

Rheology of Pastes in Thick-film Printing

R. E. TREASE and R. L. DIETZ, *Solid State Technol.*, 1972, **15**, (1), 39-43

The rheological behaviour of thick film pastes including Pd-Au and Pd-Ag compositions was measured and the results correlated with printing parameters. Two methods of relating paste viscosities to performance are described. A series of thick film pastes were tested at equilibrium and non-equilibrium conditions over a range of shear rates. The results show the danger of adjusting paste formulations using simple viscosity measurements.

TEMPERATURE MEASUREMENT

Estimation of the Effect of Uncontrolled Additions on the Electrical Resistivity of Platinum in Resistance Thermometers

YA. I. DUTCHAK, V. YA. PROKHORENKO and N. A. SKORODINSKII, *Teplofiz. Vysokikh Temp.*, 1972, **10**, (1), 198-202

The effects of various construction materials on the resistivity parameters of Pt resistance thermometers are shown in tabular form.

NEW PATENTS

METALS AND ALLOYS

Resistance Alloys

JOHNSON MATTHEY & CO. LTD.

British Patent 1,263,454

A resistance alloy contains 26-60 wt.% Ag, 0.01-2.0 wt.% B or C; or Ir, Re or Mo; or Al_2O_3 , ZrO_2 or MoS_2 , the balance being Pd.

Superconductive Alloys

SIEMENS A.G.

British Patent 1,264,298

Superconductive alloys have the general composition: $(Ce_{1-x}A_x)Ru_3$ where A is Tb, Dy or Ho, and $0.10 \leq x \leq 0.24$ for Tb, $0.12 \leq x \leq 0.27$ for Dy and $0.10 \leq x \leq 0.28$ for Ho.

Process of Preparing Noble Metal Powders

E. I. DU PONT DE NEMOURS & CO.

U.S. Patents 3,620,713 and 3,620,714

Acid chloride solutions of noble metals are prepared, the metal is precipitated as a metal ammonia complex and then is reduced to yield a relatively coarse noble metal precipitate powder. Metallisation compositions containing the noble metal powders are printed and fired to form various electrical circuit components. Au, Ag and Pt metal powders may be produced in this way. *U.S. Patent* 3,620,714 deals with metal alloy powders.

Improved Platinum Alloy

DEUTSCHE GOLD- & SILBER-SCHNEIDANSTALT

U.S. Patent 3,622,310

The high temperature strength properties of noble metals, particularly Pt, are improved by adding an element having an affinity for O_2 , preferably Zr, and heating either (1) at 800-1,200°C or (2) stepwise heating at 300-800°C followed by heating at 800-1,400°C.

CHEMICAL COMPOUNDS

Producing Palladium-Carbon Bond Compounds

UNION CARBIDE CORP.

U.S. Patent 3,632,824

Reactive compounds of Pd containing Pd-C bonds are made by reacting Pd in the zero valent state with a halogen compound containing a C bond. The compounds have utility as intermediates and as catalysts. Thus $Pd(PPh_3)_4$ reacts with MeI to give $(PPh_3)_2Pd(Me)I$.

ELECTRODEPOSITION AND SURFACE COATINGS

Light-sensitive Composition

MINNESOTA MINING & MANUFACTURING CO.

British Patent 1,263,715

A composition for use in an electroless-plating light-image-recording system includes one or more diazonium salts which will undergo photolysis when exposed to light and one or more Pd compounds which are reduced by the action of the photolysis products to Pd metal. The metal acts as a catalyst in the reduction of developer.

Electrodeposition of Ruthenium

SEL-REX CORP.

U.S. Patent 3,630,856

Thick electrodeposits of Ru can be obtained by adding Ga, In or Tl in a stable and soluble form. The deposits obtained have low stress and no surface cracks at thicknesses up to about 10 mm.

Platinum Metal Alloy Coatings

KLINGSPOR & CO. INDUSTRIE-EXPORT K.G.

