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Communications should be addressed to
The Editor, Platinum Metals Review
Johnson, Matthey & Co Limited, Hatton Garden, London EC1P 1AE
Anti-tumour Platinum Compounds

RELATIONSHIP BETWEEN STRUCTURE AND ACTIVITY

Michael J. Cleare and J. D. Hoeschele
Johnson Matthey & Co Limited  Engelhard Industries Inc.

A wide variety of platinum(II) complexes have been synthesised and tested for anti-tumour activity resulting in the identification of additional potentially active anti-tumour drugs. Several structural features have been shown to be necessary for a complex to show activity. This article follows up the article by Professor Barnett Rosenberg in the April 1971 issue.

In recent years B. Rosenberg and L. Van Camp at Michigan State University have demonstrated potent anti-tumour activity in certain platinum coordination complexes (1, 2). A previous review in this journal has described the early stages of this research (3), which has led to one compound, cis-dichlorodiammineplatinum(II), undergoing extensive human clinical trials in the United States under the auspices of the National Cancer Institute. Although these trials are far from being completed, the preliminary Phase I results are quite encouraging and indicate good tumour growth inhibition. While the necessarily lengthy clinical procedures have been getting under way, inorganic chemists have been synthesising related platinum compounds in order to determine what relationships exist between chemical structure and anti-tumour activity. A knowledge of such structure-activity relationships is useful both in designing more effective anti-tumour metal compounds and also in understanding the origin of such activity.

Testing Procedures

Two major research groups have been working in this area during the last two years (4, 5). The authors, in conjunction with Rosenberg and Van Camp, have synthesised a variety of platinum and other precious metal compounds, which have been tested against Sarcoma 180 in Swiss white female mice. P. D. Braddock, A. R. Khokhar and M. L. Tobe of University College, London, have synthesised platinum complexes which have been tested at the Chester Beatty Cancer Institute by T. A. Connors, M. Jones and W. C. J. Ross using the ADJ/PC6 plasma cell tumour in female BALB/c mice. The latter tumour has been used extensively for testing the alkylating agent drugs, some of which have been clinically successful. It is important to realise that the results obtained apply only to the particular tumour system employed and do not necessarily indicate activity against other tumour systems. In fact, several compounds are noted below which are active against ADJ/PC6 and inactive towards S 180 under the test conditions. Cis-dichlorodiammineplatinum(II) has, however, shown activity against a broad range of animal tumours—around thirty in all. Both of the tumours mentioned above were transplanted subcutaneously by means of tumour fragments on day 0 of the testing scheme. In both cases the test compounds were given interperitoneally as a solution or suspension in various solvents (usually physiological saline or arachis oil). For S 180 this occurred on day 1 and for the plasma cell tumour on day 24. Ten days after injection the animals were sacrificed and the weights of the excised tumours were compared with those from untreated control animals.

The ratio of tumour weights of treated and control animals (T/C), expressed as a percentage, is a measure of the potency of the
anti-tumour effect. T/C values which are less than 50 are generally considered significant. The therapeutic index (T.I.) is the ratio of the dose which kills 50 per cent of the animals (LD\textsubscript{50}) to that which causes 90 per cent tumour regression (ID\textsubscript{90}). Normal screening protocols were observed (6).

In the tables the dose range indicates the maximum and minimum doses which have been administered, and the dose response is termed positive (+) for cases where a consistent decrease in tumour size is observed as doses are increased up to toxic levels. In the S 180 data the toxic level is the highest dose at which survivors are greater than or equal to 85 per cent, while the T/C value quoted is the lowest obtained for a compound with a positive dose response. For compounds with marginal or negative responses the T/C values quoted are averages over the dose range given in the final column.

**Chemical Procedures**

Compounds of the general formula cis-[PtA\textsubscript{2}X\textsubscript{3}] were prepared by two methods:

1. Exchange of the X ligands was achieved via the diaquo species cis-[Pt(NH\textsubscript{3})\textsubscript{2}(H\textsubscript{2}O)\textsubscript{2}]\textsuperscript{2+}, which is formed when cis-[Pt(NH\textsubscript{3})\textsubscript{2}Cl\textsubscript{2}] is reacted with silver nitrate (7). The new complex was produced by addition of a solution containing the appropriate anion (X = Br, I, SCN, NO\textsubscript{3}, NCO; X\textsubscript{3} = ox, mal (substituted malonates)).

