PLATINUM METALS REVIEW

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The Platinum Metals in Crystal Pulling

CRUCIBLES AND OTHER APPARATUS

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The platinum metals do not react with most molten oxides and halides and therefore they have many applications in crystal pulling. They can be used not only for crucibles but also for heat shields and baffles to control both the spatial and temporal temperature distributions. The construction and use of these components is described in this article.

Single crystals of oxides and halides have an ever increasing number of uses. For example, gramophone styli, watch bearings, lasers, piezo-electric filters, and electro-optic devices are often made from oxide crystals and some optical components are manufactured from halide crystals. In many cases the most satisfactory crystals can be pulled from the melt by the method first used by Czochralski (1). One of the major difficulties with this technique is finding materials to make the necessary parts of the growth system. For oxides and halides the platinum group metals are often a good choice since they do not react with the molten charge or the atmosphere which must be maintained over it.

<table>
<thead>
<tr>
<th>Crystal†</th>
<th>Melting Point °C</th>
<th>Crucible Material</th>
<th>Atmosphere</th>
<th>Pulling Rate mm/h</th>
<th>Rotation Rate rev/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y_3Al_5O_12</td>
<td>1950</td>
<td>Iridium</td>
<td>Nitrogen</td>
<td>2</td>
<td>60</td>
</tr>
<tr>
<td>LiTaO_4</td>
<td>1650</td>
<td>Iridium</td>
<td>Nitrogen</td>
<td>10</td>
<td>30</td>
</tr>
<tr>
<td>CaWO_4</td>
<td>1650</td>
<td>Rhodium</td>
<td>Air</td>
<td>10</td>
<td>100</td>
</tr>
<tr>
<td>MnFe_2O_4</td>
<td>1500</td>
<td>Iridium</td>
<td>Nitrogen</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>NaBa_2NbO_13</td>
<td>1450</td>
<td>Platinum</td>
<td>Oxygen</td>
<td>5</td>
<td>30</td>
</tr>
<tr>
<td>Sr_2Ba_3Nb_5O_{16}</td>
<td>1406</td>
<td>Platinum</td>
<td>Oxygen</td>
<td>5</td>
<td>30</td>
</tr>
<tr>
<td>LiNbO_3</td>
<td>1250</td>
<td>Platinum</td>
<td>Air</td>
<td>10</td>
<td>100</td>
</tr>
<tr>
<td>ZnWO_4</td>
<td>1200</td>
<td>Platinum</td>
<td>Oxygen</td>
<td>5</td>
<td>30</td>
</tr>
<tr>
<td>BaClF</td>
<td>1008</td>
<td>Platinum</td>
<td>Nitrogen/Hydrogen</td>
<td>8</td>
<td>85</td>
</tr>
<tr>
<td>Bi_13GeO_{20}</td>
<td>930</td>
<td>Platinum</td>
<td>Oxygen</td>
<td>10</td>
<td>50</td>
</tr>
<tr>
<td>NaN_2O_5</td>
<td>271</td>
<td>Platinum</td>
<td>Vacuum</td>
<td>*</td>
<td>70</td>
</tr>
</tbody>
</table>

† The crystals of Y_3Al_5O_12 were for use in lasers. LiTaO_4, NaBa_2NbO_13, Sr_2Ba_3Nb_5O_{16}, LiNbO_3, and Bi_13GeO_{20} were for electro-optic devices. CaWO_4 and ZnWO_4 were for maser studies. MnFe_2O_4 was for tape recorder heads. BaClF was for a quantum counting device. NaN_2O_5 crystals were for pyroelectric devices.

* Kyropoulos method crucible cooled at 4 deg C/h

Fig. 1 A simple crystal pulling system. The melt is contained in a platinum crucible heated inductively. A seed crystal is lowered to touch the melt surface, is held there for a few minutes and then is raised slowly. The diameter of the growing crystal can be changed by varying the temperature of the crucible. The growing crystal is rotated to eliminate radial asymmetry. Both the lifting and rotary movements must be smooth if homogeneous crystals are to be grown; in this case both movements were provided by a hydraulic system (2).

Figure 1 shows a crystal being pulled from the melt. The caption explains the process and Table I enumerates conditions which have been found suitable for the growth of a number of crystals. There is an alternative process due to Kyropoulos (3) in which the crystal is not raised during growth but is allowed to grow into the melt as the crucible temperature is lowered. This process is widely used for halide crystals and requires essentially the same apparatus.

Both these processes need a crucible which does not react with the melt. For the crystals with lower melting points platinum is often satisfactory but, as Table I indicates, higher melting point materials necessitate the use of rhodium or iridium. Platinum has the advantages that it is the least reactive of these materials and is relatively easily worked. It has the disadvantage that in the pure state it is very soft at high temperatures so that it distorts in use, particularly if the melt expands on freezing. (It is unusual to remove all the melt during growth.) This problem can be overcome by alloying but some alloying elements can be leached from the crucible. Thus Whiffin and Orton (4) found that it was necessary to use high purity platinum for the growth of zinc tungstate if contamination by rhodium was to be avoided. (See Table II.) Melts containing alkali metal or bismuth ions also frequently leach impurities from platinum.

**Elimination of Distortion**

Problems with the distortion of pure platinum crucibles can be overcome in a number of ways. With some materials it is possible to supercool the melt by say 30°C before freezing is initiated and then rapidly raise the crucible temperature to a few degrees above the melting point before continuing to cool slowly. This results in the solid growing from the centre of the crucible rather than forming a solid skin locked to the crucible.
walls and trapping some unfrozen melt below it. An obvious but expensive alternative is to use a thicker crucible. However in practice it is only necessary to reinforce the rim as shown in Figure 2. A thick rim is in any case desirable in all crucibles heated inductively because small distortions can cause local hot spots producing local melting which spreads progressively. (Iridium crucibles are particularly prone to this type of failure.) Another method for preventing distortion is to hold the crucible in a rigid support; a tightly packed powder as shown in Fig. 3 is usually adequate or a casing of a castable ceramic can be used. Van Uitert (5) has described the use of an iridium crucible sealed between two platinum ones to achieve the rigidity of iridium combined with the corrosion resistance of platinum.

Clearly, in a crystal pulling system it is necessary to hold the seed crystal. Figure 2 shows one method and some alternatives are given in Fig. 4.

**High Quality Crystals**

So far, only the basic process has been discussed. However, the growth of high

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**TABLE II**

<table>
<thead>
<tr>
<th>Crucible</th>
<th>Rhodium in crystals mol. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh</td>
<td>0.075 *</td>
</tr>
<tr>
<td>Pt+10% Rh</td>
<td>up to 0.03</td>
</tr>
<tr>
<td>Pt+0.1% Rh</td>
<td>0.009</td>
</tr>
</tbody>
</table>

* This is sufficient to turn the normally colourless crystal black.
quality crystals often demands considerable refinement. The first improvement is to control (usually decrease*) the temperature gradient in the growing crystal (7). This can be done by placing a furnace over the crucible. However, a simpler and more reliable method is to use heat shields; Figure 3 gives some examples. If the most uniform possible crystals are required, it is necessary to eliminate the unsteady convection which can occur in melts heated from the side or from below. This convection produces a modulation of the growth rate which results in the presence of "growth striae" in the crystal. The effect can be eliminated by placing baffles in the melt (8, 9). In an unbaffled melt the temperature at a fixed point can oscillate several degrees with a period of a few seconds. A correctly located baffle can eliminate all measurable oscillations and so allow the production of extremely homogeneous crystals. Figure 2 shows the type of baffle used. This is lowered into the crucible after the charge has been melted. The baffle and two of the support wires are made of platinum, the third wire is 13 per cent rhodium-platinum. This wire with one of the others forms a thermocouple. The correct position for the baffle is the one which gives no variation in the output of this couple.

Precious metal thermocouples have other uses in crystal growth. With oxide and halide melts, for example, they may be used unsheathed to determine the temperature distribution in the melt, which is vital in the control of perfection (7). They can also be used to monitor the crucible temperature to ensure that the temperature control system

* It is sometimes necessary to increase the temperature gradient in order to maintain a constant diameter (6).
Fig. 4 Seed holders constructed from strip and wire. Their materials are selected to suit atmosphere and temperature. That on the left was made from platinum and was used for $B_{0,5}Sr_{1-x}Nb_2O_6$, that in the centre was for melts giving off corrosive vapours and that on the right in 40 per cent rhodium-platinum was for $Y_3Al_5O_{12}$.

is working, or even to activate it. Such couples should be welded to the crucible. Platinum: rhodium-platinum couples can conveniently be welded to platinum crucibles by heating both the couple and the crucible and then tapping the couple on to the crucible with a polished steel hammer. (This technique can also be used to fasten wires to other platinum components.) In inductively heated systems thermocouples can act as pick-up loops. This problem can be overcome by using a filter of the type shown in Fig. 5.

**Maintenance of Components**

Obviously, great care must be taken to ensure that the apparatus used in crystal growth is clean. Most melts are very reactive and will readily dissolve any contamination on surfaces which they touch. Some melts, e.g. ones containing bismuth oxide, are readily reduced by organic matter and a reduced melt will usually attack the platinum metals, so that care must be taken to remove lint and grease. The authors' colleagues soak new components in hydrochloric acid and remove traces of old melts with a fusion mixture composed of two parts of sodium carbonate and one part of disodium tetraborate. After washing away the fusion mixture with water a further soak is given usually in hydrochloric acid but for some melts (e.g.
ones containing lead ions) nitric acid is used. Large amounts of old melts are more easily removed with a trepanning drill before the use of the fusion mixture.

Apart from cleaning, precious metal components require little maintenance. Platinum parts which distort can be annealed and bent or hammered back into shape, although too much working is not desirable, and if much work must be done the material should be annealed several times. Annealing and welding are conveniently done with a gas torch but care must be taken to maintain an oxidising rather than a reducing flame.

This article discusses the main uses of the platinum group metals in crystal pulling. The ideas behind the use of the various components are given in the references so far cited and a comprehensive review is given in reference 10.

References

**Platinum in Crystal Growing and Optical Fibre Production**

Since the advent of solid state lasers in 1960 the optical and electronic industries have made significant developments in the preparation of novel oxide single crystal materials for devices such as light modulators, second harmonic generators and bubble domain memories. A further advance in materials technology is the development of optical fibre waveguides for communications. One factor common to these devices is that they are all produced with platinum apparatus.

Several grades of platinum are available for the fabrication of crucibles. The selection of a suitable grade of platinum is determined by the degree to which the optical or electrical characteristics of the end-product are influenced by specific trace impurities, and the physical and chemical properties of the crystal melt.

Where mechanical strength and thermal stability are important, as in general analytical work, platinum selectively doped with rhodium and iridium is used, although rhodium is slowly leached from the crucible by corrosive fluxes and highly reactive melts.

Platinum used for both melt and flux-melted crystal growing should be as free as possible from these and other metals, which may be detrimental to certain optical and magnetic devices. In the case of barium titanate, the ferroelectric Curie temperature may be lowered, whereas in lithium niobate the susceptibility of the crystals to laser damage may be increased. Rhodium also substitutes in the lithium niobate lattice, causing absorption in the visible region of the spectrum.

