CHEMICAL TECHNOLOGY

Spinneret Makers Enjoy Fibres Surge. Are Pushed by Economic and Technological Factors Likely to Continue Unabated for Some Time


Spinneret alloys commonly used for rayon production are 70% Au-Pt, 10% Rh-Pt, 49% Au-17% Rh-Pt. Fibre production depends on the precision with which the holes are made; 0.0001 inch tolerance for diameter, perfect shape, sharp-edged. Special shapes are used for special fibres.

Influence of Deformation and Tempering Temperature on the Electrochemical Corrosion of Titanium and the Titanium Alloy with 0.2% Palladium


Cold-rolled Ti and 0.2% Pd-Ti sheets corrode less than annealed sheets. The rate of corrosion decreases as the deformation from rolling increases.

Investigation of the Protective Action Mechanism of Palladium in Corrosion-resistant Titanium-Palladium Alloys by Radiochemical Methods


As surface corrosion commences, there is an accumulation there of Pd which passivates the surface and which leads to Pd additions of 0.1-0.2% to Ti being sufficient.

Technological Properties and Corrosion Behaviour of a Titanium Alloy with 0.2% Palladium


Tests on welded and non-welded samples of 0.2% Pd-Ti and of Ti showed that their technological, physical and processing properties are similar. Alloy and metal have the same corrosion-resistance under oxidising conditions but 0.2% Pd-Ti is superior under reducing conditions.

NEW PATENTS

METALS AND ALLOYS

Production of Ultra Pure Hydrogen

Johnson, Matthey & Co. Ltd.

**British Patent** 982,509

Ultra-pure H₂ is produced from a gas or gaseous mixture by passing it through a diffusion cell, at 50-400 ps.i.g. and 50-1000°F, consisting of a ceramic tube impregnated with an Ag-Pd alloy.

Resistor Compositions

E. I. du Pont de Nemours & Co.

**British Patent** 982,789

An electrical resistor comprises a solid ceramic base and a conductive resistor composition applied on it and consisting of 20-49 wt.% glass frit matrix and 51-80 wt.% 0.5-50 μ particle size Pd and Ag, taken in a 55:45 to 45:55 ratio by wt., the said Pd containing 0.1-1 wt.% combined oxygen.

ELECTRICAL ENGINEERING

Electrical Contact Materials in Low Current Technology


A survey of contact types, causes of failure, and contact design. Au, Pt metal and precious metal alloy contacts are particularly useful. Their properties and difficulties in use for electronics applications are described.

TEMPERATURE MEASUREMENT

Pressure Dependence of the emf of Thermocouples to 1300°C and 50 kbar


Relative temperature corrections accurate to ±1°C due to pressure are given for Pt:10% Rh-Pt, Pt:13% Rh-Pt, Chromel-Alumel, and iron-constantan thermocouples as functions of temperature and pressure. They exceed 40° in some cases. Absolute corrections ΔT were also studied and are proportional to pressure at a given temperature. ΔT can exceed 50° for Pt:10% Rh-Pt at 50 kbar, T>1300°C.

A New Method for the Computation of Temperature in Platinum Resistance Thermometry


Temperatures on the International Practical Scale of Temperature of 1948 between -182.97 and +630.5°C can be calculated from the resistance of a Pt thermometer using the equation

\[ t = t_{pt} + δ_{pt}(t_{pt} - t_{pt}) \cdot t_{pt} \cdot 4 \]

where \( δ_{pt} \) depends on the Pt temperature \( t_{pt} \) and on the thermometer constants \( δ \) and \( β \). A master table of \( δ_{pt} \) as a function of \( t_{pt} \) is given for a thermometer with \( δ = 1.492, β = 0.110 \) and tables can be derived for other values of \( δ \) and \( β \). Using such tables and a desk calculator, temperature errors should not exceed 3 x 10⁻⁴ deg C.
Production of Platinum-containing Metal Sheet or Strip
THE INTERNATIONAL NICKEL CO. LTD.
*British Patent* 983,223
Pt-containing metal sheet or strip is produced by forming a laminated stack from at least 25 sheets, each 0.001-0.1 inch thick, at least some of which consist of or comprise Pt, bonding the sheets together by forging and rolling the product to a thickness no more than 1/20 of the original stack, which may contain Pd, Rh or some other Pt group metal in addition to Pt.

