

between temperature and resistance ratio $W(T) = R(T)/R(0^\circ\text{C})$ of Pt. In this study three methods for interpolation of ΔW have been applied to experimental data. Between the boiling and triple points of O_2 the accuracy is within 1 mK; between the boiling points of O_2 and of H_2 and also between the boiling and triple points of H_2 accuracies within 2 mK are possible.

Comparison of Platinum Resistance Thermometers with the Hydrogen Vapour-pressure Thermometer

Ibid., 622-632

Pt thermometers are compared with the 20.4K equilibrium H_2 vapour pressure thermometer in three different apparatuses, using the CCT-64 scale for the Pt thermometers and the $T_{1,60}$ scale for the vapour pressure thermometer. "Best

values" on the CCT-64 scale of the fixed points of the 1968 IPTS in the liquid H_2 range are given.

The Behaviour of Pt/PtRh and Ni/NiMo Thermal Elements in the High Temperature Furnace in the Presence of Material Containing Chromium

E. LENZ, *Werkstoffe Korrosion*, 1969, (8), 651-658

Evaporation of Cr from alloy parts of the furnace during vacuum annealing at 10^{-3} to 10^{-4} Torr, $>1200^\circ\text{C}$ leads to deposition of Cr on thermocouples, which suffer reduction of service life by formation of hard, brittle intermetallic compounds. Suggested cures include use of vacuum-tight sheaths for the thermocouples, introduction of some N_2 to the vacuum above 1000°C , and replacement of Cr alloy components by ceramic materials or Mo alloys.

NEW PATENTS

METALS AND ALLOYS

Composite Metal Articles

INTERNATIONAL NICKEL LTD

British Patent 1,168,130

Articles for high temperature use in non-oxidising atmospheres consist of a core of Ir, Ru, W and Mo, a barrier layer and a coating of at least 95% Ir, Ru, W or Mo. The barrier layer between the core and coating consists of Au, Pd, Pd-Ag alloy or Pd-Cu alloy of specified composition.

Platinum-Iron Permanent Magnet Alloys

CITIZEN TOKAI K.K.

U.S. Patent 3,444,012

Pt-Fe alloys of the super-lattice type are treated to improve their magnetic characteristics by cold-working and thermal-ageing.

Dispersion Hardening of Platinum Metals and Alloys

DEUTSCHE GOLD- & SILBER-SCHNEIDANSTALT

Dutch Patent 69,00716

Materials comprising Pt group metal(s), Au or alloys thereof, together with an element having high O_2 -affinity (preferably Zr) are dispersion hardened by internal oxidation by heating at 800 - 1200°C in an O_2 -containing atmosphere for more than 5 h and preferably more than 20 h.

Production of Metallic Oxides

JOHNSON MATTHEY & CO. LTD

Swiss Patent 478,063

Electrolytic production of oxides of Pt and/or Pd or oxides of Pt and/or Pd mixed with oxides of other metals not harmful to the catalytic properties of the Pt and/or Pd oxides by electrolysis of

appropriate Pt, Pd, Pt alloy or Pd alloy anode in a molten bath of alkali metal halide and nitrate. This corresponds to *British Patent* 1,106,814.

CHEMICAL COMPOUNDS

Manufacture of Palladium Halides

FARBWERKE HOECHST A.G. *British Patent* 1,159,225

Metallic Pd is treated with O_3 (or air) in the presence of a carboxylic acid solution of a halide of a metal of Group Ia, IIa or IIIb or an ammonium halide at 10 - 150°C . The Pd used is Pd black. It becomes converted to Pd(II) halides.

Ruthenium Carbonyl

IMPERIAL CHEMICAL INDUSTRIES LTD

British Patent 1,160,765

$\text{Ru}_3(\text{CO})_{12}$ is prepared by reaction of RuCl_3 , Na naphthenate or Na acetyl-acetonate and a CO-H_2 mixture.

Production of Carbonyl Compounds

HERCULES INC.