In order to reduce to an absolute minimum trace metal contamination of the crystals, it is advisable to employ crucibles fabricated from a thermocouple grade of platinum known as Thermopure. This material is, however, comparatively soft and if a thin wall is used the crucible may need to be reinforced at the rim or to be supported in a ceramic sheath.

In optical transmission fibres, absorption in the near and infra-red spectral region is controlled largely by sub-p.p.m. levels of the first row transition metal ions. Since the purity of the bulk glass is so critical it has been necessary to introduce an ultra-high purity Fibre-optic grade of platinum to meet the stringent requirements of this comparatively new technology. This Johnson Matthey material has a total metallic impurity level of less than 10 p.p.m. (total iron plus copper content less than 5 p.p.m.).

P.M.W.
Rhodium-Platinum Thermocouples as Precision Temperature Sensors

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The standard of accuracy of all platinum:rhodium-platinum thermocouples produced by Johnson Matthey Metals Limited is extremely high. However, individual thermocouples for special purposes can be supplied to even higher standards of accuracy following their precision calibration by the National Physical Laboratory.

The choice of the platinum:10 per cent rhodium-platinum thermocouple as the instrument for defining or reproducing that part of the International Practical Temperature Scale lying between the freezing point of antimony (630.74°C) and the freezing point of gold (1064.43°C) is mainly attributable to the remarkable accuracy and stability of this thermocouple at elevated temperatures. Furthermore the smooth e.m.f.-temperature relationship enables very accurate reference tables to be constructed (1), thus permitting interpolation with a high degree of confidence. Today this is also true of the platinum:13 per cent rhodium-platinum thermocouple, which is if anything more stable and has a higher output at a given temperature. For this reason the platinum:13 per cent rhodium-platinum thermocouple may well become the preferred combination for temperature measurement up to about 1500°C.

The stability and reproducibility of both thermocouples is very dependent on the purity and consistency of the platinum limb. Many years of experience coupled with strict quality control and inspection techniques have enabled Johnson Matthey Metals to achieve a standard accuracy of ±0.3°C over the range 0 to 1100°C and the results are presented as a report. These calibrated thermocouples are used as standards in the calibration of other thermocouples, and Johnson Matthey Metals Limited are called upon regularly to supply them both to national standardising laboratories and to industrial concerns where extremely precise temperature control is necessary. One such thermocouple is shown in Fig. 1.

The calibration of platinum:10 and 13 per cent rhodium-platinum thermocouples is one service of the Measurement Group of the National Physical Laboratory. The most precise calibration of an individual thermocouple amounts, in effect, to determining by how much it differs from the appropriate reference table. This is achieved by measuring the thermocouple e.m.f. values at a series of precisely known temperatures and comparing them with the corresponding e.m.f. values given in the reference table for the same temperatures. A smooth curve of difference derived from and linking these measurement points enables interpolation between the calibration temperatures to be obtained by difference from the reference table. In practice the measurements are obtained by adopting the procedures and methods con-
tained in the recommendations of the International Practical Temperature Scale of 1968 (IPTS-68).

**Procedure for Assembly and Calibration**

The process of assembly of a thermocouple is as follows. Immediately on receipt at N.P.L. the thermocouple wires are annealed electrically, the platinum limb at 1100°C and the alloy limb at 1450°C. The wires are then threaded through a rigid and continuous twin-bore alumina insulator about 400 mm long. The hot junction is made by welding the wires together in an oxy-gas flame. While in this form the thermocouple is annealed again at 1100°C to eliminate the effect on thermal e.m.f. of any cold work or strain introduced during assembly.

The significance of the continuous length of rigid insulator lies in the desirability of maintaining the wires in a strain-free and uncontaminated condition. If these conditions do not prevail in any parts of the wire where considerable temperature gradients may occur then the thermocouple is likely to generate spurious e.m.f.s to the detriment of the calibration. It should be remarked here that subsequent use of the thermocouple at temperatures significantly above 1100°C can lead to changes in its behaviour which invalidate the high-accuracy calibration.

At the cold end of the thermocouple the reference junction is formed by winding a pure copper wire around each limb and then placing the four suitably insulated wires in a close-fitting glass tube, which is maintained with adequate immersion in a melting ice and water mixture at 0°C.

The calibration begins with measurements of thermal e.m.f. at the freezing point of gold (1064.43°C), followed by the freezing point of silver (961.93°C). Figures 2 and 3 illustrate the apparatus, the most notable features being the nickel block to promote the uniform temperature zone enveloping the ingot, and the graphite lid, crucible and re-entrant tube which safeguard the metal against risks of oxidation and contamination. The protected thermocouple is placed in the
graphite re-entrant tube and the ingot is melted. It is then cooled slowly and as it freezes a cooling curve of e.m.f. against time is plotted. The freezing point value is taken to be that corresponding to the plateau or level part of the curve. By controlling the cooling rate the plateau is readily sustained for a half hour or more, signifying that the equilibrium state is obtained. That the immersion of the thermocouple is sufficient to preclude thermal losses by conduction along the wires is demonstrated during the freeze by varying the immersion depth by about one centimetre, when the measured e.m.f. should not change by more than one microvolt.

The freezing point temperature is taken to be precisely that ascribed to the pure metal and requires that the purity of the metal, as supplied by the manufacturer, is compatible with the limits of accuracy imposed on the measurements. In this case a purity of 99.999 per cent is used, leading to a depression of the freezing point which is not likely to exceed a few millidegrees Celsius.

The calibration is continued in a uniform-temperature enclosure, available in the form of a stirred-liquid bath of concentric design and proven performance. This apparatus is shown in Fig. 4. The inner tube of the bath is about 7.5 cm in diameter and 65 cm deep, and under working conditions is constantly filling with a stirred liquid whose temperature is nominally uniform throughout. The liquid is a commercially available mixture of potassium nitrate and sodium nitrite salts, which is molten and usable in the bath from about 160°C to 630°C. [Some very real dangers attend the use of these mixtures: see H.M.S.O. Booklet No. 27, 1964, “Precautions in the Use of Nitrate Salt Baths.”]

In this medium the thermocouple is protected by a pyrex glass sheath and is calibrated by measuring its e.m.f. at a series of known
Calibration of thermocouples at N.P.L. includes plotting the thermal arrest at the freezing point of silver. The cold junctions are held in the flask of melting ice at 0°C. The use of a reversing switch eliminates the effect of stray e.m.f.s in the measuring system.

Simultaneous comparison at N.P.L. of temperature measurement by means of a platinum resistance thermometer and a.c. double bridge with the thermal e.m.f. of a J.M.M. thermocouple under test in a stirred-liquid salt bath.
and steady temperatures—generally 200, 400 and 600°C. The bath temperature is controlled electrically and is determined by reference to a standard platinum resistance thermometer used in conjunction with an a.c. double bridge having inductively-coupled ratio arms. As a secondary standard instrument the resistance thermometer is itself calibrated by the N.P.L. Measurement Group in terms of IPTS-68 and is capable of measuring temperature to an accuracy of a few millidegrees Celsius.

Throughout the tests the e.m.f. measurements are effected by means of a precision vernier potentiometer or by a digital voltmeter of comparable discrimination and as a normal precaution against the effects of stray thermal e.m.f.s a reversing switch is included in the measuring system.

The calibration is concluded with the compilation of a table recording the e.m.f. output of the thermocouple quoted to the nearest microvolt for a series of nominal temperatures covering the range. Provided that the performance of the thermocouple has been satisfactory the calibration is given an accuracy of ±0.3°C.

Sensitive devices like these thermocouples call for special care in manufacture, in carriage and in use. Johnson Matthey Metals have recently introduced a foam-lined case, shown in Fig. 1, in which each thermocouple is sent to the National Physical Laboratory for calibration. On return from N.P.L. each thermocouple is despatched in its case, together with its N.P.L. calibration report, from Johnson Matthey direct to the customer, thereby ensuring that its accuracy is not impaired in transit by cold work induced by handling during transfer from one case to another. Thereafter the life of the calibration is finite, of course, and the rate of change from calibration will depend upon the frequency and conditions of use.

**Reference**


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**Connectors for Metal Clad Thermocouples**

**PLUG-IN END CAPS FOR COMPENSATING LEADS**

A new type of end connector recently developed by Johnson Matthey Metals Limited enables the compensating lead to be disconnected from the thermocouple, so making thermocouple replacement simpler. The new unit makes it possible to connect one lead in turn to any number of thermocouples, thus saving on the number of leads and temperature recording instruments.

Housed within the anodised aluminium case are gold plated pins and sockets, to which are soldered the thermocouple wires and the compensating cable respectively. The assembly is then encapsulated in nylon to form a two-piece connector, each half bearing corresponding flats to ensure correct polarity with every connection.

These end connectors satisfactorily withstand operating temperatures of up to 100°C, the normal working temperature of the compensating lead. At this temperature stray e.m.f.s at the pin and socket junctions are negligible and do not affect output of the thermocouple.

Colour coding of the aluminium cases easily identifies thermocouples; red denotes platinum: 13 per cent rhodium-platinum, gold denotes platinum: 10 per cent rhodium-platinum, and silver or neutral colour other combinations (5 per cent Rh-Pt: 20 per cent Rh-Pt, 6 per cent Rh-Pt: 30 per cent Rh-Pt, Pallador).
Pollution from Nitric Acid Plants

PURIFICATION OF TAIL GAS USING PLATINUM CATALYSTS

By R. A. Searles
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The tail gas stream from ammonia oxidation plants for the production of nitric acid contains nitrogen oxides, which present a pollution problem. These pollutants can be eliminated successfully by reduction with a fuel gas over Honeycat platinum on ceramic honeycomb catalyst, which has been developed and is produced by Matthey Bishop Inc. and Johnson Matthey Chemicals Limited. Such Honeycat installations in nitric acid plants are becoming numerous and widespread.

The production of nitric acid by the oxidation of ammonia is an important industrial process throughout the world. Nitric acid is used in the manufacture of many products, notably fertilisers, explosives and nylon. While these products may be instrumental in improving the standard of life, nitric acid production can give rise to serious pollution problems. One way in which this problem can be minimised involves platinum metal catalysts, as described in this article.

Production of Nitric Acid

A typical nitric acid plant flow diagram is shown in Fig. 1. The first part of the nitric acid process involves the reaction of ammonia and air under pressure on a rhodium-platinum gauze to give nitric oxide. (Equation 1). After the process gases have been cooled in a series of heat exchangers, boilers and steam super-heaters, they pass into an oxidising absorption tower where with air and water they react to form nitrogen dioxide and subsequently nitric acid. (Equations 2, 3.)

\[
\begin{align*}
4\text{NH}_3 + 5\text{O}_2 & \rightarrow 4\text{NO} + 6\text{H}_2\text{O} \quad (1) \\
2\text{NO} + \text{O}_2 & \rightarrow 2\text{NO}_2 \quad (2) \\
3\text{NO}_2 + \text{H}_2\text{O} & \rightarrow 2\text{HNO}_3 + \text{NO} \quad (3)
\end{align*}
\]

The residual nitric oxide in equation 3 is in practice reoxidised to nitrogen dioxide for further conversion to nitric acid. There is an economic limit to the size of the absorption tower that is practicable and the absorption efficiency achieved is generally in the range 98.2 to 99.3 per cent (1). It is the residual concentrations of nitrogen dioxide and nitric oxide (commonly shortened to \(\text{NO}_2\)) that give rise to the pollution problem.

