 10% Rh-Pt thermocouples at 630.5-1063°C is $\approx \pm 1.0 \mu\text{V}$, based on five replicates at each of the three primary calibration points and subsequent accuracy of a calibrated thermocouple with systematic errors eliminated is $\pm 0.2^\circ\text{C}$.

NEW PATENTS

METALS AND ALLOYS

An Improved Alloy

JOHNSON, MATTHEY & CO. LTD
British Patent 1,112,766

A new alloy, especially suitable for spinnerette production, consists of 50-80% Au, 0.04-0.5% Ir, and the remainder Pt with the usual impurities.

Producing Iron-Rhodium Base Alloys Having Improved Magnetic Transition Properties

GENERAL ELECTRIC CO. (NEW YORK)
British Patent 1,117,727

An alloy with a CsCl-type ordered crystal structure and an antiferro-magnetic-ferromagnetic transition is obtained from an Fe-Rh alloy, optionally containing small amounts of Pd or Pt,

by heat treating at a temperature above 800°C to produce homogenisation of the alloy and then quenching the alloy to a temperature below 800°C.

Treatment of Palladium and Palladium-base Alloys

JOHNSON, MATTHEY & CO. LTD

British Patent 1,117,739

British Patent 1,091,051 relates to a method of treating Pd or its alloys to reduce discontinuous yielding under stress. This method may now be applied to alloys in which Na has been added to suppress the formation of Pd silicide.

Production of Platinum and/or Palladium Oxides or their Mixtures with Rhodium, Iridium or Ruthenium Oxides

JOHNSON, MATTHEY & CO. LTD

German Patent 1,266,293

A composition comprising a powder of one or more of the above oxides is produced by the anodic oxidation of Pd, Pt or a suitable alloy with the other Pt metals in a molten mixture of an alkali metal nitrate or chloride.

Permanent Magnets

DEUTSCHE GOLD- & SILBER-SCHNEIDANSTALT

German Patent 1,266,511

Methods are provided for the heat treatment of magnetic alloys containing Fe with 25–62 wt% Pd, produced by melting or sintering.

Improvement of Metal Properties

JOHNSON, MATTHEY & CO. LTD

Dutch Appln 66.14.142

Noble metals, noble metal alloys and other metals (e.g. produced from powders) are cold worked to such an extent that during subsequent tempering, recrystallisation occurs to give a grain structure highly oriented in the direction of cold working.

CHEMICAL COMPOUNDS

New Ruthenium Complexes

STE USINES CHIMIQUES RHONE-POULENC

French Patent 1,503,334

On contacting $RuCl_3$ or RuI_3 with certain nitrile or olefine ligands, new complexes are formed of formula RuX_mL_n , where m is 2 or 3 and n is 4 or 3, X is halogen and L is an olefine activated by certain groups, an aromatic nitrile or a saturated aliphatic or cycloaliphatic nitrile.

ELECTRODEPOSITION AND SURFACE COATINGS

Electrodes

IMPERIAL METAL INDUSTRIES (KYNOCHE) LTD

British Patent 1,113,421

A Ti core or a core of a similar metal is given a

coating of another metal, especially Pt group metal, without first removing the oxide film. By definition Pt group metal excludes Pd but includes the other five metals. The Pt metal is applied in the form of an alloy with a very readily dissolved metal, such as Cu.

Deposition of Ruthenium

JOHNSON, MATTHEY & CO. LTD

British Patent 1,114,595

A porous base is impregnated with Ru (e.g. to produce Ru/Al_2O_3 catalysts) by contacting it with a solution of $(NH_3)_6Ru(NO_3)_3$, and then decomposing this compound to leave behind Ru metal.

Palladium Electroplating

I.B.M. CORP.

U.S. Patent 3,376,206

Catalytic films of high activity are deposited, especially on Cu and its alloys, by using baths containing water-soluble salts of Pd and strong acids, buffering salts of weak bases and strong acids and organic complexing agents at pH 4–5.5, e.g. $PdCl_2$, NH_4Cl and disodium EDTA.