German Offen. 2,014,406

Pd alloy coatings are deposited from a bath containing, per litre, 0.05-10 g $PdCl_2$, 1-60 g

$\text{Ni}_2(\text{SO}_4)_3$, 0.1–10 g $\text{Co}_2(\text{SO}_4)_3$, 0.80% Pt metal (based on the Pd content), 0.5–60 g NaH_2PO_2 and 0.01–20 mg $\text{Na}_2\text{S}_2\text{O}_3$.

JOINING

Solderable Coating on Stainless Steel

P. R. MALLORY & CO. INC. *U.S. Patent* 3,634,048
Stainless steel is made solderable by the application of: (a) a layer of Ni, Co or Cr as a barrier against diffusion and (b) a layer Ag alloy with Au, Pd, Pt, Re or Os which is easily soldered.

LABORATORY APPARATUS AND TECHNIQUE

Chromatography Flow Controller

CALIFORNIA INSTITUTE OF TECHNOLOGY
U.S. Patent 3,624,986

A flow controller for gas chromatography has a H_2 -permeable film containing Pd between the column inlet and a H_2 supply. The H_2 permeability is controlled by electrical heating to change the film temperature.

HETEROGENEOUS CATALYSIS

Oxidation Catalyst

ASAHI KASEI KOGYO K.K. *British Patent* 1,262,219
Phenyl acetates are obtained by reaction of C_6H_5 or an alkyl benzene with O_2 and acetic acid in the presence of Pd.

Hydrogenation Catalysts

INSTITUTA KHIMICHESKOI FIZIKI A.N. S.S.S.R.
British Patent 1,262,885

The catalyst is formed by the reduction of a complex compound of Os, Ir, Pt, Ru, Rh or Pd with an aromatic hydrocarbon, alkyl-substituted quinone, aromatic carboxylic acid, aromatic amino acid or peptide.

Hydrogenation Catalysts

INSTITUT FRANÇAIS DE PÉTROLE DES CARBURANTS ET LUBRIFIANTS *British Patent* 1,264,254
Olefins are hydrogenated in the presence of organic compounds of transition metals such as Ru, Rh, Pd, Ag, Os, Ir or Pt.

Oxidation Catalysts

B.P. CHEMICALS LTD. *British Patent* 1,264,394
A mixture of ethylene and propylene may be converted to alkyl acetate by reaction with O_2 in the presence of metallic Pd and an acetate salt.

Hydrofining Catalyst

MONSANTO CO. *British Patent* 1,264,609
The catalyst consists of a noble metal, preferably Pd or Pt, supported on Al_2O_3 .

Oxidation Catalyst

KNAPSACK A.G.
British Patents 1,266,623 and 1,266,624

Vinyl acetate is produced by reaction of C_2H_4 , acetic acid and O_2 in the presence of supported Pd.

Exhaust-gas Purification

SOCIÉTÉ GÉNÉRALE DES PRODUITS RÉFRACAIRES
British Patent 1,268,420

A catalyst (e.g. Pt) for the oxidation of internal-combustion-engine exhaust gases is supported on a felt composed of monocrystalline fibres consisting of Al_2O_3 or ZrO_2 with 0–15 wt.% of SiO_2 and 0–0.1 wt.% each of Fe_2O_3 , TiO_2 , MnO_2 , K_2O and Na_2O .

Hydrogenation Catalysts

ESSO RESEARCH AND ENGINEERING CO.
British Patent 1,270,055

The octane rating of C_3 hydrocarbons is upgraded by hydrogenation in the presence of a catalyst which may be, e.g. Pd or Pt.

Exhaust-gas Purification

INSTITUT GORNOGO DELA *British Patent* 1,270,782
A device for purifying internal-combustion-engine exhaust gases includes a chamber containing granules of treated Mn ore coated with a layer of Pd or Pt.

Catalytic Hydrogenation

COURTAULDS LTD. *British Patent* 1,271,041
Caprolactam is recovered from the wash liquors of polycaprolactam extrudates by hydrogenation of the liquor in the presence of Pd, Pt or Ru.

