

## A Catalyst for the Homogeneous Hydrogenation of Aldehydes under Mild Conditions

R. S. COFFEY, *Chem. Commun.*, 1967, (18), 923

Whereas  $\text{RhCl}(\text{PPh}_3)_3$  is deactivated by aldehydes,  $\text{IrH}_3(\text{PPh}_3)_3$  catalyses homogeneous hydrogenation of aldehydes and some olefins at  $50^\circ\text{C}$ , 1 atm, e.g. *n*-butyraldehyde to *n*-butanol, in  $\text{CH}_3\text{COOH}$  solution. Ir hydrido-acetates are assumed to be the true catalysts in this reaction.

## The Decomposition of Formic Acid Catalysed by Soluble Metal Complexes

*Ibid.*, 923-924

Many phosphine-stabilised complexes of transition metals, particularly of Ir and Ru, are excellent homogeneous catalysts for decomposition of  $\text{HCOOH}$  to  $\text{H}_2$  and  $\text{CO}$ , and functional groups can also be reduced. Results for six catalysts are tabulated and discussed.

## GLASS TECHNOLOGY

### Wetting Behaviour of Glasses on Pt and Pt Alloys

R. KATZSCHMANN, *Silikat Tech.*, 1967, 18, (7), 211-214

Dynamic methods were used to study the wetting behaviour of Pt, 5% Au-Pt, 5% Ir-Pt, 5% Rh-Pt, and a Be-Pt alloy at  $400$ - $1400^\circ\text{C}$  with a heating rate of  $10^\circ\text{C}/\text{min}$ , on five types of glass. Contact angles are plotted and the results are discussed.

## NEW PATENTS

### METALS AND ALLOYS

#### Iridium Alloys

INTERNATIONAL NICKEL LTD.

*British Patent* 1,082,078

The addition of 0.1-2% Nb to an Ir of commercial purity produces easily workable alloys.

### CHEMICAL COMPOUNDS

#### Metalloacyl Organopolysiloxanes

GENERAL ELECTRIC CO. (NEW YORK)

*U.S. Patent* 3,324,157

Highly stabilised organopolysiloxanes are produced by the usual cohydrolysis method where one hydrolysable monomer is a metalloacyl silane, where "metalloacyl" is a residue of a cyclopentadienyl derivative of a transition metal. The Pt group metals are specifically mentioned.

## TEMPERATURE MEASUREMENT

### Platinum Resistance Thermometry below $10^\circ\text{K}$

R. J. BERRY, *Metrologia*, 1967, 3, (3), 53-57

An assessment of Pt resistance thermometers at  $2$ - $10^\circ\text{K}$ , based on sensitivity, stability and ease of calibration, concludes that their overall accuracy in this range is  $0.03$ - $0.05^\circ\text{K}$ , when used in a fairly convenient manner, and  $0.01^\circ\text{K}$ , when great care is taken.

### Birdcage Resistance Thermometer

D. A. TOENSHOFF and E. D. ZYSK, *Instrum. Control Syst.*, 1967, 40, (5), 109-111

A Pt resistance thermometer of "birdcage" construction was tested as a possible instrument for defining the IPTS scale and measured the gold point ( $1063^\circ\text{C}$ ) to  $\pm 0.001^\circ\text{C}$ .

### High-temperature High-vacuum Thermocouple Drift Tests

J. W. HENDRICKS and D. L. MCELROY, *Environ. Q.*, 1967, 13, (1), 34-38

Stability of  $\pm 10^\circ\text{C}$  for 1000h at  $10^{-6}$ - $10^{-8}$  torr,  $1200$ - $1450^\circ\text{C}$  was found for Pt: 10% Rh-Pt, 6% Rh-Pt: 30% Rh-Pt, W: 26% Re-W and 5% Re-W: 26% Re-W thermocouples but at  $1200^\circ\text{C}$  severe thermal emf changes occurred with Pt: 10% Rh-Pt in Ta and Nb.

### Production of Platinum and Palladium Oxides

JOHNSON, MATTHEY & CO. LTD.

*Italian Patent* 767,275

Oxidation of these metals is achieved by electrolysis of a Pt or Pd anode in a bath containing molten  $\text{NaNO}_3$  and an alkali metal halide. This corresponds to *Belgian Patent* 664,526.