Ceramic Metallising Paint

E. I. DU PONT DE NEMOURS & CO.

U.S. Patent 3,380,835

Successful metallising of ceramics with Pt group metals, e.g. Pt and Pd, is achieved by deactivating these catalytic powders previously by heating or by treatment with As oxide, Sb oxide, etc.

Chemical Platinum Plating Process

JOHNSON, MATTHEY & CO. LTD

French Patent 1,512,175

PtO_2 , alone or mixed with up to 50% of another Pt metal oxide, is reacted with a 2–5 C aliphatic alcohol to give a dispersion. The dispersion is contacted with a substrate in the presence of H_2O and a H_2O soluble mineral acid to deposit Pt (or Pt alloy) on the substrate. The deposit is dried and organic material eliminated.

Applying Designs to Metallic Bases

JOHNSON, MATTHEY & CO. LTD

Canadian Patent 785,472

A metal or alloy differing in colour from the metal base is applied in an organic base and fired to produce slight adherence, the metal or alloy then being embossed with a design. Au, Ag and Pt metals, e.g. in flake form, are suitable decorative materials. This corresponds to *French Patent 1,455,917* and *Italian Patent 767,740*.

JOINING

High Temperature Brazing Alloys

U.S. ATOMIC ENERGY COMMISSION

U.S. Patent 3,374,092

W, Ta and their alloys are brazed using a ternary alloy of 10–35 wt% Ru, 45–90 wt% W, remainder Re, melting at 2300–2800°C.

HETEROGENEOUS CATALYSIS

Epitactic Ruthenium Catalyst

E. I. DU PONT DE NEMOURS & CO.

British Patent 1,113,405

The "epitactic" catalyst is a support of $\eta\text{-Al}_2\text{O}_3$ carrying an epitaxial growth of Ru. It is produced from RuCl_3 or nitrosyl solution which is adjusted to pH 3.5-4.5 with $(\text{NH}_4)_2\text{CO}_3$ or NH_4HCO_3 and then mixed with a slurry of solid $\eta\text{-Al}_2\text{O}_3$ particles. Further alkali is added to bring the pH to 7.5-8.5 while heating at 45-85°C. After 20 min the precipitate is removed, dried and treated with H_2 .

Production of 2,3-Dimethyl Butane

UNIVERSAL OIL PRODUCTS CO.

British Patent 1,115,176

The isomerisation to 2,3-dimethyl butane of neohexane is catalysed at 100-500°C and 1-150 atm by a Group VIB or VIII metal on an acidic support, e.g. $\text{Pt}/\text{Al}_2\text{O}_3$ with small amounts of F_2 and Cl_2 . For the highest yield, the rate of flow of the neohexane should be such that 0.1-2.0 mol% of it is converted in each pass.

Catalytic Reactions and Catalyst

JOHNSON, MATTHEY & CO. LTD

British Patent 1,116,943

An improved catalyst for the isomerisation of olefines, especially $1\text{-C}_6\text{H}_{10}$ is obtained by absorbing a catalytically active Pt group metal on to a solid porous support from a thermally stable solvent, e.g. using $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ in ethylene glycol.

Catalytic Cracking of Hydrocarbons

W. R. GRACE & CO.

British Patent 1,117,210

The catalyst consists of 0.1-2 wt% Pd, Rh and/or Pt deposited on a $\text{SiO}_2\text{-Al}_2\text{O}_3$ -zeolite support. The support contains 10-40% uncombined Al_2O_3 and 5-80% of a zeolite of formula $x\text{M}_{z/n}\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 3.5-7\text{SiO}_2 \cdot 0-9\text{H}_2\text{O}$, where M is a cation of valency n and x is 0-1. 1,117,209 describes the same catalyst supports used for Co and Ni catalysts.

Selective Hydrogenation

CATALYSTS & CHEMICALS INC.

British Patent 1,120,307

Small amounts of C_2H_2 in C_2H_4 are selectively hydrogenated by adding an excess of H_2 and passing the gas mixture over a supported Pd catalyst in the usual way. The selectivity is improved by adding 5-400 ppm of CO to the olefin.

Platinum Gauze Catalyst Activation

MONSANTO CO.

