

# ABSTRACTS

## of current literature on the platinum metals and their alloys

### PROPERTIES

#### The Noble Metals in Research and Industry

H. WOLF, *Metall*, 1958, 12, (7), 585-598

Literature of the past 5-6 years on research into the mechanical and physical properties of Ag, Au and the Pt group metals, phase-diagrams and structure of their alloys, their chemical and electrochemical behaviour, including corrosion and corrosion protection properties, and their industrial applications is reviewed. (276 references)

#### Nondiffusibility of Oxygen through Platinum

F. J. NORTON, *J. Appl. Physics*, 1958, 29, (7), 1122

A capsule of Pt with 0.013 cm wall thickness was filled with oxygen at 1 atm and 25°C. No oxygen emission from the capsule was detected by a mass spectrometer on heating the capsule to 1425°C. It is calculated that at 1425° the permeation rate of oxygen through Pt is less than  $2 \times 10^{-11}$  cu. cm gas/sec/sq. cm area/mm thickness/1 atm pressure difference.

#### Low Temperature Resistivity of the Transition Elements: Ruthenium and Osmium

G. K. WHITE and S. B. WOODS, *Canad. J. Physics*, 1958, 36, (7), 875-883

Measurements of thermal conductivity from 2-150°K and electrical resistivity from 1-300°K were made for Os and Ru. The powdered metals were pressed into pellets and arc-melted in an inert atmosphere to form solid rods. The electrical resistivities of Os and Ru at room temperature (295°K) are  $9.23 \times 10^{-6}$  ohm cm and  $7.39 \times 10^{-6}$  ohm cm respectively. Extrapolation to 295°K gives values of thermal conductivity of  $0.9 \pm 0.1$  w/cm/deg. and  $1.1 \pm 0.1$  w/cm/deg. for Os and Ru respectively.

#### Thermometric Properties of some Metals and Alloys of the Platinum Group

G. B. LAPP and V. L. MAKSIMOVA, *Zhur. Neorg. Khim.*, 1957, 2, 2589-2597. (*Chem. Abs.*, 1958, 52, 8007c)

The stability of the thermal e.m.f., E, of Ir wire and Rh and Rh-Pt electrodes was studied. For Ir the maximum change in E was observed after heating *in vacuo* for 1 hr: -16 mV at 1800° and -26 mV at 2000°C. Rh and Rh-Pt alloys containing <10% Rh when heated with an electric current *in vacuo* exhibited "extinction"—a drop of 150-200° with a rising current. Rh and 30% Rh-Pt alloys were more stable than 6 and 40% alloys when heated at 1700-1800° in argon. Powdered Al<sub>2</sub>O<sub>3</sub>, MgO, and ThO<sub>2</sub> and protective

BeO tubes did not affect E of 6, 13 and 30% Rh-Pt alloys at 1500°.

#### The Grain Size and Age-Hardening of Gold-Platinum Alloys

H. SCHMID, *Metall*, 1958, 12, (7), 612-619

The effect of Rh on the grain size and age-hardening of Au-Pt alloys for use as spinnerets in the rayon industry was investigated. The following alloys were considered: 25%Pt-Au, 30%Pt-Au, 50%Pt-Au, 0.5%Rh-25%Pt-Au, 0.5%Rh-30%Pt-Au and 1%Rh-49%Pt-Au. Alloys with 25-50%Pt, after severe cold deformation and annealing at 1000°C for 14 hr, still exhibit grain segregation, the Pt-rich phase occurring with a dendritic structure. The grain size of the alloy depends on the distance between these dendrites. Rh additions are not necessary to a fine grained structure, which is dependent only on the correct choice of cooling conditions leading to a heterogeneous structure when cast. Hardness isotherms—age-hardening *v.* tempering time—were plotted for all alloys in both heterogeneous and homogeneous states. The hardness increases to a maximum with tempering time and then falls. In the heterogeneous alloys, which are those used in spinneret manufacture, Rh-free alloys reach a higher maximum hardness than Rh-containing alloys, with the exception of the 25%Pt alloy. In the homogeneous state the 0.5%Rh-25%Pt alloy is considerably harder than the binary alloy and the 0.5%Rh-30%Pt alloy has about equal hardness. The 1%Rh-40%Pt alloy cannot be obtained in a homogeneous form. Tensile strength behaves in an analogous way to hardness.