## ELECTROCHEMISTRY

### Anodes and Electrolytic Cells having Such Anodes

IMPERIAL METAL INDUSTRIES (KYNOCHE) LTD.

*British Patent* 1,076,973

A coated anode is formed from a plurality of Ti members placed side-by-side with each member coated with a Pt metal. The members are connected together by at least one transverse rib. At

least half the area of the Pt metal coating is perpendicular to the common plane of the coated members.

### Electrodes for Electrolytic Cells

IMPERIAL METAL INDUSTRIES (KYNOCHE) LTD.  
*British Patent 1,078,516*

An electrolytic cell electrode has a core of Ni with a coating of Ir or a Pt-Ir alloy. The coating which may be painted on from an organic vehicle, reduces the overvoltage of the electrode.

## ELECTRODEPOSITION AND SURFACE COATINGS

### Non-magnetostrictive Magnetic Electrolytic Deposit

INTERNATIONAL BUSINESS MACHINES CORP.  
*British Patent 1,081,316*

A Ni-Fe alloy with a small amount of Pd is electrodeposited from an aqueous bath, containing Ni and Fe in a 50-80:1 ratio, to which 700 mg/l of Na pallidichloride has been added.

### Electrically Conductive Compositions

E. I. DU PONT DE NEMOURS & CO.  
*British Patent 1,086,074*

Fired-on conductive metal coatings are produced from a mixture of (a) finely divided metallic Pd, PdO or Pd/Ag alloy, (b) finely divided Ag, (c) finely divided ceramic consisting of Bi<sub>2</sub>O<sub>3</sub> with a Cd or Pb borate frit. The component (a) must provide 22-35% Pd and component (b) 48-69% Ag, based on the total composition.

### Platinum Coating Method and Material

JOHNSON, MATTHEY & CO. LTD.  
*Italian Patent 764,009*

Dispersions of PtO<sub>2</sub> and mixtures of PtO<sub>2</sub> with oxides of Rh, Ru, Ir, and Pd, in which Pt is at least 50 wt.% metal content, are present to 1-500 g/l in a medium of C<sub>2</sub>-C<sub>6</sub> aliphatic alcohols with less than 37% HCHO. Pt metal deposits are formed by coating substrates with this dispersion.

### Applying Designs to Metallic Bases

JOHNSON, MATTHEY & CO. LTD.  
*Italian Patent 767,740*

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*.

### Electrodeposition of Palladium

JOHNSON, MATTHEY & CO. LTD.  
*Italian Patent 767,852*

The electrolyte is an alkaline or neutral aqueous

solution of a Pd compound and an NH<sub>4</sub> salt of a weak acid which does not form an insoluble product with the Pd compound. This corresponds to *French Patent 1,436,451*.

## HETEROGENEOUS CATALYSIS

### Production of Hydrogen Cyanide

MONSANTO CO. *British Patent 1,077,238*

A mixture of NH<sub>3</sub>, natural gas, H<sub>2</sub> and air or O<sub>2</sub> in the vapour phase is passed over a Pt metal or alloy catalyst at high temperature to produce HCN. A gauze made from an alloy of about 90% Pt and 10% Rh is a suitable catalyst material.

### Carbonylation of Allylic Halides

NATIONAL DISTILLERS & CHEMICAL CORP.  
*British Patent 1,077,773*

An acyl halide is produced by reacting CO and an allyl halide in the presence of a Pt metal catalyst. The preferred catalyst is Pd metal, a Pd salt or a Pd complex of an organic compound.

### Catalysts for the Isomerisation of Lower Saturated Hydrocarbons

SNAM S.p.A. *British Patent 1,081,120*

A catalyst consisting of Pt/Al<sub>2</sub>O<sub>3</sub> is activated by heating with C<sub>2</sub>Cl<sub>6</sub> vapour (at 180-500°C) before it is used to isomerise 1-6C alkane mixtures. A typical Al<sub>2</sub>O<sub>3</sub> catalyst contains 0.8% Cl<sub>2</sub> and 0.6% Pt.

