

conductivity of thick, polycrystalline RuO₂ films obtained by decomposing RuCl₃ are presented and discussed. The influence of the preparation procedure, process temperature, Cl content and nature of substrate on the electrical and structural properties is also considered.

NEW PATENTS

METALS AND ALLOYS

Dispersion Strengthening of Metals

JOHNSON MATTHEY & CO. LTD.

British Patent 1,280,815

Platinum group metals are dispersion strengthened by spraying the metal or alloy with ~0.1 wt.% reactive metal, e.g. Zr, through an atmosphere which reacts preferentially with the reactive metal to form a dispersion strengthening material, e.g. ZrO₂.

Dispersion Hardening of Pt Group Metals

JOHNSON MATTHEY & CO. LTD.

U.S. Patent 3,640,705

An oxidation resistant and high mechanical strength alloy is made by alloying a Pt group metal with an element capable of forming a stable refractory compound, and heating the alloy in a gas, e.g. air or O₂, to form the refractory compound within the alloy. This corresponds to *British Patent* 1,139,897.

Treatment of Metals and Alloys

JOHNSON MATTHEY & CO. LTD.

German Offen. 1,533,481

The mechanical properties of metals, alloys and compounds are improved by cold working and annealing. Recrystallisation, which takes place during annealing, results in an elongated crystal or grain structure orientated in the direction of working.

ELECTRODEPOSITION AND SURFACE COATINGS

Plated Polymers

GULF & WESTERN INDUSTRIAL PRODUCTS CO.

British Patent 1,277,145

It has been found that in the electroless plating of polypropylene articles, much better results are obtained if Pd(NO₃)₂ rather than PdCl₂ is used as the activator.

Platinum Coatings on Cobalt Alloys

DEUTSCHE EDELSTAHLWERKE A.G.

British Patent 1,282,530

Turbine blades and other metal parts exposed to high temperatures are made from Co alloys

Fine Line Printing for Consumer Electronics

R. A. VOGEL, *Solid State Technol.*, 1972, 15, (5), 51-54

A system for printing Ag-Pd fine lines is described. Rheology and inks are discussed, together with printer characteristics and requirements.

coated with Pt group metals, e.g., Pt itself, optionally plated on over Ni.

Iridium Plating

INTERNATIONAL NICKEL CO. INC.

U.S. Patent 3,639,219

An Ir electroplating bath is prepared by digesting an aqueous solution of IrCl₃ and sulphamic acid at 100°C for an extended period, then adjusting the Ir content of the bath to about 3-20 g/l and adding about 3-20 g/l ammonium sulphamate.

LABORATORY APPARATUS AND TECHNIQUE

Palladium Alloy

DEUTSCHE GOLD- & SILBER-SCHNEIDANSTALT

German Offen. 2,043,492

Torsion strips in electrical meters are made from an alloy of Pd with 0.6-2% B.

HETEROGENEOUS CATALYSIS

Hydrogenation Catalyst

MARUZEN OIL CO.

British Patent 1,272,728

Selective hydrogenation of polyunsaturated hydrocarbons can be carried out in the presence of specified proportions of CO and a catalyst which is preferably supported, Cu-free Pd.

Hydrogenation Catalyst

F.M.C. CORP.

British Patent 1,273,280

In the production of H₂O₂ by the anthraquinone process, the hydrogenation catalyst is Pd metal supported on Al₂O₃ spheres of specified dimensions.

Hydrogenation Catalyst

B.P. CHEMICALS INTERNATIONAL LTD.

British Patent 1,273,874

12-Aminododecanoic acid (for use in the manufacture of nylon-12) is obtained by hydrogenation of 11-cyano-undecanoic acid in the presence of Ru metal deposited on a SiO₂ support.

Dehydrogenation Catalyst

V.E.B. LEUNA-WERKE 'WALTER ULBRICHT'

British Patent 1,275,830

Normal paraffins are dehydrogenated to linear

monoolefins in the presence of a catalyst which contains 0.5–5 wt.% Pt and 0.3–0.6 wt.% alkali metal.

Rhodium Catalysts

MONSANTO CO. *British Patent 1,277,242*

Carboxylic acids and esters are obtained by reaction of alcohols with CO in the presence of a solid catalyst containing (a) a support, (b) a Rh component and (c) another metal.

Hydroreforming Catalyst

COMPAGNIE FRANCAISE DE RAFFINAGE

British Patent 1,278,001

The catalyst is a porous refractory inorganic oxide support carrying 0.02 to 2 wt.% of a metal catalyst which is a Pt group metal with 0.02–2 wt.% of Pb and/or Sn.