Production of Assemblies Comprising Titanium
IMPERIAL CHEMICAL INDUSTRIES LTD.
*British Patent* 984,973
Pt group metal or alloy plated Ti bodies are obtained by removing the surface skin of the Ti support and applying on it several coatings comprising Pt group metal compounds or their mixtures in an organic vehicle and firing each individual film in an oxidising atmosphere at 350-550°C.

Platinum Group Metal Sheet or Strip
THE INTERNATIONAL NICKEL CO. INC.
*U.S. Patent* 3,166,417
Metal sheet containing 0.1-5 vol.% dispersed hard metal oxide phase is produced by mixing metallic flake powder containing up to about 50 wt.% Au, Ag, Ni and Cu and the balance essentially a Pt group metal, in particular Pt, Pd, Rh or their alloys, with an organic solvent solution of a metal salt decomposable to said metal oxide, e.g. Th nitrate, compacting the treated flake powder, sintering at a temperature of at least 800°C and working the sintered compact into a sheet.

Noble Metal Dental and Jewellery Alloy
NOBILIUM PRODUCTS INC.
*German Patent* 1,187,378
New alloy consists of 10-50% Au, 2-15% Ga, 2-5% Ru or Ir, remainder 40-70% Pd.

Platinum Laminate for Non-cutting Shaping
DEUTSCHE GOLD- UND SILBER-SCHEIDEANSTALT
*German Patent* 1,187,804
A core of Rh, Ir, Ru or Os or their alloys is sheathed with heat resistant Pt and then shaped without cutting, e.g. to wires.

**CHEMICAL COMPOUNDS**

Production of Carbonyls
IMPERIAL CHEMICAL INDUSTRIES LTD.
*British Patent* 983,792
Ru carbonyl is produced by contacting an organic acid Ru salt, in a liquid medium consisting of or containing H₂O, with a 1:1 CO/H₂ mixture present in an inert gas at 1-3000 atm, 25-300°C.

**ELECTROCHEMISTRY**

Electrodes for the Electrolytic Protection of Metal Parts
W. MATTEWAN. *British Patent* 984,477
An electrode for the protection of metallic parts in contact with a potentially corrosive electrolyte consists of a Cu-cored Ti rod provided with a continuous or discontinuous thin Pt coating and encased in a sheath of perforated or porous plastic, which has a direct mating fit over the rod.

Catalyst Electrode for Anodic Oxidation
ESSO RESEARCH & ENGINEERING CO.
*British Patent* 989,474
An anodic oxidation electrode for use in electrochemical cells consists of a substrate formed by a Pt screen welded to a Pt plate and a catalytically active Pt-Re coating formed by treating the electrode surface with a solution of a Pt and an Re salt followed by co-precipitation of the metals with a chemical reducing agent.

Gas Diffusion Electrode
VARTA A.G. *Dutch Application* 64,08,224
The electrode has a sandwich structure consisting of a layer of catalyst, preferably a Pt metal, between two porous sinter layers.

**ELECTRODEPOSITION AND SURFACE COATINGS**

Immersion Plating
ENGELHARD INDUSTRIES INC.
*British Patent* 982,621
Au deposits are advantageously immersion-plated on to Cu substrates by a first immersion-plating of a thin layer of Pt, Pd, Rh or Ru, using a solution containing a halide or sulphamate of the metal and then immersion-plating an Au film by using a standard KAu(CN)₄ plating solution.

Plating of Palladium and Other Metals of Group VIII
AUTOMATIC TELEPHONE & ELECTRIC CO. LTD.
*British Patent* 988,174
A chemical plating bath for the electroless plating of Group VIII metals, in particular Pd, comprises a pH 1-3.5 aqueous plating solution containing a source of metal ions in a complexed form and a source of sulphamate ions, e.g. sulphamic acid and Pd diamminodinitrite.

Palladium Decorating Compositions
ENGELHARD INDUSTRIES INC.
*British Patent* 989,463
An article is decorated with Pd by applying on it a composition comprising a fluid organic vehicle and a bisthioether palladous salt coordination compound, firing the film and then burnishing it to provide a soft lustrous finish.
Deposition of Metals of the Platinum Group

DEUTSCHE GOLD- UND SILBER-SCHEIDEANSTALT
British Patent 990,174
Films of Pt group metals less than rp thick and greater than 600 A in grain size are deposited on Mo, W, Ti, Zr, Ta, Ni or stainless steel by applying on the substrate an organic solution of a Pt group metal chelate of A-CH,-A, where A is CN and/or R-Co, and R is alkyl or alkoxy, evaporating the solvent and decomposing the chelate by 1-10 min at about 400°C.

