

NEW PATENTS

METALS AND ALLOYS

Ornamental Platinum Alloy

TANAKA KIKINZOKU KOGYO

Japanese Publ. Appl. 61/34,133/4/5/6/7/8/9

An ornamental Pt alloy with excellent workability, mechanical strength and castability for jewellery applications contains 84–96% Pt, 0.5–10%Co, and one or more of Rh, Ir, Ru, Au, Ag, Cu, Y, B, Ca, mischmetal, Fe, Mn, Cr, Ni, etc.

Finely Powdered Noble Metal

KAGAKU GIJUTSU-CHO KINZ

Japanese Publ. Appl. 61/56,209

Finely powdered metal for example, Pt, Ir, Rh, Os, Ru, Au, Ag, Re, for use in catalyses or electrical conductors is manufactured using a thermal plasma generated in N_2 or in N_2 and inert gas.

CHEMICAL COMPOUNDS

Soluble Salt Production

TANAKA KIKINZOKU KOGYO

Japanese Publ. Appl. 61/6,129

The production of soluble salts of Ru, Ir and/or Rh by oxidising slightly soluble powder containing Ru, Ir, Rh and/or their oxides with a solution of alkali hydroxide and an oxidising agent, is claimed.

Transparent Iridium Oxide Preparation

NIPPON KOGAKU K.K.

Japanese Publ. Appl. 61/29,822

Transparent Ir oxide thin film is prepared on a substrate from Ir metal, and other metals by vacuum evaporation under low O_2 partial pressure or by multi-component sputtering.

Antistatic Metallised Iron Oxide

FUJI TITAN KOGYO K.K.

Japanese Publ. Appl. 61/31,318

Iron oxides consisting of reduced micaceous Fe oxide is electrolessly coated with Pt, Pd, Au, Ni, Cu, or Cr. The oxides are useful as antistatic agents for rubber or plastics or electromagnetic wave shielding materials, or additives to ceramics for changing their electrical resistance.

High Purity Palladium Acetate Preparation

MITSUBISHI CHEM. IND. K.K.

Japanese Publ. Appl. 61/47,440

Pd acetate is prepared by heating Pd powder in acetic acid in the presence of nitric acid, and then treating with an inert gas to remove the N containing impurity in the acetic acid. Trace N lowers catalytic activity.

ELECTROCHEMISTRY

Electrodes for Electrolysis

mitsui Eng. & Shipbuild.

Japanese Publ. Appl. 60/262,989

A C fibre electrode of large surface area carrying at least one of Pt, Pd, Ir, Ru, Au, Ag, Re, W, Cu, etc., its oxide and carbide, and being in contact with a diaphragm within an electrolytic cell, is claimed. The electrolytic voltage can be reduced, thus reducing side reactions and costs.

Electrolysis Electrodes

T.D.K. CORP. *Japanese Publ. Appl.* 61/52,384/5

Sea water electrolysis is carried out by electrodes coated with Pt-Ir alloy and oxides of Ir and Ru, or with a mixture of Ru oxide, Ir oxide, Pt and Sn oxide. The electrodes have good resistance to corrosion, and good characteristics, especially in low temperature sea water.

Anode for Brine Electrolysis

A.S. U.S.S.R. FAR-E CHEM. *Russian Patent* 1,139,770

A Ti anode covered with RuO_2 , CoO and TiO_2 (with $RuO_2:TiO_2 = 1:2-4$) has increased corrosion resistance for sea water electrolysis.

Insoluble Anode

G. F. POTAPOVA *Russian Patent* 1,171,566

Insoluble anodes 2–3 μ m thick are obtained when a low voltage gas phase arc-spark discharge is used to coat a Ti or Ta support with Pt, producing a Ti-Pt or Ta-Pt layer. They have more chemical resistance.

ELECTRODEPOSITION AND SURFACE COATINGS

Palladium Electroplating Process

AMERICAN TEL. & TELEG. CO.

