

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Relation Between Strength and Creep of Metals and Alloys

S. N. ZHURKOV and T. P. SANFIROVA, *Soviet Physics Tech. Physics*, 1958, 3, (8), 1586-1592 (Transl. of *Zhur. Tekhn. Fiz.*, 1957, 28, (8))

The rate of creep and the time to fracture under an axial tensile load were determined for specimens of Pt, Al, Al-Zn, Al-Mg and Ni-Co. The effect of temperature and stress on the rate of steady creep was determined. For Pt, measurements were carried out at 100, 300, 400 and 500°C. From the results it is deduced that the product of time to fracture and rate of quasi-ductile flow is a constant independent of temperature and stress.

Absorption of Hydrogen by Single Crystals of Palladium

T. J. TIEDEMA, C. KOOY and W. G. BURGERS, *Proc. Nederland. Akad. Wetenschap.*, 1959, 62B, (1), 34-40

The single crystals were examined micrographically and by X-ray diffraction before and after charging electrolytically with hydrogen. The micrographs show the formation of fracture lines on the crystal surface when hydrogen is absorbed. Comparison with X-ray results show that these fractures are parallel to the intersections of the (111) planes with the cutting planes. The fractures must thus be parallel to the (111) planes. There is no change in the crystal lattice after anodic treatment to remove the absorbed hydrogen.

Ductility of Rhodium

A. CALVERLEY and D. W. RHYS, *Nature*, 1959, 183, (Feb. 28), 599-600

The reason for the poor ductility of Rh was investigated by measurements on single-crystal and polycrystalline samples. The single-crystal bar was prepared by the electron-bombardment, floating-zone melting technique; its hardness was 190 DPN and its diameter 0.150-0.170 in. It could be cold-swaged without intermediate anneal to wire 0.050 in. diameter, a reduction in cross-section of 90%. Under similar conditions a polycrystalline bar can only be very slightly cold-worked before inter-crystalline fracture occurs. It is concluded that crystal boundaries play an important part in the cold-deformation of Rh. Grain-boundary impurities not easily detectable by normal analytical methods may be involved.

Nuclear Irradiation Effects on Permanent Magnet Materials

R. S. SERY, D. I. GORDON and R. H. LUNDSTEN, *Bull. Amer. Phys. Soc.*, 1959, 4, (3), 137 (Abstract only)

The following materials were irradiated to 10^{17} epithermal neutrons/sq. cm in 12 days in the BNL reactor: $3\frac{1}{2}$ Cr steel, 36 Co steel, Alnico II, V and XII, Cunico, Cunife, Silmanal, fine irons, Pt-Co and barium ferrites. In no case was any change in magnetic properties as a result of irradiation observed.

Some Magnetic Properties of Platinum-Rich Platinum-Iron Alloys

J. CRANGLE, *J. Phys. Radium*, 1959, 20, (2/3), 435-437 (In English)

The magnetic susceptibilities of Pt-Fe alloys near the composition Pt_3Fe , and of alloys with low Fe content, were measured as a function of temperature. For alloys near the Pt_3Fe composition the Curie-Weiss law is obeyed at higher temperatures, extrapolating towards a paramagnetic Curie point, θ_p , which depends on composition. The lowest value of θ_p , $-150^\circ K$, occurs at ~ 25.5 at.% Fe. X-ray examination shows the presence of a super-lattice in the non-ferromagnetic specimens. Cold working renders the alloys ferromagnetic indicating that the disordered state is ferromagnetic. At compositions with Fe contents $< 24\%$ ferromagnetism develops rapidly and is still present at only 2% Fe.

The Uranium-Platinum System—Final Report

J. J. PARK and D. P. FICKLE, U.S. Atomic Energy Comm. Report, NBS-5946 (1958)

Alloys over the complete range of compositions were studied by means of thermal, microscopic and X-ray analyses and by hardness determinations. A phase-diagram is plotted from the results. Two eutectics are formed, one at $1005^\circ C$ and 12 at.% Pt and the second at $1345^\circ C$ and 87.5 at.% Pt. The compounds UPt_7 , formed peritectically at 961° , UPt_6 , formed peritectically at 1370° , UPt_3 , melting congruently at $\sim 1700^\circ$, and UPt_5 , formed peritectically at 1460° , were identified. The solubility of U in Pt is 4 at.% at room temperature rising to 4.5 at.% at the eutectic temperature; U dissolves ~ 1.2 at.% Pt at room temperature and ~ 5 at.% at the eutectic temperature. The γ - β and β - α transformation temperatures of U are lowered from 762 to $705^\circ C$ and from 660 to $589^\circ C$ respectively by the addition of Pt.