Platinum Plating

SEL-REX CORP. German Patent 1,184,173
Thick, light-coloured Pt coatings are electro-deposited from a solution of Pt diaminodinitrite in an amount equivalent to at least 6 g/l in H3PO4 and H2SO4.

Chemical Palladium Plating

THE INTERNATIONAL NICKEL CO. (MOND) LTD. German Patent 1,187,886
A plating bath contains, per litre, 0.001-0.25 mol Pd (II), 2.5-14 mol NH3, 0.002-0.05 mol N2H4 and a stabiliser, e.g. 0.01-0.10 mol of a dihydroxy dialkyl sulphide.

Catalysis

Production of Organic Acetates

FAHRENFABRIKEN BAYER A.G. British Patent 981,987
Organic acetates are produced by reacting a 2-4C mono-olefine or lower alkylbenzene at 50-250°C with O2 and CH3COOH in the presence of Pd supported on a macroporous material and preferably at 2-200 atm.

Production of Aliphatic Percarboxylic Acids

LES USINES DE MELLE. British Patent 982,490
Aliphatic percarboxylic acids are produced by reacting an aliphatic carboxylic acid in organic solvent and in the presence of a strong inorganic acid, cation exchange resin or an organosulphonic acid with alkyl anthraquinone hydroperoxide produced by the hydrogenation of the corresponding alkylanthraquinone in the presence of a supported Pd catalyst.

Catalytic Hydrogenation

ABBOTT LABORATORIES. British Patent 984,516
Aromatic amino compounds are produced by hydrogenating a suitable nitro compound at 25-150°C, 1-150 atm and in the presence of 0.01-2 wt.% Rh catalyst, the activity of which as a ring-hydrogenation promoter is substantially exhausted.

Production of Alpha-olefinic Alcohols

INSTITUT FRANCAIS DU PETROLE, DES CARBURANTS ET LUBRICIERS. British Patent 984,916
\( \alpha \)-Olefinic alcohols are produced by forming a 2-85 wt.% solution of 4-20C olefinic hydrocarbon \( \alpha \)-hydroperoxide in a liquid hydrocarbon containing a hydrophilic solvent and contacting it with H2 in the presence of a catalyst obtained by treating Pd metal with an aqueous solution of Pb and/or Bi salt and a N-containing organic base.

Androstane and Androstene Derivatives

RHONE-POULENC S.A. British Patent 984,980
The reaction of 1\~\alpha\)-acetoxy-17-oxoandrost-5-ene with alkylmagnesium halide followed by hydrolysis gives 1\~\alpha\,17\~\beta\)-dihydroxy-17-alkyl-androst-5-ene, which can be hydrogenated with H2 in the presence of Adams Pd, to the corresponding androstane derivative.

Production of Halides of Unsaturated Aliphatic Acids or Derivatives thereof

IMPERIAL CHEMICAL INDUSTRIES LTD. British Patent 987,274
Unsaturated carboxylic acid halides are produced by contacting a compound containing C-C-X group, where X is halogen, with CO at 50-250°C, 50-3000 atm and in the presence of Pd or its complex or salt.

Preparation of Carboxylic Acid Halides

IMPERIAL CHEMICAL INDUSTRIES LTD. British Patent 987,516
Carboxylic acid halides are produced by reacting an organic aromatic compound with CO and halogen or with a carbonyl halide, at 200-250°C, 1-350 atm and in the presence of a catalytic amount of a Group VIII noble metal, in particular Pd or its compounds.

Purification of Olefine Polymers

COSDEN OIL AND CHEMICAL CO. British Patent 987,840
A saturated liquid polymer obtained by polymerising 2-5C olefine gas fraction and containing polyisobutylene is purified by hydrogenating the mixture at 65-730°C, 1 atm to 210 kg/cm² and in the presence of Pt, Pd or their compounds as catalyst.