World Patent Appl. 86/652A

A Pd electroplating bath for electronic applications consists of an organic ammine or ammonia complexed Pd hydroxide. The complex Pd ammine hydroxide has high solubility in water, eliminating danger of precipitates forming during the plating process.

Platinum Photodeposition

MITSUBISHI CHEM. IND. K.K.

Japanese Publ. Appl. 61/50,633

Pt is deposited from Pt halides, especially chloroplatinates, onto an inorganic semiconductor by light irradiation of a semiconductor in aqueous solution, containing a metal halide and a reducing agent. The semiconductors are used as catalysts or gas sensors. Dense deposition of final Pt particles is ensured.

Rhodium Plating Electrolyte

A.S. UKR. GEN. INORG. CHEM.

Russian Patent 1,174,496

A Rh plating electrolyte of increased stability is prepared by repeated precipitation of the hydroxide, filtration, dissolution in concentrated H_2SO_4 and sulphamic acid addition. Crack-free coatings up to $15 \mu m$ thick can be prepared.

Palladium Plating Bath

C. Z. BATZIN

Russian Patent 1,178,803

Improved electrodeposition and coating quality are obtained during Pd plating by using non-dissolvable electrodes and an anion exchange membrane between the cathode bar and the cation exchange membrane.

LABORATORY APPARATUS AND TECHNIQUE

Gas Detector

TOSHIBA K.K.

British Appl. 2,166,549A

A gas detector comprises an In-Sn oxide thin film covering the electrodes, and a laminated catalyst layer containing preferably one or more of Pt, Pd and Rh supported on Al_2O_3 of thickness $10-50 \mu m$. The detector can detect reducing gas in air with high sensitivity and selectivity, especially CO , C , CH_4 and C_2H_2 .

Oxygen Sensor Electrode

HITACHI CHEMICAL K.K.

Japanese Publ. Appl. 61/17,950

Hexachlorplatinic acid was applied to the Pt surface of a baked yttria stabilised ZrO_2 electrolyte and used to detect O_2 . The adhesion of the metal and electrolyte is strong and long lasting.

Platinum Crucible

FUJI PHOTO FILM K.K. *Japanese Publ. Appl. 61/24,982*

A crucible made of Pt or Pt alloy has a nozzle for discharging molten material. It can be used for manufacturing ferrite powder for magnetic recordings.

Crucible for Single Crystal Growth

HITACHI METAL K.K. *Japanese Publ. Appl. 61/26,588*

A columnar crucible for growth of high quality large single crystals of Mn-Zn ferrite is made of Pt or Pt-Rh with reinforcing wires of Pt-Rh at the upper end of the crucible.

Hydrogen Electrolyser

A.S. UKR. GAS INST.

Russian Patent 1,172,945

Increased H_2 purity is obtained from a filter-press electrolyser with a perforated bipolar electrode main sheet. The cathode sheet is a Pd-Ag alloy which is non-permeable and porous to H_2 to give improved separation.

Oxygen Analyser

AZERB. AZIZBEKOV PETROCHE.

Russian Patent 1,176,230

An electrochemical O_2 analyser for analysing O_2 and H_2 containing gas has separate gas cells and a Pd foil which allows H_2 , but not O_2 , to pass through. O_2 is ionised in one cell and the current flowing through a load resistor measures the O_2 concentration.

JOINING

Palladium Solder

TANAKA KIKINZOKU KOGYO

Japanese Publ. Appl. 61/20,697

A Pd solder with high corrosion resistance and low melting point of $700-800^\circ C$ comprises 5-30wt.% Ag, 0.25-7wt.% Si, 0.5-20wt.% Ga and/or Ge and balance Pd. The solder can bond Ti or Ti alloy members together, or to Cu, Ni, stainless steels, etc.

Soldering Bump

NIPPON TELEG. & TELEPH.

Japanese Publ. Appl. 61/46,052

A soldering bump with strong bonding strength, for use in electronic devices, such as Pb-based Josephson elements, is formed from two intermediate metal layers of Pd, Au, Cr or Cu.

