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The Reduction of Nitric Oxide in Automobile Emissions

STABILISATION OF CATALYSTS CONTAINING RUTHENIUM

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Catalysts containing ruthenium are used to reduce nitric oxide in automobile exhaust emissions but volatile oxides formed under transient oxidising conditions during operation can severely affect them. However, basic oxides such as alkaline earths or rare earths can stabilise the ruthenium by forming ruthenates, which have little tendency to volatilise. The ruthenates are synthesised either before the catalyst is made or in position on the catalyst support, which may be monolithic or pelleted.

In the development of catalysts for the reduction of nitric oxide in the purification of automotive exhaust emissions one of the desired attributes of a catalyst is its ability to promote selectively the reduction of nitric oxide NO to molecular nitrogen (and not to ammonia as happens over a large majority of catalysts), in the presence of hydrogen-containing compounds in the gas stream (1, 2, 3). Ruthenium-containing catalysts have been found to have a pronounced selectivity for reduction to molecular nitrogen (4, 5, 6), and several laboratories have pursued recently the development of practical ruthenium-containing catalysts.

The NOx-reduction catalysts are intended to operate in an overall reducing atmosphere in an automobile exhaust which is, on the average, a product of the carburetion of a combustible mixture richer than the stoichiometric mixture. However, relatively frequent excursions occur in the operation of the vehicle into conditions where the exhaust contains, for certain time intervals, a net excess of oxygen. Further, in some embodiments of the so-called dual catalyst system it is desirable to use the NOx-reduction catalyst as a carbon monoxide and hydrocarbon oxidation catalyst during the warm-up period, deliberately admitting an excess of oxygen during that time.

With the use of ruthenium-containing catalysts it soon became apparent that their stability under oxidising conditions is poor. Analysis of spent catalysts revealed severe losses of the active component, readily explained by the formation and removal of the volatile tetroxide (7).

Various ways were explored to minimise the tendency of the ruthenium to volatilise under oxidising conditions while still preserving the high activity and selectivity of the catalysts.

We have attempted the stabilisation of the ruthenium (or its oxide) on the catalyst by the incorporation of the basic oxide of barium. The reasoning leading to this suggestion was couched in the following chemical terms: since the highly oxidised states of ruthenium (Ru³⁺ and higher) give rise to acidic oxides, their interaction with basic oxides such as barium oxide will lead to the formation of double mixed oxides which should be more stable with respect to volatilisation in the presence of oxygen. Indeed, the higher oxidation states of Ru do form an extensive series of ruthenates, many of the latter well characterised in the literature (8). In parti-
Simultaneous testing of six honeycomb catalysts on an engine dynamometer at the Research Laboratories of the Ford Motor Company. The exhausts from each one of the six engine cylinders are fed to separate catalyst chambers. Pelleted ruthenium catalysts were also tested.

In particular, the ruthenates of the alkaline-earth metals have been investigated by Ward and co-workers (9). They tend to crystallise mainly with the perovskite structure.

Barium ruthenate BaRuO₃, in particular, has been well characterised (9a). It has a close-packed stacking of close-packed BaO₃ layers with the Ru ions in octahedral sites. There is metal-metal bonding between the ruthenium ions with an interatomic Ru-Ru distance of 2.55 Å. This is a closer approach than in ruthenium metal (2.65 Å). This structural property may have a bearing on the remarkable catalytic activity of the barium ruthenate which will be discussed later.

Another class of basic metal oxides useful for the stabilisation of ruthenium in an oxidising atmosphere is that of the rare-earth metals. With all the lanthanides, except lanthanum itself, one obtains compounds of the type (RE)₂Ru₂O₇ which crystallise as cubic pyrochlores (10). The interaction between La₂O₃ and RuO₂ leads to a perovskite phase (11) which has recently been well characterised by Bouchard and Weiher (12). It is worth noting that La₂O₃ is the most basic among the rare-earth oxides and therefore is most suitable for stabilisation. The perovskite La₂RuO₆ is considered to be unusual, as it is the only example of an oxide lattice where all the ruthenium is in the formally trivalent state. It is well known that the valence state of the B metal ion in the perovskite formula ABO₃ can be varied in wide limits by substituting mono-, di- or trivalent atoms in the A position. On the other hand, different atoms can be also substituted into the B position. This gives a very wide range of possible ruthenium-containing 'stabilised' catalysts.

The work referred to in the present article is limited specifically to the stabilisation by BaO or La₂O₃. The subject-matter is the basis for several U.S. patent applications.
Preparation of Catalysts

We have followed essentially two routes in the preparation of the stabilised catalysts. In one technique BaRuO$_3$ or LaRuO$_3$ is presynthesised. The presynthesised ruthenates were finely ground and incorporated on to monolithic supports either from American Lava Corp. or from Corning Glass Works using very dilute (2 wt. per cent) suspensions of colloidal ‘Dispal’ alumina as the binding agent. There is an obvious disadvantage to the technique, and this is the limit on the particle size achievable by the grinding. At best, the particle diameter is of the order of a few microns (or a few 10$^4$ Å), which leaves the major part of the valuable ruthenium atoms in the bulk and inaccessible to the reacting molecules on the surface. On the other hand, there is the obvious advantage that every ruthenium atom has been stabilised as the ruthenate.

The second technique consists of the impregnation of either a pelleted or monolithic support, first by a solution of the nitrate of the stabilising metal barium or lanthanum, followed by calcination to convert the nitrate to oxide, secondly by the solution of ruthenium trichloride, RuCl$_3$, which is then dried at 110°C and reduced in hydrogen at ~450°C. The very small particles of the ruthenium metal (<10 Å diameter) are then ‘fixed’ by rapid heating in air at 900°C. The fast fixation process assures very good dispersion of the resulting ruthenate. There is no direct evidence, however, that every ruthenium atom has been deposited in the vicinity of the stabilising oxide so as to assure the formation of the ruthenate.

Catalysts containing from 200 to 2000 p.p.m. ruthenium by weight were prepared by both methods.

Stability of Ruthenates in Oxidising Atmospheres

To check the stability of the BaRuO$_3$ and LaRuO$_3$ and compare it to that of RuO$_2$, thermogravimetric experiments were performed using the DuPont automatic balance. Figure 1 indicates the vast difference in the weight loss between the ruthenates and RuO$_2$ at 1180°C in flowing air.

Table I shows the percentage loss of ruthenium in a fast-flowing blend of nitrogen-oxygen from supported pelleted catalysts.
Table I
Comparison of Ruthenium Loss in a Ruthenium Catalyst and in Barium Oxide- or Lanthanum Oxide-stabilised Ruthenium Catalysts

<table>
<thead>
<tr>
<th>Temperature °F</th>
<th>Temperature °C</th>
<th>Exposure Time in hours</th>
<th>Ruthenium Loss per cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>950</td>
<td>510</td>
<td>16</td>
<td>0</td>
</tr>
<tr>
<td>1350</td>
<td>730</td>
<td>4</td>
<td>13</td>
</tr>
<tr>
<td>1450</td>
<td>785</td>
<td>4</td>
<td>45</td>
</tr>
<tr>
<td>1530</td>
<td>830</td>
<td>4</td>
<td>90</td>
</tr>
<tr>
<td>1630</td>
<td>885</td>
<td>4</td>
<td>-</td>
</tr>
<tr>
<td>1750</td>
<td>955</td>
<td>4</td>
<td>25</td>
</tr>
<tr>
<td>1820</td>
<td>995</td>
<td>4</td>
<td>75</td>
</tr>
</tbody>
</table>

Conditions: Space velocity: 38,000/h
O₂ concentration in nitrogen: 2.5–3 per cent
Ru content: 2000 p.p.m.
La or Ba (as metal) content: 3 per cent by weight
Support: UOP Al₂O₃ pellets

The cycling conditions and the possibility of switching from oxidising to reducing exhaust in the operation of an engine requires the knowledge of the changes that the stabilised catalyst undergoes under such treatment. For this purpose presynthesised ruthenates were subjected in the TGA balance to alternate oxidising and reducing conditions. The reducing agents were hydrogen or carbon monoxide (in nitrogen). Since the use of containing ruthenium alone or with BaO or La₂O₃. It should be pointed out that, this being one of the earliest preparations, the ruthenium was not prefixed by prereduction and subsequent rapid oxidation and therefore was relatively poorly dispersed (4.6 per cent of the ruthenium atoms are surface atoms). None the less, the vast improvement in stability due to the presence of BaO and La₂O₃ is quite obvious.

Fig. 2 The thermogravimetric analysis (TGA) trace of the reduction-oxidation of the ruthenate BaRuO₄ shows that the ruthenate was reduced to BaO + Ru by the reducing mixture of 5 per cent hydrogen in nitrogen but that weight was restored by oxidation back to BaRuO₄ on exposure to air. The heating rate was 10°C/min
carbon monoxide leads under certain conditions to the formation of barium or lanthanum carbonates, we give only the data for reduction by hydrogen, and only the results for BaRuO$_3$ are presented. The results for LaRuO$_3$ are analogous. Figure 2 indicates that the BaRuO$_3$ is reduced to BaO + Ru and that the weight is restored upon exposure to air. X-ray diffraction patterns after the four cycles indicate the restoration of the ruthenate, BaRuO$_3$. It is possible that frequently repeated oxidation-reduction cycling engenders the migration of the ruthenium to form gradually a separate oxide phase. To prevent this, the stabilisation of very small particles as achieved by the fixation is very important. Another possible stratagem is to dilute the perovskite ABO$_3$ in the B position by nonvolatile ions such as Mn$^{4+}$ (9a) or others. In lanthanum ruthenate, where ruthenium is trivalent, dilution by trivalent ions such as Ni$^{2+}$ and others should be feasible.

**Activity and Selectivity of Ruthenates and Stabilised Ruthenium Catalysts**

Under reducing conditions at relatively elevated temperatures the barium (or lanthanum) ruthenate reverts, as shown in the previous section, to the ruthenium metal and the stabilising oxide. Hence, its activity and selectivity under these conditions might be expected to be the same as in unstabilised Ru catalysts.

At lower temperatures and under a redox potential not quite sufficient to reduce the ruthenates, the catalyst might be required to catalytically reduce nitric oxide while the ruthenium is still coordinated in the ruthenate structure.

The available literature indicated that from simple considerations the ruthenates could be expected to be active catalysts. Thus, first, the perovskite-type ruthenates have been shown to have metallic conductivity, for which convincing explanations have been proffered (12, 13). Secondly, the Ru-Ru distances in some of the structures were shown to be actually shorter than in the metal (9a).

The metallic character should satisfy one of the important conditions required for the redox catalytic activity, the ability to chemisorb both electron-donor and electron-acceptor adsorbents. The close proximity of the ruthenium atoms should provide the dual sites required for the pairing of nitrogen atoms in the reduction of nitric oxide to nitrogen.
### Table II

Comparison of Activity and Selectivity between Stabilised and Non-stabilised Ruthenium Catalysts. System NO-H₂

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Ru Catalyst</th>
<th>Ru-BaO Catalyst</th>
<th>Ru-La₂O₃ Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% NO Converted</td>
<td>p.p.m. NH₃ Formed</td>
<td>% NO Converted</td>
</tr>
<tr>
<td>250</td>
<td>60</td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>300</td>
<td>96</td>
<td>62.5</td>
<td>96</td>
</tr>
<tr>
<td>350</td>
<td>100</td>
<td>230</td>
<td>100</td>
</tr>
<tr>
<td>400</td>
<td>100</td>
<td>250</td>
<td>100</td>
</tr>
<tr>
<td>450</td>
<td>100</td>
<td>240</td>
<td>100</td>
</tr>
<tr>
<td>500</td>
<td>100</td>
<td>—</td>
<td>100</td>
</tr>
</tbody>
</table>

Conditions: Space velocity: 20,000/h
Inlet NO concentration: 1000 p.p.m.
Inlet H₂ concentration: 1.43 per cent
Catalyst support: low-shrinkage American Cyanamid alumina pellets
Ru content: 2000 p.p.m.
La or Ba (as metal): 3 per cent by weight

### Table III

Comparison of Activity and Selectivity between Stabilised and Non-stabilised Ruthenium Catalysts. System NO-CO-H₂

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Ru Catalyst</th>
<th>Ru-BaO Catalyst</th>
<th>Ru-La₂O₃ Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% NO Converted</td>
<td>p.p.m. NH₃ Formed</td>
<td>% NO Converted</td>
</tr>
<tr>
<td>250</td>
<td>85</td>
<td>45</td>
<td>35</td>
</tr>
<tr>
<td>300</td>
<td>100</td>
<td>85</td>
<td>92.5</td>
</tr>
<tr>
<td>350</td>
<td>100</td>
<td>118</td>
<td>100</td>
</tr>
<tr>
<td>400</td>
<td>100</td>
<td>135</td>
<td>100</td>
</tr>
<tr>
<td>450</td>
<td>100</td>
<td>137</td>
<td>100</td>
</tr>
<tr>
<td>500</td>
<td>100</td>
<td>—</td>
<td>100</td>
</tr>
</tbody>
</table>

Conditions: Space velocity: 20,000/h
Inlet NO concentration: 1000 p.p.m.
Inlet CO concentration: 1.5 per cent
Inlet H₂ concentration: 1.43 per cent
Catalyst support: low-shrinkage American Cyanamid alumina pellets
Ru content: 2000 p.p.m.
La or Ba (as metal): 3 per cent by weight
Table IV

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>NO-H₂ System</th>
<th>NO-H₂-CO System</th>
<th>NO-CO-H₂O System</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% NO Converted</td>
<td>p.p.m. NH₃ Formed</td>
<td>% NO Converted</td>
</tr>
<tr>
<td>202</td>
<td>23.9</td>
<td>18.9</td>
<td>56.8</td>
</tr>
<tr>
<td>255</td>
<td>89.6</td>
<td>75.0</td>
<td>100</td>
</tr>
<tr>
<td>278</td>
<td>100</td>
<td>92.4</td>
<td>100</td>
</tr>
<tr>
<td>320</td>
<td>100</td>
<td>186</td>
<td>100</td>
</tr>
<tr>
<td>360</td>
<td>100</td>
<td>190</td>
<td>100</td>
</tr>
<tr>
<td>447</td>
<td>100</td>
<td>63.2</td>
<td>100</td>
</tr>
</tbody>
</table>

Conditions: Space velocity: 20,000/h
Inlet NO concentration: 100 p.p.m.
Inlet CO concentration: 1.5 per cent
Inlet H₂ concentration: 1.43 per cent
Inlet H₂O concentration: 10 per cent
Catalyst support: Corning monolith

Laboratory Experiments

Both monolithic and pelleted catalysts were tested in the laboratory in the flow apparatus used in our earlier studies (2, 4) and the observed activity has borne out these expectations.