Pollution by Nitrogen Oxides

Nitrogen dioxide is a red-brown acidic gas with a pungent odour; nitric oxide is colourless and odourless but is oxidised by the oxygen in air to nitrogen dioxide. The toxic effects of nitrogen dioxide are well documented (2). For example, exposure of man to nitrogen dioxide at levels of 300 parts per million (p.p.m.) may cause fatal bronchopneumonia. Long-term exposure to plants at levels of below 1 p.p.m. can cause leaf damage and decreased fruit yield.

The effluent gas from a typical nitric acid plant of 350 tons/day capacity has a volume of about 20,000 standard cubic feet/minute (34,000 normal cubic metres/hour) with a typical composition in the following range:

- \(\text{NO}_2, \text{NO}_3 (\text{NO}_2)\) : 0.08–0.30 per cent
- Oxygen : 2–3 per cent
- Nitrogen, water : Balance
Expressed in terms of weight the total NO\textsubscript{x} emissions would be over five tons/day (3).

**Removal of Nitrogen Oxides**

After the gases have left the absorption tower they possess considerable energy, still being at the plant pressure, which may be up to eight atmospheres. This energy is recovered on passing through an expansion turbine; the rotational energy recovered is normally used to drive the plant's compressor.

There are several methods by which the concentration of nitrogen oxides in the tail gas can be reduced to more acceptable levels.

**Absorption**

By increasing the size of the plant's absorption tower its efficiency may be increased. This is generally a high capital outlay, particularly for an existing plant, and this outlay is not compensated for by the small increase in nitric acid production that results.

**Adsorption**

An adsorption system using molecular sieve principles may be installed to recover the nitrogen oxide emissions and to regenerate additional nitric acid. Although impressive claims have been made for these processes, there are to the author's knowledge no commercial plants operating at the present time.

**Catalytic Combustion**

The catalytic reduction of nitrogen oxides to nitrogen gas takes place on a catalyst such as platinum or palladium on a ceramic honey-

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*Platinum Metals Rev., 1973, 17, (2)*

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comb support or alumina pellets or nickel-chromium alloy ribbon. This method involves an increase in the capital cost of the plant but recent estimates (1) show that for a 450 ton/day plant the cost for lowering the NO\textsubscript{x} outlet concentration to 300 p.p.m. would be $200,000 lower for catalytic combustion than for an increased absorption capacity at higher pressure giving the same efficiency.

**Catalytic Reactions**

The catalytic method for removing the nitrogen oxides is based on the reaction of NO\textsubscript{x} with a fuel to give colourless and harmless nitrogen and water. The reducing fuel chosen is generally determined by availability and price; typical fuels are hydrogen (for example, ammonia synthesis-loop purge gas or refinery off-gas), light naphtha, methane (natural gas), or L.P.G. (butane or propane).

The tail gas from the absorption tower is pre-heated by heat exchange with the hot gases from the rhodium-platinum ammonia-oxidation gauze to a temperature which is dependent on the design of the plant and the fuel used. This is shown in Fig. 1. Minimum inlet temperatures for good conversion efficiency and catalyst life are shown below for commonly used fuels with the Honeycat* catalyst specially developed by the Johnson Matthey Group.

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>200</td>
</tr>
<tr>
<td>Naphtha, L.P.G.</td>
<td>350</td>
</tr>
<tr>
<td>Natural gas</td>
<td>480</td>
</tr>
</tbody>
</table>

The fuel gas is introduced into the gas stream and a homogeneous mixture of tail gas and fuel passed into a reactor containing a bed of catalyst as shown in Fig. 2. Honeycat

*Registered trade mark. Marketed under the name THT in North America by Matthey Bishop Inc.
catalyst consists of platinum metals deposited on a ceramic honeycomb. The bed is built up from slabs of the catalyst. The reactions taking place on the catalyst surface can be divided into two groups. The first group of reactions involves the reaction of the fuel with oxygen and nitrogen dioxide, reducing the latter to nitric oxide. These reactions take place first and are sometimes referred to as the decolorisation reactions.

\[
\begin{align*}
\text{CH}_4 + 2\text{O}_2 & \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \\
2\text{H}_2 + \text{O}_2 & \rightarrow 2\text{H}_2\text{O} \\
2\text{C}_4\text{H}_{10} + 13\text{O}_2 & \rightarrow 8\text{CO}_2 + 10\text{H}_2\text{O} \\
\text{CH}_4 + 4\text{NO} & \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} + 4\text{NO} \\
\text{H}_2 + \text{NO} & \rightarrow \text{H}_2\text{O} + \text{NO} \\
\text{C}_4\text{H}_{10} + 13\text{NO}_2 & \rightarrow 4\text{CO}_2 + 5\text{H}_2\text{O} + 13\text{NO} 
\end{align*}
\]

In the past, plants have been designed where sufficient fuel is added to raise the temperature of the tail gas and to decolorise the nitrogen oxides. The primary purpose of this operation is to increase the amount of power recovered at the expansion turbine by operation at a higher temperature. Decolorisation is a bonus which, while it does not reduce the total acidity of the tail gas, does in fact improve the appearance of the plant and make it a less obvious polluter. However, no new plants are being built with decolorisation and the remainder of this paper will be concerned with total abatement.

The second group of reactions does not commence until reducing conditions have been achieved by all the oxygen in the tail gas being reacted with the fuel. These are sometimes referred to as the abatement reactions.

\[
\begin{align*}
\text{CH}_4 + 4\text{NO} & \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} + 2\text{N}_2 \\
2\text{H}_2 + 2\text{NO} & \rightarrow 2\text{H}_2\text{O} + \text{N}_2 \\
2\text{C}_4\text{H}_{10} + 26\text{NO} & \rightarrow 8\text{CO}_2 + 10\text{H}_2\text{O} + 13\text{N}_2 
\end{align*}
\]

Provided that a sufficient quantity of fuel is provided to react with the oxygen and the nitrogen oxides, the gases leaving the catalyst reactor will contain substantially reduced...
concentrations of nitrogen oxides and oxygen and will consist almost entirely of nitrogen gas and water vapour. Total abatement generally means NOx removal down to below 200 p.p.m. The advantages of operating a fuel-rich system are lower light-off temperature and higher conversion efficiency when compared to operation under decolorising or oxidising conditions. (Figs. 3 and 4).

The reaction of the fuel gas with the oxygen in the tail gas is, of course, an exothermic reaction and the gas leaves the catalyst at an elevated temperature. This temperature rise is proportional to the oxygen content of the tail gas but varies according to the pressure and temperature of the reaction. As a general rule, however, the following temperature rises can be used for each one per cent of oxygen that is burnt with the named fuel.

Hydrogen : 160°C
Methane, naphtha, butane, propane : 130°C

This temperature rise puts a limitation on the amount of oxygen that can be removed on a single stage. The maximum oxygen content can be calculated by subtracting the inlet temperature required with the chosen fuel from the maximum permissible operating temperature of 750°C and dividing by the temperature rise obtained if one per cent of oxygen were burnt with that fuel. For example, with hydrogen fuel and an inlet temperature of 200°C the maximum temperature rise allowable is 550°C and the maximum oxygen concentration is 3.4 per cent.

Form of Catalyst

The composition and form of the catalyst used for the above reactions has an important bearing on the flexibility of the operation, the degree of abatement achieved, the efficiency of fuel combustion, and the catalyst life.

The advantages of using ceramic honeycomb supports for platinum metal catalysts for various gas phase reactions, such as odour and NOx removal, and the treatment of diesel and petrol engine exhausts, have been covered in previous articles in this journal (4–9) and may be summarised as compact process design, high activity, low pressure drop and good catalyst life. These advantages have led to honeycomb-based systems becoming widely accepted, in preference to pelleted or metal ribbon supported systems for the application under discussion.

The activity of the catalyst is particularly important when methane is used as the reducing fuel because the methane molecule has high stability and is difficult to oxidise. The Honeycat range of catalysts is based on platinum because platinum has high stability coupled with good activity and because under reducing conditions it does not allow carbon formation, which may occur with palladium-based systems. For methane
combustion an improved version of the Honeycat catalyst has been developed to give higher activity for methane oxidation while retaining the resistance to carbon formation.

Operational Plants

A description of the method of operation of a NOx abatement system at the plant of BASF-Antwerpen in Belgium will serve to illustrate the principles involved and the advantages to be gained by catalytic abatement. The schematic flow diagram of this 540 ton/day Chemico plant is shown in Fig. 1. In this plant a Chemico Dual Combustion system is used so that the outlet temperature from the Honeycat catalyst is kept low enough to enable hot tail gas to pass directly into the expansion turbine for greater power recovery. Figure 5 shows the reactor.

A part of the tail gas is heated to the required inlet temperature of 480°C, mixed with the methane fuel and passed into the first catalyst stage. Reaction takes place on the catalyst and the hot gases leaving the catalyst are then mixed with the other part of the tail gas, which is at a much lower temperature. This quenches the hot tail gas and returns the second stage inlet temperature to the same level as that required by the first stage. By this means the average inlet temperature required is lower than the minimum inlet...
temperature and a higher percentage of oxygen can be treated without exceeding the maximum operating temperature of the catalyst.

During the first thirteen months operation of the Honeycat catalyst at BASF the average NO\textsubscript{x} outlet concentration has been 100 p.p.m. and the maximum has not exceeded 200 p.p.m. During this first year the fuel consumption has not increased and the stack has been colourless (Fig. 6).

Honeycat catalysts have now been installed in nitric acid plants operating in the USA, Canada, Australia and Belgium; some 20 plants are currently operating on purge gas and methane fuels with catalyst lives of up to five years. Further European installations will be made shortly.

References

4 J. B. Hunter, Platinum Metals Rev., 1968, 12, (1), 2-6
Artificial pacing of the heart is one of the earliest examples of electronic equipment applied to the long term treatment of patients rather than to its usual role of diagnosis. The heart pacemaker is a device which is totally implanted in the body and which provides a small electric shock to the heart to make it beat at the correct rate. This is required in patients who have a clinical condition in which the heart rate falls to 30 to 40 pulses per minute instead of the required 70 to 80 pulses per minute.

The standard method of pacing the heart is by an endocardial electrode, which is an insulated wire with a contact tip of platinum, inserted down the external jugular vein into the right ventricle of the heart. The pacemaker unit itself is inserted either over the patient's pectoral fold or in the right upper quadrant of the abdomen.

The development of a totally implanted pacemaker depends upon the ability to produce a small sterilisable unit which is inert in body tissue. The electronic circuitry presents few problems apart from the power source, which takes up about two-thirds of the volume of a pacemaker and for which mercury cells are commonly used. The only British manufacturer of an implanted pacemaker is Devices Implants Limited of Welwyn Garden City in Hertfordshire, a firm which has been developing and manufacturing them for many years. For their pacemakers, all components must pass strict mechanical, electrical and body compatibility tests.