The Equilibrium Diagram of the System Bismuth-Palladium

J. BRASIER and W. HUME-ROTHERY, *J. Less-Common Metals*, 1959, 1, (2), 157-164

The equilibrium diagram was studied up to 65 at. % Pd by thermal analysis and microscopical methods. Eutectics are formed at 5.83 at. % Pd and 256°C and at ~ 60% Pd and 577°C. Pd is practically insoluble in solid Bi. A Bi₂Pd phase and a congruently melting compound BiPd were found.

A Note on the Palladium-Boron System

W. M. LEHRER, *Trans. Met. Soc. A.I.M.E.*, 1959, 215, (Feb.), 168-169

Five alloys containing 2-6 wt. % B were studied by thermal analysis and metallographic methods. The solidus-liquidus portion of the phase diagram was constructed. A eutectic was found at about 3.5% B and 845°C and the existence of a compound with a composition very near to that of Pd₃B₂ is indicated.

The Constitution of Molybdenum-Rhodium and Molybdenum-Palladium Alloys

C. W. HAWORTH and W. HUME-ROTHERY, *J. Inst. Metals*, 1959, 87, (April), 265-269

Alloys containing up to 60% Rh and Pd were prepared by powder methods and examined by melting point measurements and X-ray and metallographic methods. The solidus and liquidus curves were determined by means of two specially constructed laboratory furnaces for use above 2000°C. The phase-diagrams constructed from the results are given. The Mo-Rh system contains a eutectic at ~ 40 at. % Rh and 1940°. The maximum solubility of Rh in Mo is ~ 20 at. % at the eutectic but falls rapidly with decreasing temperature. In the Mo-Pd system a peritectic is formed at ~ 60 at. % Pd and 1740°C. The intermediate c.p.h. phase formed by this reaction tends to decompose on quenching. A wide solid solution of Mo in Pd was found and Mo dissolves 4-8 at. % Pd at high temperatures.

Borides and Silicides of the Platinum Metals

B. ARONSSON, J. ASELIUS and E. STENBERG, *Nature*, 1959, 183, (May 9), 1318-1319

The compounds Ru₃B₃, RhB, PtB, IrB₁₋₂, Ru₂Si and Rh₂Si were examined. Their structures are discussed in some detail.

ELECTROCHEMISTRY

The Effect of Surface Oxidation on the Voltammetric Behaviour of Platinum Electrodes. The Electroreduction of Iodate

F. C. ANSON, *J. Amer. Chem. Soc.*, 1959, 81, (Apr. 5), 1554-1557

The reduction of iodate ion at reduced and

oxidised Pt electrodes was investigated by the chronopotentiometric technique. For pH 1-6 the iodate reduction proceeds much more readily at oxidised than at reduced electrodes. Since electroreduction of both the surface Pt oxides and the iodate ion occur at the same potential it is assumed that the oxide reduction catalyses the iodate reduction. For pH > 6 the oxidation has no effect on the chronopotentiograms. For pH < 1 the reduction of iodate proceeds by means of iodine as an intermediate. The mechanism of the oxide film effect is discussed.

Cyclic Alternating-Current Voltammetry with a Platinum Electrode

A. J. JULIARD, *Nature*, 1959, 183, (Apr. 11), 1040-1041

Reproducible a.c. polarograms are obtained when a 10% Rh-Pt wire electrode is polarised cyclicly between -1.0 and 1.5 V versus a standard calomel electrode in a solution stirred by nitrogen bubbles. Analytical applications for compounds reversibly or semi-reversibly reducible or oxidisable in the above potential range are described.

