

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Self Diffusion in Polycrystalline Platinum

G. V. KIDSON and R. ROSS, Atomic Energy of Canada Ltd., Report AECL 449, CRMet-702

Self-diffusion coefficients of pure Pt have been determined between 1325°C and 1600°C using the radioactive isotope Pt^{195m}. The active isotope was evaporated onto one face of an inactive Pt disc and after annealing at a known temperature the disc was sectioned and the activity of each section determined. The diffusion coefficient D is given by $D = 0.33 \exp(-2.96/kT)$, where T = annealing temperature. The value obtained for the activation energy for self-diffusion, $Q_{sd} = -2.96$ ev, does not agree with a previous value obtained from quenching measurements. It is found that there is a simple correlation between absolute melting point (T_m °K) of a metal and its activation energy. When Q_{sd} is plotted against T_m °K, values for 17 metals, including Pt, lie approximately on the same straight line.

Simultaneous Evaporation of Platinum and Carbon for Possible Use in High-Resolution Shadow-Casting for the Electron Microscope

D. E. BRADLEY, *Nature*, 1958, **181**, (Mar. 29), 875-877

It was found that simultaneous evaporation of Pt and C from electrodes containing about 85 wt.% Pt gives a substantially non-crystalline film suitable for deposition on specimens for electron microscopy. This very thin film forms a self-supporting replica. The examination of Pt/C shadowed surfaces indicates that the method is extremely promising for high-resolution shadow-casting. With crystals of methyl orange and sugar, very sharp shadows leading to good resolution were obtained. Films in use previously limited the resolution because of their large crystallites.

The Vapour Pressure of Palladium

J. F. HAEFLING and A. H. DAANE, *Trans. Met. Soc. Amer. Inst. Min. Met. Eng.*, 1958, (Feb.), 115-116

The vapour pressure of Pd was measured using the Knudsen effusion technique. A graphite vessel was used having the part in contact with solid Pd lined with W foil. The measurements were obtained under a vacuum of 10^{-5} mm or less in the temperature range 1388-1675°K. The vapour pressure was found to be higher than the estimated values in the literature by a factor of 15. The heat of vaporisation of Pd is about -80 k.cal./mole—considerably lower than the values

of -148 and -127 k.cal./mole for Ru and Rh respectively. This is consistent with values of other physical properties of Pd and indicates the abnormally weak binding in this metal due to the presence of a more complete d -electron shell than those in the other Pt metals.

Studies of the System Silver-Platinum

O. A. NOVIKOVA and A. A. RUDNITSKII, *Zhur. Neorg. Khim.*, 1957, **2**, (8), 1840-1847

The Ag-Pt system was studied by means of hardness, electrical resistance, temperature coefficient of resistance and thermal e.m.f. measurements on heat-treated alloys and on alloys annealed at 600 and 900°C. X-ray and micrographic investigations were also made. From the results an equilibrium diagram was constructed. This shows a peritectic reaction at about 1160°C, at which temperature the solid solubility of Ag in Pt is about 10 wt.% and that of Pt in Ag is 57.6 wt.%. At room temperature the solubilities are extremely limited, that of Ag in Pt being <2 wt.% and of Pt in Ag <5 wt.%. No evidence was found of the compounds which had been reported by earlier investigators. The solid solutions based on Ag which were thoroughly investigated were distinguished by their stability, the low velocity of diffusion processes and high dispersion of precipitation products.

Magnetic Susceptibility of the Alloy Pt₃Fe between 20 and 900°K

J. CRANGLE, *Nature*, 1958, **181**, (Mar. 1), 644-645

The magnetic susceptibility of the annealed 25 at.% Fe alloy containing the Pt₃Fe superlattice was measured. At high temperatures the Curie-Weiss law is obeyed, at about 200°K deviations from the law begin, the susceptibility rising to a maximum at 105°K. This behaviour suggests the presence of antiferromagnetism in the ordered alloy at low temperatures. Annealed alloys with compositions on either side of 25 at.% Fe are ferromagnetic. In the 25% alloy cold work renders the alloy ferromagnetic by destroying the superlattice.