### Carboxylic Acid Vinyl Esters

FARBWERKE HOECHST A.G.  
*British Patent 1,082,564*

C<sub>2</sub>H<sub>4</sub>, O<sub>2</sub> and carboxylic acids are reacted in a gaseous state over a supported Group VIII noble metal catalyst to give a vinyl carboxylate. Pd/Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> is a suitable catalyst.

### Process for Activating Catalysts

ESSO RESEARCH & ENGINEERING CO.  
*British Patent 1,084,354*

Finely divided Au, Ag and Pt metal catalysts (and alloys of those metals) are activated by wetting the catalyst with a basic solution having a pH of 8-14. Wetting, e.g. of a fuel cell catalyst, may be carried out with an alkali metal hydroxide, phosphate, metasilicate or carbonate or with 1N NH<sub>3</sub>.

### Preparation of Unsaturated Nitriles

ASAHI KASEI K.K.K. *British Patent 1,084,599*

Unsaturated nitriles are produced by the addition of HCN to a 2-4 C olefine in the presence of O<sub>2</sub> and Pd, Rh, Ru, Pt, Au or Cu catalyst.

### Hydrogenation of Unsaturated Aldehydes

UNIVERSAL OIL PRODUCTS CO.  
*British Patent 1,086,447*

The olefinic double bond of an unsaturated

aldehyde is reduced selectively in the presence of a Pd catalyst and a two-phase liquid system.

### Cyclododecene Production

GEIGY (U.K.) LTD. *British Patent 1,086,639*

Cyclododecatriene is hydrogenated until 2 mols of  $H_2$  are absorbed in the absence of solvent and in the presence of a hydrogenating catalyst, preferably a supported Pt group metal.

### Preparation of Vinyl Chloride

FARBWERKE HOECHST A.G.

*British Patent 1,086,785*

Vinyl chloride and optionally ethyl chloride are produced from  $C_2H_4$ ,  $O_2$  and HCl in the presence of an elementary Group VIII noble metal, especially Pd, Pt, Rh, Ru and Ir.

### Activating a Compositated Catalyst

GULF RESEARCH & DEVELOPMENT CO.

*British Patent 1,087,586*

Catalysts consisting of Pt metals on  $Al_2O_3$  are activated by heating at  $510-677^\circ$  in the presence of  $S_nO_aX_bY_c$ , where X is Cl, Y is another halogen, n is 1 or 2, a is 0-3 or 5, b is 2, 4, or 7, c is 0 or 1 and  $b+c$  is 2-8.

### Hydrogenation of Unsaturated Hydrocarbons

SHELL INTERNATIONALE RESEARCH MIJ, N.V.

*British Patent 1,087,684*

The catalysts used consist of one of the six Pt metals deposited on an  $Al_2O_3$  which has a bulk density of less than 0.78 g/ml. Smaller amounts of other refractory oxides may also be present.

### Production of Hydrogen Cyanide

MONSANTO CO.

*British Patent 1,088,903*

HCN is produced by the reaction of  $NH_3$ , natural gas and air in the presence of a metallic Pt or Pt alloy gauze which has been activated by the passage of a reactant mixture with a  $NH_3$ :gas:air ratio of 0.7-1.0:1:0.170-0.200. A preferred gauze contains 10-20% Rh.

### Catalytic Conversion of Hydrocarbons

BRITISH PETROLEUM CO. LTD.

*British Patent 1,088,933*

The catalyst for the petroleum conversion process is a crystalline synthetic mordenite having a pore opening of at least 5Å which has been decationised by direct treatment with mineral acid to give a metal cation content of not more than 2 wt.% and on to which a Group VI or VIII metal or oxide hydrogenating component has been deposited. For hydrogenation the preferred catalyst is Pt or Pd.

### Hydrogenation of Aminovinyl Ketones

EASTMAN KODAK CO.

*U.S. Patent 3,325,491*

Aminoalcohols can be produced by hydrogenating the keto and vinyl groups of aminovinyl ketones

over Ru or Rh catalysts. The amino group is not touched.