British Patent 1,164,561

Carbonyl compounds are produced by reacting an organic Group VIII noble metal compound with CO to form a CO derivative of the organic group. The Group VIII reactant is formed *in situ*, e.g., from p-carboxy-phenyl mercuric chloride and PdCl_2 . The reaction of this with CO gives terephthalic acid.

Hexaruthenium-octadecarbonyl

LONZA LTD

British Patent 1,167,691

This new carbonyl compound $\text{Ru}_6(\text{CO})_{18}$ is produced by heating trimeric $\text{Ru}(\text{CO})_4$ at 150 - 250°C in a closed vessel. O_2 is absent, and p_{CO} is 0.2-2 atm.

Trimeric Ruthenium Tetracarbonyl

LONZA LTD *U.S. Patent 3,446,591*
A basic Ru carboxylate or Ru acetylacetonate is reacted with CO and H₂ at 150–200 atm in an organic solvent at 140–250°C to yield orange-red trimeric [Ru(CO)₄]₃.

Ruthenium Complexes

RHONE-POULENC S.A. *U.S. Patent 3,449,387*
Ru halides are reacted with organic nitriles to give complexes of the form RuX_mL_n, where X is halogen and L is a nitrile. These substances may be used as catalysts for dimerisation of acetonitrile.

New Rhodium Phosphine, Arsine and Stibine Complexes

ETHYL CORP. *U.S. Patent 3,459,780*
These Rh complex monohalides have the formula RhX(ZR₃)₃, where R is a 6–10C organic group, Z is P, As and/or Sb and X is a halogen. These compounds are used as chemical intermediates, oxidation catalysts and metal plating compounds.

ELECTROCHEMISTRY

Platinum-coated Electrodes

PPG INDUSTRIES INC. *British Patent 1,159,410*
The overvoltage of a Pt metal coated Ti-base electrode is reduced by depositing metallic Bi on the Pt metal surfaces and heating to at least 200°C in a non-oxidising atmosphere.

Electrochemical Cells

LEESONA CORP. *British Patent 1,167,541*
Electricity is generated from NH₃ in a cell where the catalyst consists of more than 50 at.% Pt with most of the remainder being a second Pt group metal, e.g., 93.8% Pt, 5.3% Ru, 0.9% Pb.

Catalytic Electrode

LEESONA CORP. *U.S. Patent 3,444,003*
An electrode is made by depositing a layer of catalytic metal (Pt and Rh) from an aqueous solution of Pb and the catalytic metal on to a Pt foil or other base. This layer is followed by a second layer electrodeposited from a solution free from Pb so that the outer coating contains no Pb.

Alkali Chloride Electrolytic Mercury Cells

T. ISHIMATSU *U.S. Patent 3,445,374*
Each electrolytic Hg cell has a metallic cover, of which the inner face is coated successively with a layer of Ti and a layer of a Pt group metal (Pt, Rh, Pd and alloys) which serves as the anode in the cells.

Electrolysis Cell

ALLIS-CHALMERS MANUFACTURING CO. *U.S. Patent 3,446,725*
In an electrolysis cell for the preparation of H₂ and O₂, a noble metal screen substrate (Pt, Pd,

Rh, Ir, etc.) is interposed between an electrode of sintered Ni and the electrolyte matrix interfaces.

Brine Electrolysis Electrode

BADISCHE ANILIN- & SODA-FABRIK A.G. *U.S. Patent 3,458,423*
The anode has at least two porous layers of Ti, Ta or base alloys of these metals, the layers being arranged one above the other in the direction of the cathode, and the layer behind the layer facing the cathode is activated with a Pt group metal.

ELECTRODEPOSITION AND SURFACE COATINGS

Metallising Compositions

INTERNATIONAL BUSINESS MACHINES CORP. *British Patent 1,159,980*
A metallising composition comprises a finely divided metal alloy (Ag-Pt or Ag-Pd or Ag-Pt-Pd) and particles of a vitrifiable flux (Pb Bi trioxide and Pb borosilicate glass) dispersed in a liquid vehicle.