U.S. Patent 3,371,989

The reaction over a Pt gauze of NH_3 , natural gas and air to give HCN is improved by flowing the reactants over the gauze at 1.28-1.45 lb/hr/layer of gauze/in² in order to activate the catalyst.

Aluminosilicates Containing Platinum Metals

MOBIL OIL CORP.

U.S. Patent 3,373,110

Pt metal impregnation of a synthetic zeolite is achieved by adding a Pt metal salt solution (especially containing a Pt or Pd salt) to the aluminate and silicate solutions from which the zeolite is formed.

Selective Hydrogenation Catalyst

FARBENFABRIKEN BAYER A.G.

U.S. Patent 3,373,219

The selective hydrogenation of 4C acetylenic compound in a mainly butadiene fraction is improved when the fixed Pd catalyst is supported on a Li Al silinel.

High Octane Petrols

AIR PRODUCTS & CHEMICALS INC.

U.S. Patent 3,374,167

A full range reformat is hydrogenatively reformed over $\text{Pt}/\text{Al}_2\text{O}_3$, a heart cut is removed from the product and this cut is again hydrogenatively reformed over $\text{Pt}/\text{Al}_2\text{O}_3$. Less catalyst deactivation occurs.

Oxidisation Catalyst

UNIVERSAL OIL PRODUCTS CO.

U.S. Patent 3,377,269

The particles of catalyst are based on Al_2O_3 with a variable density of catalyst where a small part of the total surface has small localised spots of Pt with a high density of 10,000-20,000 $\mu\text{g}/\text{m}^2$ Pt and the remainder of the surface has a low density of the order of 0.9-10 $\mu\text{g}/\text{m}^2$ Pt, giving a total Pt content of 0.05-0.2 wt%. The catalyst can be used for burning I.C.E. exhaust gases.

Oxidisation of Waste Gases over Mixed Catalysts

UNIVERSAL OIL PRODUCTS CO.

U.S. Patent 3,378,334

Combustible gases (e.g. I.C.E. exhaust gases) are mixed with O_2 and passed over a fixed bed of spherical Pt catalyst particles, some of the particles (8-30%) having a Pt content up to about 5% and the remainder a low Pt content so that the overall content is 0.05-0.2 wt%.

Olefin Hydroformylation

TOA NENRYO K.K.K.

U.S. Patent 3,378,590

The production of aldehydes and alcohols from olefins, H_2 and CO is catalysed by Co promoted with Pd/C or Pt/C.

Gas Reactions Using Gauze Catalysts

MONTECATINI-EDISON S.p.A.

U.S. Patent 3,379,500

Specific mixtures of NH_3 , CH_4 , N_2 and O_2 are reacted over gauze catalysts made of Pt or its alloys at 1100-1200°C.

Low Pressure Platinum Reforming Catalyst

UNIVERSAL OIL PRODUCTS CO.

U.S. Patent 3,379,641

Low pressure reforming is catalysed by a sulphided Pt-Fe-halogen/ Al_2O_3 catalyst having an Fe content of 100-1000 ppm, uniformly distributed throughout the catalyst.

Hydrogenation of Olefine Polymers in Cumene

GULF OIL CORP.

U.S. Patent 3,379,767

Cumene contaminated with olefin polymers is passed over a Pd/ Al_2O_3 catalyst in a fixed bed at 100-300°F in the presence of H_2 to hydrogenate the olefin polymers.

Oxidation of Glucose

JOHNSON, MATTHEY & CO. LTD

Dutch Appln 67.13,891

Selective oxidation is achieved using a supported Pt metal catalyst (e.g. Pd) in the presence of Na or K carbonate or bicarbonate.

HOMOGENEOUS CATALYSIS

Ethylenic Compounds

IMPERIAL CHEMICAL INDUSTRIES LTD

British Patent 1,111,714

Vinyl or allyl alkyl ethers are produced by contacting a vinyl or allyl ester of an aliphatic carboxylic acid with a 1-20 C aliphatic alcohol in the presence of an organic solvent containing 0-10% H_2O and a salt or coordination compound of a Pt metal, especially Pd, Pt, Rh and Ru. Typical catalysts are Li_2PdCl_4 and $\text{Pd}(\text{OOC.CH}_3)_2$.