The Synthesis of Pentacyclosqualene (8,8'-Cycloönocerene) and the α - and β -Onoceradienes

E. J. COREY and R. R. SAUERS, *J. Amer. Chem. Soc.*, 1959, 81, (Apr. 5), 1739-1743

The application of electrolytic oxidation to the synthesis of C₃₀-triterpene structures from C₁₆-carboxylic acids (Kolbe coupling) is illustrated by the above syntheses. On electrolysis of the NH₄ salt of *iso*-norambrienolide in refluxing methanol at a smooth Pt anode two tetracyclic diols are obtained both of which on treatment with perchloric acid in benzene-AcOH give pentacyclosqualene. The onoceradienes are obtained by dehydration of the diols. A proof of the stereochemistry is given.

ELECTRODEPOSITION

Some Experimental Observations on the Effect of Addition Agents on Stress and Cracking in Rhodium Deposits

F. H. REID, *Trans. Inst. Metal Finishing*, 1959, 36, (3), 74-81

The origins of internal stress in electrodeposits are reviewed briefly. The effect on the stress of additions of Al, Mg and selenic acid to Rh plating baths is investigated. Additions of up to 6g/l Mg or Al to sulphate baths allowed deposition of crack-free deposits up to 0.0005 in. thick. Although these additions increased the internal stress slightly no cracks were formed probably due to the occlusion of Mg or Al oxides or hydroxides at metal faults preventing the usual contraction of the deposited Rh. These deposits were rough and required polishing. The effects of additions of selenic acid

(H_2SeO_4) are very promising. With a bath of composition Rh 10g/l, H_2SO_4 15–200 ml/l, H_2SeO_4 0.1–1.0g/l, a current density of 1–2 A/sq.dm and temperature 50–75°C crack-free deposits 0.0005–0.001 in. thick were produced consistently with a smooth surface. The cathode efficiency and hardness of the deposits are not seriously affected by the presence of H_2SeO_4 . Microscopic examination of these deposits revealed a faint pattern of extremely fine cracks. It appears that these cracks are formed in a transition from tensile to compressive stress but are closed up by further deposition. Increase in H_2SO_4 content accelerates the crack closure.

Electroless Palladium Plating

R. N. RHODA, *Trans. Inst. Metal Finishing*, 1959, **36**, (3), 82–85

A process for the deposition of Pd on catalytic surfaces by chemical reduction is described. The solution used contained a Pd-amine complex, $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$ (0.03–0.20 M/l Pd), a reducing agent, N_2H_4 (0.005–0.01 M/l), a stabiliser, EDTA (0.01–0.10 M/l), and NaOH (7.0–10.0 M/l). The EDTA minimises the tendency of the Pd complex to reduce to Pd powder. Graphs showing the effect of temperature, Pd concentration, molar ratio $\text{N}_2\text{H}_4/\text{Pd}$ and exhaustion of the bath on the rate of deposition are given. The recommended operating temperature is 30–70°C. Pure, ductile, adherent deposits of Pd up to 0.0025 in. thick were plated on to surfaces of Al, Cr, Co, Au, Fe, Mo, Ni, Pd, Pt, Rh, Ru, Ag, Sn, W, steel, graphite, carbon and on Cu pre-plated with a catalytic metal.

LABORATORY APPARATUS AND TECHNIQUE

On Quantitative Measurement of Turbulence by Means of a Constant Resistance Hot-Wire Anemometer

N. HAYASHI, *J. Phys. Soc. Japan*, 1959, **14**, (3), 360–365 (*In English*)

The technique was improved in order to permit quantitative measurements of velocity fluctuation. The hot-wire was made of Pt. For quantitative measurements the effects of resistance of galvanometer circuit and current variation due to resistance variation in the hot-wire are calculated for a general case. A direct calibrating method was developed.

A Combined Platinum-Carbon Film as a Preparative Method in Electron Metallography

F. W. GÜNTHER and D. RAAB, *Neue Hütte*, 1959, **4**, (2), 113–115

The pre-shadowing replica technique has many advantages in preparing surfaces for electron metallography. A satisfactory method for the

combined evaporation of a Pt or Pt-Ir plus C film has been developed. The Pt wire is wound on a C electrode of new design placed 100 mm from the specimen. The specimen is set at the desired shadowing angle to the evaporation source and the Pt-C is evaporated. The Pt-C film is separated from e.g. a steel specimen, by dissolving the steel electrolytically.

