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Electrodeposition of Platinum Metals from Molten Cyanides

A technique applicable to electroforming

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Platinum, palladium and iridium coatings have been electrodeposited on a variety of substrates from molten cyanides and the techniques, which are described in this paper, have also been used to electroform platinum and iridium crucibles. While the platinum and palladium electrolytes were prepared and used in vessels open to the atmosphere the molten iridium cyanide baths were kept under argon.

Atkinson (1), Withers and Ritt (2, 3), and Rhoda (4) described the electrodeposition of platinum group metals from molten cyanides under atmospheres of nitrogen or argon. However, the available information about the apparatus used in these experiments raises the possibility that the atmospheres over the molten electrolytes were not completely free of air. Later, work done by the Bureau of Mines in sealed systems showed that satisfactory deposits of iridium and rhodium do require an inert atmosphere (5, 6). On the other hand, good, thick deposits of platinum and palladium were made only in the presence of air (7, 8). Methods developed by the Bureau of Mines for electrodeposition of platinum, palladium, and iridium are described in this paper. A picture showing the tips of crucible tongs coated with platinum and electroformed crucibles of platinum and iridium appeared in an earlier issue of this Journal (9) and the Metals Research Department of Degussa, Frankfurt, Germany, has also shown objects plated with platinum in a molten cyanide bath (10).

Experimental Method

Platinum, palladium, and iridium were electrodeposited from molten sodium cyanide or from 50-50 weight per cent mixtures of sodium cyanide and potassium cyanide to which the metal ions had been added. The electrodeposition of platinum and palladium and the preparation of the corresponding electrolytes were done in vessels open to the atmosphere. Iridium electrolyte was prepared and used under argon.

Reagent grade sodium cyanide and potassium cyanide were used in preparing electrolytes. After drying the salts in a vacuum oven at 120°C for 2 hours, the metal ions were added by D.C. electrolysis using an anode of the particular platinum group metal and a cathode of the same metal or of molybdenum. Coatings were generally made with electrolytes that contained 1 to 3 per cent of the metal. Initially, the electrolyte temperature was 600°C for sodium cyanide and 550°C for sodium cyanide-potassium cyanide. When the electrolyte was prepared and used in contact with air, some of the cyanide was oxidised to cyanate and carbonate. The melting points of these baths decreased as the compositions changed and, consequently, they were operated at decreasing temperatures, generally 25 to 50°C above the melting point. Since the iridium cyanide bath was always kept in an inert atmosphere when molten, its operating...
Fig. 1 An Inconel rod, 0.32 cm diameter, and a 0.64 cm diameter Inconel-sheathed Chromel-Alumel thermocouple with platinum coatings of 9.5 mils and 6 mils, respectively.

Temperature remained constant.

Mullite crucibles with volumes of 250 to 400 ml were used to contain the electrolyte and the electrodes. They were, in turn, positioned in an Inconel pot, which was heated in a resistance furnace. Cathodes were often in the form of sheet, 0.25 inch wide and 1 or 2 inches long, but coatings were also put on short rods, the tips of laboratory tongs or forceps, and thermocouple sheaths. Crucibles were electroformed. The cell usually had two anodes of the metal being plated, each 0.25 inch wide. These were immersed to a depth of 1 inch and positioned one on each side of the cathode. When the cathode had a shape other than that of a simple rod or sheet, it was surrounded by three or more sheet anodes. Cathode current densities varied from 5 to 30 mA/cm² and anode current densities varied from one-quarter to twice the cathode current density. Cell voltages were about 0.8 volt during the initial periods of platinum or palladium electrolyte formation and 0.1 to 0.2 volt when electrodepositing coatings of these metals at current densities of 10 to 20 mA/cm². Cathodes were generally rotated at 120 rpm during electrodeposition and the direction of rotation was reversed every 30 minutes. However, cathodes with special shapes were sometimes kept stationary.

Prior to electrodeposition, metal cathodes were prepared by wet pumicing, washing in distilled water, rinsing in ethyl alcohol, and drying in a flow of warm air. When successive deposits were made on the same cathode, the coating was smoothed between deposition periods by removing loose material, filing off dendrites, and polishing with 240-grit emery paper. The total quantity of electricity used for electrodeposition was measured with a copper coulometer and the number of coulombs thus determined was used in calculating both the cathode and the anode current efficiencies.

Platinum

Bright, smooth, and adherent deposits of platinum were made on molybdenum, tungsten, Inconel, columbium, stainless steel, and copper and on graphite precoated with palladium. Cathode current efficiencies were
as high as 76 per cent on the basis of bivalent platinum ions; apparent anode current efficiencies were 98 to 150 per cent. Many deposits were approximately 63.5 μm (2.5 mils) thick and were made at the rate of 12.6 to 20.2 μm (0.5 to 0.8 mil) per hour. Much thicker coatings were sometimes made by putting successive deposits on the same cathode, with removal of loose material, smoothing, and pumicing the surfaces between deposits. Attempts to form platinum coatings in inert atmospheres resulted in thin deposits at very low current efficiencies.

Figure 1 shows a 0.32 cm diameter Inconel rod and a 0.64 cm diameter Inconel sheathed Chromel-Alumel thermocouple with platinum coatings. The 241 μm (0.5 mils) coating was put on the rod in four plating periods with a total time of 16.83 hours (rate, 14 μm/h). A freshly prepared platinum–sodium cyanide electrolyte was used. The 152 μm (6 mils) coating was put on the thermocouple in two plating periods with a total time of 9 hours (rate, 17 μm/h). The platinum–sodium cyanide electrolyte in this case had been in use for 115 hours before this coating was made; it was maintained by occasional additions of fresh sodium cyanide. Neither of these objects was rotated during the electrodeposition. The cathode current densities were 10 to 14 mA/cm² and the current efficiencies were 74 to 71 per cent, respectively. The coatings thus formed were bright, smooth and adherent.

Molybdenum rods, 0.64 cm in diameter and 2.22 cm long, were encapsulated first with 63.5 μm (2.5 mils) of iridium as a diffusion barrier and then with 101 μm (4 mils) of platinum. Iridium was electrodeposited from an electrolyte that had been in use 45 hours, and platinum from one with 100 hours of use.

**Platinum Coatings on Graphite**

The graphite surfaces were cleaned with ultrasonic agitation, first in a solution containing sodium hydroxide, sodium phosphate, sodium carbonate, and a wetting agent and then in boiling water. Before platinum coatings were put on, the surfaces were precoated with 1 or 2 mils of palladium from an aqueous bath (palladium chloride, 50 g/l; hydrochloric acid, 400 ml/l; ammonium chloride, 20 g/l). Protective coatings of platinum, 4.5 to 7 mils thick, were then applied as previously described. The precoat prevents the rapid absorption of molten salt when the sample is first placed in the bath. If this is allowed to happen, considerable quantities of salt will be trapped under the platinum coating. Later, when the specimen is heated, the salt will melt and rupture the coating, exposing the graphite to oxidation. Figure 2 shows a graphite rod encapsulated with a precoat of palladium and 114 μm (4.5 mils) of platinum. Such encapsulated specimens were evaluated in a thermogravimetric apparatus. It was found that they lost an average of 3 mg per hour at 1400°C and that the coatings were still adherent and effective after several hours at this temperature. Similar graphite specimens without coatings lost 120 mg per hour at a temperature of 600°C.

**Palladium**

Bright, smooth, adherent deposits of palladium were made on molybdenum or graphite. Figure 3 shows a 4.5 mil deposit of palladium on a molybdenum rod. Temperatures varied from 575 to 445°C for the sodium cyanide-potassium cyanide baths. Cathode current efficiencies ranged from 35 to 70 per cent on the basis of the discharge of bivalent palladium ions. Apparent anode current efficiencies were 120 to 140 per cent when the cathode and anode areas were equal, and 300 to 400 per cent when the anode area was about 4 times the cathode area. The presence of air was found to be essential for the formation of good deposits, but again there was oxidation of cyanide, and in palladium baths this oxidation was rapid. After the first few hours of electrolysis, there was a steady accumulation of white, flocculent material in the bath, chiefly sodium carbonate. Later, there was also some finely divided palladium metal. As these changes occurred,
the palladium deposits became less adherent. Eventually, in 10 to 20 hours, the bath became inoperable.

**Iridium**

The electrodeposition of iridium in adherent, compact form from molten sodium cyanide baths at 600°C under an argon atmosphere was described by Andrews and others (5). Only thin deposits, often cracked and non-adherent, were formed when these processes were conducted in the presence of air. In experiments performed after the paper by Andrews and others was prepared, deposits of iridium were made on nickel, Inconel, copper, molybdenum, AM 353 steel, and 403 steel. The cathode current densities were usually 20 to 30 mA/cm² and the anode current density was 15 mA/cm². The deposits were up to 63.5 μm (2.5 mils) thick. Cathode current efficiencies were usually 25 to 40 per cent, assuming the discharge of trivalent...
iridium ions; deposition rates were about 10 µm (0.4 mil) per hour. However, in one group of experiments 2.5 µm (0.1 mil) deposits were made on nickel discs with cathode current efficiencies up to 66 per cent. Apparent anode current efficiencies were sometimes less than 100 per cent, but more often they were 120 to 150 per cent. The best deposits of iridium were made when the cathode was rotated at 120 rpm. Deposits made on stationary cathodes were often cracked and non-adherent; deposits on cathodes rotating at 30 rpm were better, but even these had some loose material.

Electroforming

Platinum and iridium crucibles were electroformed from molten cyanide baths by the electrodeposition methods previously described, using mandrels of copper for platinum and of molybdenum for iridium. The general procedure was to electroplate the platinum group metal on the mandrel to the desired thickness in a series of successive deposits, with careful grinding and polishing of the surface between deposition periods. The initial deposit of platinum or iridium was always made over the entire surface of the mandrel, including the top. Later deposits were made on enough of the mandrel surface to give a crucible of the desired depth. When the deposit reached the desired thickness the top of the piece was cut away and the mandrel was dissolved away with nitric acid.

Crucibles electroformed in this way are shown in Figure 4. Crucible (A), made of iridium, is 0.75 inch deep and has a 1 inch inside diameter with a 5 mil wall thickness. Crucible (B) is of platinum; it is 1 inch deep, the inside diameter is ½ inch, and the wall thickness is 5 mils. Crucible (C) is also made of platinum and has a thermocouple well for differential thermal analysis work. This crucible is ½ inch deep with a ½ inch inside diameter and a wall thickness of 15 mils.

References
1 R. H. Atkinson, U.S. Patent 2,093,406; 1937
4 R. N. Rhoda, Plating, 1962, 49, (1), 69
10 Platinum Metals Rev., 1975, 19, (1), 15

Catalysts for Removing Oxygen from Stack Gases

A number of processes have been developed for the removal of air pollutants such as nitric oxide and sulphur dioxide from stack gases and one of these catalytically reduces the pollutants with carbon monoxide. Stack gases generally contain 1 to 3 per cent oxygen and there are a number of reasons why it is necessary to remove this prior to the gas entering the main catalytic reactor.

Ajay Sood, C. W. Quinlan and J. R. Kittrell of the University of Massachusetts have reported a comparison of the activities of several catalysts for the reduction of oxygen with carbon monoxide, both in the presence and in the absence of sulphur dioxide (Ind. Eng. Chem., Prod. Res. Dev., 1976, 15, (3), 176-179). Although initial testing of the catalysts was done using dry cylinder gas, three catalysts were also evaluated using wet flue gas.

The results demonstrated that in the presence of sulphur dioxide, of which 2500 ppm are typically present in stack gases, supported platinum and palladium catalysts were superior to the others tested. It is concluded that both alumina supported platinum and palladium have potential for the removal of oxygen from stack gases. The relative activity of these two was difficult to compare because of the experimental conditions; the platinum being supported on monolithic alumina while the palladium was on pellets.
Production of Optical Glass Fibres

ION EXCHANGE IN A DOUBLE PLATINUM CRUCIBLE

Since the development of the laser the concept of using optical fibres for telephone transmission has received a great deal of attention, but the manufacture of such fibres to the necessary standards has presented difficulties. A fibre for optical communication must not permit excessive radiation to escape sideways, absorption and scattering losses must be minimal, and the shape of the light pulse must be preserved over long distances.

Doped silica glass can be employed, but an alternative procedure involving the use of soft multi-component glasses is also satisfactory, while the techniques of conventional glass manufacture can be used in the latter case, employing a double crucible in pure platinum.

A report from Philips Research Laboratories at Eindhoven (H. J. M. van Ass, P. Geitnner, R. G. Goesink, D. Küppers and P. J. W. Severin, Philips Tech. Rev., 1976, 36, (7), 182-189) describes a double-crucible method in which two different glasses are employed on a continuous basis—an obvious advantage for commercial production. Two types of multi-component glass of different refractive indices are used, the glass with the higher refractive index forming the core of the fibre while the other forms the cladding.