Chemical Palladium Plating

BURROUGHS CORP. *British Patent 1,164,776*
A stable chemical plating bath which is based on the use of divalent Pd ions chelated with both EDTA and ethylenediamine and a reducing agent.

Anodes for Salt Electrolysis

ORONZIO DE NORA IMPIANTI ELETTROCHIMICI *British Patent 1,167,992*
A valve metal substrate such as Ti is plated with a Pt metal from an organic solution of a Pt metal complex of a compound having a –NH₂, –NH₁, –NH₂ or =NH group, e.g. (NH₄)₂PtCl₆.

Iridium-coated Graphite

UNION CARBIDE CORP. *U.S. Patent 3,446,607*
A graphite substrate resistant to oxidation up to 2000°C is provided with an adherent pore-free Ir coating, by applying finely divided Ir powder in a slurry, heating the substrate and Ir powder to produce a coating of sintered Ir, then vapour plating the sintered coating with Ir, and finally electrodepositing more Ir on top of this.

LABORATORY APPARATUS AND TECHNIQUE

Ionisation Gauges

EDWARDS HIGH VACUUM INTERNATIONAL LTD *British Patent 1,159,494*
The filamentary electron-emitting cathode of an ionisation gauge consists of a Pt-Rh alloy wire coated with a rare earth oxide of low work function.

Oxygen Sensor

BECKMAN INSTRUMENTS INC.

U.S. Patent 5,449,231

A polarographic cell for O determination includes an anode and a Rh cathode joined by an electrolyte and separated from the sample by a selectively permeable membrane.

JOINING

Brazing Graphite

STE NATIONALE D'ETUDE ET CONSTRUCTIONS

DE MOTEURS D'AVIATION *U.S. Patent 3,442,006*

A graphite member is welded or brazed to graphite or a refractory material by interposing between the two members a fixative layer containing refractory material and one of the Pt metals.

HETEROGENEOUS CATALYSIS

Chlorination of Toluene

TENNECO CHEMICALS INC.

British Patent 1,158,987

A chlorinated $C_6H_5CH_3$ mixture with an increased para-isomer content is produced by reacting $C_6H_5CH_3$ with Cl_2 in the presence of PtO_2 but in the absence of light or Fe.

Selective Hydrogenation of C_4 Fractions

FARBENFABRIKEN BAYER A.G.

British Patent 1,159,256

C_4 -acetylenes or C_4 -acetylene/butadienes in a butadiene containing C_4 -fraction are selectively hydrogenated in the trickle-phase at high pressure in the presence of a fixed Pd/carrier catalyst. At least 20% of the catalyst support consists of Li Al spinel.

Catalytic Reduction of Aromatic Ketones and Aldehydes

JOHNSON MATTHEY & CO. LTD

British Patent 1,159,967

Aromatic ketones or aldehydes are converted to the corresponding alcohol by hydrogenation on a Pd catalyst (5% Pd/C) in the presence of an amine (aniline, p-toluidine benzylamine, pyridine or quinoline).

Hydrocarbon Conversion Catalyst

STANDARD OIL CO.

British Patent 1,161,750

Liquid C_3H_8 and C_4H_{10} and aromatics are produced from naphtha using a catalyst comprising 0.1–2 wt% noble metal such as Pt, 2–95 wt% mordenite, 0.05–5 wt% halogen such as Cl_2 , and 5–98 wt% Al_2O_3 .

Saturated Aliphatic Mono-carboxylic Acids

KNAPSACK A.G.

British Patent 1,161,972

The oxidation of saturated aliphatic aldehydes to acids is catalysed by supported Pd metal, Pd oxide

or Pd salt together with at least one other source of metal which includes Pt, Rh, Ru, Au and Ag.