#### Contribution on the Short-Time Creep Strength of Platinum Alloys Between Room Temperature and 1250°C

G. REINACHER, *Metall*, 1958, 12, (7), 622-628

Short-time creep tests of up to 20 hr duration were carried out on 2 mm wire of pure Pt, 5%Ir-Pt, 5%Rh-Pt and 4%Pd-Pt at room temperature, 300, 500, 700, 900 and 1250°C. The elongation and necking occurring on breaking and the type of fracture involved were also investigated. The creep isotherms obtained are characterised by a decrease in strength for increasing time-to-fracture; for times greater than about 0.2 hr this decrease is exponential. At room temperature the 5%Ir-Pt alloy is the strongest. The relative strengths of the alloys vary at higher temperatures, but up to 900°C they are all stronger than Pt. At 1250° this difference disappears. The 5%Ir- and 5%Rh-Pt alloys show

an unexpected behaviour on fracturing in the temperature range 700-900°C where they break with low-ductility grain-boundary fractures showing scarcely any necking and a very low extension. Up to 500° and at 1250°C these alloys break with ductile necking fractures. Pure Pt and 4%Pd-Pt break in this way at all temperatures, the necking never falling below 90%. These results indicate that 5%Ir- and 5%Rh-Pt alloys exhibit heat embrittlement in the region 700-900°C; this may be due to oxide formation.

### On the Corrosion Resistance of Titanium Alloys, I—The Relation Between the Corrosion Resistance and the Electrode Potentials of Titanium Alloys

H. NISHIMURA and T. HIRAMATSU, *Nippon Kinzoku Gakkai-Si*, 1957, 21, (7), 465-469 (In Japanese)

The corrosion of  $\alpha$ - and  $\beta$ -solid solution binary Ti alloys in 20% HCl solution was measured and its relation to electrode potential and time-potential curves determined. The corrosion resistance of ternary Cr-Al-Ti alloys to HCl, H<sub>2</sub>SO<sub>4</sub> and oxalic acid is also determined. The effect of binary additions on the corrosion resistance of Ti is very dependent on the element added. The most beneficial additions are Pt, Pd, Mo and Zr. Additions of 2% of Pd or Pt reduce the corrosion of Ti in 20% HCl at 25°C from above 0.01 to 0.001 g/sq.cm/month. The behaviour of time-potential curves of alloys with high and low corrosion resistances is significantly different. Graphs and tables are given.

### II—The Equilibrium Diagram of the Titanium-Platinum System

ibid., 469-473

The complete range of alloys was studied by metallographic and X-ray studies, melting point measurements and differential thermal analyses. A phase diagram is constructed. Three compounds were found: Ti<sub>3</sub>Pt ( $\beta$ -W type), TiPt and TiPt<sub>3</sub> (f.c.c.). Eutectics occur between  $\beta$ -Ti and Ti<sub>3</sub>Pt at 43 wt.%Pt and 1310°C, between Ti<sub>3</sub>Pt and TiPt at 68%Pt and 1320° and between TiPt and TiPt<sub>3</sub> at 85%Pt and 1780° and a peritectic reaction between TiPt<sub>3</sub> and  $\gamma$  (Pt) at about 95%Pt. A eutectoid reaction  $\beta \rightleftharpoons \alpha + \text{Ti}_3\text{Pt}$  occurs at 840° and 12%Pt. Pt is 30% soluble in  $\beta$ -Ti at the eutectic temperature, 10% soluble at 1000° and 2% soluble in  $\alpha$ -Ti at 840°. The hardness of annealed alloys reaches a maximum at about 55%Pt. Micrographs are given.

### The Constitution of Alloys of Iron with Ruthenium, Rhodium, Palladium and Silver

W. S. GIBSON and W. HUME-ROTHERY, *J. Iron Steel Inst.*, 1958, 189, (July), 243-250

The iron-rich binary alloys were investigated by thermal analysis in the temperature range 1380-1560°C; the liquidus, solidus and  $\gamma/\delta$  trans-

formation temperatures were determined. Alloys containing up to 10.76 at.%Ru, 21.34 at.%Rh and 10.73 at.%Pd were studied and phase diagrams plotted. Ru, Rh and Pd all give equilibrium diagrams of the expanded  $\gamma$ -field type. The Fe-Ru system has a peritectic reaction at 1536°C, for Fe-Rh it occurs at 1515° and for Fe-Pd at 1478°. It was not found possible to prepare Fe-Ag alloys since the solubility of the metals in each other is negligible. The relative depressions of liquidus and solidus for the  $\delta$ -phase are Ru ( $\sim 0$ ) < Rh < Pd, which are in the same order as the size factor. The  $\gamma$ -phase liquidus and solidus curves are raised by Ru, slightly raised by Rh and lowered by Pd. The  $\gamma$ -stabilising power of the solute is in the order Pd < Ru < Rh, i.e. Rh has an abnormally high stabilising effect. An explanation of these phenomena on the basis of the electron theory of metals is given.