Both the glass manufacture and the fibre-drawing process are carried out in dust-free clean rooms. The raw materials, of high purity, are first melted in a platinum crucible, purified gas being blown through the melt to improve its homogeneity. Rods of circular cross-section, about 5 mm in diameter, are then drawn upwards through rollers.

The final production is carried out in the double platinum crucible, as shown in the diagram. Rods of the core glass are fed into the inner crucible and rods for the outer layer into the outer crucible. Melting must be conducted slowly and at a temperature sufficiently high to prevent bubble formation.

The glasses then flow out at about 800°C, and the required ion exchange between core and cladding takes place in the region between the outlets of the inner and outer crucibles where the rate of flow is very low. This composite glass is then drawn to 100 μm fibres.

The double platinum crucible for the production of optical glass fibres. The inner rod of alkali-germanosilicate glass has a high Na⁺ ion content and a high refractive index, while the outer rod of the same glass but with a high K⁺ ion content has a low refractive index. Between the outlets of the concentric crucibles there is an exchange between the Na⁺ and the K⁺ ions, giving a smooth variation of the refractive index profile in the resulting fibre.
Palladium Alloys for Hydrogen Diffusion Membranes

A REVIEW OF HIGH PERMEABILITY MATERIALS

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Group Research Centre, Johnson Matthey & Co Limited

The unique properties of palladium enable it to be used, either alone or more generally alloyed with silver, for hydrogen diffusion membranes. Recently palladium alloys containing rare earth metals have been described and some of them show considerable promise for this purpose.

Palladium holds a unique position among the metallic elements in being able to take into solution large quantities of hydrogen while simultaneously retaining a high degree of ductility. These attributes coupled with the high mobility or rate of diffusion of hydrogen in the lattice have been exploited in the use of palladium and subsequently of palladium-based alloys as hydrogen diffusion membranes. Earlier articles in this Journal (1, 2) have described the application of this principle to commercial diffusion units for the production of high purity hydrogen, and more recently to a hydrogen generator for military requirements (3). In these applications the permeability of the palladium alloy to all other gases at the operating temperatures is so low as to be negligible in practice, and the alloy therefore functions as a highly specific filter for the production of ultra-pure hydrogen, or for removing hydrogen from mixed process gases.

A limitation to the use of pure palladium for hydrogen diffusion has its basis in the pressure-concentration isotherms for the palladium-hydrogen system shown in Figure 1 (4). At temperatures below 300°C and pressures below 20 atm, increasing the hydrogen concentration leads to the formation of the β phase which can coexist with the α phase. The β phase has a considerably expanded lattice compared with α, for example a hydrogen/palladium ratio of 0.5 results in an expansion of about 10 per cent by volume. Nucleation and growth of the β in the α matrix therefore sets up severe strains in the material resulting in distortion, dislocation multiplication and hardening. After a few hydrogenation/dehydrogenation cycles splitting of the diffusion membrane may occur.

One method whereby the phase change can be avoided is to ensure that the palladium diffusion membrane is always operated in the single phase region of the Pressure-Composition-Temperature diagram (5). This may be achieved by maintaining the temperature above the critical value of 300°C as long as the membrane is in a hydrogen atmosphere, or by ensuring that cooling is allowed only when it is in a dehydrogenated condition with the hydrogen pumped from the system. Such expedients do not, of course, avoid the volume changes that inevitably occur, but in a single phase region the composition varies smoothly and the distortion phenomena associated with nucleation and growth are circumvented.

With these limitations in mind it is nevertheless possible to operate pure palladium membranes successfully for the large scale separation of hydrogen from mixed gases. Diffusion installations in the Union Carbide Corporation with individual outputs of 9 million cu ft/day have been described (6).
To overcome the drawbacks of pure metal as a membrane material, the alloying of palladium may be considered as having the following objectives. First it is desirable that the α-β phase transition should be suppressed in the alloy so that distortion is avoided. The permeability of the alloy should also be as high as possible, preferably above that of palladium, and the mechanical characteristics should be such that it can be worked to thin foil or tubing for use in diffusion units. The success of palladium as a membrane is closely connected with the catalytic activity of the surface, allowing the ready absorption and dissociation of the hydrogen molecule, and it is further desirable that the alloy should be tolerant to poisoning by impurities in the hydrogen. A large number of palladium systems have therefore been studied and described in the literature, claiming alloys with one or more of these desirable features. A selection of some of the more important of these will be considered in this brief review, and the pertinent data is summarised in the Table. For comparison purposes permeability figures are given in the table based on 350°C and 300 psi, these being typical operating conditions for commercial hydrogen diffusion cells. In this review all permeability values are given in cm³/cm²/s, referred to membranes 0.025 mm (0.001 in) thick at the pressures and temperatures specified.

Palladium-Silver Alloys

The breakthrough in hydrogen diffusion technology came with the discovery by Hunter (7) that when 20 per cent or more silver is added to palladium, the resulting alloy is dimensionally stable and does not distort on cycling in hydrogen (8). It is now well established that this is the result of the α-β miscibility gap being depressed to well below room temperature. Further and unexpectedly it was found that silver increased markedly the permeability of palladium to hydrogen. The variation of diffusion rate with silver content is indicated in the Table. The rate is found to reach a maximum at around 23 to 25 per cent silver and alloys of this composition are normally used in diffusion units. The permeability of these alloys is nearly double that of pure palladium, but falls with increasing silver content to about 10 per cent of the latter at 50 per cent silver.

It may be of interest to consider the particular features of palladium-silver alloys which give rise to the high observed permeabilities. The flow of gas by diffusion through a membrane is governed by Fick's law and the rate may be expressed in the form:

\[ V = K \frac{a}{t} DX \]

where \( V \) is volume of hydrogen diffusion per unit time,

\( K \) is constant,

\( a \) = membrane area,

\( t \) = membrane thickness,

\( D \) = diffusion coefficient,

\( X \) = concentration gradient (dc/dx in Fick's equation).

The product DX is therefore related to the permeability of the membrane. Almost without exception the value of D for palladium is decreased on alloying, and this holds for palladium-silver alloys (9). Consequently high permeabilities will only result if a high concentration gradient can be established in the alloy. The solubilities of hydrogen were measured in early work by Sieverts and others.

![Image](https://via.placeholder.com/150)
Permeability of Miscellaneous Palladium Alloys to Hydrogen at 350°C, 300 psig

<table>
<thead>
<tr>
<th>Material weight per cent</th>
<th>Permeability cm³/cm²/s</th>
<th>Remarks</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palladium</td>
<td>1.43</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>80Pd-20Ag</td>
<td>2.46</td>
<td>Hydrogen output maximum at 20 to 25 per cent Ag.</td>
<td></td>
</tr>
<tr>
<td>77Pd-23Ag</td>
<td>2.48</td>
<td></td>
<td></td>
</tr>
<tr>
<td>70Pd-30Ag</td>
<td>1.46</td>
<td></td>
<td></td>
</tr>
<tr>
<td>48Pd-52Ag</td>
<td>0.13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>95Pd-5Au</td>
<td>1.52</td>
<td>Small increase in permeability at low Au contents. Alloys more resistant to sulphur poisoning.</td>
<td>12</td>
</tr>
<tr>
<td>80Pd-20Au</td>
<td>1.37</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60Pd-40Au</td>
<td>0.60</td>
<td></td>
<td></td>
</tr>
<tr>
<td>45Pd-55Au</td>
<td>0.13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>90Pd-10Cu</td>
<td>0.69</td>
<td>Sharp maximum in output at 40 per cent Cu, corresponding with ordered β-phase in Pd-Cu system.</td>
<td>13</td>
</tr>
<tr>
<td>70Pd-30Cu</td>
<td>0.12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60Pd-40Cu</td>
<td>1.52</td>
<td></td>
<td></td>
</tr>
<tr>
<td>55Pd-45Cu</td>
<td>0.25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>45Pd-55Cu</td>
<td>0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>99.5Pd-0.5B</td>
<td>1.35</td>
<td>Interstitial boron tends to block lattice sites.</td>
<td>12</td>
</tr>
<tr>
<td>90Pd-10Ni</td>
<td>0.27</td>
<td>Low permeabilities for Fe, Ni, Ru, Pd and Rh additions.</td>
<td>12</td>
</tr>
<tr>
<td>95Pd-5Ru</td>
<td>0.47</td>
<td></td>
<td></td>
</tr>
<tr>
<td>65Pd-30Ag-5Pt</td>
<td>—</td>
<td></td>
<td>20</td>
</tr>
<tr>
<td>68Pd-30Au-2Ru</td>
<td>—</td>
<td></td>
<td></td>
</tr>
<tr>
<td>85Pd-13Ag-2Ni</td>
<td>—</td>
<td>Examples of wide range of complex alloys claimed in literature.</td>
<td>21</td>
</tr>
<tr>
<td>70Pd-20Ag-10Rh</td>
<td>—</td>
<td></td>
<td></td>
</tr>
<tr>
<td>73Pd-24Ag-3Au</td>
<td>—</td>
<td></td>
<td>22</td>
</tr>
<tr>
<td>Pd-20Ag-5Au-1.26Ru</td>
<td>—</td>
<td></td>
<td></td>
</tr>
<tr>
<td>68Pd-25Ag-5Au-2Ru</td>
<td>—</td>
<td></td>
<td>23</td>
</tr>
<tr>
<td>Pd-10Ag-1Au+0.1 each of Ru, Al, Pt.</td>
<td>—</td>
<td></td>
<td></td>
</tr>
<tr>
<td>92.3Pd-7.7Ce</td>
<td>2.24</td>
<td>The higher Ce alloy is prone to poisoning by oxidation.</td>
<td></td>
</tr>
<tr>
<td>87.3Pd-12.7Ce</td>
<td>1.27</td>
<td></td>
<td></td>
</tr>
<tr>
<td>93.4Pd-6.6Y</td>
<td>4.99</td>
<td>Estimated from 200 psi results by the $\sqrt{P}$ (Sieverts Law) relationship.</td>
<td>25</td>
</tr>
<tr>
<td>90Pd-10Y</td>
<td>5.38</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
and the results obtained are illustrated in Figure 2. The exceptionally high peak occurring in the palladium-silver system contrasts markedly with the more usual behaviour exemplified in the palladium-gold and palladium-platinum alloys. As a result the DX product for palladium-silver is high and accounts adequately for the large hydrogen throughputs for alloys in the 20 to 25 per cent silver range.

Gold and copper are, like silver, elements from Group 1B of the Periodic Table, and have therefore received a good deal of attention as alloying elements in palladium. Some slight enhancement of permeability has been reported for small gold additions by McKinley (12) but above 20 per cent the permeability is reduced. However, the gold-containing alloys were shown to be more resistant to poisoning by sulphur in the ingoing gas than palladium-silver. Consequently although these alloys do not appear to have been widely used they could be advantageous if sulphur is present in the feed gas to the diffusion unit.

Initial additions of copper cause a similar reduction in permeability, but at copper contents near 40 per cent, a sharp maximum occurs (13). This maximum is associated with the ordered body centred cubic β-phase which forms in the palladium-copper system. In earlier work by Piper (14) the diffusion coefficients for hydrogen in these alloys were measured. The ordered β-CuPd phase was found to have the highest room temperature diffusivity of any metal-hydrogen system, that is $D_{22{}^\circ{}C}=2\times10^{-5} \text{ cm}^2/\text{s}$ compared with a value of $2\times10^{-7} \text{ cm}^2/\text{s}$ for pure palladium. Unfortunately although the diffusion coefficient is extremely high, the hydrogen solubility is reduced to a low value on alloying with copper (15). As a consequence the permeability which is proportional to the DX product passes through a peak but without attaining values much in excess of unalloyed palladium.

Boron additions as a means of increasing

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*Fig. 2 Solubility of hydrogen in various palladium alloys at 1 atmosphere. The high hydrogen solubility in palladium-silver system contributes to high permeability of these alloys*
the permeability have been suggested on several occasions (16, 17, 18) but in general the results obtained are not significantly better than with pure palladium. Boron is a relatively small atom and enters the palladium lattice in octahedral interstitial sites. The boron atoms therefore cause a net expansion of the lattice and it has been argued that this expansion will result in a more open network of palladium atoms for the diffusion of hydrogen. Against this, boron occupies and thereby blocks a number of interstitial sites which are no longer available for hydrogen transport. Diffusion coefficients measured by Allard and co-workers (17) were shown to fall off much more rapidly with increasing boron content than for substitutional alloys, indicating that the blocking of lattice sites is the dominating effect.

Many isolated observations have been reported on the effect of a wide range of other elements when added to palladium, including iron, nickel, ruthenium, platinum (8) and chromium (19), together with various ternary and more complex alloys, for example (20, 21, 22 and 23), but no material significantly better than palladium-silver had emerged until the recent Birmingham University work on rare earth metals in palladium.