CATALYSIS

Surface Reactions on Evaporated Palladium Films

S. J. STEPHENS, *J. Phys. Chem.*, 1959, **63**, (2), 188–194

The reactions were studied at 0°C by allowing one gas, adsorbed as a monolayer on Pd, to react with small additions of a second gas. The extent of reaction and reaction products were measured volumetrically and by gas analysis. The systems studied were: $\text{Pd-O}_2+\text{CO}$, $\text{Pd-CO}+\text{O}_2$, $\text{Pd-O}_2+\text{H}_2$, $\text{Pd-H}_2+\text{O}_2$, $\text{PdO}_2+\text{C}_2\text{H}_4$ and $\text{Pd-C}_2\text{H}_4+\text{O}_2$. In all cases extensive reaction occurred. Surface contamination may cause an apparent increase in adsorption of a second gas due to such reactions.

Enhanced Surface Reactions III—Adsorption of Gases on Prepared Ruthenium Surfaces

M. J. D. LOW and H. A. TAYLOR, *J. Electrochem. Soc.*, 1959, **106**, (2), 138–142

The rates of adsorption of H_2 , CO and O_2 on a 0.5%Ru- Al_2O_3 catalyst treated by pre-adsorption of gases were studied. The rate and extent of H_2 adsorption are enhanced by pre-adsorption of CO on the surface. Adsorption of O_2 and CO irreversibly poison the surface. These phenomena are explained on the basis of active-site creation or destruction through recombination due to the presence of impurities (the pre-adsorbed gas).

The Adsorption of Hydrogen on Ruthenium-Alumina

M. J. D. LOW and H. A. TAYLOR, *Canad. J. Chem.*, 1959, **37**, (3), 544–552

The rate of adsorption of H_2 on Ru- Al_2O_3 was studied at four temperatures from 100–257°C and at pressures from 15–80 cm DBP. The results show two different types of adsorption, one occurring above and the other below 25 cm DBP.

Synthesis of Hydrogen Cyanide by Auto-thermic Reaction

P. W. SHERWOOD, *Petroleum Eng.*, 1959, **31**, (2), C-22–26 and (3), C-51–54

The synthesis of HCN from CH_4 and NH_3 in the presence of air is reviewed. The reaction mechanism and catalyst selection are discussed and the commercial process is considered from

the viewpoints of purity of feed, design of converters and reaction conditions. The catalyst is Rh-Pt gauze or a supported Pt catalyst. In the second part of the paper the recovery of HCN in the above process is considered and the synthesis of HCN from NH_3 and CH_4 in the absence of air is described.

Selective Oxidation of Hydrogen in Carbon Monoxide over Palladium Black, Part II—Effect of Alkali

T. SATO and K. ISHIZUKA, *J. Research Inst. Catalysis*, 1958, **6**, (2), 138-145

The activity of Pd black catalysts containing varying amounts of alkali was studied. The results are expressed graphically as the temperature dependence of the activity. Experiments were carried out both with and without HCl in the reacting gases. Heat treatment of the catalysts reduced their selectivity. Their activity is reduced both by excess alkali and exhaustive removal of alkali. It is concluded that the alkali keeps the Pd black from sintering.

Atlas Installs First C_6 Penex Unit

V. B. CHANCE and G. F. ASSELIN, *Oil Gas J.*, 1959, **57**, (Feb. 16), 146, 150-152

A Universal Oil Products Penex isomerisation unit has been in operation at the Atlas Processing Co.'s Shreveport refinery since July 1958 for the production of *iso*-hexanes. The basis of the process is the conversion of *n*- to *iso*-hexane over a Pt-containing catalyst. A flow-sheet and table showing charge and product compositions are given. The process is described. The product is a high-octane, negative-sensitivity isomerised hexane fraction suitable for motor-fuels.