### Some Aspects of the Palladium-Hydrogen System

M. van SWAAY, Univ. Microfilms, Publ. No. 23,883 78 pp. (*Dissertation Abs.*, 1958, 18, 97-98)

The permeability of Pd to hydrogen was investigated for temperatures between 150 and 450°C with hydrogen pressures between 1 and 0.1 atm. A measuring technique developed by Barrer was used to evaluate the solubility and diffusion coefficient of hydrogen in Pd.

### The Ternary System Nickel-Palladium-Manganese

W. KÖSTER and M. SALLAM, *Z. Metallkunde*, 1958, 49, (5), 240-248

The system was studied by metallographic methods, thermal analysis and magnetic, dilatometric and X-ray measurements. Eutectics are formed in the ternary system, the minimum melting point occurring at 960°C and 9%Pd-38%Ni-Mn. Isothermal sections through the system at 950, 820, 700, 650, 600 and 500°C and three temperature-concentration sections are given to show the solid-state reactions. A large continuous region of  $\gamma$ -solid solution surrounds the  $\beta$ -phase region and the two-phase  $\gamma + \beta$  region. Micrographs showing the structure of various alloys are given. The properties of the alloy 9%Mn-41%Ni-Pd as a function of annealing temperature are described. The behaviour of the properties of quenched and annealed alloys with about 10%Mn and 15-70%Pd is also given.

## ELECTROCHEMISTRY

### Corrosion of Ten Metals in Boiling Hydrochloric Acid when in Contact with Rhodium, Palladium, Iridium and Platinum

W. R. BUCK and H. LEIDHEISER, *Nature*, 1958, 181, (June 14), 1681-1682

The rates of corrosion of Al, Cd, Co, Fe, Pb, Mn, Ni, Sn, Ti and Zn were studied in boiling 2M HCl

with and without contact with Pt, Ir, Rh and Pd. With the exception of Ti, which is unique in that its rate of corrosion is reduced to a very low value when coupled to any of the Pt metals, the rates of corrosion of all the metals were much increased by coupling to a Pt metal. The relative effectiveness of the Pt metals in increasing corrosion varies with the metal undergoing corrosion. This indicates that the mechanism involved is probably a specific electronic interaction between the two members of a couple.

#### **Current Density and pH Dependence of the Electrochemical Formation and Decomposition of Oxide Films on Platinum, Palladium and Gold**

K. J. VETTER and D. BERNDT, *Z. Elektrochem.*, 1958, **62**, (3), 378-386

The anodic and cathodic charging curves were measured on smooth Pt, Pd and Au electrodes at 25°C and current densities from 0.5-240  $\mu$  A/sq.cm for the formation and decomposition of chemisorbed or oxide films. The pH dependence was determined for the range 0.3-11.7 at constant ionic concentration. The charging curves for all three metals show a change in direction at about 59 mV/pH units.

#### **The Electrolytic Separation of Hydrogen and Deuterium on Palladium Cathodes**

M. V. STACKELBERG and W. JAHNS, *Z. Elektrochem.*, 1958, **62**, (3), 349-355

The equilibrium distributions of light and heavy water were calculated and also obtained experimentally for the system aqueous electrolyte/ $\beta$ -Pd-H/hydrogen gas. The dependence of the separation factor on the D : H ratio in the system was calculated. The experimental determination was carried out by electrolytic charging of a Pd-electrode in 0.67N H<sub>2</sub>SO<sub>4</sub> with 22.87 mol.% D<sub>2</sub>. The gas evolved and that in solution in the metal were analysed mass-spectrometrically. The equilibrium separation factors obtained are: gas-solution: 3.67  $\pm$  0.02 experimental, 3.85 calculated; metal-solution: 5.66  $\pm$  0.02 experimental, 5.50 calculated; gas-metal: 0.68  $\pm$  0.03 experimental, 0.70 calculated. It can be shown that for the passage from solution to metal the kinetic separation factor is markedly higher than the equilibrium separation factor.

#### **Electrolytic Hydrogenation of 2-Butyne-1, 4-diol with Various Cathodes and the Relation between their Electrolytic and Polarographic Results**

J. KATO, M. SAKUMA and T. YAMADA, *J. Electrochem. Soc. Japan (Overseas Suppl. Ed.)*, 1958, **26**, (1-3), E43-45

The partial hydrogenation of 2-butyne-1, 4-diol to 2-butene-1,4-diol was studied using Ag, smooth Pt, Pt black-Pt, Pd black-Pt and other

electrodes. The catholyte was 2% aqueous KOH and the anolyte was saturated KOH solution. Although Pd and Pt black cathodes were thought only partially to hydrogenate 2-butyne-1,4-diol they both show polarographic reduction waves for both the butyne- and the butene-diols and some of the saturated diol was obtained in practical electrolysis using these cathodes.