HETEROGENEOUS CATALYSIS

Fruit Preservation

JOHNSON MATTHEY P.L.C. *British Appl. 2,163,637A*

Ethylene gas is removed from stored fruit and vegetables by withdrawing the air, heating it and passing it through a catalytic combustor with a catalyst containing one or more of Pt, Pd, Ru or Rh on activated Al. The air is then returned to the store.

Preparation of Pyridine

IMPERIAL CHEMICAL INDUSTRIES P.L.C.

British Appl. 2,165,844A

Pyridine is prepared by a one- or two-stage hydrogenation of 1,3-propane dinitrile(II) over a Pd/SiO₂ catalyst. The catalyst preparation is given. The process is preferably one-stage when a 1-100 times stoichiometric excess of H_2 is used.

Platinum Catalyst for Carbon Monoxide Conversion

IND. RES. INST. OF JAPAN *British Appl. 2,166,061A*

A process for the production of a CO conversion catalyst containing at least 6mg/gC for the efficient conversion to CO_2 at room temperature under humid conditions, is claimed. The catalyst is prepared by dipping activated C in chloroplatinic acid solution, drying, reducing, then treating with H_2O_2 . The activated C can additionally be treated with a monomer.

Hydrocracking Catalyst

UNION OIL CO. CALIFORNIA *European Appl.* 172,578A
A hydrocracking catalyst with controllable water content giving high and consistent activity is based on a Y zeolite exchanged with Pd or Pt cations and rare earth cations.

Shale Oil Treatment

COMMONWEALTH SCIENT. ORG.
World Patent Appl. 86/1,743A
A catalyst for the 1-step hydrocracking and hydrotreating of shale oil comprises Ru/zeolite with a Group VI and/or a Group VIII metal on a refractory support. The catalyst can deal, in 1-step, with high-boiling feeds such as heavy crude, coal and tar sands.

Catalyst for Hydrocarbon Synthesis

EXXON RES. & ENG. CO. *U.S. Patent* 4,567,205
A Ru-Re/TiO₂ catalyst is used for hydrocarbon synthesis from CO-H₂ mixtures. High quality middle distillate fuels are produced. The catalyst has high activity and low CH₄ and CO₂ selectivities, and the deactivation rate is reduced.

Catalyst for Ammonia Synthesis

M. W. KELLOGG CO. *U.S. Patent* 4,568,532
NH₃ is produced from synthesis gas over a Fe catalyst and over a Ru/C catalyst by recycling.

Alkane Dehydrogenation

ATLANTIC RICHFIELD CO. *U.S. Patent* 4,568,789
A C₂ + alkane is dehydrogenated to the corresponding olefin and water by contacting with a reducible oxide of Ru and at least one alkali or alkali earth metal, or compound. The reduced Ru oxide can be reoxidised and reused. The alkali metal increases the selectivity to dehydrogenation products.

Alkene Preparation

PHILLIPS PETROLEUM CO. *U.S. Patent* 4,570,025
Alkenes are prepared by hydrogenating one or more unsaturated hydrocarbons over a Pd/Al phosphate catalyst where Al:P=0.4-1.1:1. The catalysts are more active and/or selective than known catalysts and give high yields of (cyclo)alkenes.

Lead-Resistant Catalyst

SIGNAL APP. TECHN. IN. *U.S. Patent* 4,572,904
A Pb-resistant exhaust gas catalyst comprises a protective zirconia coating over Pt, Pd, Ir and/or Rh on a refractory inorganic oxide support. The activity is retained even with fuel containing 0.01 g/l Pb.

Dewaxing Lubricating Oil

TEXACO INC. *U.S. Patent* 4,575,417
A catalytic dewaxing process for a hydrocarbon base lubricating oil involves passing it over a calcined H mordenite catalyst with a SiO₂:Al₂O₃ ratio 10-50:1, loaded with Pt or Pd.