Transformation Characteristics of Dilute Ternary Alloys of Uranium

D. J. MURPHY, *Trans. Amer. Soc. Metals*, Preprint No. 74, 12 pp. (1958)

Ternary additions of 1 wt.% or less of Nb, Pt and Mo were made to a 0.5% Ti-U alloy. The acicular structure of martensitic α -U is less per-

sistent in forming when 0.5% Pt is added, 0.5% Mo produces a similar but lesser effect and about 1% Nb is required to give an effect equal to the Pt addition. Hardness profiles are raised as the total alloy content is increased. Peak hardness and the disappearance of acicular martensitic α -U occur at about the same cooling rates.

Structure of Superconductors, X—Thermal, Microscopic and X-Ray Investigation of the Bismuth-Palladium System

N. N. ZHURAVLEV, *Soviet Physics—JETP*, 1957, **5**, (6), 1064-1072. (Transl. of *Zhur. Eksptl. Teoret. Fiz.*, 1957, **32**, 1305-1312)

The phase diagram of the Bi-Pd system up to 65 wt.% Pd was determined by thermal analysis and microstructure investigations. The compounds Bi₂Pd, BiPd and BiPd₃ are formed and a eutectic occurs at about 584° and 38 wt.% Pd. A solid solution (γ) occurs in the region 43-54% Pd and not the compound Pd₃Bi₃ as previously reported. The density, microhardness and superconducting transition temperature (T_c) are determined for the various compounds. The compounds α and β -Bi₂Pd (low and high temperature modifications) and BiPd are superconductors. Superconductivity occurs in compounds with very diverse types of crystal lattice. Increase in minimum interatomic distance leads to an increase in T_c .

Structure of Superconductors, XI—Investigation of Alloys of Bismuth with Platinum, Ruthenium, Osmium and Iridium

N. N. ZHURAVLEV and L. KERTES, *Soviet Physics—JETP*, 1957, **5**, (6), 1073-1078. (Transl. of *Zhur. Eksptl. Teoret. Fiz.*, 1957, **32**, 1313-1318)

The phase diagram of the Bi-Pt system was determined up to 75 wt.% Pt by thermal and microstructural analysis. The compounds α -Bi₂Pt, β -Bi₂Pt (transformation temperature 390°C) and BiPt are formed and eutectics occur at about 0.2% Pt and at about 730° and 57% Pt. The density and microhardness of the compounds are determined. The presence of β -Bi₂Pt accounts for superconductivity in alloys of this composition. Bi does not form compounds with Ru, Os and Ir by direct alloying.

Superconductivity in the Palladium-Selenium System

B. T. MATTHIAS and S. GELLER, *Phys. Chem. Solids*, 1958, **4**, (4), 318-319

Melts were made with a Pd:Se ratio of 1-2.5. The superconductivity of the alloys was measured and powder photographs were taken. The two phases Pd_{1.1}Se and Pd_{2.9}Se were found. Above Pd_{1.2}Se the alloys consist of mixtures of the two phases. Pd_{1.1}Se is not superconducting when occurring alone, yet alloys above Pd_{1.5}Se are completely superconducting with a transition temperature of 2.5°K. It appears that Pd_{1.1}Se

becomes superconducting at a composition other than that of the ideal formula. Further experiments showed that the phases Pd₄Se and PdSe₂ are not superconducting above 1.5°K.

ELECTROCHEMISTRY

Effect of the Degree of Oxidation of the Platinum Anode on the Kinetics of the Electrochemical Separation of Oxygen in Sulphuric Acid Solutions

E. A. EFIMOV and N. A. IZGARYSHEV, *Zhur. Fiz. Khim.*, 1956, **30**, 1606-1614. (Transl. F. LACHMAN, R.A.E., Farnborough, Library Transl. No. 685)

The electrochemical deposition of oxygen on Pt in solutions of 1-36N H₂SO₄ was investigated. The Tafel coefficient b is dependent on the duration of preliminary polarisation of the Pt anode if this is < 15 minutes. The amount of oxygen deposited increases with polarising current density and the period for which the anode is maintained at constant potential. Simultaneously the Pt-O bonds become more stable and phase oxides are formed. It appears that the formation and decomposition of Pt oxides on the electrode surface are indispensable to the electrochemical separation of oxygen. Increased duration of preliminary polarisation causes deeper oxidation of Pt, increased stability of Pt-O bonds and consequently a decrease in the electrochemical activity of oxidic compounds and an increase of overpotential during the separation of oxygen.