## **ELECTRODEPOSITION**

#### **The Technical Uses of Noble Metal Plating**

H. W. DETTNER, *Metall.*, 1958, **12**, (6), 520-522

The properties of Ag, Au and Rh electrodeposits which results in their technical use, mainly in the electrical industry, are discussed. The method of obtaining these electrodeposits, the thicknesses used and the speed of deposition are given.

#### **Mechanical Stresses in Electrolytic Palladium Deposits**

V. V. OSTROUMOV, *Zhur. Fiz. Khim.*, 1957, **31**, (8), 1812-1819

Internal mechanical stresses in Pd deposits were studied by observing the bending of the free end of a flexible cathode. The stresses were found to depend upon the conditions of electrolysis and the composition of the phosphate electrolyte. Pd depositing on the cathode together with hydrogen forms an unstable solid phase that decomposes during, and especially after, electrolysis. The appearance of stresses in Pd deposits is associated with the formation of embedded phases of the metal and hydrogen. The internal mechanical stress can attain a magnitude of 7000 kg/sq. cm, which often leads to the formation of cracks in the deposit.

#### **Electrolytic Deposition of Palladium in Potassium Hydroxide Solutions**

V. V. OSTROUMOV, *Zhur. Priklad. Khim.*, 1958, **31**, 77-83 (*Chem. Abs.*, 1958, **52**, 8791b)

The deposition of Pd from solutions containing 20-200 g KOH and 0.3-3g Pd (as PdCl<sub>2</sub>) was studied with current densities of 3-7mA/sq.cm. The current efficiency with a brass electrode in an electrolyte containing 60g KOH and 0.5g Pd/l increased from 6-20% in a static solution as the c.d. decreased to 1mA/sq. cm and in a stirred solution reached a maximum of 82% at a c.d. of 4mA/sq.cm. In non-stirred solutions highly reflecting deposits were obtained with c.d.s. of 1-10mA/sq.cm. In stirred solutions cloudy, spongy deposits were obtained at c.d.s. of 0.4-2.0mA/sq.cm, dark, spongy deposits at 2-3mA/sq.cm and highly reflecting surfaces at 3-10mA/sq.cm.

#### **Testing Rhodium Baths in the Hull Cell**

S. DORNER and L. FROELS, *Metallwarenind.*, 1958, **49**, (7), 299-305

The influence of additives to a normal Rh plating

bath on the appearance of the Rh deposit is determined. The bath has a Pt anode and Cu cathode and contains 2.5g Rh/l. With no additive a very smooth, bright deposit was obtained using 0.2A and 2.5V. Additions of Fe, 0.135-0.890 g/l, Ni, 0.045-1.670 g/l,  $K_4Fe(CN)_6$ , 0.100-0.600 g/l,  $(NH_4)_2S_2O_8$ , 0.500-5.00 g/l,  $HNO_3$ , 1-8 cc/l and HCl, 2-12 cc/l, have no effect on the appearance of the deposit. Additions of Cu, 0.085-1.535 g/l, produce striated deposits and deposition of Cu occurs especially at low current densities; a similar effect is observed with additions of 0.005-0.020 g/l Au. Striated deposits were obtained with additions of 0.009-0.450 g/l Ag with dull deposits at very high and low current densities. Sn, 0.430-0.160 g/l and Zn, 0.030-0.915 g/l, give striated deposits and Sn gives dull deposits at high current densities.

## LABORATORY APPARATUS AND TECHNIQUE

### A New Instrumental Method for Measuring the Concentration of Dissolved Hydrogen in Water

J. M. WRIGHT and D. J. STITELER, U.S. Atomic Energy Comm. Report WAPD-BT-7, Bettis Tech Rev., March 1958, Reactor Chemistry and Plant Materials, 98-109

The instrument is based on the fact that the resistance of Pd changes in proportion to the concentration of hydrogen gas dissolved in the water. Pd and Pt wires are wound separately on a cruciform-shaped, alumina-coated Zircaloy-2 mandrel. The Pt wire compensates for resistance changes in the Pd due to temperature changes. Out-of-pile tests were carried out on the instrument at temperatures up to 550°F for a period of 1450 hr—no maintenance was required during this period. Its response rate is satisfactory (about 1 hr) at temperatures as low as 400°F, and it operates successfully in neutral, deionised water and aqueous LiOH solutions of pH 9.5-10.5.