Tertiary Amine Manufacture

MITSUBISHI PETROCH. K.K.
Japanese Publ. Appl. 60/258,145
Tertiary amines containing two long alkyl groups are prepared by reacting olefin(s), CO, H₂ and primary amines in the presence of a Rh and Ru compound catalyst in a one-step reaction.

Ethyl Acetate Production

MITSUBISHI GAS CHEM. K.K.
Japanese Publ. Appl. 61/5,050
Ethyl acetate is produced in 95% yield from acetic anhydride and H₂ in the presence of supported Pd and/or its compounds, and sulphonic acids.

Preparation of 2-Fluoropropanol

SAGAMI CHEM. RES. CENTRE
Japanese Publ. Appl. 61/7,228
2-Fluoropropanol is formed by hydroformylation of monofluoroethylene in the presence of a supported Group VIII metal compound such as a Pt, Rh, Ru or Co catalyst. Catalysts such as hexarhodium hexadecacarbonyl on activated C, SiO₂, Al₂O₃, or organic polymer in amounts 10-10⁶ moles/CH₂CFH are used at 80°C and a CO pressure of 35 atm and H₂ pressure of 35 atm, with toluene, to give 2-fluoropropanol in 95% yield.

Exhaust Gas Purification

TOYOTA JIDOSHA K.K. *Japanese Publ. Appl.* 61/18,439
A monolithic catalyst is produced by repeated immersion of the support and base material into a solution of Pt, Pd, Ir, Ru, Rh, Os, Cr, Ni, V or Cu, so that more catalytic material is loaded onto one end. The catalyst has improved durability and activity.

Reforming Catalyst

TOKYO GAS K.K. *Japanese Publ. Appl.* 61/28,451
A Ru catalyst on a solid sintered support is used for steam reforming of methane, natural gas, liquid propane gas, naphtha or in a fuel cell system. No free C is generated.

Combustion Catalyst

BABCOCK-HITACHI K.K.
Japanese Publ. Appl. 61/28,453
A catalyst with high activity at lower temperatures, for example for the combustion of CH₄, is made by loading a support of, for instance, γ -Al₂O₃ with (1) Pd and/or Rh, and (2) Ba, Sr or Ca.

Exhaust Gas Purification

MITSUI MINING & SMELTING
Japanese Publ. Appl. 61/28,455
A honeycomb support carrying Pt, Pd or Rh and also Ni oxide is used as a three-way catalyst for the purification of combustion exhaust gas. The catalyst removes 80-90% CO and HC at higher temperatures than catalysts without Ni oxide.

Production Catalyst for Ethanols

AGENCY OF IND. SCI. TECH.

Japanese Publ. Appl. 61/30,541

A supported Rh-Fe catalyst is prepared by adding Fe as an accelerator to the Rh. The amount of 2C compounds produced by CO and H₂ can be increased without increasing the amount of CH₄ formed. Selectivity to ethanols is >70%.

Double Oxide Combustion Catalysts

MATSUSHITA ELEC. IND. K.K.

Japanese Publ. Appl. 61/33,232

A catalyst A_{1-x}A'_xBO₃, where A is an alkaline earth metal, A' is Ce or Sr, and B is Rh, Pt or Ru, supported on Al₂O₃ or SiO₂, is used in small combustors for burning the lighter hydrocarbons at 700–800°C.

Methane Combustion Catalyst

NIPPON SHOKUBAI KAGAKU

Japanese Publ. Appl. 61/33,233

A catalyst for CH₄ combustion at lower temperatures comprises Pt, Pd and Ni on stabilised Al₂O₃, TiO₂ or ZrO₂. CH₄ is burned over the catalyst to heat up further fuel gas to its combustion temperature. This is used in gas turbine generators, heat recovery boilers, etc., enabling clean exhaust to be produced.

Air Purification

NIKKI UNIVERSAL K.K.

Japanese Publ. Appl. 61/35,853

Catalysts for purifying the air of CO from automobile ventilators, air conditioners, fans, waste gas from stoves or water heaters, tunnels and underground garages consist of Pt/γ-Al₂O₃, with Fe, Co, Ni, Mn, Cu, Cr, Sn, Pb or Ce deposited on it. The catalyst gives a 97% CO conversion rate.