Hydrocracking Catalyst

CHEVRON RESEARCH CO. *U.S. Patent* 3,617,485
A hydrocracking catalyst consists of 0.005–2% Pt, Pd and/or Ir, 0.005–2% Re and 0–5% flouride on an amorphous aluminosilicate support.

Hydrocracking Catalysts

CHEVRON RESEARCH CO.
U.S. Patents 3,617,489, 3,617,490 and 3,617,491
A hydrocracking catalyst consists of a layered claytype crystalline aluminosilicate containing 0.01–2% Pt, Pd, Rh, Ru and/or Ir and 0.01–5% Au, Cr and/or W or Tn and/or U.

Hydroprocessing Catalyst

UNIVERSAL OIL PRODUCTS CO.
U.S. Patent 3,617,510
A hydroprocessing catalyst has a crystalline aluminosilicate support carrying Pt (or other Pt group metal), Ge and Re components.

Gasoline Reforming

UNIVERSAL OIL PRODUCTS CO.
U.S. Patent 3,617,519
Gasoline reforming is catalysed by a supported Pt-Re halogen catalyst with controlled S content.

Naphtha Reforming Catalyst

CHEVRON RESEARCH CO. *U.S. Patent 3,617,521*
A naphtha feedstock is reformed in the presence of a mixture of a layered, crystalline, clay-type aluminosilicate and a Pt group metal on a solid support. Preferably Pt itself is the catalyst.

Lean Charge Stock Reforming

UNIVERSAL OIL PRODUCTS CO.
U.S. Patent 3,617,522
A lean charge stock is reformed over a Pt-Re catalyst in the presence of added halogen.

Purifying ICE Exhaust Gases

UNION OIL CO. OF CALIFORNIA
U.S. Patent 3,619,127
Dilute combustible gases are oxidised by contacting them at elevated temperatures with a catalyst consisting of a Group VIII noble metal and a Group VIB metal, supported on a carrier such as Al_2O_3 , e.g. Pt and Cr on Al_2O_3 .

Transition Metal Paints

MOBIL OIL CORP. *U.S. Patent 3,622,367*
Substrates may be metallised with transition metals using paints containing a metal π -complex dissolved in alcohol. Pt is the preferred metal, e.g. in the form of a diene complex of $PtCl_2$.

Ammonia Oxidation

CHEMICAL CONSTRUCTION CORP.
U.S. Patent 3,627,497
Improved Pt recovery during the oxidation of NH_3 is achieved by using a cylindrical Pt gauze catalyst with a ceramic fibre cylinder filter.

Jet Fuels

CHEVRON RESEARCH CO. *U.S. Patent 3,630,885*
Low freeze point jet fuel is obtained by hydrocracking and isomerisation over a catalyst containing Al_2O_3 , halogen and Pt, Pd or Ir.

Hydrocarbon Isomerisation Process

UNIVERSAL OIL PRODUCTS CO.
U.S. Patent 3,630,961
A catalytic composite for hydrocarbon isomerisation consists of a refractory inorganic oxide combined with a Friedel-Crafts metal halide having uniformly dispersed on it a Pt group component and a lead component. It contains, on an elemental and Friedel-Crafts metal halide-free basis, about 0.01–2 wt. % Pt group component and Pb in an atomic ratio of Pb to Pt group component of 0.05:1–0.9:1; e.g. Pt-Pb- $AlCl_3$ on Al_2O_3 .

Dehydrogenation Catalyst

CHEVRON RESEARCH CO. *U.S. Patent 3,631,315*
Composites of a Group VIII noble metal, Sn and an inorganic, solid, refractory oxide carrier have excellent dehydrogenation activities and little or no isomerisation and cracking activities.

Hydrocracking Catalyst

CHEVRON RESEARCH CO.
U.S. Patents 3,623,500, 3,632,501 and 3,632,502
A hydrocracking catalyst contains 0.01–2% Pt, Pd, Rh, Ru, Ir and/or their compounds and 0.01–5% Fe and/or its compounds on a layered clay-type crystalline aluminosilicate cracking component.