**Palladium-Rare Earth Alloys**

This work indicates that high permeabilities and dimensional stability are shown by alloys of palladium with certain of the rare earth metals. In spite of large atomic diameter differences in the systems, the solid solubility of these metals in palladium is anomalously high, and the behaviour of some of these solid solution alloys has been assessed for diffusion membranes. For example, the size difference for the palladium-yttrium system is 29 per cent, but nevertheless the solubility limit is 12 atomic per cent.

The palladium-cerium alloys (24) were among the first to be studied, but at low pressure differentials across the membranes. The initial claims of high permeabilities for these alloys, well in excess of those for palladium-silver, were not substantiated by subsequent measurements made in the laboratories of Johnson Matthey. For the latter the palladium-cerium alloys were made by arc melting, and worked to sheet 0.25 mm thick. Two compositions were studied, 7.7 and 12.7 per cent cerium (6 and 10 atomic per cent respectively) and permeability results compared directly with similar membranes of palladium-23 per cent silver alloy. The materials were tested over a wide range of conditions of practical interest, up to 500°C and 600 psig.

An example of the results obtained is shown in Figure 3. The plots for the 7.7 per cent cerium alloy and the silver-palladium alloys were obtained after the membranes were fully conditioned by heating and cooling over several cycles, and were therefore reproducible. The hydrogen throughput of the 7.7 per cent alloy is seen to be about 25 per cent lower than silver-palladium over the range studied. The 12.7 per cent cerium alloy showed quite different behaviour. For this material the membrane could not be conditioned satisfactorily and the curve given in
Figure 3 is for the initial heating cycle of this alloy. The diffusion rate increased as expected up to 350°C but started to fall off to a low value on heating to higher temperatures. After cooling and repeating the heating there were no indications that recovery of the permeability to hydrogen occurred. When removed from the cell it was found that this membrane had discoloured on the hydrogen inlet side, and it appeared likely that the fall-off in performance was due to oxidation of the alloy with the formation of an impervious layer of cerium oxide, caused by hydrogen impurities.

The poisoning of this alloy by oxidation was overcome by coating the membrane with 500Å of palladium applied by vacuum evaporation. Subsequent to this treatment reproducible results were obtained for this material also, as shown in Figure 4, but the permeability proved to be lower than the 7.7 per cent alloy.

A subsequent and more promising development has recently been reported in which palladium-yttrium alloys have been shown by the Birmingham workers to be considerably more permeable than palladium-silver (25). Measurements were made over a wide range of temperatures and pressures, with results typified by the comparative permeability plots shown in Figure 5. Hydrogen throughput for the alloys of 6 to 10 per cent yttrium are seen to be about 50 per cent higher than for palladium-25 per cent silver tested under the same conditions.

A further advantage claimed for the yttrium alloys is that they are less susceptible to poisoning by oxidation than the cerium alloy of the earlier work. Evidence from scanning electron micrographs indicates that Y₂O₃ formation results in a flaky surface layer of
oxide over a substantially pure palladium layer on the alloy surface. The non-coherent form of this oxide hence does not act as a barrier for hydrogen diffusion.

In these investigations a curious behaviour was reported in the results obtained at pressures below 100 psi for both the yttrium and silver alloys. As shown in Figure 6, a pronounced maximum permeability was present at some intermediate temperature, rather than the steady increase which normally occurs. Behaviour of this type had not previously been reported for palladium-silver alloys and is not observed in commercial diffusion units, but may occur, as for example in the palladium-cerium alloys, under conditions where some poisoning effect is present. In the work reported it is most likely that inadequate flow of gas through the inlet side of the test cell was responsible for this anomaly. Even though high purity cylinder hydrogen was used it would appear that some blanketing of the membrane has occurred, due to the accumulation of impurities. This behaviour is obviously absent in the measurements at higher pressures, where good agreement is obtained at all temperatures with earlier results such as those of Darling (26). A comprehensive review of contaminants in the hydrogen and their effect on permeability determinations has recently been published by Musket (27) these should be fully recognised if consistent results are to be obtained.

Consequently the palladium-yttrium alloys represent a considerable advance in the technology of hydrogen diffusion alloys and could lead to more effective utilisation of palladium in diffusion units. The rare earth alloys are also considerably harder and stronger than palladium-silver, which may be advantageous in the practical applications of these alloys. It remains to be seen, however, whether this extra strength will lead to problems in processing the material. The palladium-silver alloy used as thin walled tubes in the current range of Johnson Matthey diffusion units is a reliable and well-proven material, and by normal metallurgical standards is relatively easy to fabricate. Nevertheless, in the production of the thin walled tubes careful and critical working procedures are required to yield a consistent high quality product. The extra hardness of the palladium-yttrium alloys may make comparable fabrication difficult, and further work is obviously necessary on this aspect, together with the studies of the long-term stability and oxidation resistance of these materials.

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Alloying Stainless Steels with the Platinum Metals

INCREASED RESISTANCE TO CORROSION IN ACIDS

By Michael A. Streicher
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One of the earliest investigators of stainless steels, P. Monnartz (1), reported in 1911 that the rapid corrosion of iron-chromium alloys in certain acids can be suppressed either by winding a platinum wire around the corrosion-test specimen or by adding platinum as an alloying element to the steel. Contact or alloying with platinum changes the electrode potential of the corroding alloy in the positive (noble) direction. A sparingly soluble, protective, hydrated oxide film is formed on the surface of the metal which then becomes "passive". The rate of corrosion is then governed by the solubility of the oxide film in the acid. At those discrete points in the surface at which the film is dissolved, iron and chromium go into solution and react with the environment to form new oxides which repair the break in the passive film. Thus, the passive state is a dynamic, not a static or inert condition, and a continuing, small amount of metal dissolution (corrosion) is required to maintain it.

During the last 25 years Russian investigators, in particular N. D. Tomashov and G. P. Chernova, have studied the effect of alloying additions of platinum and palladium on the dissolution of stainless steels in various acids. Their publications up to 1956 were summarised by T. P. Hoar (2) in this Journal. Additions of 0.1 to 0.5 per cent platinum and 0.1 to 1.0 per cent palladium to iron-18 per cent chromium-9 per cent nickel and to iron-27 per cent chromium stainless steels reduced corrosion of these alloys in 20 to 50 per cent sulphuric acid at 20°C by as much as 99.85 per cent. These noble metal additions also were found effective in suppressing corrosion in boiling formic and acetic acids. The following is a brief summary of more recent studies on the effect of noble metals in stainless steels.

Since 1956 Tomashov, Chernova and their colleagues have concentrated their attention on the use of palladium additions to various stainless steel compositions in order to reduce corrosion in acids. It was found that an alloy of iron-24 per cent chromium-6 per cent nickel with 0.5 per cent palladium remains passive in 10 per cent sulphuric acid solution up to 100°C (3). Their findings on an alloy of iron-25 per cent chromium-3 per cent molybdenum with 0.5 per cent palladium led to a recommendation of this composition for use in hydrochloric acid solutions up to 1.6 per cent at temperatures up to 100°C. Recently they reported (4) that an iron-40 per cent chromium alloy with 0.2 per cent palladium is resistant to boiling 1 per cent hydrochloric and 40 per cent sulphuric acid at 100°C. The beneficial effects of additions of up to 1 per cent palladium were confirmed by Biefer (5) and by Agarwala and Biefer (6) using an iron-17 per cent chromium stainless steel with and without 2 per cent molybdenum, in converting these alloys to the passive state during exposure to 10 per cent sulphuric acid up to the boiling point.

Earlier this year, Tomashov et al (7) described the effect of palladium additions to austenitic 25 per cent chromium-3 per cent nickel-2 per cent molybdenum-0.8 per cent manganese steels containing up to 1 per cent nitrogen. The alloys were made by plasma
arc melting which makes it possible “to melt steels with nitrogen contents 1.5 to 2 times higher than the standard solubility level of nitrogen in steel of a specific composition at the liquidus temperature”. Such nitrogen contents greatly increase the yield strength and make the structure completely austenitic. Additions of 0.2 per cent palladium made this alloy passive in 20 to 30 per cent sulphuric acid in the range of 20 to 100°C and in 1 to 3 per cent hydrochloric acid at 20 to 50°C. No data on the effect of high nitrogen contents or of palladium additions on other forms of corrosion were included.

To observe the accumulation of palladium on the surface of an alloy undergoing self-repassivation, Tomashov et al (8) examined surfaces in the electron microscope after exposure to 10 per cent sulphuric acid at 25°C. Upon immersion in the acid the specimens were activated by cathodic polarisation which initiated dissolution of the alloy. As the 25 per cent chromium alloy dissolved, palladium was concentrated on the surface until the electrode potential changed in the positive (noble) direction and the alloy became passive. On alloys with 0.2 and 0.5 per cent palladium, particles in the range of 200 to 600 Å were found. With increasing exposure time their number, but not their size, increased.

In connection with the development of new ferritic iron-chromium-molybdenum compositions having superior pitting and crevice corrosion resistance, Streicher (9, 10) used all of the platinum metals to produce passivity in boiling 10 per cent sulphuric acid. The effects of these alloying additions on resistance to other forms of corrosion, pitting and crevice attack in oxidising chloride solutions and stress corrosion cracking, were also determined. It was found that a ferritic alloy of iron-28.5 per cent chromium-4.0 per cent molybdenum (later referred to as the 28-4 alloy), which is ductile and weldable, resists pitting and crevice corrosion in 10 per cent ferric chloride solution up to 50°C. And, unlike the austenitic stainless steels, it also resists stress corrosion cracking in various sodium chloride tests, as well as in the severe boiling 45 per cent magnesium chloride test. It has excellent resistance to uniform or general corrosion in organic acids and in oxidising, inorganic acid solutions, but not in inorganic, reducing acids. To produce passivity in boiling 10 per cent sulphuric acid at temperatures up to the boiling point, small amounts of the six platinum metals were added as alloying elements. Some results are given in Table I.

Without noble metals, the rate of attack on the 28-4 alloy is over 52,000 mils per year. Every one of the six platinum metals when present in excess of a certain minimum concentration passivates this alloy. In agreement with previous investigators, acid corrosion is increased by the noble metals when their concentration is below that required to produce passivity. This minimum concentration required to make the alloy passive on immersion in the acid solution decreases with increasing chromium content and varies from 0.005 to 0.02 per cent, depending on the noble metal used. It is independent of the atomic weight, that is, the concentration in atomic per cent.

The determining factors are probably differences in the electrochemical properties of the six platinum metals, electrode potential, hydrogen overvoltage and exchange currents of cathodic reactions taking place on those sites in the surface where the noble metals are exposed to the solution. These electrochemical factors are probably also responsible for the differences, described below, in effects produced by the noble metals on the resistance of the 28-4 alloy to pitting and crevice corrosion. Considerably larger amounts of noble metal (0.5 per cent ruthenium, Table I) additions are required to make the alloy self-repassivating, that is to say, passivity is recovered when the specimen is activated while in the boiling sulphuric acid solution by contact with an iron rod. Passivity and self-repassivation can also be produced in the 28-4 alloy by addition of 2 per cent nickel to

Platinum Metals Rev., 1977, 21, (2)
### Table 1
The Effect of Noble Metal Additions on the Corrosion Resistance of Iron–28.5 per cent Chromium–4.0 per cent Molybdenum Alloy

<table>
<thead>
<tr>
<th>Noble metal addition Weight per cent</th>
<th>Boiling 10 per cent sulphuric acid</th>
<th>Pitting corrosion (a)</th>
<th>Stress corrosion (b)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>State</td>
<td>Corrosion rate, in mil/yr (c)</td>
<td>KMnO₄–NaCl</td>
</tr>
<tr>
<td>None</td>
<td>active</td>
<td>52,180</td>
<td>R</td>
</tr>
<tr>
<td>Platinum 0.005</td>
<td>active</td>
<td>58,000</td>
<td>R</td>
</tr>
<tr>
<td>0.006</td>
<td>passive</td>
<td>48</td>
<td>—</td>
</tr>
<tr>
<td>0.20</td>
<td>passive</td>
<td>1</td>
<td>—</td>
</tr>
<tr>
<td>Palladium 0.01</td>
<td>active</td>
<td>74,000</td>
<td>—</td>
</tr>
<tr>
<td>0.02</td>
<td>passive</td>
<td>4</td>
<td>—</td>
</tr>
<tr>
<td>0.20</td>
<td>passive</td>
<td>1</td>
<td>F</td>
</tr>
<tr>
<td>Iridium 0.01</td>
<td>passive</td>
<td>112</td>
<td>R</td>
</tr>
<tr>
<td>0.10</td>
<td>passive</td>
<td>13</td>
<td>R</td>
</tr>
<tr>
<td>Rhodium 0.005</td>
<td>passive</td>
<td>14</td>
<td>R</td>
</tr>
<tr>
<td>Osmium 0.015</td>
<td>active</td>
<td>76,600</td>
<td>R</td>
</tr>
<tr>
<td>0.020</td>
<td>passive</td>
<td>26</td>
<td>—</td>
</tr>
<tr>
<td>Ruthenium 0.015</td>
<td>active</td>
<td>62,200</td>
<td>—</td>
</tr>
<tr>
<td>0.017</td>
<td>active</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>0.02</td>
<td>passive</td>
<td>60</td>
<td>R</td>
</tr>
<tr>
<td>0.20</td>
<td>passive</td>
<td>9</td>
<td>—</td>
</tr>
<tr>
<td>0.30</td>
<td>passive</td>
<td>2</td>
<td>R</td>
</tr>
<tr>
<td>0.50</td>
<td>passive*</td>
<td>3</td>
<td>—</td>
</tr>
</tbody>
</table>

*Self-repassivating: R—Resistant; F—Fails
(a) 2 per cent KMnO₄–2 per cent NaCl at 90°C, simple immersion, 10 per cent ferric chloride, FeCl₃·6H₂O, at 50°C with crevices.
(b) Boiling (155°C) 45 per cent MgCl₂, U-bend specimen. R—no cracking after 2400 h exposure.
(c) Thousandths of an inch per year.
(d) No cracking in 26 per cent NaCl at 200°C.