### A Metal through Glass Seal

E. J. DAVIS, *J. Sci. Instruments*, 1958, **35**, (8), 308  
A seal was made by sealing a length of very thin Pt tape (0.0003-0.0006 in. thick) sheathed by a short length of glass through a small hole in the appropriate place in the wall of the Pyrex vacuum tube.

## CATALYSIS

### Platinum Metals as Catalysts: A Survey

J. SAGOSCHEN, *Metal*, 1958, **12**, (7), 604-611  
A short outline of the theory of catalysis is given. The manufacture and regeneration of various types of Pt metal containing catalysts are described. The use of these catalysts in  $HNO_3$  and HCN manufacture, gas purification, effluent oxidation and a wide range of organic reactions is

outlined. A review of the use of Pt-containing catalysts in petroleum reforming is given. (139 references)

### N. I. Kobosev's Theory of Active Atomic Groupings

V. P. LEBEDEV, *Chem. Techn.*, 1958, **10**, (5), 267-278  
The basis of this theory of catalysis is that the catalytically active phase consists of atoms or groups of atoms of the catalyst not a part of its crystal lattice. The crystalline phase and carrier merely form an inert supporting surface for the active atomic groupings. This theory is demonstrated mathematically and experimentally. The number of atoms,  $n$ , in an active grouping depends on the type of reaction involved; for oxidation  $\rightarrow$  reduction reactions  $n=1$ , for hydrogenations and dehydrogenations  $n=2$  and for  $NH_3$  oxidation  $n=3$ . This concept can be confirmed by physical measurements on the catalyst such as X-ray analysis and measurement of optical and magnetic properties. Catalyst poisons and the role of the carrier are also discussed.

### The Use of Dilute Adsorption Catalysts in the Chemical Industry

N. I. KOBOSOV, V. P. LEBEDEV and V. I. SCHECHOBALOVA, *Chem. Techn.*, 1958, **10**, (5), 278-282

On the basis of the theory of atomic groupings which considers that the catalytically active phase consists of atoms or groups of atoms of the catalyst not held in the crystal lattice, it follows that the more highly atomised the catalyst the greater will be its specific activity. Higher atomisation is achieved by lowering the concentration of active catalyst on the carrier. The catalysts considered here all have degrees of surface coverage of carrier by catalyst of  $<10^{-2}$ , and are named adsorption catalysts. It is demonstrated by reference to the oxidation of  $SO_2$  and  $NH_3$ ,  $NH_3$  synthesis and organic hydrogenations that adsorption catalysts give a higher yield per unit weight of active catalyst than do normal catalysts.

### The Kinetics of the Thermal Activation and Deactivation of Platinum Catalysts

A. A. LOPATKIN, Zh. V. STREL'NIKOVA and V. P. LEBEDEV, *Zhur. Fiz. Khim.*, 1957, **31**, (8), 1820-1824

The change in catalytic activity of Pt black and Pt-silica gel in the decomposition of hydrogen peroxide was studied in relation to the time of preliminary heat treatment of the catalyst at constant temperature.

### Surface Area and Poisoning Resistance of Adams' Platinum Catalyst

H. MATSUMARU, *Yakugaku Zasshi*, 1958, **78**, 190-193 (*In Japanese*) (*Chem. Abs.*, 1958, **52**, 8705e)  
Four samples of Adams' Pt catalyst were prepared by changing the pyrolysis temperatures to 450,

500, 550 and 600°. Their specific surface area was measured by the gas and liquid adsorption methods. The amount of  $(\text{NH}_2)_2\text{CS}$  required to render H adsorption by the catalyst zero is taken as the poisoning value. It was found that the greater the specific surface area, the greater is the poisoning value, i.e. the poisoning resistance is greater. It is considered that the adsorption of a poisoning molecule on the catalyst is preceded by the formation of a unimolecular layer.

#### Investigations on Catalysts, XIX—Changes in the Sorption of Hydrogen as a Function of the Quantity of Catalyst and Carrier

Z. CSUROS, I. GECZY and J. MORGOS, *Acta Chem. acad. sci. Hung.*, 1958, **16**, (3), 301-318

Experiments were carried out on aqueous solutions of sodium cinnamate and sodium maleate using Pd-BaSO<sub>4</sub> and Pd-C catalysts. Measurement of hydrogen uptake with respect to amount of Pd in the catalyst showed that the replacement of active Pd by carrier decreases the rate of hydrogenation. The effect on hydrogen sorption of the catalyst of varying the amount of Pd and carrier was determined.