Producing Vinyl Acetate

ASAHI KASEI K.K.K.

British Patent 1,116,588

The reaction of C_2H_4 and O_2 in the presence of a chloroacetic acid to give vinyl acetate is catalysed by oxides, hydroxides and salts (readily reacting with acetic acid to give acetates) of Pt, Pd, Ru, Rh or Ir promoted with Cu, Ag, Cd, Sn, Pb, Cr, Mo, W, Fe, Co or Ni.

Manufacture of Vinyl Esters

COURTAULDS LTD

British Patent 1,116,945

The oxidation of C_2H_4 in the presence of a carboxylic acid to form a vinyl ester is catalysed by a circulating liquid solution of a palladous carboxylate, a metal salt able to oxidise Pd metal and an alkali metal carboxylate. The reaction yields Pd metal as a by-product and this is heated with a carboxylic per-acid to regenerate the palladous carboxylate.

Production of Vinyl Carboxylic Esters

CELANESE CORP.

British Patent 1,121,103

A vinyl ester of a 2-7 C aliphatic acid is produced from C_2H_4 , the 2-7 C acid and O_2 in the presence of halogen, cupric, Pd and 2-7 C acid ions, the Pd and Cu being present in at least 0.002 and 0.2 M concentrations respectively.

Olefin Oxidative Carbonylation

UNION OIL CO. OF CALIFORNIA

U.S. Patent 3,381,030

Olefins, O_2 and CO_2 react to give unsaturated carboxylic acids and aliphatic esters in the presence of an anhydrous organic solvent solution containing 0.01-5 wt% Group VIII metal, especially Pd, in a redox system at 30-300°C and at an elevated pressure.

Olefin Polymerisation Catalysts

INSTITUT FRANCAIS DU PETROLE, DES CARBURANTS ET LUBRIFIANTS

French Patent 1,505,335

The specificity and activity of Ziegler catalysts is improved by the introduction of a Group VIII noble metal salt or complex, preferably a complex produced *in situ*. Thus a complex of PdCl_2 and PPh_3 can be formed in the presence of Et_2AlCl and TiCl_3 .

Production of Fumaric Acid and Muconic Acid Dichlorides

BADISCHE ANILIN- & SODA-FABRIK A.G.

German Patent 1,263,752

The reaction of C_2H_2 , CO and PH_3 is catalysed by 0.001-5 wt% of Pd or a Pd compound at 50-120°C and 50-300 atm gauge.

Production of Alken-2-yl-1-ethers

CONSORTIUM FÜR ELEKTROCHEMISCHE INDUSTRIE G.m.b.H.

German Patent 1,269,613

The production of these ethers by the reaction of the corresponding halides with alcohols is catalysed by Group VIII noble metals, especially Pd and Rh halides or halide complexes, e.g. Na_2PdCl_4 .

FUEL CELLS

Fuel Cells

JOHNSON, MATTHEY & CO. LTD

British Patent 1,111,864

A H_2 - O_2 cell fed with NH_3 is fitted with a fuel electrode made of a base metal, Pd or Pd alloy permeable to H_2 on which the NH_3 is decomposed.

In Situ Preparation of Hydrogen and Simultaneous Hydrogen Control in Electrochemical Cells

PROTECH INC.

British Patent 1,114,851

H_2 utilisation in a fuel cell is controlled by using an anode structure coated with a layer containing Pd, (e.g. a Pd-Ag alloy) permeable only to H_2 .

Ion Exchange Membrane Electrode

GENERAL ELECTRIC CO. (NEW YORK)

British Patent 1,120,267

Electrodes particularly suitable for fuel cells are produced by electrolytically depositing a thin layer of catalytically active noble metal (especially

Pt) on a conducting base, washing and drying the deposit and finally transferring the deposit by physical contact to the surface of an ion exchange membrane. Pt alloy deposits may be produced and transferred in the same way.

Platinum-coated Fuel Cell Electrode

TEXACO INC. *U.S. Patent 3,377,204*

A porous C electrode is treated to incorporate Pt by heating the electrode in CO₂ at 700–1000°C for 1–10 hours, coating the electrode surface with H₂PtCl₆, reducing the acid to Pt metal at 200–300°C for 1–4 h in a H₂ atmosphere and finally heating the electrode at 700–1000°C for 1–10 h in a H₂ atmosphere.