Reactivities of Naphthenes over a Platinum Reforming Catalyst by a Gas Chromatographic Technique

A. I. M. KEULEMANS and H. H. VOGEL, *J. Phys. Chem.*, 1959, **63**, (4), 476-480

The reactions of 30 individual C_5 - C_8 naphthenes in excess hydrogen were studied in a micro-reactor attached to a gas chromatographic column, over a Pt- Al_2O_3 -halogen reforming catalyst at 350° and atm. pressure. Cyclopentanes and 1,1-dimethylcyclohexane are converted to aromatics much more slowly than ordinary cyclohexanes. The reactivities of cyclopentanes are explained by assuming that they first dehydrogenate to olefins which then migrate to form carbonium ions on acidic sites. Skeletal isomerisation of the carbonium ions to cyclohexyl structures is thought to be the slow step in the series of reactions, leading to aromatic hydrocarbons. The relative rates of alternative paths are given by simple ratios for relative carbonium ion stabilities multiplied by the number of possible paths. In this way rates of aromatisation and the amounts

of specific aromatic isomers formed are explained. These assumptions should hold at commercial reforming conditions of 20-40 atm and 480° .

Reforming with RD-150 Platinum Catalyst

W. H. DECKER and C. RYLANDER, *Petroleum*, 1959, **22**, (5), 165-168

This catalyst is now in use in over 70,000 bbl/day of Sinclair Refining Co.'s reforming plant with a further 3-400,000 bbl/day in design or construction. Its advantages are enumerated. The operation of the reforming plant in Sinclair's Houston refinery, using this catalyst, is described in detail. The catalyst activity has been maintained over an operating cycle of 26 months; it is regenerated by heating in a dilute air stream to remove carbonaceous deposits. For a feed-stock of typical Mid Continent naphtha a yield of 86.0 vol.% of 90 RON reformat is obtained at 350 p.s.i.g.

The Evaluation of Activation Energies Using a Rising Temperature Flow Reactor. The Dehydrogenation of Cyclohexane over WS_2 , $\text{Pt}/\text{Al}_2\text{O}_3$, $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$, $\text{NiWO}_4/\text{Al}_2\text{O}_3$ and Cr_2O_3

J. M. BRIDGES and C. HOUGHTON, *J. Amer. Chem. Soc.*, 1959, **81**, (Mar. 20), 1334-1338

The apparent activation energies, reaction kinetics and comparative activities of the catalysts were obtained using a reactor in which the temperature can be raised continuously with time. $\text{Pt}/\text{Al}_2\text{O}_3$ is the most active catalyst both on the basis of equal volumes and equal surface area of catalyst. Electron irradiation from a Van de Graaff accelerator has no permanent effect on the activity of $\text{Pt}/\text{Al}_2\text{O}_3$.

Determination of Ethylenic Bonds by Quantitative Hydrogenation

S. SWAN TIONG and H. I. WATERMAN, *Chim. et. Ind.*, 1959, **81**, (2), 204-215 and (3), 357-369

The various methods for determination of degree of unsaturation based on hydrogenation are reviewed. The present apparatus makes possible the direct and continuous measurement of the amount of hydrogen fixed. The reactions are carried out in the presence of AcOH and a Pd/C catalyst. The accuracy is very good and errors due to adsorption on the catalyst are negligible. The application of the method to a wide range of unsaturated compounds is described. The presence of aromatic ring systems has no influence on the results.

The Exchange Reaction Between Diethyl Ether and Deuterium on Evaporated Metal Films

J. K. CLARKE and C. KEMBALL, *Trans. Faraday Soc.*, 1959, **55**, (1), 98-105

The exchange reaction over films of W, Fe, Ni,

Pd, Rh, and Pt was studied using a mass spectrometer. W and Fe films produced mainly a simple exchange reaction; Ni, Rh and Pt showed intermediate behaviour; Pd caused chiefly a multiple-exchange reaction. Poisoning of the exchange with different catalysts was studied.

Carbon Monoxide Hydrogenation on Ruthenium Catalysts 3-Carbon Monoxide Hydrogenation Between 100 and 2000 Atmospheres

P. GUYER, D. THOMAS and A. GUYER, *Helv. Chim. Acta*, 1959, **42**, (2), 481-484

The hydrogenation of CO to solid paraffins on a Ru-on-Cu catalyst was studied in the range 160-220°C and 100-2000 atm. The rate of gas reaction increases fourfold on increasing the pressure from 100 to 1000 atm. The selectivity (amount of solid product) is scarcely affected by pressure change. A maximum yield of 60-65% occurs at about 180°C. For a constant rate of reaction of gas the yield of solid paraffins is increased from 35-65% by increasing the pressure from 200-1000 atm while at the same time the reaction temperature required is lowered.