#### Chemisorption and Surface Reactions of Ethylene on Evaporated Palladium Films

S. J. STEPHENS, *J. Phys. Chem.*, 1958, **62**, (6), 714-719

Chemisorption and self-hydrogenation of ethylene on evaporated Pd films and the reaction of the adsorbed hydrocarbon layer with hydrogen were studied. At 0°C ethylene is adsorbed up to a surface coverage of about 70% after which self-hydrogenation begins and continues until the surface is almost completely covered with acetylenic residues. The products are ethane and about 3% butane formed by polymerisation of the adsorbed radicals on the surface. At -78°C only 10% of the adsorbed layer undergoes self-hydrogenation and there is no noticeable desorption.

#### Study of Oxide-Metallic Catalysts for Gasoline Reforming, II—Reforming of Narrow Gasoline Fractions of the Ilsk Petroleum and Petroleum of the Second Baku on Platinum Catalysts

K. M. MINACHEV, N. I. SHUIKIN, N. F. KONONOV *et al.*, *Izvest. Akad. Nauk S.S.S.R.*, 1957, (12), 1472-1477

The catalysts 0.5% Pt-Al<sub>2</sub>O<sub>3</sub> and 0.5% Pt-SiO<sub>2</sub> were studied. The Pt-Al<sub>2</sub>O<sub>3</sub> catalyst was found to be active in reforming the 95-115° fraction of Ilsk petroleum and under selected conditions retained its activity for 2000 hr. In reforming the 85-138° fraction of Second Baku petroleum 0.5% Pt-Al<sub>2</sub>O<sub>3</sub> was much superior to 0.5% Pt-SiO<sub>2</sub>, giving more aromatic hydrocarbons and less gasification.

#### Review of Recent U.S.A. Patents on Refining

H. HEINEMANN and H. SHALIT, *World Petroleum*, 1958, **29**, (5), 126-128

Forty recent patents on various aspects of refining are discussed.

#### Sohio's New Toledo Refinery, 8—Reformer Features Compact Reactor Furnace Layout

ANON., *Oil Gas J.*, 1958, **56**, (June 23), 110-111

The reformer, which uses a Pt-containing Sinclair-Baker-Kellogg catalyst, is designed to process 12,000 bbl/day of desulphurised and denitrogenated naphtha. The five reactors in the reactor-furnace layout are specially constructed in a compact arrangement to make possible economies in investment.

#### From Natural to Super-Premium Gasolines

R. E. SUTHERLAND and D. H. BELDEN, *Petroleum Refiner*, 1958, **37**, (7), 119-123

The most economical combination of processes available for the upgrading of natural gasoline is considered. By using a scheme combining Penex and Platforming of natural gasolines with synthesis of alkylate from field butanes (Butamer process) it is possible to obtain "super-premium" quality motor fuels.

#### The Selective Reduction of Alkyl- $\alpha$ -furyl-carbinols in the Presence of Palladium

N. I. SHUIKIN and I. F. BELSKII, *Chem. Ber.*, 1958, **91**, (5), 948-951

Alkyl-furyl-carbinols were selectively hydrogenated to the corresponding  $\alpha$ -alkyl-furans in the gas phase in the presence of 10% Pd-C at 200-260°C.

#### Further Aspects of the Wittig Reaction in the Steroid Series—20-Dehydrocholesterol and 20-Isocholesterol

F. SONDEHEIMER and R. MECHOULAM, *J. Amer. Chem. Soc.*, 1958, **80**, (June 20), 3087-3090

The reaction between 21-nor-20-ketocholesteryl acetate and triphenylphosphinemethylene yields 20-dehydrocholesteryl acetate. Catalytic hydrogenation of the latter in acetic acid over a reduced Pt catalyst gives cholestanyl acetate, both double bonds being hydrogenated, whereas in ethanol using Pd-CaCO<sub>3</sub> catalyst only the substituent double bond is affected and 20-isocholesteryl acetate results.

#### Catalytic Isomerisation of Homologues of Tetrahydrofuran to Aliphatic Ketones

N. I. CHOUKINE and I. F. BELSKII, *Bull. Soc. Chim. France*, 1958, (6), 786-788

Tetrahydrofuran type compounds (i.e.  $\gamma$ -oxidised ring compounds) can be isomerised on Pt-C catalyst with ring opening giving aliphatic carbonyl compounds. When the ring has an  $\alpha$ -alkyl substituent isomerisation leads to the

corresponding ketone. Tetrahydrofuran itself under these conditions breaks down to give CO and a hydrocarbon.