Tables II and III give the comparison between a pelleted catalyst containing 2000 p.p.m. of ruthenium alone and the catalysts containing the same amount of ruthenium but stabilised by 3 per cent barium as BaO or 3 per cent lanthanum as La₂O₃. As seen from the tables, the stabilisation does not impair the activity and affects the selectivity only very slightly, if at all. At the conditions of these runs the catalysts were not reduced to the metallic state of ruthenium, because the temperature was too low (see Fig. 2).

Table IV gives the activity and selectivity in laboratory conditions of a presynthesised BaRuO₃ catalyst deposited on to a monolithic support. Similar behaviour is exhibited by the presynthesised LaRuO₃.

Table V

<table>
<thead>
<tr>
<th>Catalyst Identification</th>
<th>Stabilising Element</th>
<th>Ru Loading p.p.m.</th>
<th>NO Reduction Activity in Screening Dynamometer Test at 230,000/h, A/F ratio 13.8, 1000°F</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Total</td>
</tr>
<tr>
<td>M-176A</td>
<td>Ba</td>
<td>200</td>
<td>85</td>
</tr>
<tr>
<td>M-177AP2</td>
<td>La</td>
<td>200</td>
<td>88</td>
</tr>
<tr>
<td>M-168</td>
<td>Presynthesised BaRuO₃</td>
<td>2000</td>
<td>78</td>
</tr>
</tbody>
</table>
The Operation Parameters of the Engine Dynamometer in the Catalyst Durability Tests

<table>
<thead>
<tr>
<th>Mode</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Engine speed (r.p.m.)</td>
<td>2200</td>
<td>800</td>
<td>800</td>
</tr>
<tr>
<td>Load (ft-lb)</td>
<td>92</td>
<td>27</td>
<td>27</td>
</tr>
<tr>
<td>Air fuel ratio (at catalyst)</td>
<td>13.6</td>
<td>13.4</td>
<td>15.0</td>
</tr>
<tr>
<td>Space velocity (per hour)</td>
<td>95,000</td>
<td>25,000</td>
<td>30,000</td>
</tr>
<tr>
<td>Exhaust O₂ (per cent)</td>
<td>0.1</td>
<td>0.1</td>
<td>3.0</td>
</tr>
<tr>
<td>Exhaust temperature (°F)</td>
<td>1350</td>
<td>950</td>
<td>950</td>
</tr>
<tr>
<td>Time (min)</td>
<td>41.6</td>
<td>5.2</td>
<td>5.2</td>
</tr>
</tbody>
</table>

At periodic intervals of about 70 hours of accumulated durability time, the NO, HC, and CO conversion efficiencies are measured with the following engine and exhaust conditions:

<table>
<thead>
<tr>
<th>Air-fuel ratio</th>
<th>Engine speed (r.p.m.)</th>
<th>Vacuum (in Hg)</th>
<th>Torque (ft-lb)</th>
<th>Space timing (BTC)</th>
<th>Fuel flow (lb/hr)</th>
<th>Inlet temperature (°F)</th>
<th>Space velocity (per hour)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12.7</td>
<td>1430</td>
<td>11.2</td>
<td>86</td>
<td>40</td>
<td>14.6</td>
<td>1000</td>
<td>60,000</td>
</tr>
<tr>
<td>13.5</td>
<td>1430</td>
<td>11.2</td>
<td>86</td>
<td>40</td>
<td>13.9</td>
<td>1000</td>
<td>60,000</td>
</tr>
<tr>
<td>14.1</td>
<td>1430</td>
<td>11.2</td>
<td>86</td>
<td>40</td>
<td>13.1</td>
<td>1000</td>
<td>60,000</td>
</tr>
<tr>
<td>14.7</td>
<td>1430</td>
<td>11.2</td>
<td>86</td>
<td>40</td>
<td>12.7</td>
<td>1000</td>
<td>60,000</td>
</tr>
</tbody>
</table>

Lead-sterile fuel and ashless oil were used for the durability tests.

Dynamometer Experiments

The monolithic catalysts made in the laboratory were subjected to prolonged durability tests on engines mounted on dynamometers. Many formulations were tested, but we limit ourselves here to the presentation of a few examples only. The compositions of the catalysts of which the dynamometer tests results are discussed here are given in Table V. The last column in the table gives the performance of a fresh catalyst in a high-space-velocity screening test.

The operating parameters of the engine dynamometer are given in Table VI. The engine was a six-cylinder 200 CID Ford engine, and the exhaust of each cylinder was
The percentage of nitric oxide removed and ammonia formed as a function of air/fuel ratio at increasing times of running for catalysts M-177AP2, M-168, and M-168. The decrease in activity for the first two catalysts is very minor, notwithstanding the low loading of ruthenium. On Fig. 5 it can be seen that catalyst M-168 has suffered a sharp drop in activity in the period between 79 and 138 hours of operation. This was traced to a sharp overheating associated with a malfunction of the system. The malfunction resulted in the physical damage shown in Fig. 6. Nevertheless, a substantial activity was still exhibited by the catalyst as shown by the plots on Fig. 5 at times beyond 138 hours of operation.

Vehicle Results

The durability results accumulated in actual vehicle operation are included here to demonstrate that, notwithstanding the encouraging laboratory and dynamometer activity and stability, the catalysts deteriorated more rapidly in vehicle tests than in laboratory or dynamometer evaluation. The deterioration was faster than required for the satisfaction of the U.S. Federal 1976 requirements. As a substantial number of these catalysts have been analysed and some have shown no appreciable loss of the active component ruthenium, it is obvious that other causes of deterioration, such as poisoning or overheating (or both) operate also in the catalysts for the reduction of NOx, which is hardly surprising.

The data in Table VII were obtained on cars equipped with exhaust gas recirculation devices, with the exception of vehicle 22-C-58. The EGR was calibrated to substantially reduce inlet levels of NOx, as seen in the table. This may have resulted in increased HC and CO emissions, which does, however, not bear directly on the subject-matter of the paper. This explains the low level of NOx emissions without the use of the catalysts. The data in the table clearly indicate that in vehicle operation the ruthenium catalysts...
Fig. 6 Melting of catalyst M-168 caused by overheating from a system malfunction. The catalyst still retained substantial activity after this damage with little further deterioration of performance.

deteriorate. The stabilisation procedure is designed to minimise the deterioration associated with the volatilisation of the Ru. The extent of success in preventing volatilisation can be judged from the analytical data of the next paragraph.

<table>
<thead>
<tr>
<th>Vehicle</th>
<th>Initial CVS (C/H) Results, NOx</th>
<th>Durability CVS (C/H) Results, NOx</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wt. % Catalyst</td>
<td>Wt. % with Catalyst</td>
</tr>
<tr>
<td>21A91 (M-177) Galaxie, 429 CID</td>
<td>1.40</td>
<td>0.45</td>
</tr>
<tr>
<td>31A73 (M-190) Galaxie, 400 CID</td>
<td>1.27</td>
<td>0.48</td>
</tr>
<tr>
<td>22-C-58 (M-176B and M-177) Capri, 2.8L, d</td>
<td>2.5</td>
<td>0.47</td>
</tr>
<tr>
<td>110-T-713 (M-150C2) Galaxie, 351 CID</td>
<td>1.19</td>
<td>0.39</td>
</tr>
<tr>
<td>110-T-714 (M-190) Galaxie, 351 CID</td>
<td>1.69</td>
<td>0.44</td>
</tr>
<tr>
<td>110-T-718 (M-150G) T-Bird, 429 CID</td>
<td>0.83</td>
<td>0.26</td>
</tr>
</tbody>
</table>

a At termination
b Latest available data
c The stabilisation did not include the ‘fixation’ step
d Based upon hot CVS test.
### Table VIII
Analyses of Ruthenium Catalysts

#### a: Fresh Catalysts

<table>
<thead>
<tr>
<th>Catalyst Designation</th>
<th>Nominal Ruthenium Content p.p.m.</th>
<th>Average Ruthenium Content X-ray Fluorescence p.p.m.</th>
<th>Average Ruthenium Content Activation Analysis p.p.m.</th>
</tr>
</thead>
<tbody>
<tr>
<td>M-176</td>
<td>2000</td>
<td>2537</td>
<td>2462</td>
</tr>
<tr>
<td>M-190</td>
<td>500</td>
<td>636</td>
<td>499</td>
</tr>
<tr>
<td>M-190-A</td>
<td>1000</td>
<td>1630</td>
<td>not measured</td>
</tr>
</tbody>
</table>

#### b: Dynamometer Tested Catalysts

<table>
<thead>
<tr>
<th>Catalyst Designation</th>
<th>Hours of Service</th>
<th>Nominal Ruthenium Content p.p.m.</th>
<th>Average Ruthenium Content X-ray Fluorescence p.p.m.</th>
</tr>
</thead>
<tbody>
<tr>
<td>M-177B-1</td>
<td>200</td>
<td>700</td>
<td>643</td>
</tr>
<tr>
<td>M-176B-1</td>
<td>100</td>
<td>700</td>
<td>676</td>
</tr>
<tr>
<td>M-177B</td>
<td>200</td>
<td>500</td>
<td>425</td>
</tr>
<tr>
<td>M-190-3</td>
<td>100</td>
<td>500</td>
<td>500</td>
</tr>
<tr>
<td>M-87C2-1 a</td>
<td>130</td>
<td>2000</td>
<td>1320</td>
</tr>
</tbody>
</table>

#### c: Vehicle Tested Catalysts

<table>
<thead>
<tr>
<th>Catalyst Designation</th>
<th>Mileage</th>
<th>Nominal Ruthenium Content p.p.m.</th>
<th>Average Ruthenium Content X-ray Fluorescence p.p.m.</th>
<th>Average Ruthenium Content Activation Analysis p.p.m.</th>
</tr>
</thead>
<tbody>
<tr>
<td>M-177B</td>
<td>12,000</td>
<td>500</td>
<td>206</td>
<td>238</td>
</tr>
<tr>
<td>M-176</td>
<td>3000 b</td>
<td>2000</td>
<td>2388</td>
<td>2644</td>
</tr>
<tr>
<td>M-150G (right) a</td>
<td>5000</td>
<td>2000</td>
<td>1053</td>
<td>2144</td>
</tr>
<tr>
<td>M-150G (left) a</td>
<td>5000</td>
<td>2000</td>
<td>851</td>
<td>not measured</td>
</tr>
<tr>
<td>M-150C-2A a</td>
<td>10,000</td>
<td>2000</td>
<td>540</td>
<td>not measured</td>
</tr>
<tr>
<td>M-150C-2B a</td>
<td>10,000</td>
<td>2000</td>
<td>600</td>
<td>not measured</td>
</tr>
</tbody>
</table>

*a Catalysts stabilised without fixation
*b Operating under oxidising A/F ratio

### Analysis of Used Catalysts

To assess the extent of loss of ruthenium from used catalysts the chemical analysis of this element was carried out by two different analytical techniques.

The X-ray fluorescence analysis using the Siemens SRS-1 instrument was carried out for a series of elements present on the catalyst. These included both the active elements added in the preparation of the
Pollutant molecules labelled by isotopes such as $^{15}$N, $^{18}$O and D are used in the study of the mechanisms of their catalytic removal. The mass spectrometer serves as an important analytical tool in these studies.

catalysts and some of the contaminants accumulated during testing. Since this article deals specifically with stabilisation, the analysis results presented here are limited to ruthenium only. As mentioned before, the presence of other contaminants may have an effect on the catalyst deterioration noticed in Table VII and this matter is now under intensive investigation.

A word of caution is in order with respect to the X-ray fluorescence analysis. The presence of several contaminants on the used catalysts requires the preparation of a large matrix of standard samples. The matrix was prepared using a support from only one of the suppliers, while the actual catalysts were made with different support materials. Since all of them (with the exception of catalyst M–150G) were aluminosilicates, the effect on the analysis should not be large. Secondly, not all the interelement intensity corrections, associated with minor contaminants, were accounted for in the X-ray fluorescence analysis.

The activation analysis for ruthenium was carried out by irradiation for three minutes in the core of the Ford Nuclear Reactor at the University of Michigan. After a decay period of ~14 days, the samples were counted on a high-resolution gamma ray spectroscopy system. The 0.497 MeV radiation from $^{103}$Ru (half life 39.5d) is analysed by computer for the quantitative determination. A ground specimen of the sample is compared with another specimen to which a known amount of ruthenium has been added. Both samples are irradiated simultaneously, and the flux variations are not more than 1 per cent.

Examination of Table VIII shows considerable improvement in the prevention of ruthenium volatilisation under the conditions of dynamometer testing. This particular cycle consisted of 48 minutes of testing at 870°C, 140,000/h, under reducing conditions and 6 minutes of testing at 650°C, 50,000/h under oxidising conditions. The stabilisation without reduction followed by fixation brings about improvement, but not complete prevention. The incorporation of the fixation step virtually eliminates ruthenium loss under the dynamometer test conditions.

Under vehicle conditions the loss from the first generation of stabilised catalysts (the M–150) series is still higher than acceptable.
The data from the second generation of catalysts are not all available as yet, as these are still being tested on vehicles and the mileage accumulation is continuing (see Table VII).

In the single case where the analysis is available (catalyst M-177B, after 12,000 miles, Table VIII), there is still an apparent loss of ruthenium. This qualification is associated with the fact that no analysis is run on a fresh catalyst and the nominal intended loading can be different from the actual loading. It is, however, realised that the achieved degree of stabilisation can still be substantially improved, while mastering the technique of catalyst preparation. Further improvements can be expected by minimising the opportunities for phase separation during repeated oxy-reduction of the catalyst. This will mainly be achieved by ruthenium dilution and smaller particle-size distribution. On the other hand, better control of the air/fuel ratio in the operation of the vehicle system should also minimise the loss of ruthenium.

Another area currently under intensive investigation is the poisoning of the ruthenium-containing catalysts in the environment exhaust. A detailed effort using the techniques used previously in the poisoning studies of oxidation catalysts (14) is in progress.

We owe gratitude to many more individuals at the Ford Motor Company than we can list by name. Most importantly, we acknowledge the help of Joe Kummer, Vern Bergman, Eric Daby, Carol Smith, Gene Hancock, Henry Stepien and numerous members of the Technical Services Department.

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Russian Progress in Platinum Chemistry

The centenary of Lev Aleksandrovich Chugaev (Platinum Metals Review, 1973, 17, (4), 144-148), was the occasion for numerous biographical articles in the Russian scientific press. However, one of the most interesting manifestations was the October 1973 issue of Zhurnal Neorganicheskoi Khimii. This was entirely devoted, apart from a valedictory article on Chugaev, to papers on coordination chemistry in celebration of the anniversary.

Russian chemists have for years published more contributions in this field than has any other nation, and the Russian Journal of Inorganic Chemistry, to give its translated title, publishes several articles on the chemistry of the platinum metals every month. In this issue 13 of the 44 articles on coordination chemistry deal with the platinum metals.