2. The A ligands can be varied using an extension of Dhara’s method for preparing cis-[Pt(NH\textsubscript{3})\textsubscript{2}Cl\textsubscript{2}] (8). This consists of reacting K\textsubscript{2}[PtCl\textsubscript{4}] with the stoichiometric amount of potassium iodide to produce K\textsubscript{2}[PtI\textsubscript{4}] in solution. The latter solution reacts with most amines to precipitate cis-[PtA\textsubscript{2}I\textsubscript{2}] or [PtA\textsubscript{2}]. Reaction with silver nitrate as in the first method affords ready conversion to other cis-[PtA\textsubscript{2}X\textsubscript{3}] species. Many of the amine complexes can be prepared by direct reaction with K\textsubscript{2}[PtCl\textsubscript{4}], although this is generally a less efficient route.

**Cis and Trans Complexes**

In chemical terms the obvious similarity between the original active compounds shown in Fig. 1 is in the geometric arrangement of the chloride ligands. Each complex contains at least two adjacent (cis) reactive ligands. This feature has remained true throughout all the complexes examined to date, and where trans isomers exist and have been tested they are inactive in comparison to an active cis isomer, as shown in Table I.

Thus the major effort has been directed towards cis complexes of the type [PtA\textsubscript{2}X\textsubscript{3}], where A\textsubscript{2} is two monodentate or one bidentate amine ligand, and where X\textsubscript{3} is two monodentate or one bidentate anionic ligand.

Trans isomers are considerably more reactive than their cis analogues; thus trans-
| Table I  
Comparison of Activities for *cis* and *trans* Isomers |
<table>
<thead>
<tr>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sarcoma 180</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Complex</td>
<td>Solvent</td>
<td>Dose Range mg/kg</td>
<td>Dose Response</td>
<td>Toxic Level mg/kg</td>
<td>T/C</td>
<td>Dose mg/kg</td>
</tr>
<tr>
<td>$\text{H}_2\text{N} \rightarrow \text{Pt} \rightarrow \text{Cl}$</td>
<td>cis</td>
<td>S</td>
<td>0.5–20</td>
<td>+</td>
<td>9</td>
<td>1</td>
</tr>
<tr>
<td>$\text{HN} \rightarrow \text{Pt} \rightarrow \text{Cl}$</td>
<td>cis</td>
<td>S</td>
<td>2.5–40</td>
<td>–</td>
<td>&gt;40</td>
<td>85</td>
</tr>
<tr>
<td>$\text{HN} \rightarrow \text{Pt} \rightarrow \text{Cl}$</td>
<td>trans</td>
<td>S</td>
<td>5–20</td>
<td>+</td>
<td>15</td>
<td>30</td>
</tr>
<tr>
<td>$\text{HN} \rightarrow \text{Pt} \rightarrow \text{Br}$</td>
<td>cis</td>
<td>B</td>
<td>10–40</td>
<td>–</td>
<td>&gt;40</td>
<td>110</td>
</tr>
<tr>
<td>$\text{HN} \rightarrow \text{Pt} \rightarrow \text{Cl}$</td>
<td>cis</td>
<td>S</td>
<td>5–100</td>
<td>–</td>
<td>25</td>
<td>100</td>
</tr>
<tr>
<td>$\text{HN} \rightarrow \text{Pt} \rightarrow \text{Cl}$</td>
<td>trans</td>
<td>S</td>
<td>45</td>
<td>14</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>$\text{HN} \rightarrow \text{Pt} \rightarrow \text{Cl}$</td>
<td>cis</td>
<td>SS</td>
<td>5–20</td>
<td>–</td>
<td>&gt;20</td>
<td>105</td>
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<tr>
<td><strong>ADJ/PC6 Plasma Cell Tumour</strong></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Complex</td>
<td>Solvent</td>
<td>Dose Range mg/kg</td>
<td>Dose Response</td>
<td>LD$_{50}$</td>
<td>ID$_{90}$</td>
<td>T.I.</td>
</tr>
<tr>
<td>$\text{HN} \rightarrow \text{Pt} \rightarrow \text{Cl}$</td>
<td>cis</td>
<td>A</td>
<td>0.1–40</td>
<td>+</td>
<td>13.0</td>
<td>1.6</td>
</tr>
<tr>
<td>$\text{HN} \rightarrow \text{Pt} \rightarrow \text{Cl}$</td>
<td>cis</td>
<td>A</td>
<td>2.5–160</td>
<td>+</td>
<td>56.5</td>
<td>2.6</td>
</tr>
<tr>
<td>$\text{HN} \rightarrow \text{Pt} \rightarrow \text{Cl}$</td>
<td>trans</td>
<td>A</td>
<td>–</td>
<td>&gt;18.0</td>
<td>&lt;1.0</td>
<td></td>
</tr>
<tr>
<td>$\text{HN} \rightarrow \text{Pt} \rightarrow \text{Cl}$</td>
<td>cis</td>
<td>A</td>
<td>6–800</td>
<td>+</td>
<td>240</td>
<td>17.5</td>
</tr>
<tr>
<td>$\text{HN} \rightarrow \text{Pt} \rightarrow \text{Cl}$</td>
<td>trans</td>
<td>A</td>
<td>–</td>
<td>72</td>
<td>&gt;72</td>
<td>&lt;1.0</td>
</tr>
</tbody>
</table>