### Hydrocarbon Conversion Catalyst

UNION OIL CO. OF CALIFORNIA

*U.S. Patent 3,326,797*

The catalyst consists of Pt, Pd or another transition metal hydrogenation catalyst deposited on a crystalline, zeolitic, alumino-silicate base, the base having been prepared by digesting a crystalline zeolite, with a  $SiO_2/Al_2O_3$  ratio of about 6-12:1, in aqueous caustic.

### Catalyst for Hydrocarbon Reforming

THE BRITISH PETROLEUM CO.

*U.S. Patent 3,328,286*

Petroleum feedstocks are upgraded by hydro-reforming over a catalyst comprising Pt/ $Al_2O_3$  having a reversible  $C_6H_6$  chemisorption of up to  $5 \mu$  mol/g.

### Hydrocarbon Conversion Catalysts

ESSO RESEARCH & ENGINEERING CO.

*U.S. Patent 3,329,604*

An alumino-silicate zeolite is treated to replace alkali metal ions by Mn cations and then the product is used as a carrier for a Pt group metal catalyst. The catalysts can be used in cracking, hydrocracking, etc.

### Platinum Group Metal Catalyst Selectivity

MOBIL OIL CO.

*U.S. Patent 3,330,761*

In reforming naphtha at 100-1000 p.s.i.g., the selectivity of the Pt group metal catalyst is improved by contacting it, before major use, with a feedstock containing 100-2000 p.p.m. S to reduce subsequent undesirable exothermic reactions.

### Steam Reforming Process

IMPERIAL CHEMICAL INDUSTRIES LTD.

*U.S. Patent 3,334,055*

A Co or Ni oxide reforming catalyst is activated with 0.001-0.5 wt.% of a Pt group metal or reducible compound, preferably Pt, Pd or Rh.

### Hydrogen Peroxide Production

IMPERIAL CHEMICAL INDUSTRIES LTD.

*U.S. Patent 3,336,112*

$H_2$  and  $O_2$  are reacted together in the presence of a Group VIII metal, e.g. Pd/ $SiO_2$ , and  $H_2O$  containing a stabiliser and a condensed phosphate activator.

### Hydrogenation with Platinum Metal Sulphide Catalyst

UNIROYAL INC.

*U.S. Patent 3,336,386*

Nitro- or N-nitrosoamine groups are reduced to amine groups using a Pt metal sulphide, e.g. a supported PdS. The catalysts can also be used for other reduction processes and some of the products are rubber stabilisers.

## Dehydrogenating Hydroxy- and Oxo-cycloaliphatic Compounds

PROGIL *U.S. Patent* 3,336,399  
 $\alpha$ -Naphthol and the like are produced by dehydrogenation over a finely divided metal catalyst, selected from Pt, Ir, Pd, Rh and other transition metal catalysts.

## Hydrogenation of Cinnamaldehyde

JOHNSON, MATTHEY & CO. LTD.  
*Italian Patent* 775,456  
Selective hydrogenation of unsaturated aldehydes, in particular of cinnamaldehyde to cinnamyl alcohol, is catalysed by supported Pt metals in alcoholic solutions with alkali promoters, e.g. 5% Pt/charcoal, Ru-Pt/charcoal, Pt/Al<sub>2</sub>O<sub>3</sub>. This corresponds to *Belgian Patent* 685,368.

## Hydrogenation of Crotonaldehyde by Trickle Column Catalysis

JOHNSON, MATTHEY & CO. LTD.  
*Italian Patent* 775, 452  
Butyraldehyde is produced by hydrogenation of crotonaldehyde with H<sub>2</sub> over Pd/Al<sub>2</sub>O<sub>3</sub>, Pd/C or Pd/ceramic supports in a trickle column reactor.

## HOMOGENEOUS CATALYSIS

### Preparing High Molecular Weight Paraffinic Hydrocarbons from Carbon Monoxide and Hydrogen

H. PICHLER *British Patent* 1,076,848  
CO and H<sub>2</sub> are reacted at 80–135°C and 100–3,000 atm, to give hydrocarbons with a molecular weight of above 50,000, using a highly active Ru catalyst. This is formed *in situ* by reacting a highly active RuO<sub>2</sub> with a hydrocarbon solvent to give a hydrocarbon complex.