Three papers from the Novosibirsk State University concern platinum(II) complexes with norleucine, platinum(II) chelates with glycyglycine, and optical activity of platinum (II) complexes with mono- and bidentate L-proline. Two papers from the Leningrad Technical Institute concern platinum(II) complexes with hydrogen sulphide, and with N-methylhydroxylamine. Two from the Moscow Institute of Fine Chemical Technology deal with hydrolysis of pentahalo complexes of nitrosoruthenium, and with tert-phosphonium iridium salts. The remaining six papers originate at six other separate universities and institutes, showing the wide interest in this subject in the U.S.S.R.

Platinum Metals Rev., 1974, 18, (1)
The Growth of Oxide Single Crystals

USE AND CARE OF PLATINUM APPARATUS

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With new techniques of crystal growth new problems have been encountered with the platinum apparatus used in crystal production. Some of these difficulties are discussed in this paper, including attack by bismuth oxide, \( Bi_2O_3 \), and dissolution of the platinum in the leaching acids, together with methods of prolonging the life of platinum crucibles.

For many years single crystals of oxides have been grown by the high temperature solution technique. The conditions of growth and the properties of the solvents have been enumerated by White (1). Basically the solvents are very corrosive, which necessitates the use of platinum containers and thermocouples. In the last few years a modification of this growth technique, namely liquid phase epitaxy, LPE (2), has come to the forefront for the growth of single crystal thin films. The development of this latter technique has been accompanied by new problems with the care of the platinum. In this paper we indicate the problems and possible solutions that we have found to be of use to extend the life of the platinum. Only some of the new problems have been indicated because there are already review articles on this subject (3, 4). This paper is split into the various stages of material preparation and the difficulties encountered. No attempt has been made to be exhaustive but this paper is designed to help the crystal grower in general.

The Premelting Stage

Growth of a garnet, as a typical example of the oxides under consideration, would be from a PbO, PbF₂ and B₂O₃ flux and a typical composition for thin film growth is given in Table I. With this type of flux a well-known problem has been its attack on the platinum. In general the attack is caused by a metal or non-metal (Pb, Bi, As, Sb, B, etc.) which reacts with the platinum to form a low melting point platinum-rich alloy. Since the reaction takes place preferentially on grain boundaries, only very small amounts of the element are required to cause destruction of the crucible. The formation of lead may be the result of the non-stoichiometry in the lead compounds or of the contamination with reducing organic material, such as lead acetate, which is readily reduced to lead on heating. The organic lead salts can be removed sufficiently by washing the PbO and then redrying.

Table I

A Typical Composition for Growing \( Y_3Fe_2O_12 \) Thin Films on \( Gd_2Ga_2O_12 \) Substrates from a Lead Borate Flux

<table>
<thead>
<tr>
<th></th>
<th>g</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbO</td>
<td>275.0</td>
</tr>
<tr>
<td>B₂O₃</td>
<td>6.88</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>25.0</td>
</tr>
<tr>
<td>Y₂O₃</td>
<td>2.8</td>
</tr>
</tbody>
</table>

PbO oxide may be prevented to some extent by the addition of small quantities of PbO₂ (5) in order to prevent the formation of free lead in the melt.
To overcome the difficulties of the lead salt solvents and, in particular, their volatility at the crystal growth temperatures (1000 to 1400°C), much work has been done to find new fluxes. One such system is BaO/B₂O₃ (6) and another is BaO/B₂O₃/Bi₂O₃ (7). The addition of Bi₂O₃ to the melts has increased the number of problems because the platinum is attacked more severely and the attack is even worse with the use of platinum alloys.

Although liquid Bi₂O₃ (and PbO) should be thermodynamically stable with respect to the metal (8) up to about 1800°C, this attack can only be explained by the formation of metallic bismuth. This means that circumstances exist that prevent the system from attaining thermodynamic equilibrium. In this respect, slow heating during melting might be helpful. It has been found that there was little attack on the pure platinum crucible if a composition containing Bi₂O₃ was premelted in a slowly heated resistance furnace in an oxygen atmosphere (9). We have performed a series of tests with these fluxes in pure (99.99 per cent) platinum crucibles. In the case of fast heating with an R.F. coil in air, a failure rate of about 75 per cent was found. Even the addition of BaO₂ (decomposition temperature 800°C) could not prevent failure with fast heating. Heating at a rate of 100°C/h in a resistance furnace in an oxygen atmosphere produced no failures, even after a soaking period of 200 hours at 1150°C. The heating rate is clearly a very important factor to consider during premelting. The use of crucibles fabricated from platinum that contains certain additives in order to minimise grain growth requires more care in combination with these corrosive melts. These include mechanical failure of pure platinum crucibles. This is because the lead salt fluxes are very dense and melts can weigh up to several kilograms. This problem can be overcome by supporting the crucible in a ceramic vessel with alumina powder as padding. However, it is often undesirable to have aluminium-containing materials in the furnace, since these can lead to contamination material would cause a local reduction of the flux components when heated and hence an attack on the crucible at the grain boundaries. It would help to remove this danger during the premelting stage if crucibles were first annealed in an oxygen atmosphere at about 800°C for several hours. This not only relieves the strains produced by a previous ‘run’ but also the carbon-containing materials are oxidised and a protective oxide layer is formed on the platinum surface by reaction with the atmosphere (10) and this may help in some cases.

The Growth Stage

During the growth of crystals or films over long periods (i.e. several weeks above 900°C), certain new difficulties have been found. These include mechanical failure of pure platinum crucibles. This is because the lead salt fluxes are very dense and melts can weigh up to several kilograms. This problem can be overcome by supporting the crucible in a ceramic vessel with alumina powder as padding. However, it is often undesirable to have aluminium-containing materials in the furnace, since these can lead to contamination.

![Fig. 1 A typical double-walled crucible for crystal growth, fabricated from 5 or 10 per cent rhodium-platinum with a lining of 99.98 per cent platinum.](image-url)
Fig. 2 Liquid-phase epitaxial growth of single crystal films is carried out in this furnace at Philips Research Laboratories, Eindhoven. The internal arrangement of the furnace is shown in Fig. 3

of the desired crystals. In that case it would be better to use alloys of rhodium and platinum. However, chemical analysis has shown that the rhodium contaminates the melts, and hence the crystals. To overcome this we have successfully used double-walled crucibles, as shown in Fig. 1. The pure platinum liner stops the contamination while the 10 per cent rhodium-platinum alloy gives the strength. The rounded edge inside the base of the crucible facilitates cleaning.

In the double-walled form of crucible it is still possible to get contamination by diffusion of the rhodium through the platinum liner. It has been shown (11) that at 1000°C with a 0.5 mm thick platinum liner it takes of the order of $10^4$ hours, and that at 1400°C and the same wall thickness it takes of the order of $10^2$ hours, for 2 per cent of rhodium to diffuse through to the inner surface of the platinum liner when a 10 per cent rhodium-platinum alloy also 0.5 mm thick is used on the outside.

It has been observed that during the stirring of a LPE melt above the saturation temperature, which speeds up the homogenisation process, a crystalline form of platinum collects on the stirring rod. Also, at the end of a 'run' lasting three or four weeks there is usually a large deposit of platinum at the bottom of the crucible. It is clearly seen that the crucible wall is thinned below the level of the melt surface. This transport is not fully understood but it would appear that the stirring action accelerates the transport of platinum from the wall of the crucible to the bulk of the melt.

Here we should make some remarks about platinum: 10 per cent rhodium-platinum
thermocouples. Lead salt fluxes are some of the worst to use with platinum thermocouples since they poison them. It is possible to use platinum sheaths but even these fail after a short period of time. The thermocouples should be checked at least once a week against a standard thermocouple. In the LPE process we have found that the greatest failure of the platinum-sheathed thermocouples occurs in the cooler regions of the furnace where the lead oxide vapour condenses, as shown in Fig. 3. It appears that when the lead oxide condenses it attacks the platinum and produces a black powder, resulting in mechanical failure at this point. A typical analysis of the black powder is given in Table II. The life of the thermocouple may be extended by using a thicker platinum sheath or, better, by the use of an alumina sheath. This attack also occurs with platinum-lined furnaces and the inserted platinum baffles indicated in Fig. 3. As said before, the use of alumina may be undesirable because of contamination of the melt.

Cleaning Crucibles for Re-use

One of the quickest ways of cleaning the crucibles is to heat them upside down in a R.F. coil with a ceramic pot below to collect the melt. Final cleaning in hot dilute nitric or hydrochloric acid produces a crucible ready for re-use. This latter method creates undesired effects. First, we have found by chemical analysis that 0.25 mg of platinum is dissolved per hour from 100 cm² of platinum surface in 6N hydrochloric acid at approximately 80°C. If many crucibles are to be cleaned frequently in this way it would be desirable from the economic point of view to reclaim the platinum. Secondly, iron (one of the many elements present) is very difficult to remove from the surface of the platinum, so a different method of cleaning has to be employed. This is normally done by fusion with potassium pyrosulphate at approximately
Table II
Spectrochemical Analysis of the Black Powder Produced When the PbO Vapours Condense on Platinum
(All Values in Weight per cent)

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>bulk</th>
<th>PbO</th>
<th>Pt</th>
<th>Fe₂O₃</th>
<th>B₂O₃</th>
<th>Al₂O₃</th>
<th>Bi₂O₃</th>
<th>MnO</th>
<th>MgO</th>
<th>CuO</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0.4</td>
<td>0.3</td>
<td>0.05</td>
<td>0.006</td>
<td>0.003</td>
<td>0.002</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

700°C, but this produces grain growth in the platinum and dissolution of the platinum. We normally use a bath of K₂S₂O₇ at a somewhat lower temperature; this does not cause grain growth and only 300 mg platinum dissolves in 1 kg of K₂S₂O₇ in two months of continuous use. With the rhodium alloys the dissolution of rhodium in K₂S₂O₇ is much greater because it is more readily oxidised. Another fusion method is the use of a borax melt for 0.5 h at 1000°C. Grain growth has not been detected when using this method.

Effect of the Gas Atmosphere

The growth of garnets under various pressures of oxygen (12) and argon has produced many new and interesting results. In particular, chemical analysis of the crystals produced under these conditions has shown some interesting facts. A typical set of results is given in Table III. It is seen that the argon atmosphere produces less contamination of the crystals. However, observation inside the pressure vessel of the furnace (13) shows that with the argon the transport of platinum to the cooler regions of the furnace is far greater than in the case of oxygen atmospheres. The platinum also becomes very brittle when used in argon atmospheres and should be annealed in oxygen before re-use.

Table III
Chemical Analysis of Y₃Fe₅O₁₂ Crystals Grown from a PbO-PbF₂-B₂O₃ Flux under Various Pressures of Oxygen and Argon
(All Values in Weight per cent)

<table>
<thead>
<tr>
<th>Contaminants</th>
<th>Oxygen</th>
<th>Argon</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>6 atm</td>
<td>10 atm</td>
</tr>
<tr>
<td>PbO</td>
<td>0.4</td>
<td>0.3</td>
</tr>
<tr>
<td>Pt</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>B₂O₃</td>
<td>0.03</td>
<td>0.02</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.03</td>
<td>0.02</td>
</tr>
<tr>
<td>SiO₂</td>
<td>0.01</td>
<td>0.03</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.008</td>
<td>0.006</td>
</tr>
<tr>
<td>Rh</td>
<td>0.002</td>
<td>0.02**</td>
</tr>
<tr>
<td>Eu₂O₃</td>
<td>&lt;0.002</td>
<td>0.05**</td>
</tr>
<tr>
<td>MnO</td>
<td>0.0004</td>
<td>0.0003</td>
</tr>
<tr>
<td>MgO</td>
<td>0.0007</td>
<td>0.0006</td>
</tr>
</tbody>
</table>

* The large content of PbO and B₂O₃ is due to bulk inclusions of flux.
** These higher values are probably due to chemical batch differences.
Results in Table III are of general interest to the garnet crystal grower. They show the effect of gas species and pressure on the incorporation of impurities in the crystals and are the subject of a future publication.

Conclusions

It is possible for platinum ware to have a long life and no mechanical failures if some care is taken by crystal growers as follows:

(1) At all times handle the platinum ware with gloved hands.
(2) Premelt the fluxes slowly in an oxygen atmosphere and preferably in a resistance-heated furnace, and also check the stoichiometry of the starting compounds used.
(3) Use platinum-lined rhodium-platinum alloy double-walled crucibles for strength, but preferably for limited periods to reduce the risk of rhodium contamination of the melt.
(4) From the point of view of corrosion of the apparatus and volatility, the use of barium salt fluxes has to be considered.
(5) The use of a gas atmosphere different from air has to be considered, since it plays a role in the attack on the platinum.

Finally, it is suggested that the leaching acids should be retained because it may be economic to reclaim the dissolved platinum.

We would like to thank Mrs L. Willemsen, Mrs Staps, Mr L. van Kollenburg and Mr J. Snijders of the analytical section of Philips Research Laboratories for the chemical analyses.

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The Reliability of Dry Reed Switches

The dry reed switch is in general a highly reliable device, the inert gas contained in the glass capsule preventing any undesirable reactions that might affect contact behaviour. Because of their excellent resistance to erosion, rhodium plated contacts are commonly used on the reeds. However, the purity of the gases in the capsule may still be a cause of uncertainty, and an investigation of the effects of such impurities on the contact resistance of rhodium was reported to the 19th Annual Holm Seminar on Electric Contact Phenomena in Chicago by Hayashi, Tanaka and Hara of Fujitsu Laboratories, Kawasaki.

Gaseous impurities that can exist in the capsule included oxygen, methane and carbon dioxide, arising either from atmospheric contamination of the sealing gas or from adsorbed gases on the walls of the glass or on the reeds. The effects of these gases, in varying concentration in purified nitrogen, on the contact resistance of electrodeposited rhodium were measured, while the contact surfaces were checked for impurities by electron probe micro-analysis.

In the presence of oxygen in concentrations as low as 50 p.p.m. in nitrogen contact resistance was found to increase, while a similar effect was given by methane, and oxygen and carbon were respectively detected at the mating point of the contacts. Carbon dioxide did not appear to affect contact resistance even after many operations. Hydrogen, of course, led to no increase in contact resistance, but brought the value back to normal after operation in oxygen or methane.

Similar results were obtained in experiments using bulk rhodium instead of an electrodeposit, and an improved sealing technique to avoid contamination is discussed.
One-dimensional Metallic Conductors

A NEW CLASS OF PLATINUM COMPLEXES

By A. E. Underhill

University College of North Wales, Bangor

Certain partially oxidised transition metal complexes possess structural and electronic properties which suggest that they are capable of development as one-dimensional metallic conductors. Studies of such platinum complexes have proved the most encouraging and may lead to the development of high temperature superconductors.