An Electrochemical Investigation of Hydrogen Producing Reactions Catalysed by Nickel and Nickel-Palladium Cathodes

J. P. HOARE and S. SCHULDINER, *J. Phys. Chem.*, 1958, **62**, (2), 229-233

Hydrogen overvoltage measurements of Ni, Pd and Ni-Pd alloys in acid solution were made. The hydrogen producing mechanisms are discussed. The steady-state open-circuit potentials against a Pt/H₂ electrode are positive for Pd and high Pd content alloys but zero for alloys containing 32-99 at.% Ni. By use of Ni-Pd-H ternary alloys the number of holes/atom in the d -level can be varied from zero to 0.6. The relative catalytic activity of these metals for the hydrogen producing reaction is shown to be related to this number.

The Surface State of Platinum Anodes for Electrolytic Persulphate Manufacture by X-Ray Examination

T. INOUE, *J. Electrochem. Soc. Japan*, 1957, **25**, (11), E123 (English summary)

The surface coating of used and unused anodes was studied by a Geiger counter X-ray diffractometer technique and by X-ray fluorescence analysis. The anodes studied were of smooth Pt ribbon formed by cold-rolling and are those used in the Japanese, Loewenstein and Riedel-de-

Haen, process for persulphate manufacture. After electrolysis the abnormal surface orientation of crystal planes due to cold-rolling disappears and the smoothness of the original surface is lost. Pt_3O_4 and $\text{PtO}_2 \cdot n\text{H}_2\text{O}$ were found on the surface of a badly attacked anode.

Head-End Processes for Dissolving Stainless Steel-Uranium Dioxide Dispersion Type Fuel Elements

F. S. MARTIN and M. J. WATERMAN, U.K. Atomic Energy Authority Report, AERE C/R 2454 (1958) Two methods to facilitate the dissolution of the stainless steel content of fuel elements in HNO_3 were tested. Treatment with NH_3 or CH_4 at 1000°C renders the metal more susceptible to dissolution but the rate is very slow and is only suitable for very thin plates. Complete fuel elements can be dissolved by applying an anodic potential to the element using a Pt cathode. By varying the applied potential a range of HNO_3 concentrations can be used. The bulk of the U dissolves and recoveries of 99.5% are possible.

The Electrolytic Separation Factor of Hydrogen Isotopes on Metal Electrodes

Y. TAKAHASHI, *Bull. Chem. Soc. Japan*, 1958, **31**, (2), 220-224 (In English)

The electrolytic separation factor of hydrogen isotopes (α) was measured using the following cathodes: Pt, Au, Ag, Ni, Fe, Pb, Cu, Sn and Hg. The hydrogen gas evolved during electrolysis was analysed on a mass spectrometer. Values of α vary from 2-7 depending on the cathode material—for Pt, Ag and Au α is about 4.5. For Fe, Au and Ag α remains constant over an electrolysis period of 3 hr, but for Pt, Ni and Cu it decreases during this period.

Effect of pH on the Catalytic Activity of Hydrogen-Producing Reactions on α - and β -Palladium-Hydrogen Cathodes

S. SCHULDINER and J. P. HOARE, *J. Phys. Chem.*, 1958, **62**, (4), 504-506

In solutions of pH 10.2 and 12.0 the rate controlling step on α - and β -Pd cathodes is the slow discharge of water to hydrogen atoms, whereas in strongly acid solutions it is desorption of adsorbed hydrogen atoms. At the pH at which the rate controlling step changes from desorption to slow discharge the catalytic activity of α -Pd towards hydrogen producing reactions becomes higher than that of β -Pd.

Mechanisms of Hydrogen-Producing Reactions on Palladium, V—The Deuterium-Palladium System

S. SCHULDINER and J. P. HOARE, *J. Electrochem. Soc.*, 1958, **105**, (5), 278-284

Anodic and cathodic polarisation curves for the α -Pd-D system were found to be very similar to those for α -Pd-H, indicating that the electrode

mechanisms are the same in each case. The equilibrium potential of the α -Pd-D system in deuterium saturated solution is $\pm 0.029\text{v}$. with respect to a Pt/ D_2 reference electrode. For a β -Pd-D cathode diaphragm the reaction mechanisms are the same as for β -Pd-H.