Three-Way Catalyst

NISSAN MOTOR K.K. *Japanese Publ. Appl. 61/46,247*

A three-way catalyst giving conversion rates >80% at lower temperatures, such as 400°C, is made by loading Pt and Rh salts onto a support and calcining in a combustion exhaust gas stream.

Engine Exhaust Purification

TOYOTA JIDOSHA K.K.

Japanese Publ. Appl. 61/46,252

A monolithic catalyst for exhaust purification with improved activity (74%HC, 84%CO and 82%NO_x removal at 350°C) is formed from a columnar base material with micropores, such as cordierite, on which is deposited Pt, Pd, Ir, Ru, Rh, Os, etc.

High Calorific Value Gas

KANSAI NETSU KAGAKU

Japanese Publ. Appl. 61/57,242

A catalyst of Pt, Pd, Rh, Ir, Ru on Fe group metal substrate, with oxides of Mo and/or W on Al₂O₃ and/or SiO₂ support is used to produce a high calorific value gas from H₂ and CO.

Exhaust Gas Purification

TOYOTA JIDOSHA K.K.

Japanese Publ. Appl. 61/61,642

An engine exhaust purification catalyst has a columnar monolithic body with micropores holding Al₂O₃, loaded with catalysts of Pd, Pt and Rh. The catalyst can remove almost 100% CO at 300°C; and also needs less catalyst material.

Hydrogen Rich Gas Production

SHELL INT. RES. Mij. B.V. *French Appl. 2,567,866*

A H₂ rich gas is prepared by reacting CO with steam in the presence of a Cu and/or Pd/spinel catalyst.

Ethylene Glycol Preparation

BASF A.G.

German Offen. 3,427,138

Increased yields of ethylene glycol are produced from CO and H₂ under increased temperatures and pressures with a Rh-Co catalyst of metals or their carbonyl complexes, salts or oxides, where Rh : Co is 20 : 1 to 60 : 1.

Active Agent Evaporator

GLOBOL-WERK G.m.b.H. *German Offen. 3,436,310*

Insecticides, bactericides, disinfectants, etc., are evaporated from an impregnated porous plate by a flameless burner containing a finely distributed Pt catalyst.

Battery Catalyst

VARTA BATTERIE A.G.

German Offen. 3,437,479

A catalyst for recombining H₂ and O₂, in an accumulator, for instance in submarines, is made from PTFE, activated charcoal and acetylene black with the Pd catalyst in the core zone. This battery eliminates the need to collect the battery gases.

Palladium-Silver Catalyst

BASF A.G.

German Offen. 3,438,851

A Pd-Ag/Al₂O₃ catalyst is used in the preparation of sterically pure olefinically unsaturated compounds, by hydrogenating the corresponding acetylenically unsaturated compound.

Sulphur Oxide Gettering Agent

W. R. GRACE CO.

Australian Patent 85/46,146

A gettinger agent for removing SO_x from flue gases, and giving a reduction of >90% SO_x emissions from catalytic cracking comprises metal sulphate, preferably MgSO₄ and Al₂O₃, together with a Pt and/or Pd catalyst.

Aromatisation of Gasoline Fractions

A.S. KAZA PETRO-CHEM. *Russian Patent 1,115,464*

A method for the production of high octane gasolines and aromatic hydrocarbons giving improved yields and quality of products involves contacting the starting products with H₂ over a Pt-B-Co-Cr/Al₂O₃ catalyst at 410–528°C and atmospheric pressure. The reaction products are contacted with Pt-B-W/Al₂O₃.

Trans-Retinol Production

A.S. KAZA ORG. CATALYS. *Russian Patent* 1,141,710
Trans-retinol, an intermediate for vitamin A production, is prepared by hydrogenating retinol in the presence of an Ir-Ba/Al₂O₃ catalyst. Adding Co to the catalyst increases the productivity.