Vapour Diffusion Fuel Cell Electrode

MONSANTO RESEARCH CORP.

U.S. Patent 3,382,103

N₂H₄ is supplied to the fuel cell anode through a three-layer barrier of which the central layer contains a N₂H₄ decomposition catalyst such as Ru or Rh.

Fuel Cell Electrode Assembly

U.S. NATIONAL AERONAUTICS & SPACE ADMINISTRATION *U.S. Patent 3,382,105*

The electrode assembly consists of thin plastic ion exchange membranes coated with finely divided Pt catalyst.

CATHODIC PROTECTION

Electrodes with Activated Platinum Group Coatings

ORONZIO DE NORA IMPLIANTI ELETTOCROMICI

British Patent 1,111,767

An electrode for impressed current cathodic protection has a solid base (e.g. of Ti) coated with a Pt metal containing 0.2–2 wt% of Sb, Cd, Pb, Cu, Ta, V, Nb or their mixtures as activating element. Preferably a coating of Pt containing Sb is applied to a Ti base.

ELECTRICAL AND ELECTRONIC ENGINEERING

Cermet Resistance Element

BECKMAN INSTRUMENTS INC.

British Patent 1,112,474

A resistance layer of low coefficient of resistivity, for brazing to a non-conducting base, consists of 50–95% glass and 50–10% of a Ru-Rh alloy. Thus a layer can contain 80% glass, 10% Ru and 10% Rh.

Resistive Elements for Variable Resistors

AMPHENOL CORP.

British Patent 1,114,052

Low noise characteristics are obtained by coating an insulating base with a Ni-Cr-Fe alloy and applying a film of Pt, Rh or Ir.

Materials for an Electric Contact

HITACHI LTD

British Patent 1,116,788

Electrical contacts are made from Pd containing 0.1–10 wt% of a Pb compound or compounds. Preferably 0.1–10 wt% of PbS and/or PbO are introduced into Pd by sintering or by addition to molten Pd.

Metal Glaze Resistance

INTERNATIONAL BUSINESS MACHINES CORP.

U.S. Patent 3,372,058

Resistances are produced on ceramic dielectrics by applying and firing a glaze containing 15–70% PdO or RhO, having a crystallite size with a surface area of at least 0.75 m²/g, and up to 35% of a conductive metal, such as Ag, dispersed in 35–70% vitreous enamel frit.

Conductive Noble Metal Paint

INTERNATIONAL BUSINESS MACHINES CORP.

U.S. Patent 3,374,110

An alloy of 75–85% Ag and 25–15% Pd is produced and powdered for use with a ceramic frit to give a conductive paint. This alloy, unlike pure Ag, does not migrate and can be soldered.

Piezoelectric Lead Zirconate Titanate

NIPPON ELECTRIC CO. LTD *U.S. Patent 3,375,194*

The electromechanical coupling and mechanical qualities of these ceramics are improved by incorporating 0.01–1.0 wt% of Rh₂O₃.

Sintered Palladium Electrical Contacts

HITACHI LTD

U.S. Patent 3,380,812

Electrical contacts for use in an organic gas atmosphere are made from Pd with an added inorganic Pb compound, e.g. litharge, to reduce its catalytic action and thus eliminate the formation of brown deposits when operating in organic gases.

TEMPERATURE MEASUREMENT

High Temperature Thermocouples

GENERAL MOTORS CORP. *British Patent 1,114,874*

Balanced thermoelements and leads comprise (a) a thermoelement of 40% Pd, 50% Pt and 10% Au, (b) a second thermoelement made of 65% Au and 35% Pd, (c) one lead of chromel and (d) a second lead made of a Ni-Fe-Mn alloy.

Improved Vessel for Molten Metals

YAWATA IRON & STEEL CO. LTD

British Patent 1,117,935

In order to make measurements on molten metals, the vessel is fitted with a standard electrode for measuring the O₂ content electrochemically. The standard electrode is also matched with a metal wire, e.g. a Pt-Rh wire, to act also as part of a thermocouple to measure the temperature.