This composition with the same effect on other forms of corrosion attack as that of the 0.5 per cent ruthenium addition.

None of the noble metal additions to the 28–4 alloy affected its excellent resistance to stress corrosion cracking in the severe, boiling 45 per cent magnesium chloride test, except the large addition of 0.5 per cent ruthenium. However, when this 0.5 per cent ruthenium alloy is tested in various sodium chloride environments up to 200°C, there is no cracking observed (tr).

Because the sodium chloride tests are much more like actual service environments, they are of greater significance as a guide for practical applications of these alloys than the tests in boiling 45 per cent magnesium chloride.

Without noble metal additions the 28–4 alloy resists pitting and crevice corrosion both

*Platinum Metals Rev., 1977, 21, (2)*
### Table II
Comparison of Pitting Resistance in Halide Media

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Permanganate-chloride at 90°C (a)</th>
<th>Ferric chloride at 50°C (b)</th>
<th>Bromine-bromide at room temp. (c)</th>
<th>Sodium hypochlorite at room temp. (d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AISI 316</td>
<td>F</td>
<td>F</td>
<td>F</td>
<td>F</td>
</tr>
<tr>
<td>Carpenter 20 Cb-3</td>
<td>F</td>
<td>F</td>
<td>F</td>
<td>F</td>
</tr>
<tr>
<td>Hastelloy C</td>
<td>R</td>
<td>R</td>
<td>R</td>
<td>R</td>
</tr>
<tr>
<td>Titanium</td>
<td>R</td>
<td>R</td>
<td>R</td>
<td>R</td>
</tr>
<tr>
<td>Fe-35%Cr</td>
<td>F</td>
<td>F</td>
<td>F</td>
<td>F</td>
</tr>
<tr>
<td>Fe-28%Cr-4%Mo</td>
<td>R</td>
<td>R</td>
<td>R</td>
<td>R</td>
</tr>
<tr>
<td>Fe-28%Cr-4%Mo+Pd</td>
<td>F</td>
<td>F</td>
<td>F</td>
<td>—</td>
</tr>
<tr>
<td>Fe-28%Cr-4%Mo+Rh</td>
<td>R</td>
<td>F</td>
<td>F</td>
<td>—</td>
</tr>
<tr>
<td>Fe-28%Cr-4%Mo+Pt</td>
<td>R</td>
<td>R</td>
<td>F</td>
<td>—</td>
</tr>
<tr>
<td>Fe-28%Cr-4%Mo+Ir</td>
<td>R</td>
<td>R</td>
<td>R</td>
<td>—</td>
</tr>
<tr>
<td>Fe-28%Cr-4%Mo+Os</td>
<td>R</td>
<td>R</td>
<td>R</td>
<td>—</td>
</tr>
<tr>
<td>Fe-28%Cr-4%Mo+Ru</td>
<td>R</td>
<td>R</td>
<td>R</td>
<td>R</td>
</tr>
</tbody>
</table>

R—Resistant; F—Fails.

(a) 2 per cent KMnO₄-2 per cent NaCl. (b) 10 per cent FeCl₃·6H₂O, with crevices.
(c) 54.5 per cent Br₂+20.6 per cent ZnBr₂. (d) 0.1 per cent NaClO with Teflon® crevices.

in the potassium permanganate-sodium chloride solution at 90°C and in the 10 per cent ferric chloride solution at 50°C. Well-known alloys, such as Type 316 stainless steel (iron-18 per cent chromium-9 per cent nickel-2.5 per cent molybdenum) and Carpenter 20 Cb-3 (iron-20 per cent chromium-35 per cent nickel-2.5 per cent molybdenum-3.0 per cent copper), are severely corroded in these two oxidising chloride tests, Table II. Only the nickel-base Hastelloy alloy C (nickel-16 per cent chromium-16 per cent molybdenum) and titanium are resistant. Additions of iridium, osmium and ruthenium are without effect on the pitting and crevice corrosion resistance of the 28-4 alloy in the above two pitting tests. However, even the smallest amounts of palladium, to date the most frequently used of the noble metals to produce passivity, destroy the excellent resistance to pitting of the 28-4 alloy, Tables I and II. Rhodium does not impair resistance in the potassium permanganate-sodium chloride test, but destroys it in the more severe ferric chloride test.

Some of the alloys were tested in two even more aggressive solutions, bromine in zinc bromide and sodium hypochlorite, Table II. Note that among the materials tested for comparison, only titanium is resistant in all solutions. Platinum additions to the 28-4 alloy cause it to fail in the bromine-bromide solution. Thus, of the six platinum metals only iridium, osmium and ruthenium can be used to produce passivity of stainless steels in sulphuric acid without impairing resistance to pitting and crevice corrosion in oxidising chloride and bromide environments. Of these, ruthenium, because of its lower cost, appears to be the preferred metal for producing resistance to acid corrosion in stainless steels.
Temperature Measurement and Control

THE ADVANTAGES OF METAL-SHEATHED PLATINUM THERMOCouples

The urgent need to conserve natural resources requires that the most careful appraisal be made of the many uses to which these resources are put; in particular by the industrialised countries of the world. The recent realisation that supplies of fossil fuels are not inexhaustible has prompted the investigation of many manufacturing processes where fuel savings might be achieved, and one outcome has been a better understanding of the contribution that accurate temperature measurement and control could make to both industrial efficiency and energy conservation.

At the Tempcon '77 conference held recently at Wembley, Middlesex, papers were presented covering many aspects of the control and measurement of both low and high temperatures, either directly or by remote control. In one of these papers, by P. I. Roberts of Johnson Matthey Metals, the characteristics, development and uses of platinum metal mineral insulated thermocouples were described.

Such thermocouples, insulated with refractory but sheathed in a metal—usually a platinum group metal—have a number of important advantages compared with conventional thermocouples which are both insulated and sheathed with refractory materials. These benefits include flexibility, smaller diameter, lower thermal mass so quicker response time, and superior resistance to mechanical and thermal shock.

Metal-clad thermocouples tend to be thermo-electrically less stable than refractory sheathed ones when used at temperatures above 1200°C, and this is caused by the transfer of rhodium to the negative limb, mainly from the metal sheath but also from the positive limb. Such effects can be greatly reduced in a number of ways which were described by the author.

First the quality of the insulation is a very important factor because, when sintered, it is capable of restricting the transfer of rhodium oxide in the vapour phase. Alternatively for use at higher temperatures the air in the metal sheath can be removed and replaced with an inert gas such as argon which is then sealed into the unit. For applications at particular temperatures it is possible to select platinum alloys for the thermocouple limbs so that rhodium loss has negligible effect on the electromotive force generated. By using such techniques the advantages of these thermocouples are gained and the problem of thermo-electric drift avoided.

One particularly interesting application of metal-sheathed platinum thermocouples featured in the paper was in the French nuclear industry. It was reported that no changes were detected in the thermo-electric output of platinum : 13 per cent rhodium-platinum thermocouples, enclosed in a composite sheath of 5 per cent rhodium-platinum and stainless steel, following irradiation experiments lasting 150 days. This was most interesting as prior to the quoted work it had been considered that neutron bombardment would cause rhodium to transmute to palladium, resulting in calibration drift. Work on this subject is continuing and further papers are expected shortly.
Platinum Coordination Complexes in Cancer Chemotherapy

PAPERS FROM THE THIRD INTERNATIONAL SYMPOSIUM

By M. J. Cleare
Group Research Centre, Johnson Matthey & Co Limited

The symposium which took place at the Wadley Institutes of Molecular Medicine in Dallas, Texas, embraced a wide range of scientific disciplines from platinum metal chemistry through to clinical practice and was attended by over one hundred and fifty delegates of equally diverse backgrounds. The first two days of the meeting were largely concerned with the more fundamental aspects of platinum compounds and their biological activity, while the final day was devoted to reports of clinical efficacy and protocols.

The introductory lecture by M. J. Cleare of Johnson Matthey Research Centre discussed the basic chemistry of platinum (II) complexes and related this to their biological and anti-tumour activity. Later M. L. Tobe of University College, London, covered more specific aspects of structure-activity relationships for a series of Pt(II) and Pt(IV) amine complexes of type cis-[PtA₂Cl₂] and cis-[PtA₂Cl₂] (A=organic amine). Good anti-tumour activity and selectivity was observed in animal tests with certain alkyl, alicyclic and heterocyclic amines, but aqueous solubility was too low to make them of clinical value. However, he reported that incorporation of trans hydrophilic hydroxo groups in Pt(IV) complexes of type cis-[Pt(A)₃(OH)₂Cl₂] improved the solubility and in some cases maintained the activity as well.

A number of new compounds based on amine systems with anionic groups other than chloride were described by researchers from the Wadley Institute. The compound which attracted most attention was [Pt(A)SO₄] (A=1,2 diamino cyclohexane, active against a number of tumour systems, soluble, and having relatively low toxicity.

The chemical structure of blue platinum pyrimidine compounds, known as Platinum Blues, which have interesting biological properties, was discussed in several papers by B. Lippert, Michigan State University; S. J. Lippard et al, Columbia University, New York; and A. J. Thomson, University of East Anglia. Although these are recognised as cationic polymers of mixed or non-integral valency, their precise structure remains unknown. X-ray crystallography studies were presented on possible Platinum Blue precursors isolated from the starting material for their preparation, cis-[Pt(NH₃)₆(H₂O)₂]²⁺. These are hydroxo bridged dimers and trimers, for example [(NH₃)₂Pt(OH)₃Pt(NH₃)₃]²⁺ (C. J. L. Lock et al, McMaster University, Hamilton, Ontario; J. A. Stanko et al, University of South Florida). Dr. McAlister of Michigan State University discussed the electron microscopy staining properties of these compounds. It appears that contrary to original reports, cell surface staining is encountered with all cells and is not selective for tumour cells. The nature of this staining remains unclear although studies reported by S. K. Aggarwal of Michigan
State University indicated that it may still be a useful staining technique.

X-ray crystallographic studies on complexes between platinum and various nucleoside and nucleotides were presented by R. Bau et al, University of Southern California and confirmed the preferred base binding sites as the N7 of guanine (G) and N of cytidine (C) although some phosphate binding was also involved. The modes of binding of Pt compounds to DNA were the subject of many in vitro studies all indicating heavy G-C involvement. Evidence for binding at O6 of guanine to make a chelate ring with N7 was not forthcoming in physico-chemical studies. Intercalation studies reported by I. A. G. Roos of the University of Adelaide support the concept of intrastrand linking of DNA. Previous studies have demonstrated that interstrand cross linking is unlikely to be the major lesion leading to cell death.

An interesting new development concerns the ability of platinum compounds to sensitize cells to irradiation (R. C. Richmond et al, U.S. Army Natick Laboratories; A. H. W. Nias, Glasgow Institute of Radiotherapeutics). Of particular note is the ability to sensitize both in the presence and absence of oxygen. This could be important as anoxic cells in tumour masses are always difficult to kill by irradiation.

The distribution of $^{195m}$Pt labelled cis-[Pt(NH$_3$)$_2$Cl$_2$] in rats was reported by W. Wolf et al, University of Southern California. Two blood phases were observed, one very fast ($T_1 < 30$ minutes) and the second slow ($T_1$ approximately 19 days). An important storage compartment for the slow phase appears to be the skin which contains more than 20 per cent of the injected dose at 30 minutes and still houses 11 per cent after 72 hours. Other organs retaining more than 1 per cent of the injected dose at 12 hours were the liver (3.5 per cent), kidneys (2.8 per cent), muscle (5.1 per cent) and bone (5.1 per cent).