Hydrocarbon Reforming Catalyst

UNIVERSAL OIL PRODUCTS CO.
U.S. Patent 3,632,503
A catalyst for hydrocarbon reforming contains 0.01–2% Pt group metal, especially Pt, 0.01–5% Sn and 0.01–5% Ge on Al_2O_3 or another oxide.

Dehydrogenating Normal Paraffins

MONSANTO CO. *U.S. Patent 3,632,661*
Dehydrogenation catalysts contain Fe or its oxides or alloys and one or more Pt group metals deposited upon low acidity Al_2O_3 .

Dehydrogenation Process

MONSANTO CO. *U.S. Patent 3,632,662*
In catalytic dehydrogenation of paraffins, catalyst activity is maintained relatively constant within a desired range by using a H_2S -poisoned catalyst of Pt or Pd and a Group IB metal. The poison is gradually removed from the catalyst during the dehydrogenation reaction; e.g. Cu and Pt.

Propylene Oxidation in the Presence of Rhodium Metal

GULF RESEARCH & DEVELOPMENT CO.
U.S. Patent 3,632,833
 C_3H_6 is oxidised to acrolein, acetone, etc., by contact with O_2 in the presence of Rh metal.

Hydrocarbon Isomerisation Process

UNIVERSAL OIL PRODUCTS CO.
U.S. Patent 3,632,835
Isomerisable hydrocarbons, including paraffins, cyclo-paraffins, olefins and alkyl aromatics, are isomerised by contacting the hydrocarbon with a catalytic composite containing a Pt group component and a Re component combined with a carrier material containing Al_2O_3 and a finely divided crystalline aluminosilicate.

Nickel-Noble Metal Catalysts

KLINGSPOR & CO. *German Offen. 2,026,008*
Catalysts for the oxidation of CO and aliphatic compounds consist of alloy particles precipitated from solution by phosphite or borohydride reducing agents. The alloy contains 20–40% Ni, 10–22% Co and 10–35% Pd.

Waste Gas Purification

KALI-CHEMIE A.G. *German Offen. 2,043,031*
Waste gases, e.g. from ICE exhausts, are purified over a catalyst containing Pt or Pd on boehmite.

HOMOGENEOUS CATALYSIS

Oxidation Catalyst

ETHYL CORP. *British Patent* 1,263,366
Olefins are converted to carboxylic acids by reaction with CO and water in the presence of a mixture of a Pt salt with a Sn or Ge salt.

Catalysts

NATIONAL RESEARCH DEVELOPMENT CORP.
British Patent 1,265,564

Catalysts for polymerisation of olefins, hydrogenation, dehydrogenation, hydroformylation and hydrosilylation reactions are mixed-ligand complexes of transition metals, e.g. trimethylsilylmethyltris(triphenylphosphine)rhodium or bis(triethylphosphine)bis(trimethylsilylmethyl)platinum.

Palladium Chelates Having a Palladium-Carbon Bond

UNION OIL CO. OF CALIFORNIA
U.S. Patent 3,622,607

A Pd chelate contains Pd and a halide, alkanote or hydroxyl group in a 4- or 5-membered ring with an aromatic biphyllic ligand. The chelate is an active catalyst in hydrocarboxylation reactions.

Acrylate Production

UNION OIL CO. *U.S. Patent* 3,625,995

Acrylates are produced by the reaction of an olefin, O₂ and CO in the presence of an alcohol, Pt group metal and a heterocyclic compound. PdCl₂ and pyridine oxide are used in one example.

Olefinic Acids and Esters

UNION OIL CO. *U.S. Patent* 3,625,996

Olefinic acids or esters are produced from acids and olefins in the presence of a phosphine, arsine or stibine complex of a Pt group metal, e.g. PdCl₂ with PPh₃.