METAL WORKING

Use of Aluminium for the Deoxidation of Palladium and Palladium Alloys

R. N. RHODA and R. H. ATKINSON, *Trans. Met. Soc. Amer. Inst. Min. Met. Eng.*, 1958, (Feb.), 113-115

An improved technique is described for the deoxidation of Pd and 4.5% Ru-Pd which is especially suitable for use in making small castings with an induction-melting and casting machine. Tests were carried out on 4.5% Ru-Pd in the form of oxidised and scrap metal, melted in an alumina lined crucible, deoxidised with 0.01-0.05% Al and cast. Castings from the deoxidised scrap were of better quality than those from the oxidised metal demonstrating that, with this technique, prior oxidation may be omitted. Castings produced by melting in air were as good as those from melts in argon. The effect of crucible lining on the efficiency of the residual deoxidiser and accompanying oxide film was determined. The linings tested were ZrO_2 , Al_2O_3 and MgO cements and fused MgO; ZrO_2 was the best, Al_2O_3 being also satisfactory.

LABORATORY APPARATUS AND TECHNIQUE

A Palladium Column for Concentrating Tritium from 2-Litre Mixtures of Tritium and Hydrogen

J. CHADWICK, U.K. Atomic Energy Authority Report, AERE I/M 47, 1958, 5 pp.

Dilute mixtures of up to 16 at.% of tritium in hydrogen were separated on a Pd chromatographic separation column packed with Pd, asbestos and Dixon rings. The tritium-hydrogen mixture was contained in a pyrophoric uranium storage and outgassed storages were provided to collect the separated tritium and the mixed band of gases. The system was evacuated and the mixture passed over the column and absorbed. The absorbant was eluted by hydrogen gas passed through the column at a rate of 3 litres/hr. Tritium was eluted first and its emergence was detected by an ionisation chamber. The maximum concentration of tritium—99 at.%—was achieved with the highest tritium concentration in the original mixture.

Preparation of Zeise's Salt and Ethylene Platinum II Chloride

W. MacNEVIN, A. GIDDINGS and A. FORIS, *Chem. & Ind.*, 1958, (May 10), 557.

Zeise's salt— $\text{K}[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]$ —is prepared by

reacting an acidified solution of potassium chloroplatinite with ethylene in a closed system under pressure. Ethylene platinum II chloride is prepared from Zeise's salt by treatment with ethanol and HCl.

Precision Calorimetric Measurement

J. R. PATTISON, *Research*, 1958, **11**, (5), 192-202
The paper is confined to a consideration of "drop" methods with macro-calorimeters and direct specific heat determinations for solid and liquid phases excluding flow methods. The most accurate calorimeters are the Bunsen ice calorimeter and the adiabatic aneroid calorimeter. Temperatures are normally measured by Pt/Rh-Pt thermocouples or platinum resistance thermometers.

CATALYSIS

Catalyst as a Lyophilic Colloid

S. YAMAGUCHI, *Kolloid-Z.*, 1958, **157**, (1), 59
Since the Pt in a Pt-Al₂O₃ catalyst behaves towards the alumina carrier as a dispersed phase, the catalyst should be considered as a lyophilic colloid.

Electron Bonds in Solid Catalysts and their Connection with Catalytic Properties

G. RIENÄCKER, *Acta Chim. acad. sci. Hung.*, 1958, **14** (1/2), 173-195 (In German)

Three types of catalyst were investigated: metals and alloys, oxides with superconducting properties, and other mixed-oxide systems. In the first section particular attention was paid to alloy systems with unusual electron structures, e.g. Cu-Pd and Cu-Pt and also superstructures and Hume-Rothery phases. In all these systems a definite correlation between catalytic properties and electron-bond structure appears to exist.

Correlation of Physical Constants and Chemical Structure, VI—Graphical Statistical Methods for Studying Catalytic Processes. Characterisation of Catalysts by Parameters

H. I. WATERMAN, C. BOELHOUWER and J. CORNELISSEN, *Anal. Chim. Acta*, 1958, **18**, (5), 497-507. (See *Platinum Metals Rev.*, 1958, **2**, 33 and 67)

The activity of catalysts is determined by practical methods by correlating the most important catalytic actions—conversion of starting material (A), formation of desired product (B), and formation of by-products (C)—as functions of the process variables, temperature, pressure and nature of catalyst, by means of simple equations. Thus chemical processes can be represented graphically as "pseudo-ternary" systems in which the components are A, B and C. These graphs facilitate the rapid determination of favourable reaction conditions thus reducing the expenses of semi-industrial process development work.