The only metallic materials which have proved completely safe when implanted in the severe environment of the human body are platinum and 10 per cent iridium-platinum alloy, because of their remarkable resistance to corrosion. The latter is used on the pacemaker as the indifferent or earth return electrode, which can be clearly seen in the illustration.

The major problem still facing the manufacturer of any implanted active system is that of the power supply. The mercury cell produces 1.35 volts and will run for approximately 2½ to 3 years in a pacemaker. This means that every 2½ years the patient has to have the pacemaker removed and a new one inserted.

There are many interesting new approaches to the power supply problem. One of these is a biogalvanic cell utilising the oxygen available in the body. This oxygen is reduced...
in the cell using platinum black on a platinum grid as the catalyst. Another approach is the isotope battery, in which the heat generated by the radioactive isotope plutonium 238 is converted to electrical energy using a thermopile.

It is hoped that, by new methods of powering pacemakers, patients will be able to have trouble-free pacing for a period of at least five years. After discharge from hospital following an implantation the patient can lead a normal life, returning to hospital for checks from time to time to make sure that all is well with the system. Thousands of people who would otherwise be totally incapacitated are working and enjoying life again thanks to cardiac pacemakers for which the platinum and 10 per cent iridium-platinum electrode materials were supplied by Johnson Matthey Metals Limited.

Analytical Chemistry of the Platinum Metals

PROCEEDINGS OF THE SOUTH AFRICAN SYMPOSIUM

Techniques for the analysis of the platinum group metals and their alloys and compounds are receiving greater attention as the number of their applications increases and as the circle of consumers, refiners and producers widens. This was recognised by the holding in February of last year of a special symposium on “Analytical Chemistry of the Platinum-group Metals” at the National Institute for Metallurgy, Johannesburg. The symposium was attended by many of the most prominent workers in this fascinating field of modern inorganic chemistry. Fifteen of the 21 papers presented there have now been published in the Journal of the South African Chemical Institute (1972, 25, (3), 155-319).

As an introduction J. T. Moelwyn-Hughes (University of the Witwatersrand) gives a general survey of the chemistry of platinum metals and indicated studies which should lead to improved analytical schemes.

G. H. Faye and P. E. Moloughney (Canadian Department of Energy, Mines and Resources) described techniques for the separation and collection of precious metals using tin and showed that it is an efficient collector for all eight precious metals. R. V. D. Robért et al. (National Institute for Metallurgy) showed that nickel sulphide has several advantages over lead as a collector, except in the case of gold. A comparison of fire assay, aqua regia leach and high temperature chlorination treatments of ores and concentrates was made by I. Palmer et al. (N.I.M.) showing their general agreement, except that recovery of platinum from an ore was markedly greater by the leach methods.

Chromatographic separations of the non-volatile platinum metals on cellulose columns were shown by C. Pohlandt et al. (N.I.M.) to be relatively simple and rapid. F. von S. Toerien et al. (S.A.A.E.B.) indicated a possible series of separations of some noble metals from base metals by ion exchange.

The interferences which may be encountered in atomic absorption methods were discussed by R. G. Mallett et al. (N.I.M.) together with methods to overcome them. The graphite rod furnace technique was shown by B. D. Guerin (N.I.M.) to be useful for very low levels of the noble metals (except osmium) and the technique of pressure dissolution prior to atomic absorption was shown by D. C. G. Pearton et al. (N.I.M.) to be very effective.

J. Turkstra et al. (National Nuclear Research Centre) showed that neutron activation methods they used were not too successful on ores and flotation concentrates. A spectrometric method used by R. A. Snodgrass (South West Africa Co. Ltd.) for determining platinum group metals in gold-bearing ores encountered difficulties because of the heterogeneous distribution of the osmiridium. K. Dixon and T. W. Steele (N.I.M.) found that a spectrometric technique for determining noble metals in solution using the rotating disc method had adequate sensitivity and precision when base metals were absent.

A new method presented by P. W. Gerrard and W. Westwood (Johnson Matthey & Co. Ltd.) was concerned with the application of membrane filtration and X-ray fluorescence examination of the thin layer on the filter. B. G. Russell et al. (N.I.M.) described X-ray fluorescence analysis of ore, nickel sulphide mattes, ion exchange resins, and matte leach residues. Methods for the determination of osmium and ruthenium were reviewed by G. H. Faye.

Platinum Metals Rev., 1973, 17, (2) 65
The original metric standard of weight adopted in 1799 was a kilogram fabricated from platinum. The present international standard kilogram was made nearly a century ago from 10 per cent iridium-platinum. Johnson Matthey was deeply concerned with this work and since then has regularly supplied further national prototypes and working standards to a strict specification.

Amid the turmoil of the French Revolution a group of some of the most prominent scientists of the eighteenth century achieved one major positive step—the foundation of a new unified system of weights and measures, now known to us as the metric system. Lavoisier, while a member of the Provincial Assembly of Orléanais, had advocated the introduction of such a system to replace the confusion of separate provincial systems of weights and measures then prevailing in France (1). When he became a member of the Third Estate in the States-General of 1789 he found his views reflected widely and the National Assembly adopted a proposal by Talleyrand that the Academy of Sciences should set up a Commission to formulate the unified system.

All the members of this Commission were eminent French scientists but the most important worker on this project was Lavoisier himself. Antoine Laurent Lavoisier was born in 1743 and showed an early interest in matters of a scientific nature. After studying at the University of Paris he undertook mineralogical and chemical researches for the French Government, for example in the improvement of gunpowder manufacture. His chemical work has led to him being described as “the father of chemistry”. He also held a position in the tax-farming structure, which ultimately brought him to his death during the Revolution.

The members of the Commission were Laplace, Lagrange, Borda, Monge, and Condorcet. Lavoisier was appointed as
secretary to the Commission and also worked with Hauy to determine the weight of one cubic centimetre of distilled water, to be known as the gram. The centimetre was, of course, one hundredth part of a metre, the latter being defined as \( \frac{1}{10,000,000} \) part of the meridian quadrant passing through Paris. The work on the gram took place in Lavoisier's laboratory at the Paris Arsenal but it was interrupted by the dissolution of the Academy. Lavoisier himself was guillotined by the Revolutionary Tribunal in May 1794 but work had progressed sufficiently for prototype standards to be constructed from 1795 onwards. The metric system was finally confirmed in 1799 while Napoleon was First Consul.

The most convenient standard of weight proved to be the kilogram, defined as equal to the mass of one cubic decimetre of distilled water at its maximum density, which occurs at \( 4^\circ \)C. The material form of the standard kilogram took the shape of a platinum cylinder of height equal to its diameter. The first material prototype standards of the metric system were fabricated by Marc Etienne Janety, who was recalled to Paris to undertake the work from Marseilles, whither he had gone to take refuge from the Terror, as he had been a court goldsmith. The prototypes were called the Mètre and Kilogramme des Archives. Janety fashioned several platinum standard metres and kilograms from about 1795 (2, 3) and one of the latter is illustrated in Fig. 1.

**Bureau International des Poids et Mesures**

During the nineteenth century it was shown that the volume of a kilogram of water derived from the first standard platinum kilogram was \( 1.000028 \) dm\(^3\) at standard conditions, i.e. there had been an error of 28 parts in one million during fabrication of the man-made standard kilogram. This serious discrepancy illustrates the early difficulty in preparing accurate standards. It
thus became necessary to revise and improve the standards.

In 1870 as a result of the need for worldwide unification of measures the French government arranged a conference of representatives from 24 countries to consider such matters. This led to the Convention du Mètre and on May 20th, 1875, 28 countries agreed to set up the Bureau International des Poids et Mesures at Sèvres, a suburb of Paris. The first mission of the Bureau was to construct and maintain international prototypes of the metre and the kilogram, and to furnish copies of these standards to the various countries party to the convention.

The new standards were made by the Bureau as near as possible to the values of the Mètre and Kilogramme des Archives. The alloy chosen for their fabrication was 10 per cent iridium-platinum because of its stability, hardness, high density, and resistance to corrosion. It remains the specified material to this day.

The firm of Johnson, Matthey & Co was concerned intimately in this work (4). Already George Matthey had supplied Russian metal for standards and had assisted in its refining, melting and casting into ingots from which standards were produced in 1874. Now further orders followed with fabrication taking place in 1878 and 1879. Then agreements made in 1882 with the French government led to Johnson, Matthey & Co producing 30 standard metres and 40 standard kilograms, all in the 10 per cent iridium-platinum alloy.

The First General Conference of Weights and Measures was held in September 1889 and approved the new standards. The kilogram was redefined arbitrarily in terms of the new International Prototype Kilogram so that our present standard of mass has a permanence dependent only upon the stability of the iridium-platinum alloy. The International Prototype Kilogram is a 10 per cent iridium-platinum cylinder with diameter and height both equal to 39 mm. The national prototype kilograms in each state standardising laboratory are intercompared periodically with the working standards of the Bureau but to prevent damage and to avoid the risk of any minute change of mass the International Prototype Kilogram itself has been intercompared with other prototypes only once, in 1946, since its acceptance in 1889. State standardising laboratories determine the mass of their working standards against their national prototypes as mass references.

Production of Kilogram Cylinders

From time to time further national prototypes and working standards are required. The Johnson Matthey Group has been called upon regularly to supply them. A group of three such cylinders is shown in Fig. 2 and was produced recently by Johnson Matthey Metals Limited for the Bureau.

The specification for kilogram cylinders is very strict. It calls for an alloy composed of 89.75-90.25 per cent platinum and 9.75-10.25 iridium. The maximum proportion of metallic impurities allowed is 0.1 per cent ruthenium, 0.1 per cent iron, 0.15 per cent rhodium and palladium together, and 0.02 per cent all other metals together. Each cylinder is to be 39.2 mm diameter, 39.5 mm high and of minimum mass 1020 g as supplied. There must be no apparent surface defects and the alloy must be free of internal porosity or cracks. The density must be not less than 21.53 g/cm³ at 0°C.

Rigorous testing for defects is carried out by Johnson Matthey Metals before the cylinders are despatched to the Bureau, which carries out the final stages of comparison, applying the final adjustments necessary to give the extreme degree of precision of all kilogram standards in service.

References

3 D. McDonald, Platinum Metals Rev., 1968, 12, (4), 142-145

Platinum Metals Rev., 1973, 17, (2) 68
ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Wire of Chemically Pure Platinum Grades PLO-A and PLZ-A. Quality Requirements for Certified Products
U.S.S.R. Std. GOST 5107s-71

This Russian standard specifies the limits of diameter, purity of Pt, methods of packing and labelling for transport, and duration of guarantee for certification of Pt wire of the grades mentioned.

Enthalpy and Derived Thermodynamic Functions of Platinum and a Platinum-Rhodium Alloy from 400 to 1700°K

Revised values of the enthalpies of pure Pt and 10 wt.% Rh-Pt from 400-1700°K and molar thermodynamic properties of Pt from 300-2000K are given. It is suggested that the high temperature properties of Rh require redetermination.