Evidence concerning the nature of the renal damage produced by cis-[Pt(NH$_3$)$_2$Cl$_2$] was presented by T. F. Slater of Brunel University. The drug binds strongly at the membrane of the proximal tubule of the kidney and unlike other membrane binding this cannot be reversed by the use of cysteamine. This may explain why the kidney suffers the dose limiting toxicity.

The major discussion of cellular repair membrane was given by J. J. Roberts of the Chester Beatty Institute, Pollards Wood, who presented evidence from tissue culture studies to suggest that platinations of DNA can be circumvented by a post replication repair process. This repair protects cells from the cytotoxic and chromosome damaging effects of cis-Pt(II) and is caffeine sensitive since post treatment incubation in caffeine enhances these effects. Failure of the repair process to occur within a finite time leads to irreversible cell damage. The differing abilities of cells to perform the process rapidly may account for differing sensitivities to cis-Pt(II).

**Clinical Trials with cis-[Pt(NH$_3$)$_2$Cl$_2$]**

There was little doubt that the interest of clinicians in this drug has changed considerably since the 2nd International Symposium at Oxford in 1973. In reviewing the clinical situation I. Krakoff of the Sloan Kettering Memorial Institute indicated that the drug was now established as being useful for certain tumour types namely genito-urinary, head and neck, and held promise for several others. It would undoubtedly become an accepted chemotherapeutic drug. He also called for the apparently more promising second generation drugs to be brought along more quickly.

D. D. Von Hoff of the National Cancer Institute stated that the N.C.I. sponsorship of cis-Pt (II) started in 1971 but that a sharp increase in the interest of clinicians in this drug was noted in May 1976. In August 1976 twenty-five thousand 10 mg vials were supplied and two hundred and seven
investigations are currently in progress.

Several clinicians indicated means by which the nephrotoxicity could be significantly limited. E. Cvitkovic and his colleague also of the Sloan Kettering Memorial Institute, New York, have hydrated patients prior to treatment and administered mannitol (a diuretic) to promote urine flow, along with the cis-Pt(II). This technique allows much higher doses to be given and greatly improved therapeutic results are being obtained. There are indications that the higher dose therapy will cause a wider range of tumours to respond. C. Merrin of Roswell Park, Buffalo, reported that they had found a dose schedule comprising multiple small doses to be equally effective in this respect.

Reports on cis-Pt(II) given in combination with other chemotherapy agents were particularly encouraging and this represents another way of overcoming the toxicity. Results for testicular cancer involving cis-Pt (II) with Bleomycin and Vinblastine reported by L. H. Einhorn of Indiana University Medical Centre, were outstanding although true judgement must await a larger sample of patients. E. Wiltshaw of the Royal Marsden Hospital, London, stated that cis-Pt (II) was as good as any other single agent in the therapy of ovarian tumours and initial results indicated that in combination a considerable improvement was obtained.

Clinical Trials with Newer Platinum Compounds

The only report of clinical trials on other Pt compounds came from the Wadley Institutes of Molecular Medicine where trials on [Pt A(malonate)] (A=1,2 diaminocyclohexane) are in progress. Some responses have been observed but the results are of too preliminary a nature to draw conclusions as yet. Clinical testing of platinum uracil blue and cis-[PtA(Cl)] (A=cyclopentylamine) has been discontinued. Clinical trials on [PtA(sulphate)] (A=1,2 aminocyclohexane) will start shortly.

Exhaust Gas Sensors Aid Emission Control

ZIRCONIA DEVICES UTILISE PLATINUM ELECTRODES

The purification of automobile exhaust gases by platinum group catalysts can be most consistently achieved when the engine is operated with an exactly stoichiometric air/fuel ratio. One way of achieving this state is by monitoring the oxygen content of the exhaust gas and using the information to control the input of air to the engine. This requires an instrument which can reliably detect the variations in oxygen concentration.

Exhaust sensors consisting of a ceramic tube of stabilised zirconia closed at one end and having porous platinum electrodes on both the inner and the outer surfaces have been developed for this purpose. The sensor is inserted in the exhaust system so that the exhaust gases flow over the outer platinum anode while the platinum cathode on the inner surface is open to atmosphere. As the sensor is heated by the engine exhaust the ceramic becomes conducting to oxygen ions and, as the partial pressure of the oxygen on the two sides of the device is different, an electrical potential is generated between the two electrodes. A change in voltage occurs whenever the composition of the exhaust changes, for example from 'rich' to 'lean' or vice versa. This signal is a measure of the air/fuel ratio and can be used, via a closed loop circuit, to control any departure from stoichiometry.

While the sensor voltage can be calculated from the appropriate thermodynamic relationship, actual sensor behaviour can differ from this ideal, and such departures are detrimental to the performance of the systems they control. In a recent article W. J. Fleming of General Motors Corporation, Research Laboratories (J. Electrochem. Soc., 1977, 124, (1), 21-28) describes work to derive a physical model of a non-ideal sensor. The physical processes involved in the function of zirconia exhaust gas sensors are examined and a theory to account for the departure from ideal behaviour is presented.
Raleigh Gilchrist and His Research on the Platinum Metals

By Professor George B. Kauffman
California State University, Fresno, U.S.A.

Raleigh Gilchrist, one of America's most prominent internationally known authorities on the chemistry of platinum and of gold, was born in the small town of Windsor, Vermont on January 8th, 1893, but moved with his family to Great Falls, Montana in 1896. It was here in 1910 that Gilchrist first became involved with noble metals when, in order to earn money to enable him to attend college, he began work as an assistant for the Anaconda Copper Mining Company handling gold and silver slimes.

In September 1911 he entered the University of Montana at Missoula, from which he received his B.A. degree with a major in chemistry in 1915. He then began graduate study in inorganic chemistry at Cornell University with an assistantship in qualitative analysis. Later, in November 1917, when he had begun his doctoral research on germanium compounds he was inducted into the U.S. Army. Soon he was transferred to the Inorganic Chemistry Section of the National Bureau of Standards in Washington where, under Dr. William Francis Hillebrand, he was required “to engage upon a program of investigation of the refining and analytical chemistry of the platinum group metals”. It was during a successful career of 45 years at the Bureau, briefly at first as a soldier and later as a civilian, that Gilchrist carried out the work for which he is remembered.

In order to resume his graduate work while still remaining at the Bureau, Gilchrist enrolled at the Johns Hopkins University in Baltimore, where he began a new doctoral research problem under Dr. Joseph Christie Whitney Frazer with minors in physical chemistry and physics. He was not required to take any class work, but he audited a course in colloid chemistry from Dr. Walter A. Patrick, who played an important role in the commercial production of silica gel. Gilchrist received his doctorate in 1922 with a dissertation “The Preparation of Pure Osmium and the Atomic Weight of Osmium”, which was published in 1922 under the title “A New Determination of the Atomic Weight of Osmium” (1).

At the National Bureau of Standards Raleigh Gilchrist rose through the ranks to become Chemist in 1936, and later Chief of

Raleigh Gilchrist
1893–1966
An internationally recognised authority on the analytical chemistry of the platinum metals, the subject to which he devoted 45 years of work at the U.S. National Bureau of Standards
Photograph by courtesy of Mrs. Elizabeth R. Gilchrist

the Platinum Metals and Pure Substances Section of the Division of Chemistry. From 1948 to 1961 he was Chief of the Inorganic Chemistry Section. He retired in November 1962, after which he served as consultant to the Chief of the Chemistry Division. His duties initially consisted of planning and carrying out experimental chemical research on methods for preparing each of the six platinum metals in pure form and of developing a knowledge of their chemistry. In addition he tested for chemical composition a variety of noble metal alloys, materials, and articles from other governmental agencies, and he analysed materials where disputes had arisen between commercial chemists. He developed methods for analysing materials containing the platinum metals, gold, silver, and the base metals usually associated with them. In his later years he also worked on the purification of sulphur, nickel, zirconium, barium, strontium, germanium, and the rare earths as well as on the preparation of titanium halides and the analysis of ceramic dielectrics. The results of his systematic studies were of great practical value and have been utilised by the noble metals industry, displacing older, inadequate procedures, and by scientists in the aeronautical, dental, and industrial fields. He also supervised the preparation of pure substances and the testing of reagent chemicals.

Gilchrist travelled widely, both on official business and for pleasure, his first trip to Europe in 1926 being "to establish friendly relations with foreign laboratories in which research on the platinum metals was being done, to become acquainted with professors working on these metals and to see as much of the great platinum works as possible and to discuss problems of mutual interest" (2). Not surprisingly his first call was at the offices of Johnson Matthey and Company at Hatton Garden in London.

In 1936, 1938, and 1948 Gilchrist was a member of the United States Assay Commission, which meets yearly at the U.S. Mint in Philadelphia to check coinage. He was an official United States delegate to a number of international conferences, including, in 1934, the Third International Technical and Chemical Congress in the Agricultural Industries (Paris), the Eleventh Conference of the International Union of Chemistry (Madrid), and the Ninth International Congress of Pure and Applied Chemistry (Madrid). At the last-mentioned meeting, he presented the paper for which he was awarded the Hillebrand Prize four years later (3). In 1927-1928 and 1929-1934 he was a lecturer in chemistry (thermodynamics and advanced inorganic) at George Washington University and in 1928-1929, 1931-1932 and later years a lecturer in chemistry at the National Bureau of Standards Educational Schools.

Throughout his working career Dr. Gilchrist undertook an active part in the work of many honorary, scientific and fraternal organisations. For almost half a century he was a member of the American Chemical Society and held continuous office in the Chemical Society of Washington for 32 years, being Secretary in 1925 to 1928 and President in 1929.

A perfectionist both in his work and in his avocations, Raleigh Gilchrist died in Washington on October 26th, 1966 at the age of seventy-three.

Gilchrist's Work

During World War I when the U.S. supply of Chilean saltpetre from the Atacama Desert was threatened by German submarines it became necessary to produce synthetically the nitric acid and nitrates needed for explosives. Because of the resulting intense interest in nitrogen fixation, Dr. William F. Hillebrand's dream of creating a laboratory to refine the platinum metals and to develop methods for determining the individual metals became a reality. Young Gilchrist was assigned to work on the analysis of iridium-platinum gauzes used to convert ammonia to oxides of nitrogen and eventually to nitric acid by the process invented by Ostwald in 1901. The assignment was soon widened in
scope, and in the course of years analyses at N.B.S. under Gilchrist’s supervision were made on “a wide variety of materials, ranging from the determination of the quantity and thickness of the gold wash on the inside of a cocktail goblet to that of the composition of the highly complex native grain platinum” (4). The preparation of the platinum metals in highly pure form for the determination of various physical properties such as atomic weight required additional treatment of the commercial metals, and this task was also within Gilchrist’s purview.

Gilchrist found that most of the analytical methods in the literature for the platinum metals did not produce clean-cut separations, particularly the venerable precipitation of platinum with ammonium chloride and the extraction of metallic mixtures with acids or with molten pyrosulphate. One remarkable exception was the insolubility of iridium in molten lead, employed by Deville and Stas in analysing the iridium-platinum alloy used in fabricating the international prototype metre and kilogram (5). In this method the alloy is melted with ten times its weight of lead, producing alloys of lead and platinum, which are soluble in acids, and crystalline iridium, which is virtually insoluble in aqua regia. In his first publications (6, 7) Gilchrist confirmed the accuracy of the method and modified it to increase its ease and speed of operation. The method is an excellent one for the routine analysis of platinum alloys containing no iron, ruthenium or osmium. Beamish (8) recommends it for determining iridium in platinum or palladium alloys, in which the latter two noble metals are not to be determined. The method is readily adaptable to massive forms of alloys such as sheet or wire.

Weeks (9) has called ruthenium “the little Benjamin of the platinum family” because it saw the light of day so much later than its older brothers. Gilchrist devised a gravimetric method for this least known member of the platinum metals group that involved the principle of controlled hydrolytic precipitation (10), a principle employed in crude form as early as 1835 by Döbereiner, who used lime water to isolate platinum from osmium, rhodium, iridium, palladium and copper (11). Gilchrist added enough NaHCO₃ to the solution to turn bromcresol indicator faintly purple, and he then boiled and filtered the solution. The precipitate is ignited in a hydrogen atmosphere and weighed as metallic ruthenium.

Although distillation of OsO₄, usually from a solution acidified with nitric acid, has been generally used to separate osmium from the other platinum metals, no study of the optimum conditions or completeness of separation was made until Gilchrist’s study of 1931 (12). He found that the form in which the osmium exists in solution has a marked effect on the rate at which it is volatilised. He used a 6 N hydrochloric acid solution saturated with sulphur dioxide for absorbing the distilled OsO₄, and the osmium was recovered from this by hydrolytic precipitation with NaHCO₃. The hydrated OsO₄ was ignited in hydrogen and carbon dioxide and weighed as metallic osmium. Gilchrist concluded that a complete separation of osmium from the other platinum metals is possible by the traditional method if proper precautions are observed. More recent investigations (13, 14) resulting in low values by use of Gilchrist’s SO₂-HCl receiving solution have been shown to be due to ageing of the solution rather than to actual loss of osmium (15).