Ammonia Oxidation Catalyst

M. A. MINIOVICH et al. *British Patent 1,282,000*

A catalyst for the oxidation of NH_3 to NO consists of 75–82% Pt, 15–22% Pd, 2–3.5% Rh and 0.05–0.15 Au, Fe and Ir. This catalyst is more active but costs less than known catalysts.

Catalytic Hydrogenation of Hydrocarbon Oils

SHELL INTERNATIONALE RESEARCH MIJ. N.V.

British Patent 1,282,774

A catalyst for the hydrogenation of hydrocarbon oils consists of 0.25–5 wt.% Pt or Rh on an Al_2O_3 carrier the total alkali content of which is less than 0.01 wt.%.

Catalysis

ACCUMULATORENWERK HOPPECKE CARL ZOELLNER & SOHN K.G. *British Patent 1,283,138*

H_2 and O_2 generated by electrical accumulators are catalytically re-formed into H_2O using a Pt metal catalyst, thus minimising the need for periodic topping up.

Exhaust Gas Treatment

ESSO RESEARCH & ENGINEERING CO.

U.S. Patent 3,637,344

A new improved catalyst for the treatment of ICE exhaust gases is a mixture of Ru and Ir.

Exhaust Gas Treatment

OXY-CATALYST INC. *U.S. Patent 3,637,353*

ICE exhaust gases are treated in three coaxial chambers. The central chamber contains a Pt-plated catalyst.

Multicomponent Catalyst

CHEVRON RESEARCH CO. *U.S. Patent 3,637,527*

Hydrocracking and denitrification multicomponent catalysts are produced by co-precipitating a Pd compound (e.g. sulphide) with a Zr, Ti, Th, etc. compound and also a metal chloride.

Aromatic Hydrocarbon Hydrogenation

UNIVERSAL OIL PRODUCTS CO.

U.S. Patent 3,637,879

Cycloparaffins are produced from aromatics by reduction in contact with a catalyst containing 0.01–2% Pt group metal, 0.02–5% Ge component, 0.01–1.5% alkali metal compound and a porous carrier. Pt and Pd are preferred.

Reforming Catalyst

CHEVRON RESEARCH CO. *U.S. Patent 3,639,273*

A catalyst useful particularly for reforming is a particulate mixture of (1) a layered crystalline clay type aluminosilicate and (2) a Pt group component in association with an Al_2O_3 carrier or a SiO_2 carrier, e.g. Pt.

Ethylene Oxidation

GULF RESEARCH & DEVELOPMENT CO.

U.S. Patent 3,641,139

C_2H_4 is oxidised to CH_3COOH without O_2 in the presence of Ir metal. See also *U.S. Patents 3,641,510 and 3,641,511*.

Hydrocarbon Isomerisation Process

UNIVERSAL OIL PRODUCTS CO.

U.S. Patent 3,642,925

Hydrocarbons are isomerised using a catalytic composite of a Pt group component, a Sn component and a Re component on a porous carrier, e.g. Pt, Sn and $\text{Re}/\text{Al}_2\text{O}_3$.

Hydrocarbon Hydroprocessing

UNIVERSAL OIL PRODUCTS CO.

U.S. Patent 3,644,198

The hydroprocessing of hydrocarbons is catalysed by a supported mixture of Ni, Group VIII metal and Group IVA metal, e.g. Ni, Pt and Ge on a crystalline aluminosilicate.

Catalytic Reforming Process

UNIVERSAL OIL CO. *U.S. Patent 3,645,888*

A gasoline fraction is catalytically reformed together with H_2 and H_2O over a catalyst containing a Pt group component, Ge and a halogen on a porous support; e.g. Pt, Ge and Cl.

Dehydrogenation Catalyst

UNIVERSAL OIL PRODUCTS CO.

U.S. Patent 3,647,719

The dehydrogenation of hydrocarbons is catalysed by a mixture of Pt group metal, Ge and an alkali or alkaline earth metal on a porous support. A typical catalyst contains Pt, Ge and Li.

Dehydrogenation Catalyst

UNIVERSAL OIL PRODUCTS CO.

U.S. Patent 3,647,911

Saturated hydrocarbons are dehydrogenated over an Al_2O_3 -supported mixture of As and Pt with 0.01–1.5% Li. The ratio of As to Pt is 0.15–0.45 : 1. Other Pt group metals can replace Pt.

Selective Hydrogenation of Acetylenic Hydrocarbons

UNIVERSAL OIL PRODUCTS CO.

U.S. Patent 3,651,167

Selective hydrogenation of 4C acetylenes, for example ethylacetylene and/or dimethylacetylene, mixed with butadiene, is carried out in a fixed-bed system using a Group VIII noble metal component catalyst. A preferred catalyst contains 0.01–0.2% Pd.