There is, at present, a great interest in compounds possessing new and unique electronic properties, because the successful application of these compounds may lead to devices with as large an impact on technology as the silicon and germanium devices of the last two decades. One class of compound at present being studied in several laboratories throughout the world is that possessing structural and electronic properties which suggest the possibility of one-dimensional metallic conduction. Two main series of compounds which appear capable of development to give this type of behaviour are being investigated. One series consists of organic charge-transfer compounds containing the TCNQ (tetracyanoquinodimethane, see Fig. 1a) molecule and the other series contains some partially oxidised transition metal complexes. This article concerns the latter complexes which were briefly mentioned in a previous *Platinum Metals Review* article (1).

The transition metal complexes which appear to be capable of development as one-dimensional metallic conductors are those in which the metal atom is surrounded by a square-coplanar arrangement of ligands and in which the square-coplanar units are stacked above one another to form a chain of metal atoms running throughout the crystal (see Fig. 2). This type of complex is mainly limited to nickel(II), palladium(II), and...
platinum(I) compounds and these have been discussed in detail in a recent review (2). The electrical conduction properties of several examples of this type of complex have been studied (e.g. Ni(dmg), where dmg is dimethylglyoxime (3), Pt(NH₃)₄Cl₂ (4), and K₂Pt(CN)₄.xH₂O (5)) and they have been found to behave as semiconductors with the conductivity in the direction of the metal atom chain \( \sigma \) ranging from \( 10^{-8} \) to \( 10^{-10} \) ohm\(^{-1}\)cm\(^{-1}\) at room temperature.

In this type of complex it has been suggested (2) that the outermost \( p_x \) and \( d_{z^2} \) orbitals (Fig. 3), or a combination of these orbitals, on adjacent metal atoms may overlap to form a \( d_{z^2} \) band and, at higher energy, a \( p_x \) band. In the case of nickel(II), palladium(II) and platinum(II) complexes, each \( d_{z^2} \) orbital contains two electrons, while the \( p_x \) orbital is empty, and therefore the \( d_{z^2} \) band is completely full and the \( p_x \) band is completely empty (Fig. 4). The semiconduction properties of these compounds can therefore be understood in terms of promotion of electrons from the filled \( d_{z^2} \) band to the empty \( p_x \) band. Alternatively, the observed conductivity may result from electrons “hopping” from one square co-planar complex to the next one in the chain, the hopping process being thermally activated.

Metallic conduction is associated with an incompletely filled band, and several different types of complex having the general structure described above, and in which further partial oxidation (i.e. removal of electrons) of the central metal atom has occurred, have been characterised (6). In these compounds the \( d_{z^2} \) band, if present, would be incompletely filled and hence be expected to confer metallic properties on the complex (See Fig. 4). Because the \( d_{z^2} \) orbitals are directed along the \( z \) axis only, and not along the \( x \) or \( y \) axes, the resulting partly filled band will be confined to one axis of the crystal. Thus it is expected that the metallic properties of the crystal will exist in one dimension only and that the crystal will behave as a semiconductor along the other two axes.

There are two main types of partially oxidised complex. One type is based on the cyanocomplex ion \([Pt(CN)_4]^{2-}\) (see Fig. 1(b)) and the other on the oxalato-complex ion \([Pt(C_2O_4)_2]^{2-}\) (Fig. 1(c)). The small size of the ligand atoms and the multiple bonding characteristics of the cyanide and oxalate ligands appear to be important in the formation of partially oxidised systems. These partially oxidised complexes are at present almost exclusively restricted to platinum as the central metal. Platinum is the largest
of the elements Ni, Pd and Pt, and therefore possesses the largest orbitals. This increases the chance of effective overlap with the orbitals of the adjacent metal atoms for a given intermetallic distance and thus facilitates the formation of a delocalised d, band. In these complexes partial oxidation of the platinum can be achieved by either incorporating excess anions into the lattice (e.g. K₃Pt(CN)₄Br₀.₃₂.₃H₂O) or by the creation of a deficiency of cations (e.g. K₁.₇₄Pt(CN)₂.₁.₈H₂O or Mg₀.₉₄Pt(C₂O₄)₂.₅.₃H₂O). The extent of oxidation of the platinum is always about 2.₃₂.

Crystal Structure

The crystal structure of K₃Pt(CN)₄Cl₀.₃₃.₂₆H₂O has been determined (7) and consists of square-coplanar [Pt(CN)₄]¹⁻⁻ units stacked above one another along the c(needle)-axis of the crystal. Alternate units are staggered by 45° which reduces steric repulsion between the cyanide ligands. The Cl⁻ ions are in the centre of the unit cell surrounded by a tetrahedral arrangement of K⁺ ions. However, only 64 per cent of the unit cells contain a Cl⁻ ion and this corresponds to 0.₃₂Cl⁻ per Pt atom and hence results in an oxidation number of 2.₃₂ for the platinum. All the platinum atoms are crystallographically identical, indicating that the excess charge is delocalised along the metal atom chain. K₃Pt(CN)₄Br₀.₃₂.₃H₂O possesses a similar structure (7). The effect of the partial oxidation is to bring the platinum atoms closer together. In the platinum(II) cyanocomplexes the Pt-Pt distance is always >₃.₁Å whereas in the partially oxidised compounds it is only 2.₈₋₂.₉Å, which compares with 2.₇₇Å in platinum metal. Similar intermetallic distances have been found in the partially oxidised platinum oxalate-complexes.

The crystals of the partially oxidised compounds have a completely different appearance from their platinum(II) counterparts. Whereas the latter are either colourless or only weakly coloured, the partially oxidised compounds are a deep copper colour with a metallic reflection. The optical reflectivity spectrum has been determined (8) for K₃Pt(CN)₄Br₀.₃₂.₃H₂O with light polarised either parallel or perpendicular to the direction of the platinum atom chains. For light polarised perpendicular to the chains the reflectivity is small and essentially independent of the wavelength. For light polarised parallel to the platinum atom chains the reflectivity is about 8₅ per cent at low energy and then falls sharply to almost zero at about 6₂₅mμ. The parallel polarised spectrum can be interpreted using the Drude theory of the optical behaviour of a metal and this indicates the presence of charge carriers that are highly mobile parallel to the platinum atom chains and localised perpendicular to them. From the optical spectrum the electrical conductivity in the direction of the platinum atom chain has been estimated as 1₀⁴ ohm⁻¹ cm⁻¹ and the carrier concentration as close to that of a metal (8). The visual appearance of the crystals persists down to 4 K, indicating that the metallic properties are still present at this temperature. The presence of a Pauli temperature-independent...
Paramagnetism has been detected in crystals of $K_2Pt(CN)_4Br_{0.30} \cdot 2.3H_2O$ and also has been interpreted as arising from the presence of free metallic electrons in this compound (9).

**Conductivity**

Although the optical properties and paramagnetism of crystals of $K_2Pt(CN)_4Br_{0.30} \cdot 2.3H_2O$ indicate a metallic state for electrons parallel to the c-axis of the crystal, the electrical conduction properties of these compounds are more complicated. The d.c. conductivity of these compounds has been extensively studied and conductivities as high as $10^8$ ohm$^{-1}$ cm$^{-1}$ have been reported (10) at room temperature for single crystals in the direction of the platinum atom chains. The value of the conductivity and its variation with temperature varies, however, with the method of preparation, extent of dehydration etc. Single crystals are highly anisotropic conductors with $\sigma|| : \sigma\perp = 10^6 - 10^8$, indicating a much better conduction pathway parallel to the platinum atom chains than in the direction perpendicular to the chains, as expected from the crystal structure and optical properties. Although the conductivity is high at room temperature it falls with decreasing temperatures and below 200K the crystals are well-behaved semiconductors with a similar activation energy for conduction parallel and perpendicular to the metal atom chains (see Fig. 5) (10, 11). Above 200K the activation energy decreases with increasing temperature and eventually at about room temperature the conductivity is almost temperature-independent. At higher temperatures there are indications that a negative temperature coefficient for conduction may occur, i.e. a so-called semiconductor-to-metal transition (10). This behaviour has been observed for several of these complexes and is particularly noticeable for $K_{1.71}Pt(CN)_{1.8}H_2O$ (12). The a.c. conductivity has been determined for $K_2Pt(CN)_4Br_{0.30} \cdot 2.3H_2O$ at $10^{10}$Hz and at room temperature was the same as the d.c. value. Below 200K the a.c. conductivity decreased more slowly with decreasing temperature than the d.c. conductivity (10).

There is obviously a large anomaly between the optical reflectivity and Pauli paramagnetism studies that suggest metallic behaviour along the c-axis, and the conductivity results which indicate a semiconductor below 200K. Two theories have been proposed to explain this anomaly. In the interrupted strand theory the crystal is pictured as consisting of linear one-dimensional metallic strands of the platinum complex interrupted by insulating lattice defects. The conductivity is then controlled below 200K by a thermally activated process. The
activation energy is the energy required to transfer an electron from one metallic strand to a neighbouring strand. Alternatively, in the 'random potential' theory, complete delocalisation of the electrons along the whole length of the crystal is not expected because of the presence of anions (e.g. Br\(^-\)) or cations (e.g. K\(^+\)) in only a percentage of all the possible crystallographic sites along the platinum complex chain. This random presence of ions will, it is thought, produce a random potential which will have the effect of restricting the metallic electrons to finite lengths of the platinum atom chain instead of allowing them to move freely from one end of the crystal to the other. The behaviour of the crystal is then expected to be that of a one-dimensional amorphous semiconductor.

Both theories, therefore, picture a single crystal of these complexes as containing short chains of metal atoms, in which the electrons are delocalised, separated from one another by an area in which the electrons are localised. The reflectivity and paramagnetism are determined by the areas of the crystal in which the electrons are delocalised, whereas the electrical conduction below 200K is controlled by the process of the electron moving from one delocalised chain to the next delocalised chain. It is thought that the 'delocalised' metal chains consist of between 100 and 500 platinum atoms.

The conduction process at higher temperatures including the semiconductor-to-metal transition is not easily explained. It is clear that the thermally activated conduction process which controlled the conductivity below 200K is no longer the controlling process at room temperature. Whether at this higher temperature all the electrons have sufficient thermal energy to cross the inter-strand space or whether a new conduction mechanism begins to operate at this temperature is not known at present. Unfortunately, those complexes studied so far are hydrated and lose water just above room temperature, thus preventing conduction studies above the insulator-to-metal transition.

Several of these partially oxidised metal chain compounds have been shown to undergo a unique oxidation reduction reaction under the influence of a d.c. field of above 150V/cm \((13)\). Under these conditions a crystal of \(\text{K}_2\text{Pt(CN)}_4\text{Br}_{0.58}2.3\text{H}_2\text{O}\) changes colour at the anode from the original copper colour to give a white product \(\text{K}_2\text{Pt(CN)}_4\cdot x\text{H}_2\text{O}\). There is a sharp boundary between the two colours and bromine is expelled at the interface. The effect of the reaction is therefore to reduce the partially oxidised platinum complex to a platinum(II) complex. The occurrence of this reaction clearly sets a limit on the d.c. potentials that can be applied to these conducting complexes.

From the viewpoint of producing a one-dimensional metallic conductor the results so far are encouraging. It is clear that the platinum complexes described in this article exhibit this property over short distances within the crystal even though the whole crystal behaves as a semiconductor over a large temperature range. The “insulator-to-metal” transition which appears to occur at higher temperatures needs much further investigation and work on synthesising complexes in which this occurs at lower temperatures and on complexes possessing a greater thermal stability is being carried out. These complexes also possess an anomalously high dielectric constant which may find a practical application in the future. It has been suggested that these complexes may be capable of development as high temperature super-conductors and clearly their development as one-dimensional metallic conductors is a necessary step to this aim.

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Platinum Deposition on Sapphire and Alumina

SPUTTERED SUBSTRATES FOR FERROELECTRIC FILMS
IN COMPUTER MEMORIES

An important factor in the successful development of sputtered thin ferroelectric films for computer memories is the availability of a substrate that is smooth, electrically conductive, refractory, and inert. Platinum films sputtered on to polished sapphire or smooth alumina chips meet this requirement but there is a problem of adhesion between the noble metal film and the oxide ceramic. Even chromium and titanium, which are often used as interface layers to promote adhesion, oxidise under the platinum during the prolonged heat treatment that converts dielectric to ferroelectric films at 950°C in a corrosive atmosphere.

S. F. Vogel and I. C. Berlow of I.B.M. Corporation's Systems Development Division at San Jose, California have developed a solution to the problem by sputtering platinum on to carefully cleaned and etched sapphire and alumina substrates to give strongly adherent films, and they have now described tests carried out to verify their results (J. Vac. Sci. Technol., 1973, 10, (5), 843-846). Conventional sputtering of platinum had led to the film blistering and flaking during the heat treatment of the ferroelectric deposit at 950°C, and intermediate films of zirconium or titanium, which normally promote adhesion of noble metals to oxide ceramics or glasses, also failed during heat treatment.

The I.B.M. technique was developed empirically and consists of a two-stage deposition process followed by heat treatment. First oxygen is used as the sputtering gas for 22 minutes, giving a platinum deposition rate of 35 Å per minute. Then argon is used as the sputtering gas for a further 22 minutes, during which the deposition rate increases to 180 Å per minute. It is essential to maintain the sapphire or alumina substrates during sputtering at a temperature of at least 580°C. The heat treatment in air is a controlled temperature rise over six hours to 930°C, maintenance at this temperature for two hours, and slow cooling for 12 hours.

Adhesion tests consisted of scratching specimens with a hand-held tool until failure occurred. Satisfactory adhesion was indicated by the smeared appearance of the platinum in the centre and on the edges of the scratch. Heat treated platinum films adhered much better than as-sputtered films. Crystal structure and topography of single-crystal sapphire, polycrystalline alumina and platinum films were studied by back-reflection Laue photography, diffractometry and scanning electron microscopy. On sapphire the platinum exists either as smooth single crystal material or as material with a dull fibrous texture oriented along the [111] direction. Platinum films on alumina were also fibrous.

While the main purpose of the platinum films was to serve as substrate to ferroelectric films, platinum has also been shown to be the most satisfactory material for contact electrodes deposited on to the exposed surface of the ferroelectric films. It was sputtered in argon to 3000 to 5000 Å on the initial dielectric films, followed by joint firing at 950°C, the temperature of conversion of the dielectric to the ferroelectric films. Alternatively, platinum dots can be deposited on converted films but heating at 600°C in air is then needed to produce satisfactory contact properties. F. J. S.
Ruthenium and Refractory Carbides

TITANIUM CARBIDE COMPOSITES OF REMARKABLE STABILITY

The strong reactions that occur at high temperatures between platinum, palladium and the carbides of tungsten, niobium and tantalum were first described about nine years ago by Professor E. Raub and G. Falkenburg of the Forschungs Institut für Edelmetalle at Schwäbisch Gmünd (1). The carbides were completely decomposed, and while the metal thus released formed compounds or solid solutions with the noble metal, carbon was liberated in elemental form as graphite lamellae or spheroids. Rhodium and iridium reacted similarly with the carbides of hafnium and zirconium (2) and N. H. Krikorian of the Los Alamos Scientific Laboratory has also demonstrated that platinum and iridium decompose the lanthanide carbides (3) at temperatures as low as 1000°C. On the basis of such experimental results it seemed safe to conclude that none of the carbides were compatible with any of the platinum metals at elevated temperatures.