FUEL CELLS

Oxygen Reduction Electrode

NATIONAL RES. DEV. CORP.
World Patent Appl. 86/1,642A

An O₂ reduction electrode for use in a fuel cell, which only produces very low amounts of H₂O₂, consists of a conductive substrate with a catalyst of Ru oxide or a macrocyclic metal derivative, when used at cathodic potentials, produces very little H₂O₂.

CORROSION PROTECTION

Coated Metal Life Estimate

NIPPON PAINT K.K. *Japanese Publ. Appl.* 61/54,437
A method to estimate the service life of anticorrosion coatings for steel marine structures, ships, bridges, plants, pipelines, etc., on site, subjects the coating to 1-100V using an opposing electrode of Pt, C, etc., to measure times before current start up.

GLASS TECHNOLOGY

Molten Glass Stirrers

TOSHIBA K.K. *Japanese Publ. Appl.* 61/36,123
Glass stirrers with excellent high temperature strength are formed with Mo as main component, coated with a heat-resistant intermediate layer, then with a Pt containing material.

ELECTRICAL AND ELECTRONIC ENGINEERING

Electroconductive Fibrous Articles

AGENCY OF IND. SCI. TECH.
European Appl. 174,183A
The production of electroconductive fibrous articles involves soaking fibrous articles in a Pd hydrosol containing a surfactant and then metal plating. The articles are used in electromagnetic shields.

Sealed Contact Relay

A.T. & T. BELL LABS. *U.S. Patent* 4,573,030
The sealed relay has a catalytic metal of at least one metal selected from Pt, Pd, Ir, Rh, Ru, Os, Ni, Co and Fe, on the rubbing surface which polymerises organic matter into a solid polymer. The contacts have long life and low contact resistance.

Ceramic Wafer for Electronics

NIPPON KOATSU DENKI
Japanese Publ. Appl. 61/46,088

A ceramic wafer made of Al oxide, B oxide, SiO₂, alkali metal oxide and RuO₂, Rh₂O₃, Fe₂O₃, NiO, etc., is produced at a comparatively low temperature. A conductive paste of Pt, Au-Pt, etc., is printed onto the wafer. The wafers produced have excellent mechanical and electrical characteristics.

MEDICAL USES

Diamine Platinum Complexes

CHUGAI SEIYAKU K.K. *European Appl.* 176,005A
New diamine Pt complexes are useful anti-tumour complexes and have low toxicity; they have greater activity than Cisplatin.

Anti-Tumour Platinum Complexes

JOHNSON MATTHEY P.L.C.
Japanese Publ. Appl. 61/15,892
An anti-tumour Pt co-ordination compound with lower toxicity is prepared by reacting ammonium trichloride with KI, and then with AgNO₃ and dicarboxylic acid.

Platinum for Tooth Polishing

Y. NAKAGAWA *Japanese Publ. Appl.* 61/27,916
TiO₂ powder incorporating Fe₂O₃ n-type semiconductor, carried on a good conductivity metal, especially Pt, is used to clean teeth and the inside of the mouth. The Fe₂O₃ has a photocatalytic effect.

Organo-Platinum Anti-Tumour Complexes

MITSUI PETROCHEM. IND. K.K.
Japanese Publ. Appl. 61/37,794/95/96
New organo-Pt anti-tumour complexes can be administered parenterally or orally as injections, suppositories, ointments, tablets, capsules or syrups against leukaemia, lung cancer and melanoma.

Surgical Implants

I. BLAETTLER *Swiss Patent Appl.* 654,738
Surgical implants and repair plates are made from steel coated with Cu then with Rh, Pd, Ag or Au.

Electrodes for Blood Purification

ELECTROCHEM. INST. *Russian Patent* 1,175,494
Two Ti electrodes promoted with Pt are used in blood treatment during dialysis for detoxifying the organism. The electrodes carry current at a density of 11.2-5.6 mA/cm². This method obviates the need for additional physico-chemical treatment.

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