Hydrocarbon Isomerisation Catalyst

UNIVERSAL OIL PRODUCTS CO.

U.S. Patent 3,652,697

Hydrocarbons are isomerised using a Pt group metal-Ge-Friedel Crafts halide catalyst. A typical catalyst contains Re, Ge and Pt on Al_2O_3 treated with the chlorides of these metals to produce $AlCl_3$ as the Friedel-Crafts halide.

Hydroisomerisation Catalyst

TEXACO INC.

U.S. Patent 3,652,709

Hydroisomerisation of 4–7 C hydrocarbons is carried out in the presence of a chloride-activated metal- Al_2O_3 catalyst, the metal being Ru, Rh, Pd or Pt. The selectivity of the catalyst is improved by treating it with a C oxide at 50–400°F.

Refractory Catalyst Supports

JOHNSON MATTHEY & CO. LTD.

German Offen. 2,149,663

Refractory catalyst supports, e.g. of honeycomb structure, are produced from an Al_2O_3 structure coated with Al_2O_3/SiO_2 fibres. Pt may then be deposited on the support.

HOMOGENEOUS CATALYSIS

OXO Catalysts

BADISCHE ANILIN- & SODA-FABRIK A.G.

British Patent 1,273,042

Aldehydes and alcohols are produced by reaction of olefins with CO and H_2 in the presence of a tertiary phosphine adduct of a Group VIII metal carbonyl complex of preferably Rh or Pt.

Oxidation Catalyst

SHELL INTERNATIONALE RESEARCH MIJ. N.V.

British Patent 1,275,370

Methyl esters of aliphatic carboxylic acids are obtained by reaction of mixtures of C_2H_4 and CH_3OH in the presence of a complex of Ru with CO and a triaryl phosphine.

Hydrosilylation Catalyst

TORAY INDUSTRIES INC. *British Patent 1,278,072*

An organosilicon compound is produced by reaction of an olefinically unsaturated compound with a hydrosilane in the presence of a catalyst which is a zerovalent complex of Pd with a P-, As- or Sb-containing ligand.

Dicarboxylic Acid Production

MONSANTO CO.

British Patent 1,278,353

Dicarboxylic acids are produced by reacting a non-vicinal glycol (or one of its derivatives) with CO in a solution containing a halogen-promoted Rh or Ir compound and H_2O (where both OH groups of the glycol are substituted). Rh carbonyl bromides and chlorides and their phosphine complexes are described in the examples.

Adipic Acid Production

MONSANTO CO.

British Patent 1,278,354

Adipic acid is produced by the reaction of butane-1,4-diol with CO in the presence of a halogen-promoted Rh or Ir catalyst. The preferred catalysts are phosphine or phosphine/carbonyl complexes of Rh monohalides.

Production of Octadienes

IMPERIAL CHEMICAL INDUSTRIES LTD.

British Patent 1,278,806

1,6- and/or 1,7-octadienes are produced by contacting one or more acyclic conjugated dienes with a metallic Pt, Pd, Os, Rh or Ru or one of their compounds in the presence of a polar solvent and a reducing agent.

Catalytic Carbonylation of Nitro Compounds

OLIN CORP.

U.S. Patent 3,636,027

An organic isocyanate is produced by reacting an organic nitro compound with CO in the presence of a catalyst system containing a S-containing heteroaromatic compound and a halide of a noble metal. Thiophene and dibenzothiophene are the preferred heteroaromatic compounds, and the noble metal halide is preferably a halide of Pd, Rh, Ir and/or Pt, e.g. $RhCl_3$ -thiophene. See also *U.S. Patents 3,636,028 and 3,636,029*.

Unsaturated Ester Production

MOBIL OIL CORP.

U.S. Patent 3,646,115

Unsaturated esters are prepared from an olefin, carboxylic acid and O_2 in the presence of a Rh or Ir catalyst complexed with CO, phosphine, arsine or stibine.

Aromatic Isocyanate Production

OLIN MATHIESON CHEMICAL CORP.

U.S. Patent 3,637,785

Aromatic isocyanates are produced by the reaction of an aromatic nitro compound with CO in the presence of a noble metal halide and an amide or thioamide, e.g., Pd halide and dimethyl formamide. See also *U.S. Patent 3,637,786*.

Diene Synthesis Catalyst

E. I. DU PONT DE NEMOURS & CO.

U.S. Patent 3,640,898

Dienes are synthesised from olefins and conjugated dienes in the presence of Rh(III) salt catalysts complexed with amides, phosphoramides, phosphine oxide, etc.