A recent paper, again by Raub and Falkenburg (4) highlights the danger of such premature generalisations. Although the four cubic platinum metals appear to decompose all the refractory carbides, hexagonal ruthenium is perfectly compatible with titanium, tantalum and vanadium carbides even when the two constituents are fused together in the argon-arc furnace.

Ruthenium, with titanium carbide, forms a quasi-binary eutectic containing about 40 molecular per cent of titanium carbide which melts at 1820°C. Up to this temperature nominally pure ruthenium co-exists with pure titanium carbide, the microstructure of such alloys showing a fine eutectiferous matrix surrounding primary crystals of either ruthenium or titanium carbide. The nominally pure ruthenium is in fact a dilute solid solution, which can contain up to about 4 molecular per cent of titanium carbide at 1500°C. Above this concentration finely divided carbide starts to form round the ruthenium grain boundaries.

An intermetallic compound TiRu appears when more than about 5 atomic per cent of titanium is added to these eutectiferous alloys, but the ternary system Ru-TiC-Ti is generally of great simplicity, only the phases Ru, TiRu, TiC and Ti being present. No evidence of carbide decomposition or graphite precipitation was observed within this triangular field. The ruthenium-tantalum carbide and ruthenium-vanadium carbide systems were less fully, though adequately studied, and the results obtained demonstrate the remarkably high stability of these refractory carbides with respect to ruthenium. The solubility of tantalum carbide in ruthenium was shown to be approximately 5 molecular per cent at 1850°C, and after heat treating the duplex eutectic alloys below 1650°C a complex carbide Ru₄Ta(C) of unknown carbon content was precipitated.

The importance of these findings is considerable. Thermodynamically they appear to indicate that the ability of the platinum metals to decompose carbides is not greatly affected by the stability of the carbides concerned, but is largely controlled by the position of the platinum metal within its triad. In this respect it might be concluded that osmium would behave similarly to ruthenium, although experimental evidence for this is still lacking. The stability of titanium carbide in contact with ruthenium, and its instability with respect to platinum agrees with the predictions of Brewer and Engel, and is supported by the work of Gingerich and Grisby (5). These investigators showed that stable gaseous compounds are formed between titanium and platinum, and titanium and rhodium, although titanium-
ruthenium molecules appeared to have a weaker bond.

From the practical viewpoint, the ability of titanium carbide to retain its identity in the presence of ruthenium at high temperatures suggests many intriguing possibilities. In view of the significance of titanium carbide as a cutting tool material, the mechanical properties of duplex noble metal alloys containing major quantities of carbide obviously require attention. Electrical contacts of ruthenium strengthened by a uniformly dispersed titanium carbide phase might have useful characteristics in the medium duty range, and such components could be produced by standard powder metallurgical techniques. One is also encouraged to consider instrument bearings, pivots and pen points which could profitably utilise the characteristics of these corrosion and abrasion resistant composite materials. The equilibrium diagram of the quasi-binary system Ru-TiC is similar to that of the Co-WC system so familiar to workers in the hard metal industry, and sintering in the presence of a small quantity of liquid phase appears to offer the possibility of high density components.

With the hexagonal close packed carbides of tungsten (6) and molybdenum (7) rhenium forms unbroken series of solid solutions which have interesting superconducting properties. Ruthenium also has a hexagonal unit cell, the parameters of which are close to those of rhenium, and it is tempting to inquire whether it behaves in a similar way to rhenium with respect to hexagonal carbides. The ability to change mechanical properties, gently and controllably without phase change or discontinuity, from those of a hard brittle carbide to those of a relatively ductile metal is a variable which has hitherto been unavailable to the practical metallurgist. In spite of the high cost of these rare hexagonal metals, the remarkable characteristics of their carbide solid solutions should, therefore, stimulate a good deal of speculative research.

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Standard Platinum Resistance Thermometers

The revision of the International Practical Temperature Scale which resulted in the publication of IPTS-68 has led to a careful reappraisal of methods of temperature measurement to take into account the slight modifications from the former scale IPTS-48. This journal has already reported on the implications of such work on the use of rhodium-platinum thermocouples.

The U.S. National Bureau of Standards has now published NBS Monograph 126: “Platinum Resistance Thermometry”, which describes the methods and equipment used there for calibrating standard platinum resistance thermometers to IPTS-68. The text of the scale, the authorised English version of which is given in Appendix 1, is clarified and its characteristics are described. A number of thermometer designs are illustrated in detail, together with possible sources of error in their use.

Three classes of reader will find this Monograph valuable. Users of platinum resistance thermometers will find guidance as to their mechanical and thermal treatments and to transporting them. Calibrators will find a full guide to the techniques of calibration, including the fixed points used to establish the scale of temperature. Those wishing to submit their own instruments to N.B.S. for calibration will learn of the methods employed there.

F. J. S.
Very pure metals of the actinide, lanthanide and alkaline earth series can be prepared from their oxides by coupled reduction by hydrogen in the presence of platinum group metals. During the process the platinum group metals form intermetallic phases with the metals from the oxides. These phases are decomposed to yield the pure metals in gaseous form and the platinum group metals in solid form. The pure gaseous metals condense to produce pure solid specimens.

In the course of our investigations dealing with phase equilibria in uranium oxide-rare earth oxide systems, we made the following unexpected observations (1):

1. In fluorite phases with a high content of rare earth oxides it is not possible to reduce higher valency states of uranium to tetravalent uranium, at least when using hydrogen and at temperatures below 1000–1100°C.

2. At higher temperatures and when using noble-metal crucibles, we observed weight changes which indicated a reduction of the uranium to valencies below four. The metallic appearance of the reaction product made a chemical reaction between the substance and the crucible very possible. Detailed studies proved this assumption and we were able to demonstrate that the hydrogen reduction of metal oxides in the presence of noble metals (platinum, palladium, rhodium, iridium) can be applied to prepare very pure noble metal alloys with actinide, lanthanide and alkaline earth elements, titanium, zirconium, hafnium, vanadium, niobium, tantalum, and even with lithium (2–6).

The direct synthesis of alloy phases of noble metals with base metals involves many serious problems caused by the relatively high vapour pressure of the base metals. In addition, the choice of the crucible material and of the gas atmosphere affects the results. Furthermore, ordered phases are obtained only by repeated homogenising and by prolonged and careful annealing. Also the usual methods of preparation of highly radioactive metals are somewhat difficult, and in some cases the elements, such as protoactinium ($^{231}$Pa) and curium ($^{244}$Cm), are only prepared in milligram quantities and have not yet been investigated sufficiently. Further methods for the preparation of intermetallic phases are the reactions of platinum metals with nitrides (7,8), sulphides (9), borides (10), or carbides (11,12) of the base metals; the reactions of the carbides with platinum metals have been investigated more thoroughly. However, the results of the reactions of base metal carbides with platinum metals do not give single-phase products but mixtures, e.g. $\text{UMe}_3$ and $\text{U}_2\text{MeC}_2$ ($\text{Me}=\text{Ru, Os, Rh, Ir, Pt}$), or $\text{UMe}_3$ and carbon corresponding to the initial metal concentration. The application of these methods to the preparation of intermetallic phases is further hindered, as the stoichio-
metric constitution of the carbides or nitrides must be examined by analyses before starting the reaction. The preparation of the pure oxygen-free carbides and nitrides of the transuranium elements is also complicated by practical problems. In the cases of curium and protoactinium no carbides and nitrides have yet been prepared.

From metallurgical practice it is known that oxides difficult to reduce are more easily reduced in the presence of nobler metals. This is the case for the preparation of ferrous alloys and results from the fact that with higher temperatures the oxygen partial pressure of the oxide is raised by the presence of the more noble metal. Reduction is then possible if both metals form mixed crystals and this is explained by the affinity forces occurring during the formation of the mixed crystals (13).

On this basis it was possible for Klemm and Bronger (14) to prepare some noble metal alloy phases by reduction of base metal oxides with platinum metals in the presence of hydrogen or ammonia. Reaction mechanisms of coupled reactions in the case of the refractory oxides with practical reference to platinum thermocouples have been studied by Darling and his colleagues (15-19).

Details of this method of obtaining the very pure noble metal alloy-phases are as follows. When heating the oxides with finely powdered noble metals in an extremely pure stream of hydrogen, a reaction takes place which we have called "coupled reduction", i.e. the reduction of a metal oxide (carbonate)/fluoride in the presence of a noble metal, leading to the formation of a base metal-noble metal alloy.

The formula is general for the method used (in the case of an oxide):

$$xPt + Me_xO + H_2 \rightarrow Pt_xMe_y + H_2O$$

Up to the present time we have been able to show that coupled reduction is possible when using platinum, palladium, iridium and rhodium as the noble metals. Attempts to prepare alloy phases with ruthenium, osmium,
nickel, or cobalt by means of coupled reduction have been started. The temperature needed to achieve complete reduction increases when going from platinum to iridium and decreases with increasing atomic number of the actinide element. Furthermore, alloys with a high noble metal : actinide ratio are more easily prepared than compounds having a lower ratio. This means, for example, that Pt,Cm may be prepared at about 1200°C, whereas the preparation of the iridium compound requires temperatures of 1550°C. The table shows the platinum-, palladium-, iridium-, and Rh-actinide intermetallic phases prepared by coupled reductions, among them the twenty compounds prepared for the first time.

**Intermetallic Phase Structure**

The structure of Pt,A phases (A=Th, Np-Cm) was elucidated by comparison with compounds of the Pt,RE type which were prepared by coupled reduction and were investigated by Bronger (20). The hitherto unknown structure of Pt,Th and Pt,Pu proved to be isostructural with Pt,Sm; Pt,Pa and Pt,U crystallise in the cubic Ni,U-structure type.

The structure of the other new alloy phases could be established by comparison with known types of structures. The 2:1 compounds crystallise in the cubic Laves-phase type, whilst most 3:1 phases have the ordered Cu,Au-structure type. Deviation from this structure type could be observed only for the platinum alloy phases of the light actinide elements. Four different types of structures were found for the 3:1 compounds of the platinum system. Pt,Th is the only compound whose type of structure is unknown. The Pt,Pa and Pt,U alloy phases crystallise in the hexagonal Cd,Mg-structure type, Pt,Np has the hexagonal Ni,Ti-lattice, while the Pt,Pu phase has the expected Cu,Au-structure type. This fact is remarkable because no case has been reported as yet in which a simple compound of three neighbouring elements in either the lanthanide or the actinide series has the same stoichiometric formula but different lattice structures. The structures of these different lattice types, however, are very similar, only the stacking order being different. The lattice constants of the isostructural series follow a trend which is generally known when comparing the radii of the actinide elements. In the case of the Ir,A (A=Th, U-Cm) and Rh,A (A=Th-Cm) compounds this may be seen in Fig. 1. A mini-
mum in the lattice constants is to be seen between uranium and neptunium, both of which metals have been shown to possess the highest valency in their metallic state. Such a dependence of molar volume with the atomic number could not be observed in the series of platinum compounds because of the different types of structures, having more or less dense packing of the atoms.

The preparation of the Pt$_3$RE phases (RE=La-Tm, Y) by coupled reduction was first performed by Bronger (20), who also prepared some Pt$_3$RE phases (RE=Ho-Lu, Sc).

Apart from the Pt$_3$RE (RE=La-Tm, Y) and Pt$_3$RE (RE=Tb-Lu, Sc, Y) compounds we have been able to prepare other types of alloy phases of the lanthanides, such as Pt$_4$RE (RE=La-Gd) and Pd$_4$RE (RE=La-Lu, Sc, Y) and also Rh$_3$Sc. All these compounds have been prepared earlier by conventional metallurgical techniques except Pd$_4$Tm, which could not have been prepared in pure form owing to the relatively low Δ$H_V$ of thulium metal. Further information on Pd$_4$Tm is available elsewhere (3,4).

The hydrogen used was the purest cylinder hydrogen available with oxygen and water vapour contents of about $10^{-5}$ p.p.m. each. In order to prepare high purity hydrogen from it several stages of purification by physical and chemical methods were necessary (3, 22). After passing through heated titanium cuttings, heated platinum/asbestos and molecular sieves, the hydrogen was further purified by bubbling through a series of three bottles containing liquid potassium-sodium alloy (approximate composition K:Na =2.5:1 (23)) and finally by cooling to liquid nitrogen temperature to remove organic contaminants.

The hydrogen thus purified had an oxygen content of less than $10^{-26}$ torr and a partial water vapour pressure of less than $10^{-7}$ torr (22, 24). The oxygen content of the purified gas was determined by using a ThO$_4$ solid galvanic cell with Fe/FeO as the reference electrode. The water vapour content was measured with an "Hygrometer PA 1000" made by Panametrics, Waltham, U.S.A. The same method was also used to purify helium and argon, which sometimes were used as inert gas when cooling reaction products.

Coupled reductions for the preparation of most of the platinum alloy phases and all of the palladium, iridium and rhodium alloy phases were unsuccessful when performed with two commercial hydrogen diffusion apparatuses (3).

Some comment should be made concerning the analytical purity of the alloys. Because the noble metal:base metal ratio does not change during the coupled reduction the ratio of the elements in the final products is the same as in the initial mixtures; this has been demonstrated by chemical analyses on several characteristic compounds. Exceptions to this rule will be discussed later. Determinations of the oxygen contents were made on most of the alloy phases; some phases were also analysed for nitrogen and hydrogen. All determinations were performed by vacuum hot extraction. The oxygen contents of most of these alloy phases do not exceed 500 p.p.m.; the hydrogen and nitrogen contents are always less than 100 p.p.m. This means that these phases are not stabilised by the incorporation of oxygen or nitrogen (3).