Physical Characteristics of Electrodeposited Finely Divided Platinum-Cobalt Alloys
A. I. ZAYATS, A. A. PAVLYUKOV and N. A. PEREKHREST, Porosh. Met., 1972, 12(4), 7-11

Pt-Co alloy powder was electrodeposited from a solution of constant Pt and Co ion concentration. The structure and coercive force of the alloy depended on its Pt content; its dispersion was unaffected by electrolysis conditions.

Features of the Fine Structure and Magnetic Properties of Iron-Platinum Alloys with 32 and 35 at.%Pt

Monocrystals of 32 and 35 at.% Pt-Fe were studied by X-rays in the equilibrium and high coercivity states, and during isothermal annealing. The change in magnetic saturation and in coercive force during annealing at 750°C was also studied. Relation of structural changes to magnetic properties led to conclusions as to the structural features responsible for the high coercive force.

Effect of Plastic Deformation on the Structural Composition and Coercive Force of Some High Coercivity Alloys

X-ray and electron microscopy studies of the effect of plastic deformation on the structure and coercive force of ordered FePt, FePd and CoPt show that deformation induces partial heterogeneity together with breakdown of lamellar domains with double orientation. The coercive force is related to the stage of plastic deformation according to these factors.

Preparation, Single Crystal Growth, and Characterisation of PtSi and PtGe

Large polycrystalline ingots of PtSi and PtGe were prepared by lowering a coiled 99.999% pure Pt wire into molten Si or Ge at a controlled rate under an Ar atmosphere. Single crystals up to 1.8 x 3.5 cm were then grown. Both materials show diamagnetism and good electrical conductivity; their bulk densities and Seebeck coefficients are also reported.

Superconductivity in the Palladium-Hydrogen and the Palladium-Deuterium Systems
B. STRITZKER and W. BUCKEL, Z. Physik, 1972, 257(1), 1-8

Superconducting transitions were observed in the Pd-H and Pd-D systems up to 9K and 11K, respectively. The high concentrations necessary for superconductivity are obtained by implanting H or D ions into the Pd at T_{liq.He}.

Lattice Spacings and Magnetic Susceptibilities of Palladium-Lanthanum, Palladium-Cerium and Palladium-Praseodymium Alloys
J. D. SPEIGHT, J. Less-common Metals, 1973, 30(11), 159-163

Lattice constants and magnetic susceptibilities of rapidly quenched 1-4 at.% La-Pd and Pr-Pd and of 2-8 at.% Ce-Pd alloys were measured. Results suggested that the f states in Ce in solid solution in Pd are not occupied, the effective valency then being four.

The Alloys of Palladium with Yttrium, Samarium, Gadolinium, Dysprosium, Holmium and Erbium

Phase diagrams of Pd-Ln alloys were determined by D.T.A., X-ray diffraction and metallographic techniques. In general seven phases occurred: LnPd$_{10}$, LnPd$_{4}$ and LnPd (and LnPt$_{4}$ when Ln=Y, Dy, Er), all melting congruently; and
Ln₃Pd, Ln₅Pd₂, and LnPd₄ (and Ln₃Pd₂ when Ln = Sm, Gd, Ho), formed by peritectic reactions. Structural data are given for LnPd₃, LnPd, Ln₅Pd₂ and Ln₃Pd₂.

Excess Specific Heat of a Glassy Pd₀.775Cu₀.06Si₀.165 Alloy at Low Temperature


The specific heat of Pd₀.775Cu₀.06Si₀.165 was measured at 2.0-18.0 K. The electronic specific heat of the glassy phase is much smaller than the value calculated assuming the electrons to be free, suggesting a strong association between Pd and Si and a high degree of short range order. The glassy phase has a greater specific heat than the crystalline phase, very similar in position and magnitude to the excess shown at low temperatures by other glass-forming solids.

The Electrical Resistivity of Iridium at High Temperatures

R. T. WImBer and J. J. HAlYorSon, J. Mater., 1972, 7(4), 564-567

The electrical resistivity of Ir was measured in the range 293-2275K and an expression was derived to T⁴. Values for the temperature coefficient of resistivity are given.

On the Constitution of the Rhodium-Lead System

M. EL-BorAGy, K. C. JAIN, H. W. MAYER and K. SCHUBERT, Z. Metallkd., 1972, 63(11), 751-753

The phase diagram of the Rh-Pb system and lattice parameters of several of its crystal structures were determined. Stability of the phases is discussed.

On the Tensile Properties of Recrystallised Molybdenum Wire Alloysed with Ru and C


The modification of the tensile properties of recrystallised 0.02 wt.% C-Mo by 0.14 wt.% Ru was investigated. Ru increases strain-hardening but decreases hardness and yield strength at room temperature, thus increasing ductility; it increases yield strength at high temperatures and decreases temperature- and strain-rate-dependence. Ru increases the uniform elongation and “working range” at room temperature.

The Ru-Y Constitution Diagram


Physical and chemical methods were used to construct the constitution diagram of the Ru-Y system and measurements of the alloy properties confirmed the limits of the phases in the system.

Phase Equilibria in the System Ruthenium-Titanium-Hafnium


The complete phase diagram is established for the Ru-Ti-Hf system.

CHEMICAL COMPOUNDS

How to Buy Platinum Group Metals Chemicals


Factors peculiar to the procurement of Pt group metal compounds are discussed, including quality, economic and delivery considerations.

The Electrical Conductivity Behaviour of K₃Pt(CN)₆Br₀.3-2H₂O at High Pressures


K₃Pt(CN)₆Br₀.3-2H₂O was studied at up to 100,000 atm using X-ray and conductivity methods. Changes in conductivity are interpreted in terms of the effect of pressure on the interatomic distance and are discussed in the context of the electronic structure of this material.

Effect of cis-Dichlorodiammineplatinurn(I1) on Cytological and Morphological Changes in Bone Marrow of Mice. Long-term Observations

M. ŽAK, J. DROBNÍK and Z. ŘEŽNÝ, Neoplasma, 1972, 19(4), 305-310

After an intraperitoneal injection of 8 mg/kg cis-Pt(NH₃)₂Cl₂, cell count, mitotic index and relative frequency of individual elements in the bone marrow of mice followed decreasing oscillatory patterns with normalisation within 28 days.

Effect of cis-Platinous Diamminodichloride on Graft Rejection. Prolonged Survival of Skin Grafts against H₂ Histocompatibility


Maximum suppression of skin graft rejection in mice by cis-Pt(NH₃)₂Cl₂ is achieved by a single injection of 8 mg/kg body weight on the day of transplantation.

Synthesis and Distribution of a Radio-labelled Anti-tumour Agent: cis-Diamminodichloroplatinum(I1)


The antitumour compound, cis-Pt(NH₃)₂Cl₂, was synthesised from metastable ¹²⁵Pt; its structure was verified by chemical and biological methods. Following i.v. injection into rabbits
Chemistry of Complexes Related to cis-Dichlorodiammineplatinum(II) Anti-tumour Drug
An extensive review of complexes related to \( \text{cis-Pt(NH}_3\text{)}_2\text{Cl}_2 \) is presented. Their chemistry, photochemistry, physico-chemical properties and biological interactions are discussed and related to their potential in the elucidation of causes and cure of cancer.

Hydroxy Complexes of Platinum(II) and Palladium(II)
The preparation and structure of the hydroxy-bridged complexes \( [\text{M}_2(\text{OH})_6\text{L}_2][\text{BF}_4]_2 \), where \( \text{M} = \text{Pt} \) and \( \text{L} = \text{triethylphosphine, triphenylphosphine or pyridine} \), or where \( \text{M} = \text{Pd} \) and \( \text{L} = \text{triphenylphosphine} \), are described. These complexes are stable and resist bridge cleavage by tertiary phosphines under conditions which easily cleave analogous chloro-bridged complexes.

A Superconducting Ternary Sulphide AggPd_3S
Only one intermetallic compound, AggPd_3S, was found to exist in the Ag-Pd-S system; it has a \( \beta\)-Mn(A-13)-type structure. It is the first ternary Ag-Pd compound observed to be superconducting and undergoes a sharp transition at 1.13K. It is suggested that it may undergo a metal-semiconductor phase transition 300K.

ELECTROCHEMISTRY

A Rechargeable Hydrogen Permeable Palladium Electrode
H\(_2\) was adsorbed on the palladised surface of a Pd black/Pd foil/Pd,Pt black electrode and diffused through the membrane to the KOH electrolyte where it was anodized to H\(_2\)O. Up to 600 mA/cm\(^2\) at 100mV overpotential was obtained. Cathodic polarisation fully reversed the process, producing H\(_2\) at up to 10 atm and 300 mA/cm\(^2\).

Polarisation Characteristics of an Iridium Electrode
T. OKAMURA, Denki Kagaku, 1972, 40, (11), 796-799
The electrochemical properties of Ir were studied in 1N H\(_2\)SO\(_4\), 0.1N NaOH and 5M NaCl. An oxide layer, less stable than that of Rh, forms in both acidic and alkaline solutions but is reduced at almost the same potential as that of formation. The very low chlorine overvoltage of an Ir electrode makes it suitable for use as a brine electrolysis anode, but a small amount of contamination of the Cl\(_2\) with O\(_2\) may be expected.

ELECTRODEPOSITION AND SURFACE COATINGS

Metallising Nonconductors. VI. Vapour Plating
E. GROSHART, Metal Finishing, 1972, 70, (8), 49-51, 54
Very thick, pure deposits of Pt on nonmetal substrates may be obtained by the vapour deposition process. Pt salts of carbonyl-chloride or acetylacetonate are thermally decomposed on the heated substrate. Seamless Pt tubing can be produced by the process, using a C rod as the substrate, which is later removed.

Electrodeposition of Dispersed Platinum-Cobalt Alloys
A. I. ZAYATS and N. A. PEREKHREST, Zh. Prikladnoi Khim., 1972, 45, (10), 2248-2252
Pt-Co deposits can be obtained from both acidic and alkaline electrolytes. Nearly equiatomic Pt-Co deposits can be obtained from ammine electrolytes under optimum conditions.

Electroless Metal Deposition on Hydrophobic Surfaces
Polyimide, polyester, epoxy resin, PTFE, PE and PP were uniformly metallised using a Sn(II) electroless process after immersion in a colloidal sensitising dispersion to render them hydrophilic. No other pretreatment was necessary. Sn(II) was deposited and then used to deposit Pd(0) by reduction of Pd(II) in acid solution. Pd(0) is catalytic to electroless metal deposition. Selective UV oxidation of Sn(II) prevented Pd deposition on exposed areas.

Investigation of the Electrodeposition and Some Physical Properties of Dispersed Palladium-Cobalt Alloys
Properties of Pd-Co electrodeposits depend on the conditions of electrolysis. Dispersion of Pd-Co
powders rises with increased current density and decreased temperature and metals concentration. Alloy structure depends upon alloy content. Coercivity of the alloys also rises with increased current density and decreased temperature and metals concentration.