During the period 1915 to 1943 only two chemical determinations of atomic weights of the platinum metals were made—osmium by Gilchrist (1) and ruthenium by Gleu and Rehm (16). From the osmium content of (NH₄)₂OsCl₆ and (NH₄)₂OsBr₆, Gilchrist, returning to the topic of his doctoral dissertation, proposed the value 191.5, one considerably below today’s accepted value of 192.2, obtained from isotopic abundance ratios (17).

Gilchrist’s work, however, was not limited to research on the individual platinum metals but encompassed the separation and determination of each of the metals in the presence
of the others. An important step in this direction was his paper on “Purification of the Six Platinum Metals”, published in 1928 (18). In 1923 Wada and Nakazono noted that rhodium is precipitated by the reducing action of Ti$_2$(SO$_4$)$_3$, while iridium is not if the chloride solution of each metal is treated separately (19). Gilchrist developed this qualitative observation of selective reduction into a quantitative separation of the two metals and their gravimetric determination (20). The rhodium is redissolved in boiling sulphuric acid, reprecipitated by hydrogen sulphide, ignited in hydrogen, and weighed as metal. The titanium, now in the tetravalent state, is precipitated from the filtrate with cupferron (C$_6$H$_5$N(NO)ONH$_2$). The iridium is precipitated from the filtrate hydrolytically with NaHCO$_3$, and the IrO$_2$•H$_2$O is ignited in hydrogen and weighed as metal. The recent chromatographic method of Rees-Evans et al. (21), modified by Payne (22), has been reported to be simpler than Gilchrist’s titanium method.

In 1934 Gilchrist devised a procedure for the separation of ruthenium from platinum, palladium, rhodium and iridium based on hydrolytic precipitation (23). In the same year he employed hydrolytic precipitation by NaHCO$_3$(pH6) in the presence of NaBrO$_3$ (which prevents hydrolysis of PtCl$_6^{2-}$) to remove palladium, rhodium and iridium from a solution containing platinum (24). The platinum remaining in solution is precipitated by hydrogen sulphide, dissolved in aqua regia, precipitated with sodium formate, ignited, and weighed. Palladium is precipitated with dimethylglyoxime (25), ignited, and weighed as metal, while rhodium and iridium are determined gravimetrically by Gilchrist’s earlier procedure (20).

By 1934 Gilchrist and his colleague Edward Wichers had developed a new and reliable procedure for the separation and gravimetric determination of all six platinum metals based largely on Gilchrist’s work of the previous decade cited above. The method, which was simpler than the methods previously used, was discussed in the paper “A New System of Analytical Chemistry for the Platinum Metals” (3), presented by Gilchrist at the Ninth International Congress of Pure and Applied Chemistry, for which he and Wichers received the Hillebrand Prize (26). Osmium and ruthenium are first removed by distillation, and palladium, rhodium and iridium are separated from platinum by a hydrolytic precipitation with NaHCO$_3$ under conditions of controlled acidity (pH 6 to 8) that leaves platinum, whose chloride complex undergoes no appreciable hydrolysis, alone in solution. The detailed analytical procedure appeared in the Journal of the American Chemical Society (27) and has been experimentally reevaluated (28; 29, p. 67). It should be noted that researchers comparing hydrolytic methods with other methods are in effect examining their ability to use the method, which requires considerable experience and skill, especially with small samples (29, p. 75). Gilchrist also authored a number of review articles on the platinum metals in books, encyclopaedias, and journals (30-35).

Conclusion

At the beginning of Gilchrist’s career, the state of development of the analytical chemistry of the platinum metals lagged far behind that of the other groups of metals, the methods then used being incomplete, inefficient, inaccurate, and inconvenient. Although in a number of cases, the methods developed by Gilchrist have been superseded by more modern methods, the fact that today the separation of the platinum metals is no longer shrouded in mystery is due in no small part to his pioneering efforts. Thanks to Raleigh Gilchrist and those who followed him, reliable procedures based on simple reactions are now available for the analysis of platiniferous materials—procedures comparable in accuracy with the best in use for more common metals.

Acknowledgements

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Platinum Process for Photographic Prints

A nearly forgotten photographic process which produces platinum prints with a most attractive appearance and a permanency which far exceeds those produced by more conventional processes is recalled in a recent article by G. L. Wakefield (Amat. Photogr., 1976, 154, 25), 67-69). Processes employing platinum group metals have been known for over a hundred years and as early as 1873 William Willis was granted a patent for “Improvements in Photo-chemical Printing” where he employed salts of platinum and iridium. In more recent times commercial availability of the sensitised materials has been progressively reduced and at the same time the development of newer techniques has displaced the necessary processing data from many of the photographic textbooks.

Prints of considerable age produced by one or other of these platinum processes can still be seen in many of the larger collections of photographic prints where their intrinsic beauty can be admired and the technical skills of the photographer appreciated. Although unlikely to have much influence on the present photographic situation the techniques still appear to offer considerable potential to the creative enthusiast.

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Platinum Metals Rev., 1977, 21, (2)
ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

The Wetting of High Temperature Oxides by Molten Platinum and Its Work of Adhesion
Studies of the wetting of BeO, MgO, Y2O3 and ZrO2+20% Y2O3 by molten Pt were carried out in He atmosphere at temperatures ranging from the melting point of Pt up to 2100°C, using the sessile drop method. It is shown that BeO is least wetted by Pt. The wetting angle θ of Pt on BeO changes from 120° at 1800-2000°C, and the work of adhesion changes from 800 to 1100 MJ/m² in this temperature range. The wetting angles on MgO and Y2O3 were 92 and 88° respectively and were found practically constant with temperature. The value of θ on ZrO2 +20% Y2O3 decreases with increasing temperature from 85 to 60° and the work of adhesion increases from 1950 to 2400 MJ/m².

Effect of Carbon and Water on Wetting and Reactions of B2O3-containing Glasses on Platinum
The wetting characteristics of molten B2O3 and B2O3-containing glasses on Pt were studied using the sessile drop method, at 700-1000°C under ambient pressures of 10⁻⁴ torr to 1 atm. It is shown that in atmospheres free of carbonaceous gases, the contact angle for all glasses on Pt was small and independent of pressure and temperature. Adsorption of C at the metal surface increased the contact angle. Absorption of H₂O vapour by the glasses resulted in a reaction at the solid/liquid interface, spreading of the glass and adherence.

Interaction of Hydrogen with Pt(111): The Role of Atomic Steps
K. CHRISTMANN and G. ERTL, Surface Sci., 1976, 60, (2), 365-384
The interaction of H₂ with stepped Pt(S)-9(111) ×(111) surface was studied using LEED, AES, TDS, thermal desorption and work function techniques. It was found that the saturation coverage with dissociatively adsorbed H₂ at 120K is near unity. The presence of steps increased the initial sticking coefficient by a factor of four to a value of 0.34. The activity for H₂-D₂ exchange reaction was enhanced by an order of magnitude. A model in which two different types of adsorbed H atoms are associated with the atomic steps is proposed.

Ductile-Brittle Transition in Metallic Glasses
Studies of the ductile-brittle behaviour in (M₁₋ₓNₓ)₀.₇₅P₀.₁₄B₀.₆₆Al₀.₀₂ alloy with M = Fe, Co, Ni, Cr and Mo show that the Fe, Co, Mo and Cr metallic glasses are very brittle in comparison with the Ni, Pd and Pt based glasses. It is suggested that the incomplete d-shell orbitals of the Fe, Co, Cr and Mo atoms lead to higher resistance to shear strains and brittle behaviour. The Ni, Pd and Pt glasses by filling the d-shell of the transition metals ensure a relatively low shear modulus and ductile behaviour.

Strengths and Stiffnesses of Metallic Glasses
The elastic and plastic properties of a number of metallic glasses including Pd₀.₉₀Si₁₆₀, Pd₇₇₅Cu₂₂₅ and Pd₄₀Ni₄₀P₂₀ were studied and a simple correlation of the strengths and stiffnesses of these glasses was observed. The correlation between the strengths and stiffnesses is given in terms of the Vickers hardness, Young's modulus, density and the velocity of extensional mode ultrasonic waves.

The Motions of Hydrogen Impurities in α-Palladium Hydride
Studies of the intensity distribution of inelastically scattered thermal and hot neutron on H impurities in α-palladium hydride were made as a function of concentration, temperature, momentum transfer and different annealing procedures.
The results show that at higher concentrations and with insufficient annealing treatment clusters of H atoms formed even in the α-phase, producing a local lattice distortion.

Superconductivity in the Pd$_1$-xM$_x$H$_c$ (M is Noble Metal) and PdB$_x$H$_c$ Alloy Systems


The dependence of the transition temperature $T_c$ on the H$_c$ content in several Pd-Cu and Pd-Ag alloys and on the H + B content in several Pd-B alloys was studied. The results show that the increase of H$_c$ concentration causes an increase of $T_c$ and that the higher the Cu, Ag or B concentration the lower is the c-value corresponding to the appearance of superconductivity. The presence of noble metal and also B) atoms in the Pd alloy considerably reduces the solubility of H$_c$.

Metallic Glasses


A review of the physical properties of metallic glasses including Pd-Au-Si, Pd-Cu-Si, Pd-Si, Pd-Ni-P and Pt-Ni-P, is presented. The formation, stability and glass transition as well as structure, structure relaxation and crystallisation are discussed. The mechanical behaviour and magnetic properties are summarised. Acoustic and electron transport properties are described.

The β→α Phase Transformation in Palladium-Hydrogen Alloys


A room temperature study has made of the β→α phase transformation in thin foils of annealed β-palladium hydride using electron microscopy and diffraction techniques. Initially coherent precipitation of α was observed close to the surface of the foil while the transformation proceeds in a discontinuous manner accompanied by the formation of a high dislocation density and microcracks in the α phase. It is thought that the rate of transformation is controlled by the formation of molecular H$_2$ at the foil surface.

The Internal Friction and Elastic Modulus of Amorphous Pd-Si and Fe-P-C Alloys


Internal friction of an amorphous Pd-Si alloy was measured from room temperature to ~550°C using a specially designed micro-tension pendulum. It is shown that the internal friction of the amorphous alloy increases steeply with temperature. A wide range of distribution in activation energies was observed. The shear modulus was found to increase by ~30% upon crystallisation.

The Influence of Adsorbed Carbon on the Condensation of Molecular NaCl on Ir and Pt


Studies of the nucleation and growth of NaCl crystals on Ir and Pt show that the condensation rate on clean substrates is considerably higher than that on substrates covered with adsorbed C. This is attributed to a lower energy of adsorption of the NaCl on the C covered surfaces of Pt or Ir.

Thermal Expansion Measurements Near the Antiferromagnetic Phase Transitions in K$_3$ReCl$_6$ and K$_3$IrCl$_6$


The linear thermal expansion coefficient measurements for K$_3$IrCl$_6$ and K$_3$ReCl$_6$ show anomalous behaviour near the antiferromagnetic phase transition. The results show that the contribution of the next-nearest-neighbour exchange interaction to the thermal strain is of opposite sign for the two compounds.

Studies of the Phase Composition and Electrical Transport Properties of the RuO$_2$-TiO$_2$ System


X-ray studies of the RuO$_2$-TiO$_2$ phase diagram at 900, 1200 and 1350°C show that there are two regions of limited solubility, one near the TiO$_2$ and another near the RuO$_2$. In the remaining concentration range there exist two rutile phases which are solid solutions of TiO$_2$ in RuO$_2$ and RuO$_2$ in TiO$_2$. The dependence of electrical conductivity and thermal e.m.f. of the Ti$_{1-x}$Ru$_x$O$_2$ ($x=1-6$ mole%) solid solutions on the composition, temperature and partial pressure of O$_2$ is discussed. The defect structure in the crystal lattice of these solid solutions is presented.

CHEMICAL COMPOUNDS

An Analytical Study of Platinum Silicide Formation


AES, secondary ion mass spectroscopy and electron probe microanalysis were used to study the kinetics of Pt silicide formation and the surface effects were found to relate to O$_2$ and Al contamination of the films. The contaminants moved with the Pt-Pt silicide interface during subsequent annealing, while additional oxidation occurred at the surface due to some very small amount of O$_2$ in the annealing ambient.
Crystal Structure of \( \text{Pd}_4\text{S}_7 \)


Crystallographic studies of the Pd-S system show that the phase \( \text{Pd}_4\text{S}_7 \) has a cubic body-centred structure with 46 atoms in the cubic cell and is related to the \( \gamma \)-brass structure. The phases \( \text{Pd}_4\text{S}_7, \text{Pd}_6\text{S}_8, \text{Pd}_8\text{S}_9 \) were interpreted as energetically favourable in terms of the two-electron correlation model.