An increase in stability, however, is to be observed when carbon is incorporated in the lattice of the compounds of Cu$_3$Au-type structure. The reaction, for example, of ThRh$_9$ with carbon yields ThRh$_9$C$_x$ with a maximum value of $x=0.5$ (25, 26). The increase in stability may be obtained from thermodynamic data. Using a high temperature galvanic cell of the type

$$(\text{--)Ta|}\text{U}_3\text{UF}_5|\text{CaF}_4|\text{UF}_5\text{UPt}_5\text{Pt|Ta(+)}}$$

a preliminary $\Delta G_{1000K}$ value of $-49.1$ kcal/mole for UPt$_5$ was obtained (27). Using similar galvanic cells the following data were obtained:

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta G_{1000K}$ (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>URu$_5$</td>
<td>$-45.5$</td>
</tr>
<tr>
<td>URh$_5$</td>
<td>$-62.4$</td>
</tr>
</tbody>
</table>

*Platinum Metals Rev., 1974, 18, (1)*
The increase in stability of the carbon-doped compounds may be seen by comparing the $\Delta G$ values of URu and URu$_2$C$_6$, the compound with the highest carbon content (12). By using a galvanic cell of the type

$$(-) \text{Pt|U}_2\text{UF}_6|\text{CaF}_2|\text{UF}_6,\text{URu}_2\text{C}_6,\text{Ru}_2\text{C}|\text{Pt}(+)$$

a $\Delta G_{1000^\circ \text{C}}$ value for URu$_2$C$_6$ of $-60.1$ kcal/mole was obtained. The increase in stability increases with the carbon content of the intermetallic phases. The influence of carbon in the octahedral positions on the stability of the metal lattice can be interpreted by an increase of the effective valency of the platinum metals.

**Preparation of Metals**

When preparing americium-platinum alloys at temperatures in excess of $1300^\circ \text{C}$ we observed mainly a loss of americium in the reaction product. Detailed studies showed that the americium-platinum alloys decomposed at temperatures of about $1300^\circ \text{C}$ or higher, in vacuum or inert gas atmospheres, to yield solid noble metal and americium. These could be condensed at cooled parts of the reaction apparatus.

We also have been able to demonstrate that not only americium but also other volatile metals (e.g. Cf, Ca-Ba, Li) could be prepared by this method (3, 5, 6).

Not yet investigated by us is the preparation of the rare earth metals by this method. However, remembering the above-mentioned fact, that the conventional metallurgical technique for the preparation of Pd$_2$Tm was not successful (21), it should obviously be possible to prepare rare earth metals, at least those with a relatively low $\Delta H_T$ (e.g. thulium).

Note that we were able to prepare calcium also from the mineral fluorite practically in one step by coupled reduction to the compounds Pt$_4$Ca or Pt$_3$Ca followed by decomposition in vacuum at higher temperatures. Detailed studies of these processes and their thermodynamic relationships are now under our investigation.

This means that metals like Am, Cf, Cm, Ba-Ca, and Li can be prepared by direct hydrogen reaction of the corresponding oxides, the noble metals only serving as a catalyst. This is shown by the scheme in Fig. 2.

The significance of this type of reduction is that using alloy phases as intermediates it is possible to prepare volatile metals by hydrogen reduction of the oxide. Preliminary data even indicate that it is possible to separate the two elements, for example, californium from americium or from curium, by utilising the difference in volatility of the actinide metals. With tracer amounts of $^{252}\text{Cf}$ we have been able to show that californium is volatilised by more than 90 per cent at $1250^\circ \text{C}$ in extremely pure hydrogen or in vacuum from californium oxide-platinum mixtures, at which temperature curium does not volatilise. Detailed studies of these processes and their thermodynamic relationships are now under investigation.

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Science Awards to Platinum Metals Research Workers

PROFESSOR GEOFFREY WILKINSON AND DR VLADIMIR HAENSEL

The achievements of two research workers prominent in the platinum metals field were recognised in October 1973, when awards to Professor Geoffrey Wilkinson and Dr Vladimir Haensel were announced. Both recipients have contributed to past issues of Platinum Metals Review. In the January 1959 issue Dr Haensel described “The Penex Process for Pentane Isomerisation”. In January 1964 he contributed “Duofunctional Catalysts in the Petroleum Industry”, while Professor Wilkinson reviewed “Organometallic Compounds of the Platinum Metals”. Wilkinson then reviewed “Tertiary Phosphine Complexes of the Platinum Metals” in the April 1968 issue.

Professor Wilkinson, now of Imperial College, London, has been awarded the Nobel Prize for chemistry jointly with Ernst Fischer. The award was made for determining the structure of “sandwich” compounds, initially of ferrocene, and subsequently synthesising many other such compounds. Ruthenocene is one such platinum metal compound. The original work was carried out in 1952 when Wilkinson was teaching at Harvard. Since returning to London in 1956 his interests have gradually shifted to other areas, among which the development of some of the most active homogeneous catalysts is of particular importance to the chemistry of the platinum metals. His name is closely associated with the family of catalysts based on tristriphenylphosphinochlororhodium, (Ph₃P)₃RhCl, from which the carbonyl complexes RhCl(CO)(Ph₃P)₂ and RhH(CO)(Ph₃P)₂ used in hydroformylation reactions have been developed.

The National Medal of Science, the U.S. Federal Government’s highest award for distinguished achievement in science, mathematics and engineering, was presented by President Nixon at the White House on October 10th to ten scientists, among whom was Dr Haensel, Vice-President for Science and Technology of the Universal Oil Products Company, Des Plaines, Illinois, for “his outstanding research in the catalytic reforming of hydrocarbons which has greatly enhanced the economic value of our petroleum natural resources”. Dr Haensel’s work has, of course, included responsibility for the development and improvement of the series of U.O.P. Platforming catalysts since their inception. Platinum-based catalysts for the reforming of hydrocarbons were first developed at U.O.P. and Haensel’s team has constantly upgraded their performance, more recently by the introduction of bimetallic catalysts in which a second metal synergistically improves the reforming performance of platinum.

F. J. S.
ABSTRACTS
of current literature on the platinum metals and their alloys

PROPERTIES
An X-ray Diffraction Study of Atomic Ordering in Platinum-rich Copper–Platinum Alloys
Ordering was studied in the Cu–Pt system at Pt concentrations of 48, 54, 61, 66 and 70 at.%. An ordered structure exists for the near-equiatomic composition, CuPt, and for the composition near CuPt2. There is, however, no evidence for the existence of an ordered structure for CuPt3.

The Domains of Homogeneity of the Superconducting Phases in the Molybdenum–Platinum System
Mo–Pt (up to 55 at. % Pt) was studied by metallography, X-ray diffractometry, hardness measurements, superconductivity and resistivity measurements for various thermal treatments. Results show that the phase diagram at high temperatures needs revision. In particular, the partially ordered ε′ hexagonal phase of the Ni3Sn (DO19) type is responsible for the maximum superconducting transition temperatures.

The Superconductivity, Structure and Magnetic Susceptibility of NbAuPt(1–x) A-15 Type Phases
The superconducting transition temperature, lattice parameter and magnetic susceptibility of ternary Nb–Au–Pt alloys in the as-cast and annealed states were measured. Annealing reduced most of the alloys to A-15 structure as observed by X-ray diffraction, but metallographic microstructures of some of these alloys showed them to be still inhomogeneous, which affected the values of Tc and χ. All the alloys are nearly paramagnetic and χ varies with Tc in most cases.

The Debye Temperature of Pure Pd and Dilute Pd–Ni Alloys
The temperature dependence of the Debye temperature of dilute Pd–Ni alloys was studied. Results are compared with those for pure Pd and Pd–Cu and show that in pure Pd there is no observable paramagnon contribution to the apparent lattice specific heat.

Effect of High Pressure on the Superconducting Transition Temperature of Pd–H
Under hydrostatic pressure Pd–H exhibits a negative value of dTc/dp comparable to that of non-transition superconductors. The isotope effect in Pd–H(D) is discussed in terms of a simple model which is in agreement with the observed pressure effect.

Kinetic and Magnetic Properties of Palladium-Iron Alloys. II. Temperature Dependence of Magnetisation and Thermal E.M.F.
Measurements of the temperature dependence of magnetisation and of thermal e.m.f. of 0.5–99.5 at.% Fe–Pd alloys at 4.2–300 K enabled the values of magnetic saturation at 0 K to be used to calculate the mean magnetic moment and the moment on dissolved Fe atoms. Curie temperatures of dilute Fe–Pd alloys were determined by the thermodynamic potential method. An attempt was made to estimate the relative importance of the factors contributing to the thermal e.m.f.s. at various ranges of temperature.

On Some Phases in the Pd–Pb Mixture
Pd10Pb, hitherto thought to be a homogeneous phase, is composed of four different phases, Pd10Pb5(h1), Pd9Pb5(h2), Pd8Pb3 and Pd11Pb4. All phases are variants of the NiAs type. The structure of Pd10Pb5(h1) is confirmed; the structure of Pd8Pb3 is isotypic to Ni3Ge2, and Pd11Pb4 has a monoclinic cell.

The Diffusion of Hydrogen through Membranes of Palladium and Its Alloys with Silver
Studies at 250–700°C and pressures up to 3 atm showed that the diffusion rate of H2 through Pd and 25% Ag–Pd membranes is related to pH by Svert's Law.
Diffusion of Hydrogen from Converter Gases through Membranes of Palladium and Its Alloys

Ibid., 1702–1706

Studies at 300–650°C and pressures of up to 3 atm showed that the rate of diffusion for H₂ from converter gases through Pd and 25%Ag-Pd membranes is related to p₁₀ by Sivert’s law. An approximate equation for the rate of diffusion for H₂ from membranes is related to p₁₀ by Sivert’s Law.

The Chromium-Rhodium Constitution Diagram


The Cr-Rh system was studied over the entire converter gases through Pd and 2.5%Ag-Pd to 68 at.%. at 1475°C. The Chromium-Rhodium Constitution Diagram of the Cr-Rh system was studied over the entire composition range. Two intermediate phases exist in this system. The β phase has a Cr₃Si (A15) type structure and is stable from 77–78 at.%. Cr. The location of the f.c.c. (γ-Rh) to h.c.p. (ε phase) transition is strongly temperature dependent. Precipitation of a metastable h.c.p. structure occurs during rapid cooling of the b.c.c. (α-Cr) solid solution. A peritectic reaction, an eutectic reaction and a peritectoid reaction occur when R = R' = Me, but when R = Me or Et and R' = Ph₂, 2-metallation and 4-chlorine substitution of the phenyl group occurs as evidenced by the X-ray structure [PtCl₄(CIC₄H₄NH)(NHMe)] (PEt₃)₃ ClO₄.

Investigation of the Ternary System Iridium-Tantalum-Nickel


The isothermal section of the Ir-Ta-Ni system at 950°C showed four intermetallic phases not previously noticed.

CHEMICAL COMPOUNDS

Radical Cation Formation during the Adsorption of Polyenic Aromatic Hydrocarbons on Platinum Oxide


Experimental conditions are reported for resolving the hyperfine splitting of e.p.r. spectra obtained from the interaction of polycyclic aromatic hydrocarbons with PtO₂·2H₂O. The adsorbed species are shown to be radical cations.

New Compounds of Na₂Pt₃O₄ Structural Type


New members of the Na₂Pt₃O₄-type platinates, Me₅Pt₃O₄, where Me = Li, K, Ca, Ba, Co, Zn, and Cd and 0 ≤ x ≤ 1 were prepared and are characterised by their lattice constants. Details of the thermal stability of both new and known platinates and palladates are given. Thermalysis of the palladates starts at 844–1020°C and of the platinates at 725–798°C. Decomposition gives either Pt metal and binary oxide or more stable palladates and platinates.

Metallation of a Phenyl Group in a Platinum (II) Carbene Complex during Oxidation to Platinum(IV)


Reaction of Cl₂ with cis-[PtCl₂(C(NHR)(NHR'))] PEt₃ and trans-[PtCl₂(C(NHR)(NHR'))(PEt₃))₂ ClO₄ gives analogous Pt(IV) carbene complexes when R = R' = Me, but when R = Me or Et and R' = Ph₂, 2-metallation and 4-chlorine substitution of the phenyl group occurs as evidenced by the X-ray structure [PtCl₄(CIC₄H₄NH)(NHMe)] (PEt₃)₃ ClO₄.

Dimeric Triphenylphosphine Complexes of Platinum(II)


The preparation of a new pale yellow isomer (probably cis-) of the bridged complex [(PPh₃)₂ PtCl₂] and its reaction with p-toluidine and CO are described.

Addition Reactions on Coordinated Olefinic Ligands. VII. Reaction between Amines and Pt(II) Olefin Complexes: Factors Affecting Reactivity and Stereochemistry


The addition reaction between diethylamine and simple α-olefins coordinated in a variety of Pt(II) complexes was studied. Details of the reactivity of the unsaturated ligands towards the nucleophile and also data on the stereochemistry of the addition are given. The influence of relevant factors is discussed.

Antitumour Action of Dichloro(4,5-dimethyl-o-phenylenediamine)platinum(II)


Dichloro(4,5-dimethyl-o-phenylenediamine-N,N')platinum(II) is effective against the Ehrlich ascites tumour and L1210 leukemia in mice and increases survival times by 176% and 74% respectively. At 4 × 10⁻⁵ M concentration there is a 50% inhibition of DNA, RNA and protein synthesis in Ehrlich ascites tumour cells grown in vitro. Details for the synthesis of this compound is given.
The Antitumour Agent cis-Pt(NH₃)₂Cl₂: Distribution Studies and Dose Calculations for ¹⁹³⁷-²⁰⁴⁷ and ¹⁹⁳⁷-²⁰⁴⁷


When cis-Pt(NH₃)₂Cl₂ labelled with ¹⁹³⁷Pt was injected into mice bearing sarcoma 180, the tumour: blood ratio of radioactivity varied from 1:3 to 2:1 at 4-5 days after treatment. Details of organ distribution and of the metabolic pathways of this compound are discussed.

K₂Pt(CN)₄Br₂·3(H₂O) a Diamagnetic One-dimensional Metal?


The magnetic susceptibilities of K₂Pt(CN)₄ Br₂·3(H₂O)₂, K₂Pt(CN)₄(H₂O)₃, and K₂Pt(CN)₄Br₂ were measured. Results show that any metallic type of contribution to the susceptibility of the first compound is at least an order of magnitude smaller than that expected from simple band theory or from an interrupted strand model.

Optical Conductivity and Electron Interaction in the One-dimensional Metal K₂Pt(CN)₄Br₂·3H₂O


The optical conductivity of K₂Pt(CN)₄ Br₂·3H₂O single crystals was studied for photon energies near the plasma edge. The imaginary part of the dielectric function is determined by inelastic scattering of holes by the Coulomb potentials of randomly distributed Br ions and by inelastic scattering by excitation of plasmons.

Optical Excitation of the Electronic Plasma Oscillation in the One-dimensional Conductor K₂Pt(CN)₄Br₂·3H₂O


Reflectivity measurements with p-polarised light under non-normal incidence at a (001) surface of K₂Pt(CN)₄Br₂·3H₂O showed a resonance near the electronic plasma frequency. Results are discussed using the Fresnel formula for anisotropically absorbing crystals and classical dispersion theory for the description of the plasma oscillation.