Combustion of Methane and Hydrogen on Incandescent Platinum: Transfer of Energy and Mechanism of the Reaction

P. DEVORE, C. EYRAUD and M. PRETTRE, *Compt. rend.*, 1958, **246**, (Feb. 24), 1200-1203

The combustion of the mixtures, 3% CH₄ in air, 3% CH₄ in oxygen, 3% CH₄ in air plus a little nitrogen and 3% hydrogen in air, were studied using Pt ribbon as catalyst. In all cases the thermal effects of the reaction occur on or near the ribbon at relatively low temperatures. On increasing the temperature the thermal effects, of the final stage at least, occur further and further from the ribbon. This can be explained by a reaction mechanism consisting of a stage in the heterogeneous phase followed by a chain reaction in the gaseous phase.

Nitric Plant Optimises at Medium Pressure

ANON., *Chem. Eng.*, 1958, **65**, (May 5), 56-58

U.S. Steel have installed a nitric acid plant at their Geneva works at Provo, Utah, which uses the Montecatini process for ammonia oxidation. Whereas most U.S. processes operate at a pressure of 120 lb/sq in and a temperature of about 1720°F, this process uses a pressure of 40 lb/sq in and a temperature of 1500°F. A lower pressure means a higher ammonia conversion but a larger plant and therefore higher running costs, while a lower temperature reduces Pt loss from the catalyst but also lowers the ammonia conversion. It is estimated that at 40 lb/sq in and 1500°F a minimum in the overall cost is obtained. Under these conditions the loss of Pt is only 0.08 g./metric ton and shut-downs for catalyst repair need only occur every 3-4 months. Within the reactor is a heat-recovery boiler which enables the process to operate at zero power input. The NO₂ from the reactor is absorbed by a cascade process in horizontal stainless steel absorbers which also act as heat exchangers. The plant has an output of 160 tons of 100% HNO₃ per day.

Nitric Acid Production

W. FLETCHER and N. W. ROBERTS, *Brit. Chem. Eng.*, 1958, **3**, (3), 124-127

The development of nitric acid manufacture is reviewed briefly. The chemistry of the ammonia oxidation reaction is given. A modern plant with a capacity of 150 tons/day of 100% HNO₃, produced at 65% concentration, is described. Ammonia is reacted with oxygen at 120 p.s.i.g. pressure on a Rh-Pt gauze catalyst.

Nitrogen Industry of the U.S.S.R.

E. Y. MELNIKOV, *Brit. Chem. Eng.*, 1958, **3**, (4), 194-199

Describes the manufacture of synthetic ammonia, nitric acid and nitrogenous fertilisers. Nitric acid is produced by three processes all of which use a Pt catalyst; one is operated at high pressure, one

at atmospheric pressure and in one the oxidation of NH_3 is at atmospheric pressure and absorption at high pressure. Most new plants use one of the high pressure processes. Efforts are being made to improve these by achieving higher yields and lower consumption of Pt.

Morphy Richards Install an Oxycat

ANON., *Fuel Efficiency*, 1958, 6, (2), 36-37

A Houdry Oxycat air treatment and heat recovery unit has been installed at the Morphy Richards Ltd. paint stoving and bonderising plant in Kent. The effluents from the enamelling oven are passed over the Pt containing catalyst where the organic materials are oxidised and the heat produced is used to heat the enamelling and dry-off ovens. This has resulted in a reduction in fuel consumption and a saving in running cost.

Aromatics from Petroleum

H. G. McGRATH, *Petroleum*, 1958, 21, (3), 95-96

Aromatics are synthesised from petroleum by catalytic reforming processes. An outline of the reforming process over molybdena-alumina and platinum based catalysts is given. The synthesis of benzene from petroleum is also described.

Mina al Ahmadi Refinery

ANON., *Petroleum*, 1958, 21, (5), 158-160

The existing refinery is expanding from a daily capacity of 30,000 bbls. to 190,000 bbls. New distillation units and storage facilities are already complete. A U.O.P. "Hydrobon" Platformer is due on stream this year. The "Hydrobon" unit desulphurises the feed to the Platformer.

Recent Developments in Refining

W. J. NEWBY, Preprint of paper given at Institute of Petroleum Meeting, May 1958, 10 pp.

The increase in octane requirements of motor fuel is reviewed. The following processes for upgrading such fuel are described in some detail: reforming, isomerisation, cracking, alkylation, polymerisation, chemical treatments, and hydrofining. Future requirements in Europe will be for the highest possible severity in catalytic reforming and for processes which will upgrade light gasolines.