Hydrogenation of Acetylene on a Palladium Catalyst

A. GRIGNON-DUMOULIN and C. THONON, *Rev. Inst. Franc. Petrole*, 1959, **14**, (2), 214-222

The selective hydrogenation of acetylene to ethylene over a 0.01% Pd-silica gel catalyst was investigated. The reaction mechanism was studied on a hydrogen-acetylene mixture. Below 160°C it is a simple reaction, 1st order with respect to H pressure with an activation energy of 17 kcal/mole. Above 160°C the rate of reaction increases to a maximum with H pressure, then decreases for further increases in pressure. Reaction rate increases rapidly with temperature from 160-200°C, then more slowly up to 303°C. The catalyst activity decreases with temperature rise above 160°C and secondary reactions become more important. The reaction mechanism could not be elucidated in this region but may be explained by the co-existence of two mechanisms. The selectivity of the catalyst was studied on mixtures of acetylene and ethylene in hydrogen. The selectivity is very high. At both 180° and 299°C the acetylene was 100 times more reactive than ethylene.

Effect of Alkali Salts on the Steric Course of Hydrogenation of a Cyclic Allylic Alcohol

M. C. DART and H. B. HENBEST, *Nature*, 1959, **183**, (Mar. 21), 817-818

Alcholesterol was hydrogenated in ethanol using Adams' PtO₂ catalyst. Cholestanol and a hydrocarbon fraction (hydrogenolysis product) together with coprostanol were always obtained as products. The trace of Na salts normally

present in Adams' catalyst has a considerable effect on the course of the reaction. When the salts were deliberately removed higher yields of hydrocarbon were obtained at the expense of the coprostanol.

Preparation of *p*- and *m*-Aminomethylcyclohexylcarboxylic Acids

M. LEVINE and R. SEDLECKY, *J. Org. Chem.*, 1959, **24**, (1), 115-116

These acids are of possible importance in the preparation of fibre-forming polymers. They were obtained from *m*- or *p*-tolunitrile by oxidation with Cr₂O₃ to *m*- or *p*-cyanobenzoic acid followed by reduction of the nitrile group with Raney Co and the aromatic nucleus with PtO₂ in AcOH to give *m*- or *p*-aminomethylcyclohexylcarboxylic acid.

Synthesis in the 5-Hydroxyindole Series. N-Acetyl-5-hydroxytryptophan and Related Compounds

J. KOO, S. AVAKIAN and G. J. MARTIN, *J. Org. Chem.*, 1959, **24**, (2), 179-183

The synthesis of N-acetyl-5-hydroxytryptophan, 5-hydroxytryptophol and related substances are described and an improved method is given for the large-scale preparation of the pharmaceutically important compound, 5-hydroxytryptophan. The latter is prepared from 5-benzyloxygramine by a multistage process. In the last stage 5-benzyloxytryptophan is catalytically debenzylated in 5% NaOH solution, using 10% Pd-C as catalyst, to give 5-hydroxytryptophan in 91% yield.

Polymerisation through Catalytically Activated Hydrogen

Z. CSUROS and I. GECZY, *Periodica Polytech.*, 1958, **2**, 65-88 (*Chem. Abs.*, 1959, **53**, 1905g)

Methyl methacrylate, methyl acrylate and ethyl acrylate were polymerised in MeOH in the presence of H and Pd/BaSO₄. The H radicals formed initiate the polymerisation. Acrylonitrile, styrene and vinyl acetate require a peroxide in addition to the activated H. The rates of the reactions were measured.

The Hydrogenation of Castor Oil II

J. VAN LOON, *Fette-Seifen Anstrichmittel*, 1959, **61**, (3), 201-205

The hydrogenation of castor oil and the ethyl esters of its total mixed fatty acids was studied using a Pd-C catalyst at different reaction temperatures, H pressures, catalyst-oil ratios and catalyst activities. At 1 atm and 180°C the hydrogenation proceeds more quickly over Pd-C than over Ni-kieselguhr catalyst and less decomposition of the products occurs. The double-bonds are hydrogenated first. Hydrogenation of the -OH groups is always less complete and stops completely on saturation of the double

bonds. The degree of —OH bond reduction is very dependent on catalyst activity. The reaction mechanism is discussed.