Reactions of Palladium(II) Compounds with Carbon Monoxide in Alcohol/Amine Systems: a New Route to Palladium(0) Carboxyl- and Carboxalkoxy-palladium(II) Complexes


Pd(d) carbonyl complexes, Pd(CO)(Ph₃P)₃, Pd₄(CO)₆(Ph₃P)₃ and Pd₄(CO)₆(Ph₃P)₄ were prepared by reacting (Ph₃P)₂PdCl₂ with CO at room temperature in MeOH/amine systems involving primary and secondary amines; these carbonyl complexes are interconvertible. The use of tertiary amines, however, gives selectively a carbomethoxy complex, (Ph₃P)₂PdCl(COOCH₃).

Cyanoalkyl Complexes of Transition Metals. I. Preparation and Properties of Some Palladium Complexes


PdCl₂(CH₂CN)(Ph₃P)₂ was synthesised by reacting Pd(Ph₃P)₄ with CICH₂CN. Compounds having the formula PdX(CH₂CN)L₂ where X = Cl or Br and L = PPh₃CH₂CH₂PPh₃, PPh₃CH₂CH₂PPh₃, or o-phenanthroline, were obtained by an exchange reaction of PdCl₂(CH₂CN)(Ph₃P)₂ with the ligands. The structure of these complexes is discussed.

The Carbonylation of RuCl₃·xH₂O in Refluxing Ethanol


The red solution formed by passing CO through a refluxing solution of RuCl₃·xH₂O in EtOH is shown to contain Ru(CO)₃Cl₂·fac-[Ru(CO)₂Cl₂]⁻ and Ru(CO)₃Cl₂/[Ru(CO)Cl₄]⁻. Ambiguities in the preparation and spectra of these and other Ru carbonyl halides are discussed.

Infrared Spectroscopic Evidence for Di-hydridotricarbonyl(triphenylphosphine)ruthenium


The reactions of Ru(CO)₃PPh₃ and Ru(CO)₅ under pressures of H₂ were studied using a high pressure spectrophotometric cell. Infrared spectral evidence was obtained for the formation of H₂Ru(CO)₅PPh₃ in reversible equilibrium with Ru(CO)₅PPh₃ and H₂. Reactions of Ru(CO)₅ with H₂ at low temperatures affords H₂Ru(CO)₄ as the initial product. Above 20°C decomposition occurs resulting in the formation of polynuclear products.

ELECTROCHEMISTRY

On the Influence of the Annealing Temperature and Heavy Current Treatments on the Porous Structure of Platinum Electrodes and on the Kinetics of the Oxygen Reaction at High Temperatures


The influence of high temperature annealing and anodic heavy current treatments of porous Pt electrodes was studied by scanning electron microscopy. Results are discussed on the basis
of the kinetic behaviour of the electrodes, whose structure and catalytic activity are affected by these treatments.


The adsorption of n-propanol on a platinised Pt electrode was investigated by tracer methods. The process is an irreversible chemisorption that cannot be characterised by an equilibrium isotherm. The apparent concentration and potential dependences of adsorption are assumed to be due to certain oxidation-reduction reactions.

LABORATORY APPARATUS AND TECHNIQUE

A Thermistor Bimetal Thermocouple Hemisphere Electrode for Simultaneous Electrochemical/DTA Measurements


The construction of a thermistor bimetal thermocouple sensitive to thermal changes at the single electrode during scanning electrochemical experiments in liquid solutions is described. A Pt: 13% Rh-Pt thermocouple is incorporated in this device to permit caloric standardisation of differential thermal analysis thermogram peak areas from the known Peltier effect enthalpy change for passage of a known change across the couple.

HETEROGENEOUS CATALYSIS

Deactivation of Reformation Catalysts by the Growth of Platinum Crystals


Crystal size data are used to make approximate determinations of the specific Pt areas in reformation catalysts and thus to predict the relative activity of the catalysts.

The Reduction of Nitric Oxide with Carbon Monoxide and Hydrogen over Supported Noble Metal Catalysts


The reduction of NO with H₂, CO and equimolar mixtures thereof was studied on Pt, Pd, Rh and Ru catalysts. Details of comparative catalytic activity for each reducing agent are given and a new reaction path, not involving the NH₃ decomposition step is proposed.

Effect of the Pressure of Hydrogen on the Course of C₅⁻ and C₆⁻-Dehydrocyclisations of n-Octane over Platinised Carbon


During C₅⁻ and C₆⁻-dehydrocyclisations of n-C₈H₁₈ at 375°C over 20% Pt/C, increasing pH₂ causes more formation of 1,2-disubstituted rings, e.g. o-xylene and 1,2-methylethyclobutane. Reactions proceed via the general stage of formation of monoadsorbed complexes followed by subsequent conversion to the five- or six-membered rings.

Isoeyanate Intermediates in the Reaction NO + CO over a Pt/Al₂O₃ Catalyst


The intermediates formed by the interaction of NO and CO on a Pt/Al₂O₃ catalyst were studied by i.r. spectroscopy. Results show the existence of a Pt-NCO species and a (NCO)⁻ anion, and provide a new mechanistic pathway and possible alternative to previous explanations of NH₃ formation in the catalytic treatment of automobile exhaust gases.

A Study of Platinum-Polyamide Catalysts. Catalytic Behaviour in the Benzene Hydrogenation Reaction


Studies of CO₉H₆ hydrogenations over Pt/polyamides, Pt/polyacrylonitrile, Pt/molecular sieves, Pt/ion exchange resins, and Pt/Al₂O₃ showed the effect of the supports on catalytic activity and selectivity. Only when Pt/polyamides are used is cyclohexene found as a reaction product. Various techniques showed that a bivalent Pt complex on the polyamide surface gives these catalysts their special selectivity.

Kinetics of Dehydrogenation of Cyclohexane on Platinum/Alumina Catalyst in a Pulsed Regime


Studies of the kinetics of cyclohexane dehydrogenation over Pt/Al₂O₃ by the pulsed microcatalytic method in a stream of H₂ and He enabled the kinetic constants to be determined. The reaction products in these conditions inhibit the reaction.

Formation of Coke in Conditions of Reforming Aromatic and Naphthenic Hydrocarbons on Platinum/Alumina Catalyst


The yield of coke during aromatisation of hydro-
Pt/zeolites and surpass Pt/Al₂O₃ in this respect. Platinum Metals Rev., 1974, 18, (1) 39

Hydrogenation of Aromatic Hydrocarbons of Jet Fuel Fractions on Platinum Catalysts

Ptlzeolite catalysts have greater hydrocracking activity if the zeolite has a high silica content. Platinum Metals Rev., 1974, 18, (1) 39

When vitrinite is catalytically dehydrogenated in the presence of phenanthride as vehicle, the H₂ yield is not greatly influenced by the catalyst support or concentration but by the metal used. The highest H₂ yield is achieved by Pd.

Platinum and Palladium Catalysed Hydrogenation, Racemisation, Exchange and Double Bond Migration in Substituted Cyclohexenes

Partial deuteration of methyl-substituted cyclohexenes showed considerable exchange and double bond migration over 5% Pd/C but over 5% Pt/C hardly any double bond migration occurred in the cyclohexene ring although up to 60% of the recovered molecules were on the surface and 25% of them exchanged at least one H for D.

Hydrogen-Oxygen Titration Method for the Measurement of Supported Palladium Surface Areas

The dispersion of Pd in 0.25-2.0% Pd/y-Al₂O₃, measured by titration by H₂ or D₂ at 100°C of O₂ preadsorbed on the catalyst, agrees with results of other methods and has distinct advantages over them because of the method’s sensitivity and its suitability for use where the catalyst has been exposed to the air.

Dispersion and Activity of Palladium in Catalysts for Hydrogenation of Phenol

The dispersion of Pd on 0.25-2.0% Pd/γ-Al₂O₃ during hydrogenation of C₆H₅OH was determined by electron microscopy and by O₂ chemisorption studies. The specific activity of Pd on this support remains constant while the kinetics of the reaction are steady. Selectivity and efficiency of the catalyst are related to the thickness of the active Pd layer on the catalyst particles.

Heterogeneously Catalysed Vapour-phase Oxidation of Ethylene to Acetaldehyde

A heterogeneous catalyst for vapour-phase oxidation of C₂H₄ to CH₂CHO consists of Pd-doped V₂O₅ with a third component such as Ti, Ru, Pt, or Ir. The Pd ions play an important part in the redox mechanism. This catalyst operates well at 110-175°C, 1-30 atm with high space-time yields.

Supported Metals. Preparation of Palladium on Silica, Alumina, Magnesia, and Aluminium Silicate

Catalysts prepared by the impregnation of Al₂O₃, SiO₂, MgO and silica-aluminas with either...
Palladium(I) and Platinum(I) Complexes

The preparation of a polymeric diphenylbenzylcatalysts is discussed. 0.5 wt. %, Ir/Al₂O₃ at 370-490°C space velocity in the Presence of Iridium/Alumina Catalysts

Heterogeneous Selective Catalysis of the Hydrogenation of Olefins by Polymeric Palladium(II) and Platinum(II) Complexes


The preparation of a polymeric diphenylbenzylphosphine ligand and of its Pd(II) and Pt(II) dichloride complexes is described. The effectiveness of these complexes as olefin hydrogenation catalysts is discussed.

Dehydrocyclisation of 2-n-Butylnaphthalene in the Presence of Iridium/Alumina Catalysts


Studies of 2-n-butylnaphthalene conversion over 0.5 wt. % Ir/Al₂O₃ at 370-490°C; space velocity 0.8-0.2 h⁻¹ showed that C₅- and C₆-dehydrocyclisation at the α- and β-C atoms of naphthalene depends on the temperature; at 370-410°C cyclisation at the β-C atom predominates but at 450-490°C cyclisation at the α-C atom predominates.

HOMOGENEOUS CATALYSIS

Palladium(II) Acetate Catalysed Reactions of Olefins in Acetic Acid


The results of several investigations of Pd(II) acetate catalysed reactions are summarised. These include vinyl and allylic ester exchanges with solvent to give vinyl and allylic acetates and also some olefin oxidation reactions.

Palladium(II) Catalysed Aromatic Acetoxylation. II. Nuclear Acetoxylation of Aromatic Compounds: A Reversal of the Usual Isomer Distribution Pattern in Aromatic Substitution


The reaction between monosubstituted aromatics and Pd(II) acetate in CH₃COOH in an O₂ atmosphere was studied. The monoaetoxylation products from compounds containing o,p-directing substituents consist of predominantly meta isomer, whereas one compound with a meta-orienting substituent gives mainly o,p-acetoxylation. Isomer distributions are thus reversed with respect to ordinary electrophilic aromatic substitutions. Polymethyl-substituted benzenes give side chain acetoxylation products.

Noble Metal Catalysis. II. Hydrato-carbonylation Reaction of Olefins with Carbon Monoxide to Give Saturated Acids


The hydrato-carbonylation reaction of olefins with CO to give saturated acids was studied in the presence of a catalyst – probably a zerovalent Pd-phosphine complex. The reaction rate is dependent on olefin concentration and CO pressure and reaches a maximum with a H₂O concentration of 5-10%. The catalyst system undergoes a number of changes between the zero and plus two valence states, some of which probably involve the carbon moieties attached to the phosphine ligand.

Isomerisation and Hydrogenation of Iso-pentenes in the Presence of Chlorodimethylsulphoxide Complexes of Palladium


Chlorodimethylsulphoxide complexes of Pd catalyse the hydrogenation and isomerisation of 3-methylbutene-1 to form a mixture of isopentenes. Isomerisation of 3-methylbutene-1 takes place with the aid of hydride complexes according to the β-allyl mechanism. 2-Methylbutene-1 is formed directly from 3-methylbutene-1 rather than by successive transfers of the C==C bond.

Properties of Sodium Bis-(2-methoxyethoxy) aluminium Hydride. XIV. Dehalogenation in the Presence of Palladium Complexes


Dehalogenation of aliphatic and aromatic halogeno derivatives with NaAlH₄(OC₂H₅OCH₂)₃ is accelerated by catalytic amounts of Pd complexes, the strongest effect being in the aromatic series where even fluorobenzene is reduced. The effects of the amount of catalyst and nature of the halogen are discussed.

Catalytic Codimerisation of Styrene with Lower Olefins by Rhodium and Ruthenium Catalysts


The codimerisation reaction of styrene with lower olefins such as ethylene, propylene or 1-butene were studied in the presence of a number of Rh(III) and Ru(III) compounds. Details of reaction products and comparative yields are given.
Rhodium Complexes of Chiral Phosphines as Catalysts for Asymmetric Homogeneous Hydrogenation


The use of a series of soluble Rh complexes, prepared from chiral tertiary phosphines, as catalysts for asymmetric homogeneous hydrogenation is discussed. These catalysts show nearly complete, enzyme-like stereoselectivity and represent a vast improvement in performance over that of simpler chiral-supported heterogeneous catalysts.

Hydrogenation of $\text{TiPCl}_3$(triphenylphosphine).chlororhodium(I)


The reactivities of $\text{RhCl(PPh}_3)_2$, $\text{RhCl(PPh}_3)_3$, and $\text{Rh}_2\text{Cl}_4(P\text{Ph}_3)_4$ towards $\text{H}_2$, and the contributions of each of these species to the overall rate of hydrogenation of $\text{RhCl(PPh}_3)_3$ in solution were determined. $\text{RhCl(PPh}_3)_2$ is at least $10^4$ times as reactive as the other two species.

Hydrogenation and Dehydrogenation of Chlorotris(triphenylphosphine)rhodium(I)


The amount of $\text{H}_2$ absorbed per mole of $\text{RhCl(PPh}_3)_3$ differs from that recovered by an inert gas purging technique when using $\text{C}_2\text{H}_6$, $\text{CH}_2\text{Cl}_2$, and $50\% \text{C}_2\text{H}_5\text{OH-CHCl}_3$ solutions. In the last case the reversibly bound $\text{H}_2$:Rh ratio is only $\sim 0.3$ at 298K because $\text{RhHCl(PPh}_3)_2$ has been formed, whereas in $\text{C}_2\text{H}_6$ the ratio is 0.85 and in $\text{CH}_2\text{Cl}_2$ it is 0.66.

NEW PATENTS

METALS AND ALLOYS

Novel Platinum-Rhodium-Tungsten Alloy

UNITED STATES ATOMIC ENERGY COMMISSION

U.S. Patent 3,737,309

A new alloy composition comprising 25-30% Rh, 6-10% W with the remainder Pt, is useful for encapsulating radioisotope fuels. It has a melting point of 1980-2050°C.

Wrought Dispersion Strengthened Metals by Powder Metallurgy

INTERNATIONAL NICKEL CO. INC.