2,4-Diaminopteridine Derivative

THE WELLCOME FOUNDATION LTD. British Patent 987,916
2,4-Diamino-6-hydroxy-7,8-dihydropteridine is produced by catalytic hydrogenation, in the presence of PtO, of 2,4-diamino-6-hydroxypteridine or 2,4-diamino-6,7-dihydroxypteridine.
Production of Hydroxy Benzaldehydes
RHÔNE-POULENC S.A. British Patent 987,947
The oxidation of a suitable hydroxybenzyl alcohol in an aqueous medium with inert gas-diluted oxygen and in the presence of a Pd catalyst produces m- or p-hydroxybenzaldehyde.

Production of 1,4-Cyclohexanedimethanol
EASTMAN KODAK LTD. British Patent 988,012
1,4-Cyclohexanedimethanol is produced by reacting a dialkyl terephthalate with H₂ at 100-400°C, 50-500 atm and over a fixed bed catalyst containing 0.25-10 wt.% Pd, passing the effluent through a second hydrogenation stage using Cu chromite as catalyst.

Manufacture of Amines
MONSANTO CO. British Patent 989,257
Amines are produced by heating, at below 350°C and in the presence of Pt group hydrogenation catalyst and optionally an H acceptor, a six-membered alicyclic ketone and an ammonia compound retaining at least one H on the N atom.

Treatment of Hydrocarbons
THE BRITISH PETROLEUM CO. LTD.
British Patent 989,269
A hydrocarbon feedstock containing alkyl aromatics is dealkylated by contacting it at 450-900°F, 50-1500 p.s.i.g. and in the presence of H with decationised zeolite Y supporting 0.1-5 wt.% Pt group metal, preferably Pd.

Platinum Metals Rev., 1965, 9, (3) 110

Hydro-refining Catalysts
UNIVERSAL OIL PRODUCTS CO.
U.S. Patent 3,161,586
A continuous process for hydro-refining unsaturated, coke-forming hydrocarbon distillates utilises refractory metal oxide-supported Ru, Rh, Pd, Os, Ir, Pt or their mixtures as catalysts and is operated at 250-500°F.

Production of Benzimidazolinones
RESEARCH LABORATORIUM DR. G. JANSEN N.V.
U.S. Patent 3,161,645
In the production of 1-(1-aroylpropyl-4-piperidyl)-2-benzimidazolinones, the stage of catalytic hydrogenation to remove the benzyl group is carried out in the presence of Pd/C catalyst.

Carbonylation of Conjugated Diolefines
EGIES CHEMICAL CORP. U.S. Patent 3,161,672
Mono-olefinically unsaturated monoesters are produced by carbonylating 4-20°C conjugated diolefines in a 1-20°C alkanol solvent at 125-225°C, 500-3000 p.s.i.g. and in the presence of 0.001-5 wt.% Rh metal, oxide, nitrate or carbonyl.

Preparation of Vinyl Esters
RHÔNE-POULENC S.A. British Patent 990,447
Vinyl esters are produced by reacting ethylene with 1-4°C aliphatic carboxylic acid at 50-80°C, 10-100 atm and in the presence of a noble metal halide, e.g. PdCl₂, p-quinone and an alkali metal salt of such an organic acid, separating the vinyl ester formed and the noble metal catalyst, reoxidizing the diphenol produced to the quinone with O in the presence of carbon black supported Rh catalyst and using the regenerated p-quinone in further reaction.
Hydrogenation Catalysts
ALLIED CHEMICAL CORP.
U.S. Patent 3,167,888
Unsymmetrical-dialkylhydrazines are produced by forming a slurry of nitrosodialkylamine, Pt or Pd supported on C, TiO₂ or Al₂O₃ and H and feeding it through a reaction zone at 25-125°C, 10–1000 p.s.i.g. and then separating the catalyst at 70–120°C and 20–1000 mm Hg.

Production of Carbonyls
SHELL OIL CO. U.S. Patent 3,168,553
Carbonyl compounds are produced by reacting a 2–20°C mono-olefinic hydrocarbon with CO at 75–250°C and 800–3000 p.s.i.g. in the presence of a catalyst consisting of Co, Ru, Rh and Ir in complex combination with Co and trialkyl phosphine.