CATHODIC PROTECTION

Cathodic Protection for Naval Vessels

L. J. WALDRON, M. H. PETERSON and M. C. BLOOM, *Corrosion*, 1959, **15**, (2), 87-92

The paper describes the field programme carried out under the direction of Naval Research Laboratory personnel, to apply cathodic protection to vessels of the U.S. Navy's Reserve Fleet and to active vessels. In tests on the Reserve Fleet graphite or Mg anodes were used and on active vessels Mg anodes or Pt anodes. The latter were installed in submarines. Full details of the installations are given. In all cases they were successful in reducing corrosion.

ELECTRICAL ENGINEERING

Telephone Relays Suitable for Exposure to the Atmosphere

B. THIEL and W. REISER, *Nachrichtentechnik*, 1959, **9**, (3), 117-122

The requirements of relays to be exposed to the atmosphere and testing of such relays are described. A life of ~ 20 years should be aimed for. Suggestions for adapting relays to such requirements by changes in materials and surfaces without any constructional changes are discussed. For contacts, the use of 30% Ag-Pd or Rh-plated Ag in place of Ag is recommended.

ELECTRONICS AND TELECOMMUNICATIONS

Temperature Coefficients of Resistance of Metallic Films in the Temperature Range 25 to 600°C

R. B. BELSER and W. H. HICKLIN, *J. Appl. Physics*, 1959, **30**, (3), 313-322

Measurements were carried out *in vacuo* on films of sputtered Au, Ir, Mo, Ni, Pd, Pt, Rh, Ta and W, of evaporated Al, Cr, Ti and Zr and of the alloy films Pt-Au, Pt-Ir and Pt-Ni. The range of film thickness was 75-2000 Å. The substrates used were soft glass, steatite, Al₂O₃, Pyrex, Vycor, fused quartz and Stupalith. Changes in resistance on annealing the films were observed. After annealing, films of Pt and Ir can be heated in air to 600°C with very little reversible resistance change. Only films of Pt, Au and Ir can withstand extended heating in air at 600°C. Partial protection is afforded other films by coating with SiO and this also reduces agglomeration in all

the films. The temperature coefficient of resistance (TCR) of the films is not greatly affected by film thickness or nature of substrate. Low TCRs are obtained for Pt alloy films, e.g. 0.0007 per °C for Pt-Ir, 0.0002 for Pt-Ni and 0.0004 for Pt-Au; these films have resistivities 3-4 times those of either constituent. Films of Mo, W, Ta, Cr, Zr and Ti contain oxide inclusions and have low TCRs and high resistivity which is a useful combination for electronic component applications.

What Makes the 'Solion' so Promising?

ANON., *Canad. Chem. Proc.*, 1959, (March), 88-92

Describes work being carried out at the University of Ottawa on the development of 'solions'—electronic components based on the properties of ions in solution. The theory is discussed briefly. The simplest solion has Pt gauze anodes and a Pt wire cathode in KI-I₂ solution with a diaphragm made of Teflon. The basis of operation is a transducer effect based on variation in current output due to movement of the diaphragm caused by the application of external forces. It should eventually be possible to record and control liquid and solid levels in tanks, static pressures, fluid flow and temperature by this method.

TEMPERATURE MEASUREMENT

Instrumentation in the Glass Industry in Great Britain

L. WALTER, *Glass. Ind.*, 1959, **40**, (March), 125-130, 158-162

Recent developments in temperature measurement and control and liquid glass level control are reviewed. In forehearth and spout temperature control bare or sheathed thermocouples are located below the glass surface. An assembly for automatic feeder temperature control is described in which a Pt sheathed thermocouple is used as the sensing element. Optical pyrometers are also described.

Instrumentation for the Production of Hexachlorocyclohexane

A. B. GREVENSTUK and A. H. VAN GORCUM, *Philips Serv. Sci. & Ind.*, 1958, **5**, (6), 77-83

Hexachlorocyclohexane is used both as an insecticide and as starting material in various syntheses. It is prepared commercially by the photochemical addition of chlorine to benzene. The control of temperature and pressure during the reaction is extremely important. The temperature is accurately measured and controlled by installing three Pt resistance thermometers in each reaction vessel and connecting these to a 12-point recorder with a measuring range of 15-65°C. An alarm signal is set off if any ther-

meter is reading too high or too low. The resistance elements are mounted in the glass reaction vessel by means of tubes protruding to the inside.