Comparison of Ratings of Sulphate, Nitrosocloride and Sulphamine Electrolytes for Ruthenation

N. M. SHMELEVA, A. L. ROTINIAN, P. M. VYACHESLAVOV and E. P. LEONENKO, Zh. Prikladnoi Khim., 1972, 45, (8), 1728–1733

Studies of sulphate, nitrosocloride and sulphamine electrolytes prepared from Ru hydroxycloride showed that the easiest to prepare and adjust to deposit Ru are the sulphamine electrolytes, which give the thickest deposits with the least internal stress. The deposits depend upon the electrolyte composition and process regime. Deposits of Ru on Ni are stable after preliminary degreasing of Ni in organic solvent and electrochemically in alkaline solution, followed by electrochemical activation.

LABORATORY APPARATUS AND TECHNIQUE

Separation of $^1$H and $^3$H on a Palladium Filter


A Pd filter has been developed to separate $^3$H at concentration $10^{-12}$ from $^1$H at 60–250 torr. Range of temperature for concentration of $^3$H with low specific activity is 200–250°C; for exclusion of tritiated “memory” filters it is above 350°C.

HETEROGENEOUS CATALYSIS

Concentrated Nitric Acid Made at Lower Pressure


The Peroxide process produces concentrated HNO$_3$ from dilute (<68%) HNO$_3$ liquid N$_2$O$_4$ and air at ~8 atm. Air and NH$_3$ are reacted over Rh-Pt catalyst gauze to form NO, from which the dilute acid is produced.

Some Recent Developments in Nitric Acid Manufacture


Developments in catalysts and pollution control in HNO$_3$ production and new processes for direct concentrated HNO$_3$ production are described. Pt catalysts may be recovered by introducing a heat-resistant stainless steel mesh and then one or two 20% Au-Pd gauzes immediately downstream of the catalyst gauze. Pt is captured from the gas stream by exchange with Pd and is then reprocessed. Pt or Pd on honeycomb or spherical supports is used in the catalytic reduction of tail gas to control pollution.

Two Regions of Platinum Crystallisation on the Surface of Aluminium Oxide

N. M. ZAIDMAN, Kinet. Kataliz, 1972, 13, (5), 1254–1257

Studies on the dispersion of Pt on Al$_2$O$_3$ reveal two regions of crystallisation differing in structure and in the stoichiometric reaction of H$_2$ with surface Pt atoms. In one region there is a critical size of nucleus for crystallisation and isolated Pt atoms; in the other there are trimeric crystals at relatively low temperatures in two types, the sizes of which decrease as the temperature of roasting increases.

Effect of the Metal Particle Size in Supported Catalysts on the Selectivity and the Reaction Mechanisms


10% Pt/Al$_2$O$_3$ and Pt/SiO$_2$ catalysts, prepared by several methods to give different mean crystallite diameters (d), gave selectivity in methycyclopentane hydrogenolysis dependent on particle size; isomerisation of hexane occurred by a cyclic mechanism except when d > 150 Å; interconversion between methylpentanes occurred by a cyclic mechanism when d < 50 Å but predominantly by bond shift for d > 50 Å. d influences the formation of various types of defects which are responsible for the different reaction mechanisms.

Catalytic Properties of Platinum Catalysts. Relative Activity of Various Platinised Carbons in Pulsed Regime Conditions


The basis of the catalytic activity of 11% Pt/C in C$_7$-dehydrocyclisation of isooctane, hydrogenolysis of cyclopentane, dehydrogenation of cyclohexane, and configurational isomerisation of cis-1,2-dimethylcyclopentane to the trans form was studied by the impulse method. More activity is possessed by catalysts impregnated and not promoted by KOH. Catalysts using C calcined at 1000°C are somewhat more active than those using C heated to 300°C.

Selective Hydrogenation Catalysed by Polymeric Palladium and Platinum Complexes


PtCl$_4$ and PdCl$_4$ complexes, with organic polymeric ligands containing diphenylbenzylphosphine groups, are highly selective in the hydro-
Hydrocracking of Saturated Hydrocarbons
Extensive experimental material is reported and interpreted concerning hydrocracking of numerous pure feed hydrocarbons using Pd/Ca-Y-zolite and Co-Mo catalysts.

Formation of Dimethyl Ether from Hydrogen and Carbon Dioxide over a Graphite-PdCl₂-Na Catalyst
PdCl₂-Na/graphite shows good reactivity and selectivity for the formation of dimethyl ether from H₂ and CO. O₂ inhibits the reaction but CH₃OH and HCHO enhance it. Other transition metal chlorides show poor reactivity or selectivity.

Catalytic Oxidation. V. Mechanisms of Olefin Oxidation over Supported Iridium
N. W. Cant and W. K. Hall, J. Catalysis, 1972, 27, (1), 70-78
The selectivity and kinetics of oxidation of 2-5 C olefins over Ir/Al₂O₃ and Ir/SiO₂ were studied. CH₃COOH was the most important product of all but 1-butenes and isobutene. A double bond cleavage mechanism was proposed.

Kinetics of the Catalytic Vapour Phase Carbonylation of Methanol to Acetic Acid
Low pressure carbonylation of MeOH to AcOH is catalysed in the vapour phase by I⁻-promoted Rh/C, an analogue of the homogeneous catalyst used for the reaction in the liquid phase. In both phases the reaction is first order in I⁻ and independent of [MeOH] and [CO], suggesting similar mechanisms.

Activation of Nitrogen by Alkali Metal Promoted Transition Metal. I. Ammonia Synthesis over Ruthenium Promoted by Alkali Metal
The rate of NH₃ synthesis over Ru is greatly increased by addition of alkali metals (effect of Cs > K > Na). At 250°C, the rate over K-promoted 5% Ru/C is 10 times the rate over K₂O-promoted Fe/Al₂O₃. It is suggested that the
alkali metal increases the electron density in Ru, thus promoting activation of $N_2$, and that active C and $Al_2O_3$, which further increase the rate when used as supports, act as a medium for the electron transfer.

**Homogeneous Platinum(II)-catalysed Hydrogen-Deuterium Exchange at a Saturated Carbon Atom**


In the presence of $K_2PtCl_4$, RC(CH$_3$)$_3$CH=CH$_2$ alkenes (R has 1-4C) undergo H-D exchange in the alkyl chain almost exclusively at C-5. A five-membered ring intermediate is suggested.


II. The effects were investigated of concentration and solvent and catalyst compositions on H-D exchange in alkanes and aromatic hydrocarbons, catalysed by platinum(II) chloro-complexes in acetic [H$_3$] acid in D$_2$O. Cl:Pt ratios of 4.0-2.3 were used. Exchange rate varied exponentially with ionisation potential of the hydrocarbon, except when excessive complex formation occurred. III. Halogen-substituted alkanes, aromatic compounds and certain branched-chain hydrocarbons were studied by photoelectron spectroscopy and in H-D exchange reactions catalysed by PtCl$_2$.

**Reduction of Carbon Dioxide by Molecular Hydrogen in the Presence of Complexes of the Transition Metals**


Various Pt metal complexes were tested as catalysts for HCOOCH$_3$ synthesis from CO$_2$, H$_2$, and CH$_3$OH. (PPh$_3$)$_3$IrH$_3$ gave the highest yield of the complexes tested.

**Homogeneous Hydrogenation of Unsaturated Compounds Catalysed by Pd Complexes. I. Scope and Effect of Variables. II. Deuterogenation of Mono- and Diolefins**


I. Catalysis of the hydrogenation of unsaturated compounds by Pd complexes was studied. Conversion rate and product distribution were dependent on the catalyst and nature of the reaction mechanism.
substrate. O_2 treatment of Pd(o) complexes increased the rate. Pd hydrides are probably the active species. II. Deuteration of olefins catalysed by (Ph,PCHPHPh_2)_2Pd on several substrates was studied to determine the mechanism of olefin hydrogenation.

Catalysis by Metal Complexes. VII. Hydro-silation Catalysed by Tetrakis(ethylene)dichlororhodium(I)
The competitive addition of couples of silicon hydrides of the type (C_5H_5)nSiHCl_2, where n=0-3, to 1-heptene catalysed by [RhCl(C_5H_5)n]_2 was found to yield only the products of the addition of the hydride containing the greater number of Cl atoms, in contrast to preparative additions which give individual hydrosilation products in 40-65% yields. The reason for this discrepancy is discussed.

Polymerisation of Propadiene. III. Catalyst Systems Based on Various Rhodium(I) Complexes
The catalysis of the polymerisation of propadiene to 1,2-polyallene by various Rh(I) complexes was investigated. It was found that activity decreases in the order: cis-Rh(CO)_5P(C_5H_5)Cl > [Rh(CO)_5Cl]_2 > [Rh(CO)_3Cl]_2 > Rh[P(C_5H_5)Cl]_2. Differences in activity are due to differences in the catalytic action of various intermediates.

[RhCl(C_5H_5)_2]_2 reacts with an excess of Me_2NPF_2 at room temperature to give RhCl(Ph_2NMe_2)_2Cl in 1:4 ratio. Both complexes exist as discrete entities in solution and both catalyse the decarbonylation of benzaldehyde.

Selective Catalytic Route to Bifunctional Silanes. Catalysis by Rhodium and Ruthenium Complexes of the Alcoholysis of Diarylsilanes and the Hydrolysis of Carbonyl Compounds
RhCl(PPh_3)_2 and RuCl_2(PPh_3)_2 are effective catalysts for the selective production of diarylalkoxysilanes by the alcoholysis of diarylsilanes and by the hydrolysis of carbonyl compounds; the Rh complexes are more efficient.

Kinetics of Ethylene Polymerisation and Butadiene Polymerisation Catalysed by Solutions of Hydridochlorotris(triphenylphosphine) ruthenium(II)
Polymerisation of C_2H_4 and of C_4H_8, catalysed by HRuCl(PPh_3)_3 in N,N-dimethylacetamide at 50-85°C, is first order in catalyst and in C_2H_4 in the former system but independent of [C_2H_4] in the latter, due to stronger complexing of the diene. A common mechanism is proposed where, after coordination of the monomer to the metal, the polymer chain grows by insertion of the monomer at a polarised Ru-C bond. The catalyst can be regenerated by H_2.

Investigation of the Homogeneous Transfer of Hydrogen from Pentanol-2 to Cyclohexanone, Catalysed by Tris(triphenylphosphine)dichlororuthenium in the Presence of Alkali
KOH promotes cyclohexanone reduction via H_2 transfer from pentanol-2 with subsequent hydrogenation and condensation in the presence of RuCl_2(PPh_3)_2. H_2 transfer is greatest for KOH concentrations 1.64 x 10^-3 M in Ar or 4.08 x 10^-2 M in H_2. As KOH concentration rises so does the hydrogenation by H_2 and the condensation. H_2 transfer increases from 50°C to 84°C, but hydrogenation is maximum at 70°C, due to the catalytic action of various intermediates.

FUEL CELLS

Low Power Methanol-Air Battery
A nine-cell stack weighing 5.6 lb operated in a 600/68, 45mW/15W duty cycle for more than 1000 h before failure due to leakage. Each cell contained a PTFE-bonded anode containing 25% Pt-Pd catalyst, two cathodes containing Ag, MeOH-KOH electrolyte and an air inlet.