Conversion of *n*-Nonane in a Flow System in the Presence of Platinised Aluminosilicate and Hydrogen at Elevated Temperature and Pressure

K. M. MINACHEV, N. I. SHUIKIN, L. M. FEOFANOVA and Y. P. EGOROV, *Izvest. Akad. Nauk, S.S.S.R., Otdel. Khim. Nauk*, 1957, 1218-1222. (*Chem. Abs.*, 1958, 52, 4967c)

A 1% Pt-aluminosilicate catalyst was tested in a flow system for its action on C_9H_{20} at 400° and 360°C in the presence of hydrogen at 20 atm. pressure. At 400°, 100% conversion is obtained with isomerisation, hydrocracking and dehydro-

cyclisation predominating. At 400° and a hydrogen pressure of 20 atm. the conversion over an aluminosilicate catalyst is only 14% which indicates that promotion of the catalyst by Pt is useful for the reforming of gasoline.

Effect of Amines on the Catalytic Hydrogenation of Chlorobenzene

E. R. A. PEELING and D. K. SHIPLEY, *Chem. & Ind.*, 1958, (March 22), 362-363

The effect of certain alicyclic amines on the hydrogenation of chlorobenzene in aqueous ethanol using Adam's PtO_2 catalyst was studied. The hydrogenation occurs in two stages: hydrogenolysis to give benzene followed by hydrogenation to cyclohexane. All the tested amines are more toxic to the ring hydrogenation than to the hydrogenolysis, suggesting that the mode of absorption of the reactant in the two reactions is different. Cyclohexylamine and pyridine are more toxic than the tertiary amines.

The Preparation of Amines and Hydrazo Compounds using Hydrazine and Palladised Charcoal

P. M. G. BAVIN, *Canad. J. Chem.*, 1958, 36, (1), 238-241

The reduction of nitro-compounds to amines by ethanolic hydrazine and 10% Pd-C catalyst is described. The method is more rapid and gives higher yields than classical reducing agents and requires no special apparatus. The reductions probably proceed through the nitroso and hydroxylamine derivatives. The reduction of azo to hydrazo-compounds can also be carried out in this way, which is an improvement on the normal Zn-KOH reduction.

Total Synthesis of Pseudoionone and an Isomeric Ketone

W. KIMEL, N. SAX, S. KAISER, G. EICHMANN, G. CHASE and A. OFNER, *J. Org. Chem.*, 1958, 23, (2), 153-157

Full chemical details are given of the process described in *Platinum Metals Rev.*, 1957, 1, (4), 119-120. Pseudoionone is synthesised from acetone and sodium acetylide. The key step is a pyrolytic rearrangement of a disubstituted propargyl acetoacetate (dchydrolinalyl acetoacetate) to pseudoionone.

Catalytic Perhydrogenation of Rosin

J. B. MONTGOMERY, A. N. HOFFMANN, A. L. GLAZEBROOK and J. I. THIGPEN, *Indust. & Eng. Chem.*, 1958, 50, (March, Part 1), 313-316

In a commercial process using a Ni catalyst rosin is hydrogenated to improve its oxidation resistance properties, but one constituent, dehydroabietic acid, is resistant to hydrogenation by this method. Perhydrogenation (complete hydrogenation) was attempted using Os, Pt, Rh and Pd catalysts. Rh and Pd were found to

be very active. Extended tests on the hydrogenation of dehydroabiatic acid were carried out using a 5% Pd-C catalyst. Metal ions present in the rosin at the time of reaction poison the catalyst and must be removed. In order to design a continuous pilot plant the effect of the process variables, catalyst-rosin ratio, temperature and pressure, on the reaction rate were determined. An equation is given summarising these effects. The rate of hydrogenation increases with increase in catalyst concentration, temperature and pressure. Reaction conditions of high temperature (about 260°C) and high pressure (about 5000 lb/sq in) were therefore chosen. The resultant perhydrogenated rosin is colourless and very resistant to oxidation while retaining the other physical properties of rosin. It should find use where oxidation causes undesirable effects such as darkening, loss of tack or odour, as for example, in lacquers and adhesives.