## ELECTRICAL ENGINEERING

### Noble Metals and their Alloys as Electrical Contact Materials

H. HOLZMANN, *Metall*, 1958, **12**, (7), 630-636

The properties required of electrical contact materials are enumerated. The use of Ag, Au, Pt metals, W and Mo, alloys of these metals and sintered materials as electrical contacts is described. A table of physical and mechanical properties of many of these contact materials is given. Pt metals and their alloys are used in low-current applications.

### Physical Processes in Contact Erosion

L. H. GERMER, *J. Appl. Physics*, 1958, **29**, (7), 1067-1082

Pd and Ag contacts were studied in circuits which make or break currents of 0.5A or less and voltages <600V. Contact erosion on making and breaking the circuit was investigated. Erosion occurring on closure is due to arcs between the contacts which can be of either anode or cathode types. There is a critical distance, dependent on electrical conductivity, below which arcs are of the anode type. This distance is about  $0.5 \times 10^{-4}$  cm for Pd and  $3-4 \times 10^{-4}$  cm for Ag. The type of arc occurring is independent of arc current, of energy/unit area and of the total arc time at constant current. For inactive Pd contacts the transfer of metal from anode to cathode decreases from  $4 \times 10^{-14}$  cc/erg at 50V to a fraction of this at 300V, but is not greatly dependent on current up to 100A. For Ag transfer is almost independent of potential. Correlation between measured transfer and type of arc is excellent. For active contacts there is generally no net transfer of material. Activation favours cathode loss at low currents but at high currents anode loss predominates for both metals. The phenomena occurring on break are more complex. Cathode erosion occurs exclusively for both Pd and Ag contacts. The erosion increases with circuit energy, being about  $1 \times 10^{-14}$  cc/erg for Pd in high-energy circuits. The lower erosion in low energy circuits is associated with the shielding effect of the surface carbon. For inactive Pd and Ag contacts glow discharges and showering arcs must be considered and the erosion behaviour of the two metals is different. For Pd all erosion is produced by showering arcs; the first of these are of the anode type with transfer of about  $4 \times 10^{-14}$  cc/erg, but for electrode separation  $>0.5\mu$  they are of cathode type with transfer about  $1 \times 10^{-14}$  cc/erg. For Ag contacts erosion occurs during glow-discharge due to sputtering and showering arcs continue to be of the anode type up to greater separations.

## ELECTRONICS AND TELECOMMUNICATIONS

### Characteristics of Electron Tubes having Clean Electrodes

J. E. BEGGS, *Inst. Radio Eng. Trans. (Electron Devices)*, 1958, **ED-5**, (2), 55-58

Electron tubes in which the grid and anode do not become contaminated by material evaporated from the cathode can be obtained by using active metal surfaces and high degassing and exhaust temperatures with oxide-coated cathodes having a passive base metal. A good combination was found to be a Ti anode and an oxide-coated Pt cathode. Such diodes have been operated, with anode and cathode at the same temperature, for over 10,000 hr with no contamination of the electrodes. Diodes with clean anodes operate reliably in the emission limited region. Triodes with Ti anode and grid and Pt as cathode base metal were tested. When grid and cathode are at the same temperature the grid remains clean almost indefinitely. The characteristics remain stable for long periods of time; no changes were apparent in a triode operated for 5000 hr in a multivibrator circuit at 500-600°C. Triodes with a clean grid surface can be made to have a built-in grid bias of 2V or more.

### Design of Valves for Submerged Telephone Cable Repeaters

F. H. REYNOLDS, *Research*, 1958, **11**, (8), 310-314

The modifications in design necessary in producing long-life valves suitable for underwater installations are discussed. These include replacing the conventional Ni cathode core by Pt.

## TEMPERATURE MEASUREMENT

### The Intermediate Metal Thermocouple in Metal/Mould Interface Temperature Measurements

D. V. ATTERTON and D. H. HOUSEMAN, *Brit. Foundryman*, 1958, **51**, (February), 77-82

An intermediate metal thermocouple was developed for temperature measurements at the mould/metal interface of steel castings. The Pt and Rh-Pt wires are sheathed separately in silica sheaths and the protruding ends are left unjoined. The hot junction is formed on contact with the molten metal. Intermediate metal and sheathed thermocouples with the composition Pt/13% Rh-Pt and 1% Rh-Pt/13% Rh-Pt were compared in experiments using 280 lb and 13½ lb castings. With the 280 lb castings the intermediate metal thermocouples record a substantially higher temperature than the sheathed thermocouples. Results from the latter are rendered unreliable by temperature gradients across the sheath. Values

obtained using intermediate metal thermocouples are in accord with practical observations and with theory. The results obtained for the 13½ lb castings were unsatisfactory with both types of thermocouple due to the response time of the instruments being too long for the rapid solidification which occurs. Recalibration of the intermediate metal thermocouples after use showed no serious error due to contamination of the wires by steel from the castings.