**ELECTROCHEMISTRY**

The Effect of Anions on Hydrogen Chemisorption and Oxide Formation on Pt in Aqueous Acids


A potentiodynamic cyclic voltammetry method was used to study the component processes of H chemisorption on Pt and Pt oxide formation in \( \text{H}_2\text{SO}_4 \), \( \text{HClO}_4 \) and HF aqueous acids. Processes of H adsorption/desorption and Pt oxide formation occurred only in \( \text{H}_2\text{SO}_4 \) and not in \( \text{HClO}_4 \) or HF, and thus represent anion interference with the faradaic reactions. The strong H species were observed in \( 1 \text{M HClO}_4 + 10^{-2} \text{M H}_2\text{SO}_4 \).

Effect of the Addition of Ruthenium Trichloride on Oxygen Overvoltage at a Platinum Anode in Aqueous Acidic Solution


The effect of the addition of RuCl\(_3\) on \( \text{O}_2 \) overvoltage was studied at a Pt anode in aqueous acidic solution using cyclic voltammetry, potential-time curves and by determination of evolved \( \text{O}_2 \) gas. The RuCl\(_3\) addition noticeably decreased the overvoltage for the anodic evolution of \( \text{O}_2 \) at low anodic potentials which was attributed to the presence of Ru species as active sites, incorporated in the oxide film of the Pt anode. The results at relatively high anodic potentials showed that RuCl\(_3\) additions slowed down the \( \text{O}_2 \) evolution due to simultaneous oxidation of the Ru species.

Reduction of Nitric Oxide at a Platinum Cathode in an Acidic Solution


Studies of the reduction of NO were carried out at a Pt electrode in \( 4 \text{M H}_2\text{SO}_4 \) using the measurement of potential/current relations and by the determination of the current efficiencies for \( \text{N}_2\text{O}_5, \text{NH}_3, \) hydrazine and \( \text{H}_2 \) formation at fixed potentials from 0 to -400mV. The results showed that in the potential range of the first wave (\( > -30 \text{mV} \)), NO was reduced only to \( \text{N}_2\text{O} \). In the second wave (from -50 to -250mV), NO was reduced to hydroxylamine, \( \text{NH}_3 \) and \( \text{NO}_2 \).

**ELECTRODEPOSITION AND SURFACE COATINGS**

Electrodeposited Noble Metal Coatings from the Present Day Point of View


A review of the current methods of plating Pt group metals and Au for decorative purposes is presented.

Increase of the Corrosion Resistance of Electrolytic Chromium Coatings by Modification with Palladium


Studies of the corrosion resistance and the electrochemical behaviour of electrodeposited coatings...
of Cr modified with 1–3% Pd were carried out. The results show that these coatings are considerably more corrosion resistant in 20% H₂SO₄ and 5% and 10% HCl solutions than the unmodified coatings.

**HETEROGENEOUS CATALYSIS**

New Hydrogenation Catalysts with Platinum Deposited on Polyamide-66. IV. Comparison of the Activities of Different Catalysts in the Hydrogenation of Styrene


Specetroscopic studies of the catalytic activity of the Pt/polyamide-66 catalyst made during the hydrogenation of styrene into ethylbenzene at 100°C showed that the activity of the catalyst did not depend on the total Pt content but was proportional to the amount of Pt at surface of the nylon. The influence of the preparation of the catalyst, of the solvent and of the nature of the Pt compound on its catalytic activity was discussed.

Catalytic Reforming of Benzine Fractions on Polymetallc Catalysts


The catalytic reforming of benzine was carried out over polymeric 0.6 wt.% Pt/Al₂O₃ and 0.35 wt.% Pt/Al₂O₃ catalysts at pressures of 15–35 atm. The results show that high benzene and toluene outputs are obtained during reforming over the 0.35 wt.% Pt/Al₂O₃ catalyst. The lowering of the working pressure down to 14 atm led to a further increase of the hydrocarbon output.

Relative Importance of Thermal and Chemical Deactivation of Noble Metal Automotive Oxidation Catalysts


The reactivation of a series of monolithic Pt/Al₂O₃ and Pt+Pd/Al₂O₃ catalysts was studied after operation in vehicles for 50,000 miles. It is shown by transmission electron microscopy that the metal particles grew from ~60Å to 1000Å. The CO chemisorption techniques show that the available metal area decreased to 3 × 10⁻⁴ m²/g. The thermal sintering causes loss of 95% of the original metal area and poisons deactivate 95% of the remaining metal area.

**Platinum-Rhenium-Alumina Catalysts. III. Catalytic Properties**


Studies of the activity of Pt-Re/Al₂O₃ and Pt-Re/γ-Al₂O₃ catalysts in five different reactions showed that the activity is not the sum of the activities of Pt and Re. The activity vs. composition curves have one or two maxima in benzene hydrogenation, benzene-deuterium exchange, hydrogenation, benzene-deuterium exchange, isomerisation, and para selectivity.

**A Study of the Chemisorption of Nitric Oxide on PdY Zeolite, Evidence for a Room Temperature Oxidative Dissolution of Pd Crystallites**


Studies of NO adsorption on a PdY zeolite in oxidised and reduced forms were carried out using i.r. and E.P.R. spectroscopies. It is shown that NO can be reduced in N₂O and the Pd can be reoxidised to such an extent that all the metal atoms are redispersed as cations on the support. These results are of practical interest for the elimination of NO in automobile exhaust and are important in the problem of catalysts ageing.

**On the Catalytic Reduction of Nitric Oxide in the Presence of Oxygen**


Studies of the reduction of NO by H₂ and CO over a number of Pd, Ag and Fe mixed catalysts supported on γ-Al₂O₃ showed that the three-component catalyst Pd/Ag/Fe had a remarkable
selectivity for the NO reduction by H₂ and CO even at O₂ concentrations of 2% at the inlet. The relatively low excess temperatures of the Pd/Ag/Fe catalyst indicated a reduced selectivity for the CO oxidation by O₂ as compared to the other catalysts.

Study of Adsorption Properties of a Pd/Al₂O₃ Catalyst

Studies of the H₂ sorption and specific adsorption of Zn and Cd cations on 0.05g Pd/Al₂O₃ catalyst were carried out using 1N H₂SO₄, H₂O and NH₄OH solvents. It is shown that the quantity of adsorbed cations depends on their concentration in the solution and on the nature of the solvent. The effect of temperature on the amounts of sorbed H₂ and adsorbed cations is discussed.

Organic Hydrogen Getters

A 5% Pd-CaCO₃ catalyst in combination with an unsaturated dimerised phenyl propargyl ether-DPPE was developed for gettering H₂ irreversibly from closed systems via a chemical reaction. The activation energy for H₂ uptake was found to be 9.4 kcal/mole at 22-25°C. The getter material can be used as a powder or be packaged in a bag through which H₂ can permeate. The getter is shown to be non-explosive and non-pyrophoric.

Electrochemical Study of Palladium-Copper Catalysts

The correlations between the H₂ sorption and catalytic activity of Pd-Cu powder catalysts with 0.1, 10, 20, 30, or 40 at.% Cu were studied using galvanostatic and potentiodynamic methods in 1N NaOH and 1N H₂SO₄ respectively. The catalysts activities were measured in liquid-phase hydrogenation at 25°C and 1 atm. The quantitative decrease of the dissolved H₂ was observed on 0-20 at.% Cu-Pd catalysts while for 20-40 at.% Cu-Pd catalysts, the decrease was primarily in the adsorbed H₂.

The Effect of Thermal Treatment on the Catalytic Activity of Skeleton Iridium in the Acetone Reduction

Studies of the catalytic activity of a skeleton Ir electrode catalyst in the acetone reduction show that thermal treatment of the catalyst in a H₂ atmosphere at 100-600°C has no significant effect on the adsorption and hydrogenation of acetone.

The Catalytic Activity of Rh, Ru and Ir Blacks, Deposited on Pt Supports, in the Processes of Reduction and Electroreduction of Maleic Acid

The catalytic activities of Pt supported Rh, Ru and Ir black electrodes were studied in the electro-reduction and hydrogenation of maleic acid. The results show that the catalytic activity changes in the following order: Rh > Ir > Ru.

The Kinetics and Mechanism of Carbon Monoxide Hydrogenation over Silica-Supported Ruthenium-Copper Catalysts

Studies of the activity of Ru-Cu/SiO₂ catalysts for CO hydrogenation at 530-670K show that the activity decreases with increasing Cu content, while the activation energy remains constant at 21 kcal/mole. The catalyst containing 5% Ru and 0.32% Cu initially produces less ethane and propane than does the pure Ru catalyst.

Ruthenium Zeolite Hydrogenation Catalysts

The catalytic activities of Ru L, A, X, Y and mordenite zeolites, catalysts with widely different cation densities, cation binding energies, pore structure and molecular sieve properties were studied in the hydrogenation of benzene. The results show that a Ru-L zeolite in which the Ru metal is highly dispersed is an excellent hydrogenation catalyst. Good activities were also observed for Ru zeolites X, Y and mordenite in which the metal is not so well dispersed.

HOMOGENEOUS CATALYSIS

The Isotopic Exchange of Benzo furans with Heavy Water in the Presence of Potassium Tetrachloroplatinate

Studies of H-D exchange between heavy water and benzo furans were carried out at 120°C in the presence of homogeneous K₂PtCl₆ as a catalyst. The difference in reactivity of benzo furan and its alkyl derivatives was discussed in terms of a homogeneous dissociative π-complex mechanism.

Transition Metal Catalysed Rearrangements of Small Ring Organic Molecules

The literature on the molecular rearrangements, catalysed by transition metals, in organic molecules with three- and four-membered rings is critically surveyed. (132 Refs.)
CHEMICAL TECHNOLOGY
Enhanced Low Temperature Sintering of Tungsten
The influence of Pd, Pt, Fe, Co, Ni and Cu additions on the sintering of a fine W powder was studied using the isothermal and constant heating rate experiments at 900-1400°C. The results show that Pd is the best activator for the densification of W, followed by Ni, Co, Pt and Fe. A considerable acceleration of the sintering process is obtained when four atomic monolayers of Pd are present on the W powder surface. Near-theoretical densities are achieved at temperatures as low as 1200°C.

ELECTRICAL AND ELECTRONIC ENGINEERING
Differences between Platinum- and Gold-doped Silicon Power Devices
The effects of Au and Pt diffusions on the properties of Pt- and Au-doped p+-n- junctions were studied. It was found that there are substantial differences between the energy levels introduced by these impurities. Pt shows improved high-temperature properties and turn-on performance and is better for devices which are switched on rapidly.

NEW PATENTS
METALS AND ALLOYS
Solution Hardened Alloys Containing Palladium
U.S. ENERGY RESEARCH & DEVELOPMENT ADMINISTRATION
U.S. Patent 3,976,479
Solution hardened alloys of Cu, for example, containing equal atomic percentages of Pd and Al are formed by using at least two solutes which form associated solute pairs in the solvent metal lattice.

Ruthenium Powder Alloy
GENERAL MOTORS CORP.
U.S. Patent 3,977,841
Ductile Ru alloys are prepared by mixing 70-80% Ru powder with 20-30% prealloyed powder (containing Co, Ni, Cr, W and Si), both powders being of less than 200 mesh size, pressing at 35,000-50,000 psi, and sintering in dry and/or in a vacuum, at 2150-2250°F for 30-45 min.

Materials Selection in Hybrid Product Design
The Pd-Ag conductor paste was found to be economical and reliable as a solderable conductor when used with a Sn-free Pb-Ag-In solder, in the manufacture of power hybrid voltage regulators.

MEDICAL USES
Anti-tumour Agents Synthesised from K₂PtCl₄ and Polymeric or Cyclic Phosphazenes
Complexes between a square-planar Pt unit, K₂PtCl₄, and polymers such as the phosphazenes [NP(NHMe)₂]ₙ, [NP(NHMe)₃]ₙ, or [NPMe₄]ₙ were obtained. These complexes of the type [H₂N₄P₄R₈]²⁺[PtCl₄]⁻ show significant anti-tumour behaviour in preliminary testing.

An Explanation for the Efficacy of Attack by Platinum Blue Drugs on Biopolymers
Platinum halides and amides can react to form platinum blues, useful anti-tumour agents which are used as stains for biological specimens. Studies made of the interaction of these polymeric compounds with protein crystals have suggested a possible mode of action.

Ruthenium Alloy for Use in Composite Seals
W. H. FENGLER
U.S. Patent 3,991,229
A base metal, such as the Al or Fe housing of a rotary or reciprocating-piston I.C.E. and a sealing member for its pistons or rotor are coated with a layer of a wear resistant alloy such as Ru-W.