Oxidation—Reduction Studies in the Realm of Indole Alkaloids

E. WENKERT and D. K. ROYCHAUDHURI, *J. Amer. Chem. Soc.*, 1958, **80**, (Apr. 5), 1613-1619

A generally applicable method was required for the elucidation of ring skeletons of the yohimbine-, ajmalicine-, and corynantheine-type natural products. Dehydrogenation of the C-ring of these indole alkaloids by Pd black and maleic acid fulfils this requirement and relative rate data can be used as a diagnostic test for these systems. Catalytic hydrogenation (PtO₂ at pH 10) or sodium borohydride reduction of the tetrahydro compounds lead mainly to *normal*- and *allo*-products. The structure of sempervirine was determined by oxidation-reduction studies. An infra-red spectrophotometric method for the determination of the steric configuration of C-3 in indole alkaloids is presented.

Platinum-Catalysed Addition of Triethylsilane to Methyl Methacrylate

J. W. CURRY and G. W. HARRISON Jr., *J. Org. Chem.*, 1958, **23**, (4), 627-628

Triethylsilane was reacted with methyl methacrylate in the presence of a Pt-C catalyst. The compound formed is α -methyl- β -(triethylsilyl)propionate. The Pt catalysed addition of methyl dichlorosilane to methyl acrylate gives methyl- α -(methyl-dichlorosilyl)propionate. It can be seen that the presence of the α -methyl group in the unsaturated compound reverses the direction of addition of the silane.

CATHODIC PROTECTION

Further Aspects of Anodic Polarisation of Titanium

J. B. COTTON, *Chem. & Ind.*, 1958 (April 28), 492-493

Ti can be protected by coating with a very thin, porous film of Pt or by welding to it a small

piece of Pt foil (see *Platinum Metals Rev.*, 1958, **2**, (2), 45-47). An anodic film is formed on the Ti which is capable of withstanding very high anodic current densities. Ti coated with a porous film of Pt withstood sea-water corrosion at anodic current densities of 100 amp./sq ft for a period of 250 hr without failure. This has practical value in providing non-corrodible anodes for impressed current cathodic protection.

ELECTRICAL ENGINEERING

Selection of Contact Materials

Z. R. SMITH, *Machine Design*, 1958, **30**, (March 6), 129-133

Contact materials are divided into four groups: Ag and Ag base alloys; noble metals (Au, Pt and Pd) and their alloys; W and Mo; sintered metal powders. The conditions under which each type of contact material is used are given. Causes of contact failure are enumerated.

Line Selector Using High-Speed Noble-Metal Relays

R. GROTE, *Siemens-Z.*, 1958, **32**, (4), 239-240

In the new line selector, high-speed noble metal relays with Pd contacts, of the type used in modern Siemens PABXs, are arrayed at either end of each main trunk. Resulting advantages are high transmission performance, service reliability and flexibility with respect to the number of main trunks and subscribers.

Metal Oxide Film Potentiometers

G. V. PLANER, Paper given at the International Symposium on Component Design, Malvern, Sep. 1957. (Extended summary in *J. Brit. Inst. Radio Eng.*, 1958, **18**, (3), 177)

As well as oxide film potentiometers which formed the main part of this paper, reference was also made to metal film potentiometers where a deposit of Pt-Au alloy is fired on to a glass substrate. For high total resistance meandering patterns are applied by a photo-abrasion technique giving tracks with resistance up to 500,000 ohms on a 2 in. diameter.

ELECTRONICS AND TELECOMMUNICATIONS

Effect of Electrode Metal on the Insulation Ageing of Ceramic Dielectrics

I. E. BALYGIN and K. S. POROVSKII, *Soviet Physics, Techn. Physics*, 1958, **2**, (3), 459-460 (Transl. of *Zhur. Tekhn. Fiz.*, 1957, **27**, (3))

The effect of Ag, Pt and Al electrodes on the insulation ageing (breakdown in electrical properties) of two ceramic materials, one basically Al₂O₃ + SiO₂ and the other basically SiO₂ + MgO, is studied. In both ceramics a Ag anode with cathodes of Ag, Pt or Al caused breakdown after times of from 3-380 hr. With anodes of Pt and

Al, however, no breakdown occurred over a period of 707 hr. This establishes that a considerable part of the insulation ageing occurs because of the penetration of Ag from the anode into the ceramic. For reliable operation for long periods at increased or high temperatures the anode, at least, should be made of burnt-in Pt.