#### **Design of an Immersion Thermocouple and its Application in Open-Hearth Steelworks**

H. LÖSCHER, *Neue Hütte*, 1958, 3, (7), 416-425

A review of literature on the developments in design of immersion thermocouples and sheaths for use in the steel industry. The thermocouples 6%Rh-Pt/30%Rh-Pt and Pt/10%Rh-Pt are described. The dependence of the mean temperature increase of the bath on the admission temperature and heat supply is discussed. The improvement of steel quality by observing the correct tapping and casting temperatures is described.

#### **Error in Temperature Measurement due to the Interdiffusion at the Hot Junction of a Thermocouple**

A. J. MORTLOCK, *J. Sci. Instruments*, 1958, 35, (8), 283-284

Theoretical expressions are derived for the error in e.m.f. due to interdiffusion for the case where one arm of the thermocouple is a pure metal and

the other is an alloy of this metal. The error is less when the thermocouple leads are anti-parallel than when they are parallel. For the normal parallel arrangement a Pt/13%Rh-Pt thermocouple in a gradient of 10°C/cm may, according to the equations derived, have an error of up to 1.3°C at all temperatures in the normal operating range following a heat treatment equivalent to 100 days at 1500°C.

#### **On the Accuracy of Temperature Measurement of Molten Steel with Immersion Thermocouples of Various Types**

A. N. GORDOV and N. N. ERGARDT, *Zavods. Lab.*, 1957, 23, (6), 727-730. (In Russian)

The thermocouples in use in the Russian steel industry at present are Pt/10% Rh-Pt and W/Mo. Errors obtained with the latter are due to oxidation and crystallisation on immersion and amount to about ±20°C. The noble metal thermocouples which are used give errors since the Pt is not sufficiently pure and the sheathing is ineffective. The use of spec. pure Pt and effective sheathing is recommended. Work is described on the thermocouples 6%Rh-Pt/30%Rh-Pt and 13%Rh-Pt/30%Rh-Pt which are more stable at high temperatures than Pt/10%Rh-Pt. They have sufficiently high e.m.fs. for technical use in the temperature range 1500-1700°C. The 6%Rh-Pt/30%Rh-Pt couple seems the most promising. A method of calibrating shallow-immersion thermocouples for the temperatures met with in industry is described.

## **NEW PATENTS**

#### **Catalytic Reforming of Hydrocarbon Mixtures**

N. V. DE BATAAFSCHE PETROLEUM MAATSCHAPPIJ  
*British Patent 794,650*

Hydrocarbon mixtures of the gasoline type with a naphthene content of less than 30% by weight are reformed by contacting the mixture, together with an 8-fold molar proportion of hydrogen, at at least 10 atm. A 1% platinum-on-alumina catalyst activated with halogen is used.

#### **Hydrogenation of Petroleum Fractions**

ESSO RESEARCH AND ENGINEERING CO. *British Patent 794,809*

Petroleum fractions, containing aromatic compounds boiling in the range of 300-650°F are upgraded by hydrogenation at a temperature of 500-675°F, a pressure of 100-1,000 p.s.i.g. in the presence of 2,000-15,000 standard cubic feet of hydrogen per barrel of feed in contact with a catalyst comprising platinum supported on eta alumina. 0.001-5% (preferably 0.05-1%) by

weight of platinum is used. Chloroplatinic acid or platinum sulphide is preferred. Method of making catalyst is described.

#### **Catalytic Processes**

THE M.W. KELLOGG CO. *British Patent 794,915*

A catalyst of platinum- or palladium- on alumina is used in a process for the catalytic converting or reforming of hydrocarbons in which the reactant material is passed at reaction temperature and pressure through a fixed bed of the catalyst along paths of equal length and flow resistance.

#### **Higher Fatty Alcohol**

CALIFORNIA RESEARCH CORP. *British Patent 795,181*

A ruthenium-containing hydrogenation catalyst is used in a process for the production of higher fatty alcohols from fat.

#### **Manufacture of Aromatic Hydrocarbons**

FARBWERKE HOECHST A.G. *British Patent 795,235*  
Aromatic hydrocarbons containing a substantial