T. SHIROMA, Denki Kagaku, 1972, 40, (5), 390-395
The diffusion coefficient of H in a 25 at.% Ag-Pd electrode is half that in pure Pd, necessitating only half the thickness of metal. The alloy electrode showed no deterioration after repeated absorption and desorption of H.
Hydrogen-permeable Electrodes of Pd-Ag-Au Alloy
T. SHIROYAMA, Denki Kagaku, 1972, 40, (8), 605-610.
The ternary alloy 66.6 wt. % Pd-13.4 wt. % Ag-20 wt. % Au combines good polarisation characteristics with excellent mechanical properties for use as a H-permeable membrane electrode with a high resistance to pinholing. The lattice parameter and electrode potential as a function of dissolved H were measured and the diffusion coefficient of H through the membrane was determined.

Preparation of Highly Dispersed Platinum on Carbon
The preparation, characterisation and properties of Pt-doped C for fuel cell electrodes are described. A high degree of dispersion of Pt (crystallites <15 Å) was achieved only by pyrolysis at 500-800°C of the Ca2+ form of Amberlite IRC50 and CG50 resins on which Pt ions had been localised by exchange. The mechanism and influence of the pyrolysis are discussed.

TEMPERATURE MEASUREMENT
Resistance Thermometry in Magnetic Fields, I. Thermistors and Platinum Thermometers at 77K
At 77K, in magnetic fields up to 16 kG, both negative temperature coefficient thermistors and Pt resistance thermometers show a virtual rise in temperature due to the field. Pt thermometers seem more desirable for this application.

The Calibration of Resistance Thermometers at Low Temperatures
Details are given of an apparatus for comparing resistance thermometers at 4-90K and for the routine calibration of Pt resistance thermometers in accordance with IPTS-68.

The Automatic Calibration of Platinum-Pt, Rhodium Thermocouples in the Temperature Range 0 to 1100°C
Equipment for the automatic calibration of Pt : Rh-Pt thermocouples from 0-1100°C is described. The uncertainty of calibration is only ±0.3°C and the time for calibration is 1 h compared to 46 h for the fixed-point method.

A CENTRALISED TEMPERATURE CONTROL SYSTEM FOR DIFFUSION FURNACES
The installation of a centralised temperature control system at the Allentown Works of Western Electric Co., Inc., has led to increased yields and significant savings in the manufacture of diffused-junction npn transistors. The system uses three Pt : 10% Rh-Pt in each of 35 diffusion furnaces. Automatic, continuous temperature measurement gives close control over quality, enabling a sampling method of testing to be established.

NEW PATENTS
METALS AND ALLOYS
Tarnish Resistant Alloys
PENNWTALT CORP., British Patent 1,296,879.
An alloy which resists tarnishing contains 39-47% Au, 9-12% Pd and the balance Ag and Cu in a 1:1-1:5:1 ratio. The alloy can be used for jewellery, dental work and electrical contacts.

Dental Gold Alloy
A gold alloy for bonding to dental porcelain for capping teeth contains 67.7 wt. % Au, 16.7 % Pd, 11.6% Pt, 1.3% Ru, 2.0 % Ag, 0.6% Sn, 0.1% Cu.

Degassed Platinum Powders
Degassed Pt powders are prepared by mixing finely divided Pt with at least an equal volume of a diluent metal oxide powder, heating the mixture to dissipate all gases from the Pt powder, cooling the mixture and separating the Pt from the diluent. The Pt powders are suitable for application to "green" ceramic sheets used to produce monolithic multi-layer ceramic circuit components.

Platinum Group Metal Alloys
Pt group metal alloys, especially 9-45 (preferably 20-40) % Rh-Pt, are dispersion hardened by the presence of up to 1 wt. % of Ti, V, Zr, Nb, Hf and/or Ta.

Superconducting Alloy
M. WILHELM et al., U.S. Patent 3,684,495.
A superconducting alloy has the formula
(Ce_{1-x}A_2)Ru_x, where A is Tb, Dy or Ho and x is 0.10-0.25, depending on the nature of A.

**Beryllium Alloy**

Soc. Trefimetaux G.P. U.S. Patent 3,685,988

A Be alloy contains 0.05-3% Ca and 0.15-3% of at least one additional metal selected from Pd, Pt, Ir, Rh, Au and Fe.

**Sprayed Metal Articles**


Metal articles or ingots with a fine stable grain structure and superior properties may be made by arc, flame or plasma spraying the metal or alloy on to a cold target so that the droplets form a coherent deposit in which most retain their identity. The method is very suitable for Pt group metals, an alloy of 49 wt.% Pt, 50 Au and 1% Rh being used in one example.

**Dispersion Strengthened Metal**


A strengthened ingot, e.g. of Pt, is obtained by spraying a target with a molten metal and a reactive constituent (e.g. Pt and Zr). In its passage through the atmosphere the reactive constituent is converted to oxide, carbide, etc.

**CHEMICAL COMPOUNDS**

**Platinum Group Metal Oxides**

Diamond Shamrock Corp. U.S. Patent 3,677,975

Solid solutions of Pt group metal oxides and valve metal oxides (Ti, Zr, Nb, Ta) are formed by flame spraying a solution of salts of the two classes of metal, e.g. RuCl_3 and Ti(OBu)_3. The products are useful as solid electrolytes.

**ELECTROCHEMISTRY**

**Electrolysis Electrodes**

P.P.G. Industries Inc. U.S. Patent 3,677,917

Electrolysis electrodes are coated with a layer of PdO containing (a) a film-forming metal oxide (Al, Bi, Nb, Ta, Ti, etc.), (b) a second Pt group metal oxide, such as RuO_2, and (c) an Fe group oxide.

**ELECTRODEPOSITION AND SURFACE COATINGS**

**Chemical Plating**

Farbenfabriken Bayer A.G. British Patent 1,299,102

Ni-B coatings are deposited by chemical plating on to surfaces previously cleaned and dipped in acid PdCl_2 solution.

**Noble Metal Alloy Chemical Plating**

Mobil Oil Corp. British Patent 1,299,413

A mixture of metals, especially Au, Ag and Pt group metal alloys, are deposited chemically from a non-aqueous solution of the metals, at least one being in the form of a π-complex, and then the metal compounds on the surface are reduced. In one example a PdCl_2-cyclooctadiene complex is used with chlorosuccinic acid in chloroform solution.

**Cementing Metal Powders to Metals**

Dr. W. Kampschulte & Cie. British Patent 1,303,712

A metallic powder is deposited and adhered to an electrically conducting surface by electrophoretically depositing the metal powder and then electroplating the deposit and surface. Pt and Au alloys are among the metals described.

**Sensitising for Chemical Plating**

Allied Research Products Inc. U.S. Patent 3,674,550

Substrates are treated with a Pt group metal nitrite, ketocarboxylate or diglycollate and then with a reducing agent to produce a sensitising deposit. Pd, Rh and Pt are the preferred metals.

**Palladium-Nickel Coatings**

K. Yanamura et al. U.S. Patent 3,677,909

Pd-Ni coatings are electrodeposited from a Pd-Ni salt bath containing NH_3 which is brightened with a sulphonamide.

**Metal Patterns on Insulators**


Al_2O_3 or another insulator substrate is sensitised, Pd catalyst is deposited and then a continuous Au film is formed. The Au/Pd film is shaped to make patterns.

**Noble Metal Sensitising Solutions**

Kollmorgen Corp. U.S. Patent 3,682,671

Surfaces are sensitised for subsequent chemical plating by treatment with a solution containing a Pt group metal, Au or Ag and a Group IV metal stabilised with a polyol. Pd and Sn are suitable components.

**Metallisation Compositions**


Metallisation compositions for screen printing circuits on substrates contain noble metal powders in 3-15% of bismuthate glass-ceramic precursors. These give better adhesion of the composition.

**Metallised Fibres**

Asahi Kogyo K.K. U.S. Patent 3,686,019

Nylon and other fibres are given a metal coating.
to improve their antistatic properties. Metalisation involves the deposition of a noble metal catalyst (e.g. Pd) on the fibres, processing of the fibres by the usual textile treatments and the subsequent deposition of Pd, Au, Co, Ag, Cu, Ni, etc.

**Heater Coating**
G.T.E. SYLVANIA INC.  
*U.S. Patent 3,691,421*
A double layer coating on a wire support consists of a layer of Al₂O₃ and a layer of AlₓOₙ mixed with ZrO₂ or BeO. This layer is coated with Pt, Ir, etc., to prevent the oxidation of W.

**Protection of Cobalt-Based Alloys**
DEUTSCHE EDELSTAHLWERKE A.G.  
*U.S. Patent 3,692,554*
Co-based alloys are protected by diffusing into their surfaces a mixture of Ni, Pt (or other Pt group metal) or Al.

**Ruthenium Alloy Plating**
SEL-REX CORP.  
*U.S. Patent 3,692,641*
Thick electroplated coatings of low stress are obtained by plating from an ammonium ruthenate bath containing a Group IIIA metal (In, Ga or Tl) and optionally another Pt group metal.

**Osmium Electroplating**
INTERNATIONAL NICKEL CO. INC.  
*U.S. Patent 3,692,642*
Os is electroplated from a bath containing diammonium hexachloroosmate acidified with H₂SO₄ or HSO₃NH₂.

**Platinum Chemical Plating**
F. H. LEAMAN  
*U.S. Patent 3,698,939*
Metallic and non-metallic surfaces are chemically plated using an ammoniacal chloroplatinate solution mixed with hydrazine or a hydrazine derivative.

**Transparent Conductive Coating**
HUGHES AIRCRAFT CO.  
*U.S. Patent 3,698,946*
Transparent coatings able to conduct electricity are produced by the vacuum deposition of thin consecutive layers of TiO₂, noble metal such as Au or Pd, and TiO₂.

**LABORATORY APPARATUS AND TECHNIQUE**

**Detecting Reducing Vapours**
T.R.W. INC.  
*U.S. Patent 3,676,188*
Reducing vapours are detected by the change in resistance of a noble metal strip applied to a non-corrodible backing and coated with a reducible metal salt. The strip can consist of Pt, Rh, Au, Ag, etc. Suitable reducible salts contain Au or Ag, e.g. AuI/KI.

**JOINING**

**Solderable Stainless Steel**
P. R. MALLORY & CO. INC.  
*U.S. Patent 3,698,880*
Stainless steel is rendered solderable by applying a barrier layer of Ni, Co or Cr and covering it with a layer of Ag alloyed with Au, Pt, Pd, Re or Os.

**HETEROGENEOUS CATALYSIS**

**Unsaturated Aldehyde Hydrogenation**
UNIVERSAL OIL PRODUCTS CO.  
*British Patent 1,296,448*
Anisaldehyde is hydrogenated continuously to anisyl alcohol in the presence of a Pt/alkali metal catalyst. A preferred catalyst contains Pt and Li₂O on an Al₂O₃ support.

**Production of Biphenyls**
ASAHI KASEI K.K.K.  
*British Patent 1,296,721*
Benzenes are converted to biphenyls by oxidation in the presence of Pd or a Pd compound and H₂SO₄.