U.S. Patent 3,738,817

Powder metallurgy is used to produce Pt-based alloys by dispersion hardening with uniform distribution of the dispersed agent transversely and longitudinally.

Homogeneous Olefin Hydrogenation Catalysed by Dichlorodicarbonyl-bis(triphenylphosphine)rhodium(I)


The relative hydrogenation rates for a variety of alkenes and alkadienes catalysed by $\text{RuCl}_2$(CO)$_2(P\text{Ph}_3)_2$ were measured in the presence of added $\text{PPh}_3$. Reaction rates and the means of obtaining selective hydrogenation are discussed.

GLASS TECHNOLOGY

Observation of Contact Phenomena in Glass/Metal Systems


A study of the glass droplets found near the wetting edge of glass sessile drops on Pt has clarified the deposition process and the influence of the Pt grain structure on their nucleation and growth. The mode of grain boundary movement during grain growth is discussed.

TEMPERATURE MEASUREMENT

A Reciprocal Kelvin Temperature Sensor


A simple bridge circuit using a Pt resistance thermometer is described which generates a signal proportional to $1/T$ with an error $<0.1\%$ over a wide range. The superiority of Pt over other materials is discussed.
CHEMICAL COMPOUNDS

Rhodium Molybdenum Oxide
SOLVAY & CIE. British Patent 1,330,589
A new oxide for use as an electrolysis electrode, oxidation catalyst and composite semiconductor is a mixed oxide of formula Rh<sub>m</sub>MoO<sub>n</sub> formed from hydrated rhodium trichloride and molybdc oxide.

Silyl Metal Complexes
DOW CORNING CORP. German Offen. 2,260,215
Disilanes and hydrosilanes having Cl substituents are reacted with Pd or Pt phosphine complexes to give silyl complexes of the type Pd( SiPhCl<sub>2</sub>)(PBu<sub>3</sub>)Br.

ELECTRODEPOSITION AND SURFACE COATINGS

Chemical Plating Process
UNITED KINGDOM ATOMIC ENERGY AUTHORITY British Patent 1,324,653
Insulators such as glass and plastics are chemically plated by ion bombardment to produce an activated surface which is then contacted with a suitable plating bath. The examples show the use of positive Pd ions for bombardment.

Ruthenium Alloy Electroplating
SEL-REX CORP. British Patent 1,328,928
Stress in Ru electroplated coatings may be reduced by the co-deposition of another Pt-group metal and optionally a Group IIIB metal such as Ga, In or Ti. The bath used contains 0.5-50 g/1 Ru as (NH<sub>3</sub>)<sub>6</sub>(Ru<sub>2</sub>Cl<sub>6</sub>(H<sub>2</sub>O)<sub>2</sub>N) and 0.5-20 g/1 of other Pt-group metal as a water-soluble salt, e.g. Na<sub>3</sub>PtCl<sub>6</sub>.

Rhodium Plating
AMERICAN CHEMICAL & REFINING CO. INC. U.S. Patent 3,729,396
An aqueous acidic Rh plating bath contains Rh ions, Al ions, SO<sub>4</sub> ions and a polycarboxylic organic acid. Optionally PO<sub>4</sub> ions are also present.

Electrolyte for Rhodium Deposition
AMERICAN CHEMICAL & REFINING CO. INC. French Appl. 2,150,988
An electrolyte for the deposition of Rh, in the manufacture of jewellery and ornaments, comprises 1.0-30.0 g/1 Rh ions, 0.05-5.0 g/1 Al ions, 50.0-400.0 g/1 sulphate ions and 1.0-25.0 g/1 of an organic polyacid, e.g. azelaic, oxalic, maleic acids. The pH is within the range 0.1-2.0. The electrolyte may also include 10.0-70.0 g/1 PO<sub>4</sub> radicals.

Ruthenium Plating Bath
INTERNATIONAL NICKEL LTD. German Offen. 2,261,944
Bright flash coatings of Ru are obtained using baths of pH 4 or lower containing a N-bridged Ru complex and at least 1.5 g/1 SO<sub>4</sub> ion. [Ru<sub>3</sub>N(H<sub>2</sub>O)<sub>3</sub>Cl<sub>6</sub>]<sup>3-</sup> is a suitable complex.

HETEROGENEOUS CATALYSIS

Paraffin Hydrocracking and Isomerisation
TEXACO DEVELOPMENT CORP. British Patent 1,324,480
Control over catalyst activity and selectivity when using fluoroated Pt, Pd, Rh, Ru or Re catalysts on Al<sub>2</sub>O<sub>3</sub> supports is achieved by adding an oxide of C.

Organosiloxane Composition
DOW CORNING CORP. British Patent 1,324,964
Adhesives are produced from a mixture of organosiloxane and vinyl triacetoxyxilane in the presence of a Pd catalyst.

NO<sub>x</sub> Abatement
JOHNSON, MATTHEY & CO. LTD. British Patent 1,330,841
Tail gas from HNO<sub>3</sub> plants is mixed with excess CH<sub>4</sub> or other gaseous reducing fuel and passed over a layer of Pt-Rh deposited on a wash-coated ceramic honeycomb. The metallic layer contains 20-50% Rh-Pt.

Oxidation of Methane
JOHNSON, MATTHEY & CO. LTD. British Patent 1,330,842
A gaseous compound of C is mixed with O<sub>2</sub> and passed over a Pt-Rh alloy deposited on a wash coated ceramic honeycomb. The alloy contains 20-50% Rh-Pt. The feed gases may be C-enriched HNO<sub>3</sub> tail gases or engine exhaust gases.

Azole Derivatives
MERCK PATENT G.m.b.H. British Patent 1,331,408
In the synthesis of azole derivatives the hydrogenation of nitro to amine and the hydrogenolysis of benzyl groups may be catalysed by Pd catalysts.

Benzotriazoles
RHEIN-CHEMIE RHEINAU G.m.b.H. British Patent 1,331,606
Benzotriazoles can be hydrogenated smoothly and rapidly in the presence of Pd, Pt or Rh catalysts to give the hitherto unknown 4, 5, 6, 7-tetrahydrobenzotriazoles in good yields.

Cyclohexanone Production
V.E.B. LEUNA-WERKE WALTER ULBRICHT British Patent 1,332,211
The hydrogenation of phenol to cyclohexanone is catalysed by an Al<sub>2</sub>O<sub>3</sub>-supported mixture of 0.1-5% Pt-group metal and 5-50% alkaline earth metal hydroxide and/or alkaline earth metal oxide. The catalyst must have a specific area of 110 m<sup>2</sup>/g and at least 40% of the pores in the range 100Å-500Å.
Hydrogenation Catalysts
ESSO RESEARCH & ENGINEERING CO.
British Patent 1,332,483
The activity of supported catalysts is increased by treating the supports before impregnation with a Group I-III metal alkyl, aryl, etc. For example 0.6% Pt can be deposited on an alcolohate alumina pretreated with AlEt3.

Hydroformylation
JOHNSON, MATTHEY & CO. LTD.
British Patent 1,332,894
Catalysts suitable for hydrogenation, hydroformylation and carbonylation may be prepared by absorbing into the pores of a solid porous support solutions of hydrido carbonyl complexes of Rh such as RhH(CO)(PR3)2 or RhH(CO)(PR3)3 where R is an organic substituent.

Methane Production
CLARKE CHAPMAN-JOHN THOMPSON LTD.
British Patent 1,333,251
CH4 is produced from CO and H2 in the presence of a Ru, Pt, Co or Ni catalyst, stripped of H2O and then the reaction is repeated to increase the yield.

Paraffin Hydrocracking and/or Isomerisation
TEXACO DEVELOPMENT CORP.
British Patent 1,324,209
Control over temperature and reaction during hydrocracking and/or isomerisation over a Pt:Al2O3 catalyst containing Cl2 is achieved by introducing CO during the reaction.

Lubricating Oils
SHELL OIL CO.
U.S. Patent 3,730,877
Lubricating oils are produced by the treatment of paraffinic-naphthenic oils with hydrogen over a Pt:Al2O3 catalyst containing up to 4% alkali or alkaline earth metal.

Palladium-Gold Catalyst
KNAPACK A.G.
U.S. Patent 3,743,607
An improved catalyst for the catalytic vapour phase production of CH3COOCH2CH3 from C2H4, CH3COOH and O2 is disclosed. A catalyst for the synthesis reaction is metallic Pd and an alkali metal acetate or formate supported on a carrier activated by metallic Au.

Ammonia Oxidation Catalyst
JOHNSON, MATTHEY & CO. LTD.
French Appl. 2,148,525
Gas reactions, e.g. NH3 oxidation for HNO3 production, are catalysed by two sets of gauzes. The reactant gases first come into contact with noble metal gauzes (e.g. 10% Rh-Pt alloy), and then with less volatile catalytic gauzes such as austenitic 21% Ni, 23% Cr stainless steel or a Pt-Ni-Cr alloy.

Ring Hydrogenation of Arylamides
UNIROYAL INC.
Dutch Appl. 73.02459
N-aliyclic polyamides are produced from N-aryl polyamides by hydrogenation in the presence of a catalyst such as Rh, Ru, Pd, Os, Ir, Ni or Co.

Hydrocarbon Conversion Catalyst
SHELL INTERNATIONALE RESEARCH M.V. N.V.
Dutch Appl. 73.07241
Petrols containing straight chain paraffins are treated to raise the octane number by selective hydrocracking using a catalyst, e.g. Pt deposited on a porous support with a pore diameter of 0.42-0.58 µ and a C content of at least 2.5%, especially a zeolite.

HOMOGENEOUS CATALYSIS

Nitro Compound Reduction
AMERICAN CYANAMID CO.
U.S. Patent 3,729,512
Nitro compounds are reduced to amines with CO/H2 in the presence of Ru carbonyls or their precursors.

Rhodium Based Catalysts for Diene Synthesis
E. I. DU PONT DE NEMOURS & CO.
U.S. Patent 3,742,080
Improved catalysts are provided for the synthesis of 1,4-diienes from α-monoolefins and conjugated dienes. The catalysts are Rh(III) salts in combination with amides, phosphoramides, phosphine oxides, or water. The improved catalysts allow control of the trans-cis ratio of the 1,4-diene formed and are operable at useful rates in a wide range of solvent systems, both protonic and aprotic.

Carboxylic Acid or Anhydride Production
Monsanto Co.
Dutch Appl. 73.02968
Carboxylic acids are produced by the reaction of olefins and CO in the presence of an Ir complex of an arson, phosphine and/or stibine, e.g. HRh(CO)(PPh3)3.

FUEL CELLS

Electrochemical Cells
NATIONAL RESEARCH DEVELOPMENT CORP.
British Patent 1,332,295
A cell for operating a cardiac pacemaker or the like uses Pt-black in an O2 proof seal as one electrode.

CHEMICAL TECHNOLOGY

Noble Metal Image Stabilisation
POLAROID CORP.
U.S. Patent 3,730,716
Noble metals below Ag in the electromotive series, e.g. Pt-group metal, are used to enhance Ag halide image stability.
Chemical Plating of Fibres
COPPERTECH INC. U.S. Patent 3,733,213
Fibres or fabric are degreased with solvent, oxidised and then sensitised using Pd and Sn solutions.

Silver Halide Grains Sensitised with a Rhodium Salt
EASTMAN KODAK CO. U.S. Patent 3,737,313
Rh salts are used to sensitize Ag-halide emulsions used in non-destructive testing.

Sensitising Composition
NAUCHNO-ISLEDOVATELSKI TECHNOCHEMICHESKII INSTITUT
Photographic compositions are sensitised with a mixture of organic dyestuff, a water-soluble Pt or Pd salt and a complexing agent.

GLASS TECHNOLOGY
Coating Refractory Metals
JOHNSON, MATTHEY & CO. LTD. U.S. Patent 3,736,109
Articles for use at high temperature, for example in the glass industry, have a refractory core made from Nb, Ta, Cr, Zr, V, Hf, Re or their alloys, a barrier layer of MgO and a sheath of a Pt-group metal. The oxides of the core metal or alloy are chosen to be less volatile than the oxides of Mo at operating temperature within the range 1100° to 1500°C.

ELECTRICAL AND ELECTRONIC ENGINEERING
Electric Lamps
THORN ELECTRICAL INDUSTRY LTD. British Patent 1,327,363
Heat is conducted away from a lamp seal by the use of a contact cap arrangement having a high thermal conductivity. A Cu sleeve is brazed to Pt-clad Mo conductors by a high Ag-content Cu brazing alloy, which also serves to protect the embedded ends of the conductors from oxidation.

Monolithic Capacitors
N.L. INDUSTRIES INC. British Patent 1,327,902
A fired capacitor has stacked alternating layers of Bi-containing barium titanite and electrode layers, inert to bismuth, consisting of up to 90% Pd with the remainder Au and/or Pt.

Memory Discs
PHILIPS ELECTRONIC & ASSOCIATED INDUSTRIES LTD. British Patent 1,328,016
Improved performance memory discs have a Co-P layer applied to a disc over an intermediate layer of Pt.

Electrical Lead Structures
INTERNATIONAL STANDARD ELECTRIC CORP. British Patent 1,329,050
External leads on vidicon tubes are eliminated by placing the leads, e.g. of Pt, in grooves formed internally in the envelope and then sealing with a melted glass frit.

Circuit Patterns
WESTERN ELECTRIC CO. INC. British Patent 1,329,287
A layer between a circuit pattern and the substrate has a discontinuous, etch resistant portion of Pd which is highly adherent to the base. A thicker layer of easily etched material, such as Au, Cu or Ni is then applied. The resulting composite has good adhesion and can be easily etched.

Electroless Deposition
K.C.A. CORPORATION British Patent 1,332,000
An apertured colour TV selection mask is produced by first depositing a pattern of catalytic material such as Pd and then depositing enough metal chemically on the pattern to form the opaque pattern required.

Sandwiched Eutectic Reaction Anticompromise Circuits
An anticompromise circuit has a thin film circuit sandwiched between two eutectic reaction films separated by electrical insulating films. The eutectic reaction films consist of a mixture of Pd and Al and are adapted to be coupled to a switched electrical source to produce a eutectic reaction to destroy the thin film circuit.

Schottky Diode
SIGNETICS CORP. German Offen. 2,264,322
A Schottky diode is produced by the application of a Pt-Ni-Si alloy layer to a Si block.

Grid Electrodes
BROWN, BOVERI & CIE. Dutch Appl. 72.17592
Grid electrodes for discharge tubes have an intermetallic layer, such as ZrPt3, coated with a noble metal layer such as Pt.

TEMPERATURE MEASUREMENT
Platinum Resistance Temperature Sensors
ROSEMOUNT ENG. CO. LTD. British Patent 1,325,451
A Pt resistance temperature sensor is described which does not deteriorate in stability, provided that the pressure is prevented from rising substantially within the sheath.