Production of Phenol by Catalytic Dehydrogenation

INSTITUT FRANCAIS DU PETROLE DES CARBURANTS

ET LUBRIFIANTS

British Patent 1,162,397

The dehydrogenation of cyclohexanol and/or cyclohexane is catalysed by a substrate of SiO_2 supporting 0.1–2 wt% Pt, 0.05–1 wt% Ir and 0.5–3 wt% alkali or alkaline earth metal. The specific surface of the catalyst must be 100–300 m^2g^{-1} and the pore volume 0.7–1.1 ml g^{-1} .

Process for Converting Hydrocarbons

SHELL INTERNATIONALE RESEARCH

MIJ N.V.

British Patent 1,162,969

Hydrocarbons are converted by contacting them at high temperature and pressure, in the presence of H_2 , with a Pd/zeolite catalyst. The zeolite is specially treated to have an alkali metals content of < 1% and a molecular SiO_2/Al_2O_3 ratio 3–7.

Vinyl Acetate Production

KURASHIKI RAYON K.K.

British Patent 1,164,194

C_2H_4 , O_2 and aqueous CH_3COOH are reacted over a metallic Pd catalyst, e.g., 0.1–5% Pd on a support, to give vinyl acetate, and CH_3COOH in a form suitable for recycling.

Catalytic Isomerisation

ESSO RESEARCH & ENGINEERING CO.

U.S. Patent 3,442,973

Normal 4–8 C paraffins are isomerised on a catalyst comprising Au and Pd on an Al_2O_3 support. It preferably contains Pd in an amount representing 5–83 wt% of the Au present.

Catalytic Dehydrogenation

UNIVERSAL OIL PRODUCTS CO.

U.S. Patent 3,448,165

Mono-olefines are produced from 10–18°C n-paraffin without skeletal rearrangement, by contacting at 400–600°C with an As-attenuated Pt catalyst on lithiated Al_2O_3 (0.05–5 wt% Pt). See also *U.S. Patent 3,448,166*.

Catalytic Reforming

CHEVRON RESEARCH CO.

U.S. Patent 3,449,237

A reforming process using a Pt-Re catalyst on a process support is started up by contacting the naphtha with the catalyst in the presence of an inert gas (N_2) at 650°F. Thereafter the catalyst temperature is increased to 900°F when a pressure of H_2 is built up.

Hydrogenation of Pyrolysis Gasoline

UNIVERSAL OIL PRODUCTS CO.

U.S. Patent 3,451,922

The olefines and dienes of pyrolysis gasoline are removed selectively to stabilise the product by (a) hydrogenation of the heavier fraction over Pd

and desulphurisation over Ni and (b) bulking the fractions and hydrogenating over Pd.

Hydrocracking of Feedstocks

CHEVRON RESEARCH CO. *U.S. Patent 3,453,204*
An improved catalyst is produced by co-gelling or co-precipitating the hydrogenating and cracking components which consist of 50–90 wt% SiO₂, Al₂O₃ and 0.01–0.05 wt% of Pt, PtS, Pd or PdS.

Haloacetyl Halide Production

NATIONAL DISTILLERS & CHEMICAL CORP.
U.S. Patent 3,454,632
A process is provided for preparing haloacetyl halides from polyhalomethanes by reaction with CO in the presence of a Pt or Pd triad catalyst, and optionally, a promoter for the catalyst.

Hydrogenation of Hydroxy-containing Diene

SINCLAIR RESEARCH INC. *U.S. Patent 3,459,814*
Hydroxy-containing diene polymers (e.g., H₂O₂-polymerised polybutadiene) are hydrogenated, using as a catalyst Pt supported on a large pore Al₂O₃, i.e., an Al₂O₃ having at least 0.22 ml/g of pore volume in pores above 500 Å.

HOMOGENEOUS CATALYSIS

Oxidation of Organic Compounds

CELANESE CORPORATION *British Patent 1,159,250*
Organic compounds are partially oxidised in a system including a solution of Ru catalysts and an oxidising agent for maintaining the Ru in solution. The oxidation potential of the system must be maintained within the range represented by the values for Ru(V) and Ru(VII).