*a* Only 66 per cent survivors.  
*b* Slurry at higher concentrations  
*c* Sporadic toxicity over this range.
[Pt(NH$_3$)$_2$Cl$_2$] aquates approximately four times faster and undergoes ammoniation some thirty times faster than its cis isomer (9, 10). This suggests that trans compounds will react faster and with a wider variety of body constituents than their respective cis isomers, making them less specific in their action. Preliminary distribution and excretion studies involving $^{185m}$Pt-enriched [Pt(NH$_3$)$_2$Cl$_2$] isomers indicate that the cis isomer is excreted initially faster than the trans isomer, although the amounts retained after five days are comparable. However, the relative levels of isomers in the blood indicate a trans concentration which is initially some three times higher than for the cis compound, and with a higher retention after five days (11). Since only cis compounds have the potential to form chelates (assuming that only the chloride ligands are reactive) this might imply that the anti-tumour activity is largely associated with a chelating interaction. DNA appears to be a principal receptor site (12, 13) and both inter- and intrastrand chelated crosslinking is possible; indeed, the former has been demonstrated for HeLa cells in culture (14).

### Table II

Variation of $X$ in $\text{cis-}[\text{Pt}(\text{NH}_3)_2X_2]$ with Sarcoma 180 Tumour

<table>
<thead>
<tr>
<th>$X$</th>
<th>Solvent</th>
<th>Dose Range (mg/kg)</th>
<th>Dose Response</th>
<th>Toxic Level (mg/kg)</th>
<th>T/C</th>
<th>Dose (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{NO}_3^-$</td>
<td>W</td>
<td>6-12</td>
<td>-</td>
<td>7&lt;sup&gt;e&lt;/sup&gt;</td>
<td>54</td>
<td>6</td>
</tr>
<tr>
<td>$\text{NO}_2^-$</td>
<td>S</td>
<td>2.5-12</td>
<td>+</td>
<td>11</td>
<td>8</td>
<td>10</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}$</td>
<td>W</td>
<td>2-20</td>
<td>-</td>
<td>5&lt;sup&gt;e&lt;/sup&gt;</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\text{Cl}^-$</td>
<td>S</td>
<td>0.5-20</td>
<td>+</td>
<td>9</td>
<td>1</td>
<td>8</td>
</tr>
<tr>
<td>$\text{Br}^-$</td>
<td>B</td>
<td>5-20</td>
<td>+</td>
<td>15</td>
<td>30</td>
<td>14</td>
</tr>
<tr>
<td>$\text{Br}^-$</td>
<td>S</td>
<td>2-6&lt;sup&gt;d&lt;/sup&gt;</td>
<td>+</td>
<td>5-6&lt;sup&gt;d&lt;/sup&gt;</td>
<td>13</td>
<td>5</td>
</tr>
<tr>
<td>$\text{I}^-$</td>
<td>WS</td>
<td>10-25</td>
<td>-</td>
<td>&gt;25</td>
<td>110</td>
<td>10-25</td>
</tr>
<tr>
<td>$\text{SCN}^-$</td>
<td>S</td>
<td>5-100&lt;sup&gt;b&lt;/sup&gt;</td>
<td>-</td>
<td>~50</td>
<td>70</td>
<td>20-35</td>
</tr>
<tr>
<td>$\text{NO}_2^-$</td>
<td>SS</td>
<td>5-100</td>
<td>-</td>
<td>&gt;100</td>
<td>99</td>
<td>5-100</td>
</tr>
</tbody>
</table>

<sup>b</sup> Slurry at higher concentrations  
<sup>d</sup> Daily injections for 9 days  
<sup>e</sup> Highly toxic — convulsions  
<sup>f</sup> Cationic complex ion (2+)