Intercomparison of Eleven Resistance Thermometers at the Ice, Steam, Tin, Cadmium and Zinc Points

E. H. MCLAREN, *Canad. J. Physics*, 1959, **37**, (4), 422-432

Eleven standard thermometers comprising three different types of construction were compared. Temperature coefficients determined from measurements at the ice, steam and Zn points were used to calibrate the thermometers for measurements at the Sn and Cd points. The precision of measurement was $\sim 0.0002^{\circ}\text{C}$ at each fixed point. No significant error in the readings with any thermometer was observed. Since the quadratic resistance-temperature relations were used in these calculations their applic-

ability to Pt resistance thermometers in this range is verified. The results also indicate the reliability of the liquidus points of In, Sn and Cd as precision alternatives to the steam point on the International Temperature Scale.

Equipment Used for Vacuum Melting and Casting in the Iron and Steel Industry

A. S. D. BARRETT and M. E. HARPER, *J. Iron Steel Inst.*, 1959, **191**, (4), 366-374

Vacuum metallurgy is being used in the production of specialised alloys. The development of a 56 lb furnace for research and pilot-plant work and one of 5 cwt for production work is described. Equipment used in the operation and control of such furnaces is outlined. Temperature measurement of the melt is carried out by means of two 5% Rh-Pt/20% Rh-Pt immersion thermocouples. Using molybdenum-alumina sheaths up to 30 dips can be achieved without replacement of the sheath.

NEW PATENTS

Production of Tetracyclonitrile

AMERICAN CYANAMID CO. *British Patent* 808,701

Tetracyclonitrile is prepared by reducing chlor- or brom-tetracyclonitrile by hydrogenation in the presence preferably of a Pd-charcoal catalyst and an inert organic solvent such as methyl "Cellosolve" (RTM).

Electrodeposition of Rhodium

THE MOND NICKEL CO. LTD. *British Patent* 808,958

In order to reduce or prevent cracking of a rhodium deposit, deposited from an aqueous electrolyte composed mainly of rhodium sulphate, rhodium phosphate, rhodium fluoborate or a mixture of any of them, selenic acid or an alkali metal salt thereof is added to the electrolyte, preferably in the amount of 0.4 to 1 g/l.

Combustible Gas Indicator

MINE SAFETY APPLIANCES CO. *British Patent* 809,215

In a combustible gas indicator comprising a detector filament heated electrically and electrical means responsive to the increase in temperature of the filament, the filament is formed of a coil of Pt having a narrow band at the mid-section surrounded by a thin adherent coating of glass of melting point above the operating temperature of the coil.

Organochlorosilanes

MIDLAND SILICONES LTD. *British Patent* 809,317

Reference is made to the use of activated Pt on

charcoal (5% by wt. of Pt) in the preparation of organochlorosilanes.

Reduction of Carbonyl Compounds

SOC. DUMONT FRERES ET CIE. *British Patent* 809,339

A carbonyl compound, i.e. aldehyde, hydroxyaldehyde, ketone or hydroxyketone, is reduced to form the corresponding alcohol by catalytic hydrogenation in the presence of a non-soluble anion-exchange resin. Pd or Pt oxide may be used as catalyst.

Preparation of Carboxylic Acid Esters

E. I. DU PONT DE NEMOURS & CO. *British Patent* 809,496

Carboxylic acid esters are made by reacting carbon monoxide, a non-aromatic unsaturated hydrocarbon (each carbon atom bonded directly to only one other carbon atom) and a monohydric primary or secondary alcohol in the presence of a catalyst comprising a combination of an alcohol-soluble salt of Sn or Ge with an alcohol-soluble salt of a Group VIII noble metal at 30-325°C and pressure of 100-1000 atm. The catalyst may comprise tin chloride and platinum chloride or chloroplatinic acid. Palladium chloride or ruthenium dioxide may also be used.

Upgrading of Gasoline

UNIVERSAL OIL PRODUCTS CO. *British Patent* 809,635

Reference is made to the use of a supported Pt catalyst in a process for upgrading gasoline. A