Platinum-Rhodium Containing High Temperature Alloy Coating
CHROMALLOY AMERICAN CORP.
British Patent 1,463,447
The heat resistance of Ni- and/or Co-based alloys is improved by cleaning the surface of the alloy, thermally diffusing first and second coatings of Rh and Pt respectively on to the alloy surface and pack-aluminising the alloy.
**Electroless Metal Plating**

**IMPERIAL CHEMICAL INDUSTRIES LTD.**

*British Patent 1,463,803*

A substrate is exposed to sensitising radiation when coated with a H₂O soluble quaternised bipyridilium compound dissolved or dispersed in a H₂O permeable film forming matrix, activated by contact with a solution of PdCl₂ and HCl, contacted with an aqueous solution of a reducing agent other than formaldehyde solution and contacted with an aqueous electroless metal such as Co plating bath.

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**Electrical Heating Unit with a Protective Overglaze**

**CORNING GLASS WORKS U.S.**

*Patent 3,974,360*

An integral element type heating unit consists of a Pt film bonded to a supporting ceramic plate. The platinum film element is electrically stabilised and physically protected by a PbTiO₃ overglaze.

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**Titanium/Silver/Palladium Metallisation System**

**MOTOROLA INC. U.S.**

*Patent 3,978,517*

A glass encapsulated double-plug diode has a semiconductor substrate on which are disposed successive layers of Ti, Ag and Pd.

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**Coating Noble Metals on Bonding Tools**

**TRIBOTECH U.S.**

*Patent 3,986,653*

Os, Ru and/or their alloys are electrodeposited from their alkali metal salts in a non-aqueous solvent, such as methanol or DMF on to the tips of bonding tools. The tips may also optionally be coated with a chemically bonded Si layer on top of the metal layer.

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**Ruthenium Coated Oxide Supports**

**EXXON RESEARCH AND ENGINEERING CO. U.S.**

*Patent 3,990,998*

The high surface area, multilayered oxide supports with a Ru coating have the composition Ru-MgO-MgAl₂O₄-MgAl₂O₄ + Mg₃SiO₄-Core. The products are used in the treatment of waste gases especially I.C.E. exhaust gases.

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**Thallium Palladate Anode Coating**

**C. CONRADTY U.S.**

*Patent 3,991,158*

TIPd₃O₄ for use as a coating layer for metal anodes is prepared by heating TINO₃ to 350°C to give TI₃O₃ and NO and NO₂, heating the TI₃O₃ to 500°C to give TI₅O₃ and O₂ and adding PdO to the TI₅O₃ to give TIPd₃O₄.

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**Noble Metal Coated Lamp Current Conductors**

**U.S. PHILLIPS CORP. U.S.**

*Patent 3,991,337*

The outer Mo current conductors of electric lamps with quartz glass lamp envelopes and pinched seals have a corrosion metal coating of Pt, Pd, Au or Ir on a primer layer of Ni or Cu.

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**LABORATORY APPARATUS AND TECHNIQUE**

**Oxygen Sensor**

**NISSAN MOTOR CO.**

*British Patent 1,462,336*

A sensor for use in an I.C.E. exhaust system has a cylindrical solid O₂-ion electrolyte which is a ceramic composed of ZrO₂ and CaO whose inner and outer surfaces are coated with Pt.

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**Oxygen Sensors**

**ROBERT BOSCH G.m.b.h.**

*British Patent 1,462,639*

An electrochemical sensor for determining the O₂ content of I.C.E. exhaust has an O₂ concentration cell with an ion conducting solid electrolyte in the form of a tube which is closed at one end and on the outer surface of which is located an electron conducting layer for catalysing the attainment of gas equilibrium. The electron conducting layer is formed of Pt, Pd or Ir (alloy) and may have additional refractory metal such as Ag or Au layers.

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**JOINING**

**Heat Resistant Sealing Materials**

**NATIONAL RESEARCH DEVELOPMENT CORP.**

*British Patent 1,455,428*

A new heat resistant material for sealing bodies together in TV screens consists of 5-40% Ca oxide, 35-70% SiO₂, 9-30% MgO₂ and 3-30% Al₂O₃. Several examples illustrate the bonding of a Pt disc, Pt or Pt-Rh wires or Pt alloy discs to Al₂O₃ or ZrO₂ in thermocouple production.

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**Metallisation Process for Bonding a Semiconductor Die to Terminals**

**MOTOROLA INC. U.S.**

*Patent 3,987,217*

A metallisation system for metallurgically bonding a semiconductor die to metallic conducting slugs and terminals uses a combination of Pd, Al and Sn, for bonding to Mo.

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**HETEROGENEOUS CATALYSIS**

**Dehydroxylation of Aminoglycosides**

**TAKEDA CHEMICAL INDUSTRIES LTD.**

*British Patent 1,460,039*

New deoxyaminoglycoside antibiotics may be prepared by reduction of intermediate halogenated compounds using Pt group metal catalysts.

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**Stabilised Ruthenium Catalysts**

**JOHNSON MATTHEY & CO. LTD.**

*British Patent 1,460,273*

A catalyst is formed by a mixed oxide having one of the empirical formulae: RuO₂ₓTiO₂ₓ; RuO₂ₓZrO₂; RuO₂ₓHfO₂; RuO₂ₓNb₂O₅ and RuO₂ₓBi₂O₅ where x > 1. The catalyst is used in the purification of I.C.E. exhaust gases.
High Severity Reforming Process with a Platinum-Iridium Catalyst
EXXON RESEARCH AND ENGINEERING CO.
British Patents 1,461,946-7
A naphtha feedstock having a Watson characterisation factor of 11.4-12.2 and H₂ are contacted with a catalyst comprising 0.15-0.75% Pt, 0.15-0.45% Ir and 0.3-2% halogen. The catalyst is supported on Al₂O₃.

Purifying Hydroquinone
GOODYEAR TYRE AND RUBBER CO.
British Patent 1,464,072
Photographic grade hydroquinone is prepared by treating a solution of technical grade hydroquinone in the presence of a Pd catalyst with H₂, while the solution is at a pH of 3-6.

Platinum Containing Molecular Sieve Catalyst
JOHNSONMATTHEY & CO. LTD. U.S. Patent 3,979,329
A selective molecular sieve catalyst is prepared by treating furfuryl alcohol with an aqueous solution of chloroplatinic acid and warming the mixture to initiate polymerisation of the alcohol, drying the polymer by heating under N₂ and curing by heating to 400°C for 4 h. Similar catalysts can be prepared, using Ru, Rh, Pd, Os, Ir, Fe, Co, Ni and Cu, and all catalysts are very selective for hydrogenation reactions.

Multimetallic Conversion Catalyst Containing a Noble Metal
UNIVERSAL OIL PRODUCTS CO. U.S. Patent 3,986,948
A catalyst for hydrocarbon conversion reactions is a porous carrier material on which is deposited 0.01-2.0% Pt or Pd, 0.01-2.0% Rh, 0.01-5.0% Sn, 0.1-3.5% halogen and 0.01-1.0% S. The Pt or Pd, Rh and Sn are uniformly dispersed throughout the carrier and the noble metals are in the form of their sulphides.

Platinum Group Metal Catalyst for Decomposition of Carbohydrate Wastes
U.S. ENERGY RESEARCH & DEVELOPMENT ADMINISTRATION U.S. Patent 3,989,480
Carbohydrate waste materials are decomposed to form a gaseous fuel product by contacting with a metal chosen from Rh, Ir, Pd, Pt, Ni, Co or Cu-Ni or Ni-Fe-Cr alloys and heating in the absence of H₂O.

Crosslinked Platinum Catalyst-Inhibitor
DOW CORNING CORP. U.S. Patent 3,989,666
The composition is prepared by heating in a closed system for 10-30 h, at 50-90°C a mixture of a siloxane, an acetylenic alcohol and a Pt catalyst, followed by removal of unreacted alcohol. When combined with a vinyl containing siloxane polymer it retards the actions of Si-bonded H atoms with aliphatic unsaturation catalysed by Pt.

Rhodium Catalyst for Propionic Acid Production
MONSANTO CO. U.S. Patent 3,989,747
A one step process for propionic acid production involves the reaction of C₃H₄ with CO and H₂O at mild pressure in the presence of a Rh catalyst and a bromide promoter.

Multiple Group VIII Metal Containing Catalyst
STE. FRANCAISE DES PRODUITS POUR CATALYSE French Appl. 2,287,496
The catalyst, for hydrocarbon conversion processes, has a support, 0.005-2.0% Pt, 0.005-1.0% of a metal chosen from Ir, Rh and Ru, 0.05-0.8% Co, 0.005-1.0% of at least one metal chosen from Cu, Mn, Ag and Au and 0.1-10.0% halide.

Platinum Metals Rev., 1977, 21, (2) 71
**Hollow Spheres for Encapsulating Precious Metals**  
**CANADIAN PATENTS & DEVELOPMENT LTD.**  
*U.S. Patent 3,975,194*

Microballoons which can incorporate small particles of Pt, Ag or Au, for jewellery purposes, or can be used to form hollow Pt/Al₂O₃ catalyst beads, are prepared by uniformly dispersing a soluble film-forming solid into a core solvent, shaping this mixture while still in the molten state, cooling to solidify as a shaped blend, slowly transforming the solid cone into a gas and removing and recovering the microballoons which have an inner sponge lining. The metal particles can be dispersed in the core while it is liquid and will migrate to form part of the shell.

**Noble Metal Halides as Colour Stabilisers**  
**MONSANTO CO.**  
*U.S. Patent 3,975,408*

The colour stability of refined dicarboxylic acid anhydrides, such as maleic anhydride, is improved by the addition of 0.01–1,000 ppm of a halide of Ru, Rh, Pd, Os, Ir or Pt.

**Platinum, Silver and Palladium Reaction Rate Modifiers for Hydrogen Production**  
**U.S. SECRETARY OF THE NAVY**  
*U.S. Patent 3,977,990*

H₂ gas evolution rates and the gas temperature of hydrogen generating solid compositions are modified by the addition of small amounts of various compounds including PtO₂, Pd, Ag₂CO₃, PdCl₂.

**Refining Platinum Group Metals**  
**MATTHEY RUSTENBURG REFINERS (PTY) LTD.**  
*U.S. Patent 3,979,207*

The separation and purification of platinum group metals, especially mixtures of Rh, Pt and Ir, which are present as salts in aqueous solution is achieved by adjusting the pH as necessary, to provide an acidic solution, contacting this with an oxidising agent sufficient to oxidise all Ir present to Ir(IV), then contacting the solution with a N₂-containing organic compound (chosen from secondary and tertiary amines and quaternary ammonium compounds), removing an organic phase which contains all the Pt and Ir present, removing the Ir from this phase by contacting with an aqueous solution of a reducing agent and removing the Pt remaining in the organic phase with an aqueous stripping solution.

**ELECTRICAL AND ELECTRONIC ENGINEERING**

**Light Emitting Display Device**  
**TOKYO SHIBAURA ELECTRIC CO. LTD.**  
*British Patent 1,455,195*

The device has an electric insulation base plate bearing printed conductive layers and conductive light reflectors of which one is made of one metal from the group Pt, Ag, Au, Ni and Al and the other is made from one metal of the above group but having a different colour.

**Resistance Composition**  
**C.T.S. CORP.**  
*British Patent 1,462,526*

An electrical resistance composition comprises a mixture of glass particles, a conductive phase consisting of RuO₂ and Ir, the Ir being present as an organometallic compound in solution, and a liquid carrier.

**Silver-Palladium Film with Improved Adhesion**  
**JOHNSON MATTHEY & CO. LTD.**  
*German Offen. 2,616,060*

A composite film, such as a Ag-Pd and Bi oxide thick film for a circuit, is obtained by using the molten oxide constituent to hold particles of the metal in place as a conducting layer.

**MEDICAL USES**

**Determining the Perfusion Efficiency Factor of Animal Tissue**  
**L. ESCHWEILER & CO.**  
*British Patent 1,461,345*

The rate of perfusion of an indicator substance is percutaneously measured in the tissue at a specified locus, and the indicator concentration is simultaneously measured at the same locus. Signals are obtained in dependence on the measurements and the signals are combined to obtain a composite signal corresponding to the factor. The apparatus used includes Ag/AgCl sensors and Pt electrodes.

**Palladium Dental Alloys**  
**FA. DR. TH. WIELAND**  
*German Offen. 2,523,971*

Pd alloys which are readily joined to porcelain for dental purposes contain 45–62% Pd, 25–42% Au, 5–22% Ag, up to 2% Sn and up to 1% Ti. The presence of Pd increases the adherence to porcelain and colour reproduction.

**Reduced Gold Dental Alloy**  
**JOHNSON MATTHEY & CO. LTD.**  
*Dutch Appl. 76.02206*

An alloy for use in restorative dental treatment contains 45–62% Pd, 25–42% Au, 5–22% Ag, up to 5% Ga, up to 2% In and up to 1% Sn.