**Jet Fuels**
SHELL INTERNATIONALE RESEARCH MIJ. N.V.  
*British Patent 1,296,772*
Jet fuels are obtained by hydrogenating kerosene fractions over a catalyst consisting of at least 1% Pt or other Pt group metal and at least 0.5% F on an Al₂O₃ support.

**ICE Exhaust Gas Treatment**
UNIVERSAL OIL PRODUCTS CO.  
*British Patent 1,296,874*
ICE exhaust gases are treated in two catalyst beds, the first containing 0.01-1% Pt/oxide catalyst while the second contains a refractory oxide supporting 1-20% CaO, SrO or BaO and 0.01-1% Pt.

**Selective Hydrogenation**
INSTITUT FRANÇAIS DU PETROLE, DES CARBURANTS ET LUBRIFIANTS  
*British Patent 1,296,943*
Unsaturated byproducts are removed from 3-10C hydrocarbons by selective hydrogenation, e.g. over a Pd catalyst.

**Reduction Catalyst Alloy**
BUSH BOAKE ALLEN LTD.  
*British Patent 1,301,300*
Reduction processes with organic compounds are catalysed by a crystalline alloy of Sn with Pt and/or Pd, preferably on a support. A typical catalyst contains 3% of a 1:1 mixture of Pd and Sn on SiO₂ gel support.

**Unsaturated Carboxylic Esters**
TORAY INDUSTRIES INC.  
*British Patent 1,301,465*
Unsaturated esters are obtained when a con-
jugated diene and a carboxylic acid are reacted in the presence of Pd and an alkali metal carboxylate.

Steam Reforming
IMPERIAL CHEMICAL INDUSTRIES LTD.
British Patent 1,301,836

"Reduced carbon lay-down" in the steam reforming of hydrocarbons is achieved using a Ru metal catalyst deposited on a refractory oxide support, optionally together with CaO, SrO and/or BaO. In an example 0.08% Ru and 0.55% CaO are deposited on Al₂O₃ pellets.

Hydrogenation Catalyst
PRODUITS CHIMIQUES Pechini-St. Gobain
British Patent 1,302,269

Dienes and other impurities in olefins are selectively hydrogenated in the presence of a catalyst containing 100–800 p.p.m. Pd promoted by 50–1000 p.p.m. V, supported on Al₂O₃ or Al₂O₃ plus SiO₂ having a surface area of up to 150 m²/g. Au, Ag, Rh, etc., may be present as additional selectivity promoters.

Dehydrogenation Catalyst
INSTITUT FRANCAIS DU PETROLE, DES CARBURANTS ET LUBRIFIANTS
British Patent 1,302,737

Straight chain paraffins and other saturated hydrocarbons are dehydrogenated over a catalyst based on Al₂O₃ of 1–100 m²/g surface area carrying 0.05–0.7% Pt and Ir and/or Ru in an amount 0.05–0.3 times the amount of Pt. An alkali or alkaline earth metal is also present.

Alkyl Aromatic Compound Isomerisation
ASHLAND OIL INC.
U.S. Patent 3,679,769

Alkyl transfer in alkyl aromatic compounds is catalysed by Pt, Pd, Rh, Ru, etc., on a zeolite support. U.S. Patent 3,679,773 uses the same catalyst for dehydrogenation reactions.

Serial Reforming
J. H. SINFELT
U.S. Patent 3,684,693

Serial reforming of hydrocarbons uses Pt/Al₂O₃ as a catalyst in the first zone(s) and Ir/Al₂O₃ in the tail zone(s).

Hydrogen Cascade Process
UNIVERSAL OIL PRODUCTS CO.
U.S. Patent 3,691,059

An economical H₂ cascade process uses Pt group metal catalysts in multiple stages with the hydrocarbon feedstock being treated in aliquot portions in each stage.

Hydrocracking Catalyst
UNIVERSAL OIL PRODUCTS CO.
U.S. Patent 3,692,666

A hydrocracking catalyst for a low pressure process consists of a Pt group metal and Ni on a reaction product of Al₂O₃ and a sublimed Friedel-Crafts halide, e.g. Pt-Ni/Al₂O₃-AlCl₃.

Olefin-Alkyl Iodide Exchange
SHELL OIL CO.
U.S. Patent 3,697,611

Higher olefins are produced by exchange between a lower olefin and a higher alkyl iodide in the presence of supported Pt, chloroplatinic acid, Pt trisphosphine or Ru bispinephosphate carbonyl.

Fuels from Cellulosic Wastes
JOHNSON MATTHEY & CO. LTD.
German Offen. 2,214,295

Organic fuel oils are produced by reduction of cellulose-based materials, chiefly waste products, at elevated temperature and pressure using at least one Group VIII metal and/or Cu as catalyst. The preferred catalyst is Ru and its compounds.

Reduction and Oxidation Catalyst
JOHNSON MATTHEY & CO. LTD.
German Offen. 2,212,616

Oxidation of organic compounds with O₂ or NO reduction in the presence of a gaseous reducing fuel takes place at low temperatures in contact with an alloy or mixture of 1–50 wt.% Rh, 0.01–25 wt.% base metal and remainder Pt on an inert support, preferably a ceramic honeycomb optionally coated with a refractory oxide.

Heat Exchanger Catalyst
JOHNSON MATTHEY & CO. LTD.
German Offen. 2,213,935

A catalyst support contains a thermally conductive base metal in the form of a metal strip, honeycomb or the fluid conducting conduit of a heat exchanger such that it can conduct heat away in a controlled manner. The catalytic metal is preferably a Pt group metal, Au, Ni, Cr or alloys thereof and the base metal is preferably Cu or stainless steel.

HOMOGENEOUS CATALYSIS

Hydroformylation Catalysts
British Patent 1,298,331

The hydroformylation of olefins is catalysed by a Rh carbonyl hydride complexed with two or three mols of a tertiary phosphine, arsine or stibine, e.g. RhH(CO)(PPh₃)₂ or RhH(CO)(P₂Hₙ)₃ or RhH(CO)(P₂Hₙ)₄, in the presence of an aldehyde (or alcohol corresponding thereto) which is a product of the reaction and excess of free trisubstituted phosphine, arsine or stibine.

Ruthenium Carboxylate Catalysts
JOHNSON MATTHEY & CO. LTD.
British Patent 1,301,739

Ru(II) carboxylates, Ru₄(OCOR)₆, especially the acetates, may be prepared by heating together soluble Ru and carboxylate salts and the carboxylic acid. Its adducts with stabilising ligands,
e.g. pyridine or a trisubstituted phosphine, arsine or stibine, are also claimed. The compounds are useful as catalysts and catalyst precursors.

**Olefin Oxidation**

**UNION OIL CO.**

U.S. Patent 3,686,287

Olefins are oxidised to unsaturated esters, including vinyl esters, by vapour phase oxidation in the presence of a heterogeneous catalyst containing a Group VIII noble metal, a nitrogen oxide as the oxidant and an aliphatic carboxylic acid. The metal is preferably in the form of a Pt, Pd, or Rh complex.

**CHEMICAL TECHNOLOGY**

**Nuclear Fuel Elements**

**U.K. ATOMIC ENERGY AUTHORITY**

British Patent 1,295,251

The nuclear fuel element is enclosed in a sheet coated with Rh, Ir, Ru, Au, Cu, Ag and/or Re.

**Separating Hydrogen from Water**

**NATIONAL AERONAUTICS & SPACE ADMINISTRATION**

U.S. Patent 3,678,654

Dissolved H₂ in H₂O is removed by contact with a thin metallic film of Pd or Pd-Ag alloy coated with Pd black, preferably by rubbing with PdCl₂ powder and reducing. There is a reduced pressure on the opposite side of the film.

**Diffusion Unit**

**JOHNSON MATTHEY & CO. LTD.**

German Offen. 2,213,599

A diffusion unit of two superimposed metal foils, e.g. Ag/Pt, is described in which at least one foil, preferably both, is corrugated. A wire helix, e.g. of stainless steel, is situated in each corrugation trough to prevent collapse under high pressures and facilitate diffusion and collection of H₂.

**ELECTRICAL AND ELECTRONIC ENGINEERING**

**Pyrochlore Conducting Oxides**

**E. I. DU PONT DE NEMOURS & CO.**

British Patent 1,295,517

Electrically conducting, pyrochlore-type oxides have the formula \((M₂Bi₃₋ₓ)(M'₃-M''₂₋ₓ)O₇₋₂\) where M is Y, Ti, In, Cd, Pb or a lanthanide, M' is Pt, Ti, Cr, Rh, Sb, Sn or Ge, M'' is Ru or Ir, x is \(0-1\), y is \(0-0.5\) and z is \(0-1\). y is \(0-1\) when M' is Rh or more than one metal. These oxides, e.g. Bi₁Ir₀.₅O₇, are used in ceramic film resistances.

**Electrodes on Piezoelectric Ceramics**

**PLESSEY CO. LTD.**

British Patent 1,299,616

Pt foil may be used to produce electrodes on Li niobate piezoelectric ceramics.

**Glass-covered Gold Pattern**

**BELL TELEPHONE LABORATORIES INC.**

U.S. Patent 3,676,087

A Au conductor pattern on a substrate is more easily wetted by glass when it is covered with a thin film of Rh.

**Oxide Resistors**

**INTERNATIONAL NICKEL CO. INC.**

U.S. Patent 3,679,607

Resistors are made from RuO₂ and/or IrO₂ of fine crystallite size.

**Solar Cell with Metal Layered Contact**

**TELEFUNKEN PATENTVERWERTUNGS A.G.**

U.S. Patent 3,686,036

A solar cell consists of a semiconductor body having one or both contacts of three-layer construction comprising Ag/Ti, Cr, Mo or Ta/noble metal, e.g. Pt or Pd. A method of contacting a solar cell by vapour deposition is also included.

**Uranium Oxide Electrode**

**INTERNATIONAL BUSINESS MACHINES CORP.**

U.S. Patent 3,689,378

A high impedance voltmeter has a standard reference electrode and a low impedance electrode consisting of Ir or another noble metal wire coated with a thin smooth layer of uranium oxide.

**Dispenser Cathode**

**SIEMENS A.G.**

U.S. Patent 3,692,575

A W dispenser cathode is coated with Os, Ir or another Pt metal by displacement from solution, heating and reduction.

**TEMPERATURE MEASUREMENT**

**Thermistor Compositions**

**E. I. DU PONT DE NEMOURS & CO.**

U.S. Patent 3,679,606

A ceramic support is glazed with a mixture of 20–50% noble metal powder and 50–80% frit. The noble metal powder contains 15–85 wt.% Pt and/or Ru, 15–85% Rh and 0–12% Ag and/or Au.

**Thermocouple Compensating Leads**

**JOHNSON MATTHEY & CO. LTD.**

German Offen. 2,204,613

A compensating apparatus for a thermocouple, preferably Pt:13% Rh-Pt, comprises two compensating leads, one of which includes at least two insulated conductor limbs, of which one limb is formed from material having thermoelectric properties different from any other conductor limb. The thermoelectric e.m.f. of the combined thermocouple and compensating leads is adjustable.