Dehydrogenation Catalysts
SINCLAIR RESEARCH INC. U.S. Patent 3,168,587
4–8°C aliphatic hydrocarbons are dehydrogenated at 800–1300°F and 0.05–100 p.s.i.g. by introducing into the reaction vessel 0.01–10 mol.% O and a catalyst comprising a non-acidic refractory support carrying a minor proportion of a Pt group metal.

Hydrocracking Catalysts
SOCONY MOBIL OIL CO. INC. U.S. Patent 3,169,107
A hydrocarbon charge is subjected to hydrocracking by contacting it under the usual conditions and in the presence of H with a catalyst comprising 25–75 wt.% SiO₂, 0.05–10 wt.% Pt or Pd and the balance Al₂O₃.

Ketene Polymerisation
SHELL INTERNATIONALE RESEARCH M.IJ. N.V. French Patent 1,370,507
Ketenes are polymerised at 10–50°C by being contacted with a catalyst selected from PdCl₂ or (Ar₂X)₂PdCl₂, where Ar is an aryl, in particular phenyl, and X is P, As or Sb.

Hydro-reforming Catalysts
UNION CARBIDE CORP. French Patent 1,372,742
Organic compounds are hydrogenated by contacting them with H₂ and a catalyst obtained by reacting, at elevated temperature and in an inert liquid, Ru, Rh, Pd, Os, Ir or Pt with 10–20 molar excess of organosilicon possessing Si-H bonds, whereby the precious metal component is reduced to lower valency state, preferably zero.

Exhaust Gas Purifiers
DEUTSCHE GOLD- UND SILBER-SCHWEIZERSTALT French Patent 1,373,299
A purifier for combustion engine exhaust gases contains a first thin layer composed mainly of a noble metal, in particular Pt or Pd and a second thick, fluidised layer containing only a minor amount of such metal.

Polymerisation Catalysts
IMPERIAL CHEMICAL INDUSTRIES LTD. French Patent 1,375,869
Elastomeric compositions comprise 100 wt. parts diorganono-polyorganosiloxane, 0.1–100 wt. parts another organosilicon compound, 0–10 wt. parts structure controlling agent, 0–150 wt. parts reinforcing filler, 0–200 wt. parts semi- or non-reinforcing filler and up to 0.2 wt.% Pt, Ru, Rh, Pd, Os or Ir.

Hydrocarbon Conversion Catalysts
INSTITUT FRANCAIS DU PETROLE, DES CARBURANTS ET LUBRIFIANTS. French Patent 1,376,480
5–6C paraffins are converted to 3–4C paraffins by hydrogenating them at 350–450°C, 10–250 atm and in the presence of a Pt group metal catalyst, preferably Pt or Pd.

Molecular Sieves
INSTITUT FRANCAIS DU PETROLE, DES CARBURANTS ET LUBRIFIANTS. French Patent 1,376,483
3–4C paraffins are obtained by subjecting 5–6C paraffins to hydrocracking at 350–550°C, 10–250 atm and in the presence of a molecular sieve of about 6 Å pore size activated by 0.2–1 wt.% Pt group metal, preferably Pd.

Hydrogenation of Organic Compounds
UNION CARBIDE CORP. French Patent 1,376,744
Organic compounds are hydrogenated by contacting them with H₂ and a catalyst obtained by reacting, at elevated temperature and in an inert liquid, Ru, Rh, Pd, Os, Ir or Pt with 10–20 molar excess of organosilicon possessing Si-H bonds, whereby the precious metal component is reduced to lower valency state, preferably zero.

Production of Enolic Ethers of 3-Keto-5ω-androstanes
FRANCESCO VISMARA S.P.A. French Patent 1,377,260
Enolic ethers of 3-keto-5ω-androstanes are produced by the hydrogenation of ethers of 3-hydroxy-androsta-3,5-dienes at 5–30°C, in an inert organic solvent and in the presence of a Pt or Pd catalyst on an inert support, preferably Pd/CaCo₃.

Catalysts for Exhaust Gas Filters
W. R. GRACE & CO. French Patent 1,377,737
Catalyst for the oxidative purification of exhaust gases of internal combustion engines are produced by impregnating a high specific surface area
refractory oxide support, e.g. Al$_2$O$_3$ to provide 3-15 wt.% CoO and 0.01-0.1 wt.% Pd, drying the material at 127°C and then calcining for 3-19 h at about 760°C.