### Carboxylic Acid Preparation

SHELL INTERNATIONALE RESEARCH MIJ. N.V.  
*British Patent* 1,080,867  
The reaction of an optionally substituted olefine with CO, to produce a carboxylic acid or its derivatives, is catalysed by a halide or  $\pi$ -complex of Pd, Rh or Ru, e.g. PdCl<sub>2</sub> or an C<sub>2</sub>H<sub>4</sub>-Pd complex.

### Chemical Compounds

IMPERIAL CHEMICAL INDUSTRIES LTD.  
*British Patent* 1,081,304  
Copolymers of an olefine and CO are produced by heating them in the presence of a catalyst comprising an alkyl phosphine complex of a Pd salt, especially (Bu<sub>3</sub>P)<sub>2</sub>PdCl<sub>2</sub>.

### Preparation of Carboxylic Acid Esters

ESSO RESEARCH & ENGINEERING CO.  
*British Patent* 1,083,597  
A substituted allyl ester is produced by reacting a tertiary olefine with a source of carboxylate ions

in the presence of a Pd salt and a high boiling anhydrous polar solvent at 50–150°C.

### Production of $\alpha$ , $\beta$ -Ethylenically-unsaturated Carboxylic Acids and/or $\beta$ -Acyloxy Carboxylic Acids

UNION OIL CO. OF CALIFORNIA  
*British Patent* 1,083,880  
These acids are produced by the oxidative carbonylation of olefines in an anhydrous reaction medium containing an aliphatic carboxylic acid solvent and 0.001–5 wt.% of a Pt metal, preferably of the Pt or Pd subgroups, as a finely divided metal, salt or chelate.

### Production of Vinyl Acetate and Acetaldehyde

E. I. DU PONT DE NEMOURS & CO.  
*British Patent* 1,083,959  
The oxidative carbonylation of C<sub>2</sub>H<sub>4</sub> takes place in an acid solution of a Pd salt, an ionisable metal chloride, cupric acetate and 0–20 wt.% of H<sub>2</sub>O.

### Production of Acetaldehyde

E. I. DU PONT DE NEMOURS & CO.  
*British Patent* 1,086,347  
CH<sub>3</sub>CHO and optionally vinyl acetate are produced from C<sub>2</sub>H<sub>4</sub>, O<sub>2</sub> and CH<sub>3</sub>COOH in the presence of 0.001–0.1 mols/l palladous salt and at least 0.5 mols/l of a Zn/Cu redox mixture.

### Manufacture of Ethers

BRITISH CELANESE LTD. *British Patent* 1,086,351  
C<sub>2</sub>H<sub>4</sub> is reacted with a palladous salt and a metal salt able to oxidise Pd metal in an alcohol to form the vinyl ether of the alcohol and then the metal salt is reoxidised and regenerated with O<sub>2</sub>.

### Production of Vinyl Acetate

E. I. DU PONT DE NEMOURS & CO.  
*British Patent* 1,087,508  
C<sub>2</sub>H<sub>4</sub> is reacted with an CH<sub>3</sub>COOH solution of a palladous salt and a cupric salt at 100 psig or higher and also in the presence of 0.05–2.6 mol/l KCl.

### Palladium Catalysts for Ketone Polymerisation

SHELL OIL CO. *U.S. Patent* 3,321,442  
The catalysts are PdCl<sub>2</sub> and (Ar<sub>3</sub>X)PdCl<sub>2</sub>, where Ar is Ph and X is P, As or Sb.

### Hydrido-iridium and -osmium Complexes in Hydrogenation

STANDARD OIL CO. (INDIANA)  
*U.S. Patent* 3,324,018  
Non-aromatic C-C unsaturation is hydrogenated selectively using a number of specified hydrido-iridium and -osmium complexes of triphenyl arsines, stibines and phosphines, e.g. IrHCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>.

### Organosilanol Preparation

DOW CORNING CORP. *U.S. Patent 3,328,448*  
The conversion of a SiH group to a SiOH group by reaction with H<sub>2</sub>O is catalysed by either H<sub>2</sub>PtCl<sub>6</sub>, Zeise's salt, Pd, Rh or Ru.