Vinyl Ester Production

KNAPSACK A.G. *U.S. Patent* 3,627,821

A new catalyst for the production of vinyl esters from the reaction of an olefin, oxygen and a carboxylic acid consists of Pd, U and alkali metal acetates.

Hydrocarbon Isomerisation Catalyst

UNIVERSAL OIL PRODUCTS CO.
U.S. Patent 3,632,525

A catalytic composite for isomerisation consists of a Pt group metal component, a Sn component and a Friedel Crafts metal halide component combined with a refractory inorganic oxide.

Acrylate Production

ATLANTIC RICHFIELD CO. *U.S. Patent* 3,634,501
Na acrylate and methacrylate are produced by the oxidation of allyl Pd complexes of C₃H₆ and C₄H₈ respectively.

Hydroformylation Catalyst

JOHNSON MATTHEY & CO. LTD.
French Patent 2,069,322

The hydroformylation or carbonylation of organic compounds in the gas phase is catalysed by a Rh carbonyl hydride complex of a tertiary phosphine, arsine or stibine, e.g. RhH(CO)(PPh₃)₃, which is deposited upon a solid support.

Rhodium Hydroformylation Catalyst

JOHNSON MATTHEY & CO. LTD.
French Appl. 2,072,146

The hydroformylation or hydrogenation of gaseous olefins is improved by the use of a complex of Rh hydride carbonyl with a P-containing stabilising ligand, e.g. RhH(CO)(PPh₃)₃.

Rhodium Compounds

JOHNSON MATTHEY & CO. LTD.
German Offen. 2,136,470
Dutch Appl. 71.10,076
Belgian Patent 770,310

New compounds are complexes of monovalent Rh with a stabilising donor ligand. They are used to catalyse hydrogenation, oxidation, decarbonylation and other reactions. The preferred compounds have the general formula RhAn(CO)_xL_y where An is an anion other than halogen or pseudohalogen, L is a stabilising donor ligand such as a tertiary phosphine, x is 0 or 1 and y is 2 or 3. A typical complex is Rh(PPh₃)₃NO₃.

FUEL CELLS AND BATTERIES

Fuel Cell Electrode

VARTA A.G. *German Offen.* 1,771,242

An electrode for a fuel cell consists of a porous C or metal base coated with a layer of 70-99% Pt and/or Pd and 10-1% Pb.

CHEMICAL TECHNOLOGY

Spinnerets

C.T.A.-CIE. INDUSTRIELLE DE TEXTILES INDUSTRIELS ET SYNTHÉTIQUES *British Patent* 1,264,346

Spinnerets of large dimensions may be produced from sheets 0.026 mm thick made from 93 wt.% Pt, 4 wt.% Au and 3 wt.% Rh, or 29.5 wt.% Pt, 70 wt.% Au and 0.5 wt.% Rh.

Sprayed-metal Articles

JOHNSON MATTHEY & CO. LTD.
British Patent 1,270,926

Articles such as sheets, rods, wires, spinnerets which are made of precious metal, e.g. an alloy containing 49 wt.% Pt, 50 wt.% Au and 1 wt.% Rh, are fabricated from metal made by flame-spraying the metal in droplet form on to a cooled stationary target whereby the droplets solidify into a coherent deposit. The deposit is removed from the target and worked.

GLASS TECHNOLOGY

Manufacture of Glass Fibres

P.P.G. INDUSTRIES INC. *British Patent* 1,266,212
Electrically heated Pt or Pd bushings are supported on a bushing frame made of ferritic nodular cast iron.

Glass Fibres

NIPPON SELJOC CO. LTD.
British Patents 1,266,521 and 1,266,524
Concentric Pt melting pots are used in the production of glass-fibre bundles of non-homogeneous composition for light conducting applications.

Platinum Alloy Spinneret

OWENS-CORNING FIBERGLAS CORP.
U.S. Patent 3,622,289
A glass feeder is made from an alloy containing 14-79% Pt, 20-85% Rh and 0.01-10% Mo. The Mo is present in an amount sufficient to increase the ductility of the alloy.