Cyclic Olefin Isomerisation

SUN OIL CO. *U.S. Patent 3,647,896*
Exocyclic-unsaturated olefins are produced by isomerisation in the presence of a Group VIII complex, especially an Os or Ru phosphine halide and/or carbonyl.

Palladium Complexes

OLIN MATHIESON CHEMICAL CORP.
U.S. Patent 3,654,279
New catalysts, especially for isocyanate production, have the formula $\text{PdL}(\text{CO})\text{X}_2$, where X is halogen and L is a Lewis base and particularly a heteroaromatic N compound such as pyridine.

Stabilised Rhodium Carbonyl Complexes

BADISCHE ANILIN- & SODA-FABRIK A.G.
German Offen. 2,044,651
Rh carbonyl complexes used in the oxo synthesis are stabilised by a formylalkyl ester.

FUEL CELLS AND BATTERIES

Fuel Cell Electrodes

ALLMANNA SVENSKA ELEKTRISKA A.B.
British Patent 1,273,045
The fuel electrode in a fuel cell is a porous Ni plate coated with a mixture of Pd, Pt and Ru and the air electrode has an active layer consisting of a mixture of Ag and Ni particles sintered together.

CHEMICAL TECHNOLOGY

Platinum in Silicone Elastomers

DOW CORNING CORP. *U.S. Patent 3,652,488*
A flame resistant elastomer is obtained from a mixture of 100 parts silicone polymer, 10-100 parts SiO_2 reinforcing agent and 0.05-2 parts S-free C black cured with 10-150 p.p.m. Pt.

GLASS TECHNOLOGY

Glass Fibre Production

CERTAIN-TEED PRODUCTS CORP.
U.S. Patent 3,647,382
A cooling tube assembly for use in a glass fibre spinneret is made from commercial Pd metal.

ELECTRICAL AND ELECTRONIC ENGINEERING

Anode

ELECTRONOR CORP. *British Patent 1,273,486*
A Ti anode for use in electrolysis of brine is coated with an electrocatalytic layer of a semiconductor composition. The composition contains a major portion of TiO_2 and a minor portion of an oxide of a Pt group metal.

Semiconductor Device

TELEFUNKEN PATENTVERWERTUNGS G.m.b.H.
British Patent 1,274,500
A solar cell includes a semiconductor body and a contact which consists of a layer of Ag, a layer of Ti and a layer of a noble metal other than Ag (e.g. Pd or Pt).

Heater Elements

JOHNSON MATTHEY & CO. LTD.
British Patent 1,278,411
An electrical heater element is made from a high temperature resistant non-conducting substrate with a layer of the resistor composition of *British Patent 1,210,493*. This consists of 91-20% finely divided glass and 9-80% of the product of heating RuO_2 with one or more Group V oxides, e.g. Nb_2O_5 .

Resistor Composition

JOHNSON MATTHEY & CO. LTD.
U.S. Patent 3,637,530
A resistor composition suitable for firing on to a ceramic substrate has the form of an oxide containing Nb and Ru in which the atomic ratio of metal to O_2 is 1 : 2 and in which the atomic ratio of Nb to Ru is within the range 1:2000-1:1.

Palladium Films on Silicon Semiconductors

MATSUSHITA ELECTRONICS CORP.
U.S. Patent 3,642,528
Pd films on SiO_2 layers peel off when exposed to H_2 . This discovery is used in making selective deposits on Si semiconductors. The area not to be coated is treated to produce a layer of SiO_2 . The whole body is coated with Pd and treated with H_2 so that the Pd over the oxide peels off.

Palladium Phosphide Chalcogenides

E. I. DU PONT DE NEMOURS & CO.
U.S. Patent 3,655,348
At high pressures and $\sim 1,000^\circ\text{C}$, Pd, P and a chalcogen, S or Se, combine to form compounds of formula $\text{PdP}_y\text{X}_{2-y}$ in which y is 0.67 when X is S and y is 0.4-0.8 when X is Se. The compounds have a pyrite-type crystal structure. They are electrical conductors with a zero temperature coefficient of resistance from liquid He temperature to room temperature. They are useful as electrical resistors.

TEMPERATURE MEASUREMENT

Resistance Thermometer Alloys

CALIFORNIA INSTITUTE RESEARCH FOUNDATION
U.S. Patent 3,644,863
Alloys with a negative temperature coefficient of electrical resistance contain a Pt group metal, Si or Ge and a first series transition metal. A preferred alloy is $\text{Pd}_{80-x}\text{Si}_{20}\text{Cr}_x$, where x is 1-8.