Vinyl Acetate

CELANESE CORPORATION *British Patent 1,159,528*
C₂H₄ is converted to vinyl acetate in a redox system comprising an CH₃COOH solution of a salt of a Group VIII metal (a Pd(II) salt) a source of CH₃COO⁻ ions and Cl⁻ ions, Cu(II) ions and O₂.

Chlorinated Hydrocarbons

IMPERIAL CHEMICAL INDUSTRIES LTD
British Patent 1,159,950
The H atoms of hydrocarbons are replaced by Cl by contacting a hydrocarbon (acyclic paraffin, olefin, C₆H₆ and its homologues) with a mixture of molten LiCl and PdCl₂, (additionally KCl).

Oligomerisation Process Using a Ruthenium Catalyst

GEIGY (U.K.) LTD *British Patent 1,165,286*
Oligomers of butadiene and/or isoprene with methyl methacrylate are produced using a Ru catalyst (e.g., RuCl₃) in a 1–6 C alcohol.

Preparation of Stable Polysulphones

SHELL OIL CO. *U.S. Patent 3,444,145*
C₂H₄ is oxidised to vinyl acetate in the presence of a Pt metal salt, e.g., PdCl₂ and a nitrogenous oxide compound, e.g., HNO₃ or a nitrate.

Polyester Compositions

GENERAL ELECTRIC CO. *U.S. Patent 3,448,072*
A polyester and an isocyanate are contacted to provide for the introduction of aliphatic unsaturation into the polyester. This reaction takes place in the presence of a Pt catalyst (H₂PtCl₆, Pt-C₂H₄ complex, etc.) with a Si hydride-bearing hydrolysable radical to produce curable compositions of a polyester with terminal silylurethane groups.

Ethyl Vinyl Sulphone

SHELL OIL CO. *U.S. Patent 3,448,159*
C₂H₄ and SO₂ react in aqueous solution in the presence of a Pdhalide catalyst (PdCl₂) and a co-catalyst (halide ion, especially KCl) to yield ethyl vinyl sulphone.

Preparation of Vinyl Acetate, Acetaldehyde and Acetic Acid

UNION OIL CO. OF CALIFORNIA
U.S. Patent 3,450,748
C₂H₄ is oxidised (O₂) in contact with a liquid phase containing a noble metal catalyst (PdCl₂) and a soluble halide. The products are separated and recovered.

Homogeneous Hydrogenation Catalyst

SHELL OIL CO. *U.S. Patent 3,454,644*
Keto, nitrile, unsaturated and formyl compounds are hydrogenated in the presence of the Ru or Os complex of formula L_nMZ₂, where n is either 3 or 4, M is Ru or Os, Z independently is Cl, Br or H, and L independently is CO or tertiary phosphine with at least three L's being tertiary phosphine.

Iridium Phosphine Complexes

IMPERIAL CHEMICAL INDUSTRIES LTD
U.S. Patent 3,458,547
New catalysts for reactions involving unsaturated bonds have the formula IrH₃(PR₃)₂, where R is the same or different alkyl, aryl, arylky, alkenyl, cycloalkenyl, alkoxy, aryloxy or heterocyclic group. They are produced by the hydride reduction of IrY₂(PR₃)₂, where Y is an anion.

FUEL CELLS

Recovery of Hydrogen

UNITED AIRCRAFT CORPORATION
British Patent 1,159,150
H₂ is recovered from H₂-containing feedstocks in a fuel cell in which the anode contains a dehydrogenation catalyst. A cathode membrane (of

Pd-Ag alloy) is spaced from the anode. The cathode is selectively permeable to H₂.

Electrodes

LEESONA CORPORATION *British Patent 1,159,343*
An electrochemical cell electrode comprises a porous metal (Ni) substrate with one surface in intimate contact with a catalyst layer. The latter consists of Pt black and a hydrophobic polymer (PTFE) uniformly distributed throughout the catalyst layer. See also *British Patents 1,159,344-1,159,346*.