### Polybutadiene Isomerisation

UNIROYAL INC. *U.S. Patent 3,330,817*  
A polybutadiene containing *cis*, *trans* and vinyl isomers in a non-equilibrium ratio is isomerised by contacting it with a Rh salt selected from the chloride, bromide, iodide, sulphate, nitrate or acetate at a temperature of 20–80°C.

## FUEL CELLS

### Fuel Cells

THE SPERRY GYROSCOPE CO. LTD.  
*British Patent 1,084,238*

A fuel cell is provided with a hydrogen-permeable membrane of Pd substantially free from pinholes. Preferably the Pd is alloyed with a minor proportion of one or more metals, such as up to 27% Ag, to improve its strength.

### Plural Coated Fuel Cells

STUDEBAKER CORP. *U.S. Patent 3,322,576*

The electrode consists of a porous metal support in the form of a Ta or Ti sheet member, a first coating of graphite in a fluorocarbon polymer and a second coating of Pt black in an amount of 0.1–20 mg/cm<sup>2</sup>.

### Metallised Paper Fuel Cell Electrode

AMERICAN CYANAMID CO.  
*U.S. Patent 3,328,205*

A new form of electrode consists of an unfused, fibrillated, substantially hydrophobic paper sheet on which an active metal catalyst (preferably selected from Pt, Pd and Ru) is deposited in an amount of 25–65%, based on the resulting sheet.

## GLASS TECHNOLOGY

### Alloy Resistant to Wetting by Glass

JOHNSON, MATTHEY & CO. LTD.  
*Italian Patent 764,901*

An alloy for use in the glass industry consists of 60–97 wt.% Pt, 2–25 wt.% Rh and 1–10 wt.% Au. This corresponds to *Belgian Patent 682,754*.

## ELECTRICAL AND ELECTRONIC ENGINEERING

### Electrical Contact Elements and Contact Assemblies

JOHNSON, MATTHEY & CO. LTD.  
*British Patent 1,088,541*

A series of contact elements are produced on a backing strip of a different metal which is pro-

vided with a plurality of locating members corresponding to the numbers of contact elements. The object of the locating members is to locate the strip in a press tool accurately to that contact members can be pressed out precisely without leaving waste material between them. The contact metals are preferably formed of noble metals, such as Ag, Pt, Pd or Au.

### Electrical Resistance Wire

JOHNSON, MATTHEY & CO. LTD.  
*U.S. Patent 3,320,039*

The wire consists of an outer tube of Pt group metal or alloy filled with a refractory oxide selected from Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub> and MgO. A suitable tube is made from Pt with 10–40% Rh.

### Cermet Resistance Element

BECKMAN INSTRUMENTS INC.  
*U.S. Patent 3,326,645*

A thin resistance layer is produced on a non-conducting base layer from a cermet composition. This contains 50–95 wt.% glass and 5–50 wt.% of a Ru-Rh alloy, such as a 1:1 alloy (by weight). The composition of the alloy is matched to the glass so that the glass has a lower melting point than the alloy and at least 10 wt.% Ru is present. See also *U.S. Patent 3,326,720*.

### Electrical Resistance Element

CTS CORP. *U.S. Patent 3,329,526*

The resistance element consists of a resistant insulating base coated with a glass film not thicker than 0.0002 inch and containing particles of Ru having hexagonal close-packed crystalline structure and acicular growth.

### Sparking Plug Electrodes

JOHNSON, MATTHEY & CO. LTD.  
*U.S. Patent 3,331,685*

Ru and Ru-Ir alloy powders are compressed and sintered to form an electrode resistant to contamination by Pb. Ranges of preferred particle sizes, sintering temperatures, and compacting conditions are claimed.

### Strain Gauge Alloy

HITACHI LTD. *U.S. Patent 3,333,462*

A new alloy useful for strain gauge wire of foil consists essentially of 20.0–52.2 at.% Pt, 11.3–33.5 at.% Rh and about 14.3–50.0 at.% Pd.

## TEMPERATURE MEASUREMENT

### Tungsten-Osmium Thermocouple

U.S. ATOMIC ENERGY *U.S. Patent 3,320,098*

The thermocouple consists of a first leg consisting of 0.5–1.0 at.% Os and the remainder W and a second leg consisting of 26 at.% Re and the balance W.