**Catalysts for Exhaust Gas Purification**

W. R. GRACE & CO. French Patent 1,377,776

Catalysts for the oxidative purification of exhaust gases of internal combustion engines are produced by impregnating a high surface area refractory metal oxide with solutions of Mn and Pd salts so that after 3-9 h calcination at 538-760°C the catalyst contains 5-20 wt.% MnO$_2$ and 0.01-0.1 wt.% Pd.

**Vinyl Acetate Production**

FARBENFABRIKEN BAYER A.G. German Patent 1,185,604

The reaction of C$_2$H$_4$ and O$_2$ is catalysed by a Pd catalyst on a macroporous support having an internal surface of less than 50 m$^2$/g.

**Tritium Introduction Catalyst**

U.K. ATOMIC ENERGY AUTHORITY German Patent 1,187,235

Tritium is introduced into tetrasodium-1,4-dihydroxy-2-methyl-1,4-dihydonaphthalene-(1,4)-diphosphate using Pt or Pd hydrogenation catalysts.

**Organosilicon Compound Production**

IMPERIAL CHEMICAL INDUSTRIES LTD. German Patent 1,187,240

The reaction of silanes with organic compounds is catalysed by a Pt (II) salt complex with an olefine.

**Nitroaromatic Reduction**

E. I. DU PONT DE NEMOURS & CO. German Patent 1,187,243

Amines are produced from nitroaromatic compounds by reduction in the presence of a Pt catalyst and a cycloaliphatic N base.

**Production of Dihydrotriazine**

VITAMINS LTD. German Patent 1,187,626

4,6-Diamino-1,2-dihydro-2,2-dimethyl-1-hydroxy-1,3,5-triazine is produced by hydrogenation of the corresponding unsaturated compound in the presence of a Pd catalyst.

**Benzene Production**

SUN OIL CO. German Patent 1,188,063

The aromatisation of methylcyclopentane is catalysed by a Pt catalyst, on an Al$_2$O$_3$ support containing a halide, in the presence of NH$_3$ or an amine.

**Hydroxybenzaldehyde Production**

RHONE-POULENC S.A. German Patent 1,188,069

The oxidation of hydroxybenzyl alcohols to the corresponding aldehydes is effected by O in aqueous-alkaline medium in the presence of a Pd catalyst.

**Selective Acetylene Hydrogenation**

SNAM S.p.A. Dutch Application 64.05.225

Water-miscible acetylenic compounds are hydrogenated selectively in an aqueous Zn salt solution in the presence of a Pd catalyst.

**Production of Halohydrocarbons**

IMPERIAL CHEMICAL INDUSTRIES LTD. Dutch Application 64.06.346

The reaction of alkenes with a halogen acid is catalysed by a mixture of a Pt metal and one of its compounds, e.g. Pt and chloroplatinic acid.

**Ketone Production**

F. HOFFMANN-LA ROCHE & CO. A.G. Dutch Application 64.07.001

A catalyst for ketone production consists of a Pd-Fe compound mixture.

**Carboxylic Acid Production**

Dutch Application 64.08.476

The reaction of unsaturated compounds with CO to form acids is catalysed by a Group VIII noble metal, e.g. Pd.

**FUEL CELLS**

**Fuel Cells**

LEESONA CORP. British Patent 986,837

A porous reducing electrode for fuel cells is formed of 1-100µ particle size powder of a Pd alloy containing 0.25-10 wt.% Ag.

**Precious Metal Fuel Cell Electrodes**

SHELL RESEARCH LTD. French Patent 1,374,387

Improved microporous electrodes for fuel cells may consist of a microporous substrate which has been coated with a thick film of Pd, Pt, Os, Ir, Rh or their alloys, which may be further thickened by application over almost the entire surface of another metal selected from the same group.

**Fuel Cell Electrode**

SHEMENS-SCHUCKERTWERKE A.G. Dutch Application 64.06.694

A porous ferromagnetic electrode core is used and the catalytic metal, e.g. Pt, is introduced by magnetic forces.

**Porous Fuel Cell Cathode**

SHEMENS-SCHUCKERTWERKE A.G. Dutch Application 64.07.594

A Ru catalyst is obtained with a spinel catalyst on a fuel cell electrode by co-deposition from a solution of a heavy metal salt, an Al salt and a Ru salt.