Glass Melting Pot

JOHNS-MANVILLE CORP. *U.S. Patent* 3,623,857
Glass is melted in a Ni-Cr-Fe alloy pot and then drawn through holes in the bottom lined with Pt.

Platinum Clad Niobium, Tantalum etc.

JOHNSON MATTHEY & CO. LTD.
French Appl. 2,084,651
An article for use at high temperatures, e.g. in the glass industry, consists of a refractory core made from Nb, Ta, Cr, Zr, V, Hf, Re or alloys thereof, a barrier layer of MgO and a sheath of Pt metals or alloys thereof.

Glass Fibre Production

JOHNSON MATTHEY & CO. LTD.
German Offen. 2,053,059
A method of manufacture of glass fibre using Pt-Rh-Au alloys which are suitable for use in contact with molten glass is described. These contain 9-25% Rh, 1-4% Au and balance Pt.

ELECTRICAL AND ELECTRONIC ENGINEERING

Semiconductor Device

GENERAL ELECTRIC CO. *British Patent* 1,267,828
A semiconductor device has ohmic contact regions consisting of an active metal such as Pd and a contact metal such as Au, Ag or Pt.

Stable Semiconductor

COGAR CORP. *U.S. Patent* 3,627,647
Stable semiconductor devices are formed by coating their SiO₂ surfaces with a noble metal-Si-O layer. The noble metal is preferably Pt but Au, Ag, Rh, Pd and Ir may be used.

Etched Platinum Thin Films

MOTOROLA INC. *U.S. Patent* 3,629,022
Pt masks are produced by first applying an Al film to the Pt thin film. The Al film is then etched away to leave the reverse image of that required in the Pt film. The Al pattern is then diffused into the Pt to give a more readily etched Pt-Al alloy. The alloy is then etched away.

Platinum Oxide Electrical Resistor

E. I. DU PONT DE NEMOURS & CO.
U.S. Patent 3,629,156
Electrical resistors are made by applying to a ceramic base and firing a rhombohedral PtCo oxide of formula Pt_xCo_yO₂, where x and y are about 0.85 and 0.15.

Brine Electrolysis Electrode

ELECTRONOR CORP. *U.S. Patent* 3,630,768
A coating of a Pt group metal on a valve metal base (e.g. Ti) is formed by coating the base with a complex of the Pt metal with an amine, NH₃, etc., and then heating the coating.

Electrochemical Electrode

CHEMNOR A.G. *U.S. Patent* 3,632,498
An electrode has an electrically conductive base selected from Al, Ta, Ti, Zr, Bi, W, Nb and their alloys. Part of the surface of the base has a coating of a mixed crystal material consisting essentially of an oxide of a film-forming metal and an oxide of a Pt group metal. Typically an aqueous alcoholic solution of Ti(OBu)₄ and RuCl₃ is painted on a Ti base and fired.

Ruthenium Oxide Resistors

JOHNSON MATTHEY & CO. LTD.
U.S. Patent 3,637,530
An electrical resistor contains RuO₂ and NbO₅ in a glass matrix. The atomic ratio of metal to O₂ is 1:2 and of Nb or Ru is between 1:2,000 and 1:1.

Gas Diffusion Electrode

ROBERT BOSCH G.M.B.H. *German Offen.* 1,771,179
A porous catalyst layer is formed on a gas diffusion electrode by applying catalyst particles (e.g. PtO₂/Au) in a liquid organic paint medium.

Contact Alloy

W. C. HERAEUS G.M.B.H. *German Offen.* 2,039,100
An alloy for electrical contacts contains 30-55% Pd, 35-50% Co and 15-40% W and/or Mo.

TEMPERATURE MEASUREMENT

Liquid Level Indicator

K. J. WOOD *British Patent* 1,266,887
A liquid level indicator e.g. an oil-level indicator for internal combustion engines, includes a Pt temperature-sensitive resistance element.