Rhodium Plating Techniques

R. R. BENHAM and I. J. WARWICK, *Brit. Commun. & Electronics*, 1958, 5, (4), 266-269

The uses of Rh plating in the electronics industry are described. The high wear and corrosion resistance and constant resistivity of Rh deposits make them particularly suitable as a contact material. An outline of the plating procedure is given.

TEMPERATURE MEASUREMENT

The Accurate Measurement of Temperature

J. A. HALL, *Research*, 1958, 11, (4), 147-151

The International Temperature Scale and some of the most accurate temperature measuring instruments are described. The platinum resistance thermometer can be used in the temperature

range -182.97°C to 1062°C ; up to 630.5°C it has a reproducibility better than 0.01°C . Mercury thermometers have the advantage of simplicity in use but are not very accurate unless special precautions are taken. Pt/Rh-Pt thermocouples can be used in the range $400-1700^{\circ}\text{C}$, with an accuracy from $\pm 1^{\circ}\text{C}$ at 1063°C to $\pm 5^{\circ}\text{C}$ at 1600°C . Other thermocouples are also described. Above the range of rare-metal thermocouples a disappearing filament pyrometer is used, but this is only accurate when the emissivity of the surface is known. With a black-body source accuracies of $\pm 10^{\circ}\text{C}$ at 1600°C can be obtained.

Immersion Thermocouple Sheaths

O. M. MARGULIS, K. G. ROMANCHENKO and I. A. GETMAN, *Stal'*, 1957, (8), 714-715

Research was carried out on the development of sheaths capable of repeated use in liquid steel temperature measurement. In general ceramic sheaths were found to crack at the liquid metal-air interface. This cracking can be prevented if the sheaths are covered with a protective coating of a composition based on magnesite or on ZrO_2 stabilised with CaO. Sheaths prepared in this way can be used for several brief immersions or for a prolonged immersion of up to 4 hrs.

NEW PATENTS

Supported Platinum Catalysts

W. R. GRACE & CO. *British Patent* 790,431

A catalyst is prepared by commingling alumina shapes with an aqueous chlorplatinic acid-hydrogen halide solution 0.1-1.0 normal with respect to the hydrogen halide, drying at $200-400^{\circ}\text{F}$ and then converting the adsorbed platinum to the metallic state. The hydrogen halide may be hydrofluoric acid or hydrochloric acid. Suitable for reforming of gasoline.

Catalytic Reforming

SOCONY MOBIL OIL CO. INC. *British Patent* 790,476

A reforming catalyst having a surface area of from 650-100 g/sq metre comprises platinum and/or palladium in amount from 0.05-2% by weight deposited on silica which contains alumina in amount from 0.25-7% (based on weight of catalyst), the amount being correlated with the surface area to define a point falling within an area given on an accompanying graph.

Manufacture of a Cyclic Ketone

F. HOFFMANN-LA ROCHE & CO. A.G. *British Patent* 790,607

A platinum hydrogenation catalyst is used in a process involving the oxidation of 2,6,6-trimethyl-cyclo-hexen-(1)-one-(4) with an organic peracid,

hydrolysing the product, followed by isomerisation to form 2,6,6-trimethyl-hexan-dione-(1,4), which is then reduced with hydrogen in the presence of the catalyst to give 2,6,6-trimethyl-cyclo-hexanone-(1)-ol-(4).

New Carotenoid Compounds

F. HOFFMANN-LA ROCHE & CO. A.G. *British Patent* 790,614

A palladium/calcium carbonate catalyst is used as a hydrogenation catalyst in a process for the manufacture of 4,4¹-disubstituted-15,15¹-dehydro-beta-carotenes.

New Carotenoid Compounds

F. HOFFMANN-LA ROCHE & CO. A.G. *British Patent* 790,615

A palladium/calcium carbonate hydrogenation catalyst is used in a process for the manufacture of 4,4¹-diketo-15,15¹ dehydro-beta-carotene and 15,15¹ monocis, 4,4¹-diketo beta-carotene.

Di (2,2,2-Trifluorethyl) Acetal of Acetaldehyde

AIR REDUCTION CO. INC. *British Patent* 790,824

Di (2,2,2-trifluorethyl) acetaldehyde acetal is heated in the presence of a dehydration catalyst to produce 2,2,2-trifluorethyl vinyl ether. The