Fuel Cell Electrode

TOKYO SHIBAURA ELECTRIC CO. LTD
British Patent 1,165,679
The fuel cell has a H₂ electrode, composed of Pd or a Pd alloy of a Group IB metal or metals, which is coated on one side with Pt black and on the other side with a layer of Pd alloyed with Pt and/or Rh in the form of a "black".

Fuel Cell Electrodes

LEESONA CORPORATION
British Patent 1,167,542
Catalyst compositions for NH₃ fuel cells comprise 75-98 at. % Pt and 2-25 at. % Rh or Ru.

Fuel Cell

ESSO RESEARCH & ENGINEERING CO.
U.S. Patent 3,443,998
The anode is an electrically conducting substrate coated with a physical mixture of Pt and Au. This is immersed in an anolyte containing Na molybdate dissolved in H₂SO₄.

Fuel Cell

CHEVRON RESEARCH CO. *U.S. Patent 3,449,169*
Pt phosphide of high surface area is used as an electro-catalyst in fuel cells.

CHEMICAL TECHNOLOGY

Catalytic Reforming

UNITED AIRCRAFT CORP. *U.S. Patent 3,450,500*
The catalytic (Ni) conversion of a mixture of H-containing carbonaceous feedstock and steam is effected close to a Pd membrane so that H₂ formed in the conversion is simultaneously abstracted to drive the equilibrium to increase H₂ production.

GLASS TECHNOLOGY

Alloys for Parts in Contact with Molten Glass

INTERNATIONAL NICKEL LTD
British Patent 1,160,748
Articles and parts which come into contact with molten glass are made of an alloy containing 0.5-4% Ti, the remainder Pt.

Coating Glass with Platinum

J. GISBIES *East German Patent 66.003*
The object to be clad is covered with a methanolic solution of platonic acid methyl ester. On evaporation of the solvent, a Pt mirror remains. The ester is prepared from the reaction between PtF₄ and methanol.

ELECTRICAL AND ELECTRONIC ENGINEERING

Ion Source

PHILIPS ELECTRONIC & ASSOCIATED INDUSTRIES LTD
British Patent 1,159,634
An ion-source comprises a porous W body forming a closure for a supply of alkali metal compounds. The body has a thin Os-Ir coating.

Coated Cathode for Electrical Equipment

PHILIPS ELECTRONIC & ASSOCIATED INDUSTRIES LTD
British Patent 1,164,413
A cathode, e.g., for electric discharge tubes, is made with a porous W body filled with Ba compounds and coated with a thin porous layer of an Os-Ir or Os-Ru alloy. The Ir alloy can contain 30-70 at. % Os and the Ru alloy 20-80 at. % Os.

Printed Circuits

WESTERN ELECTRIC CO. *British Patent 1,166,659*
A metallic pattern is formed on a substrate by depositing a layer of Ti and then a layer of Pt, masking the surface and etching away the exposed Pt. The mask is then removed and Au applied to the remaining Pt pattern.

Thin Film Conductors

PLESSEY CO. LTD *British Patent 1,166,992*
The precursors of a ceramic glaze, plus Ru and/or Rh compounds, are added to a solvent to produce a solution or emulsion which is applied to a substrate. The film left after eliminating the solvent is fired to give a conducting film. A typical coating composition contains Pb stearate, Si resinate and Ru resinate in diacetonol alcohol.

Noble Metal Metallising Compositions

E. I. DU PONT DE NEMOURS & CO.
U.S. Patent 3,450,545
The metallising compositions comprise 60-95% of a noble metal powder (Ag, Pd, Pt or Au), an inorganic binder powder and at least one oxide precursor (Rh, Ir, Ru, Cu, SiC or BN).

Electrode for Electrolysis Reactions

ORONZIO DE NORA IMPIANTI ELETTROCHIMICI
Dutch Patent 68.17957
A metal electrode base, e.g., produced from Ti, is coated with a mixture of semiconducting oxides. In an example, a coating of Ir, Ru and Ti metals is applied and then converted to the oxides. See also *Dutch Patent 68.17966*.