### Variation of Anionic Ligand

Table II shows the effect of varying $X$ in $\text{cis-}[\text{Pt}(\text{NH}_3)_2X_2]$. Chemical studies on $\text{cis-}[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ have clearly established that the chlorides are the reactive ligands (15, 16), whereas the platinum ammine bonds are very stable and rather inert to nucleophilic attack. Thus it is likely that biological interactions occur with $X$ (in $\text{cis-}[\text{Pt}(\text{NH}_3)_2X_2]$) as the leaving group. Although no definite information has been obtained about the effective anti-tumour site(s) of action, the effect of varying the presumed leaving group $X$ can be observed. The order of leaving ability has been established for the reaction

$$[\text{Pt}^{\text{II}}(\text{dien})X]^++\text{py}^->[\text{Pt}^{\text{II}}(\text{dien})\text{py}]^{2+}+X^-$$

where the order of decreasing rate constants is $X=\text{NO}_2^->\text{H}_2\text{O}^->\text{Cl}^->\text{Br}^->\text{I}^->\text{SCN}^->\text{NO}_3^-$ (17).

This seems to be generally true for Pt(II) substitution reactions (18). The spread in reaction rates for the above sequence is nearly $10^4$, showing the influence of the Pt-X bond strength on the intrinsic reactivity.

The screening results reflect this order of leaving ability. Where the $X$ ligands are
readily replaced (H₂O, NO₃) the complexes only show activity when administered in saline, wherein the chloro species is reformed prior to and during inoculation. In aqueous solution cis-[Pt(NH₃)₂(H₂O)₂][NO₃]₂ shows a remarkably high and immediate toxicity, which appears to be due to action at the neuromuscular junction. Recent studies indicate that the solution containing this species has potential as an anti-viral agent (19).

When X is of intermediate leaving ability (Cl, Br) the compounds show considerable anti-tumour activity, which follows the leaving order with chloride somewhat more effective than bromide. The latter appears to require a higher dose (in terms of platinum) to register its maximum effect and has a correspondingly high toxic level. However, its lower solubility must be taken into account. The iodide is extremely insoluble but is inactive up to the doses shown when given as a slurry. This order of halogen complex activity holds for other cis amine complexes.

The strongly bound thiocyanate (-SCN) and nitrite (-NO₂) ligands give inactive complexes, which the animals can tolerate at relatively high doses. In these cases the ligands are so tightly bound that little or no reaction occurs within the body.

Thus the activity of these complexes is largely dependent on the nature of the Pt-X bond. Labile complexes will react rapidly and indiscriminately, thus preventing a sufficient amount from reaching the site(s) responsible for the anti-tumour activity. Inert compounds, which reach these site(s) in higher concentration, will not react sufficiently to elicit the anti-tumour response. Complexes with mixed monodentate anionic ligands, i.e., cis-[Pt(NH₃)₂XY] where X≠Y = Cl, Br, I, NO₂, SCN, have been prepared but the activity was not enhanced (4).

When Xₚ is replaced by a chelated dicarboxylate anion, as in Fig. 2, (e.g. oxalate C₂O₄²⁻ and malonates O₂C.CH(R).CO₂⁻, where R=H, CH₃, C₆H₅) considerable activity is observed (Table III). Indeed, [Pt(NH₃)₂mal] is more effective against the ADJ/PC6 tumour than the parent compound cis-[Pt(NH₃)₂Cl₂] and is equally as effective against S 180. It is also active against S 180 tumour after eight days of growth. These chelated complexes are expected to be relatively inert to substitution, and indeed spectral and conductivity changes occur extremely slowly at 37°C (4).

Accurate kinetic studies for reactions with chelating N-donor ligands (such as are found in DNA) are desirable. However, at present it is difficult to rationalise the anti-tumour activity in terms of leaving ability of the chelated ligands. A different mechanism could operate, such as biological activation (e.g. enzymatic removal) of the chelated groups. Coordination to a metal should make the methylene (-CH₂-) group in malonate more susceptible to nucleophilic attack.

Variation of the Amine Group

Table IV shows the effect of varying the A group. By far the majority of A ligands have been N-donors such as mono- and bidentate neutral aliphatic, aromatic and heterocyclic amines. Whereas the X group largely determines the reactivity of the amine complexes, the nature of the A ligands will modify this in a secondary manner due to differing steric, electronic and basic properties. However, as Tables IV and V illustrate, the nature of the A group has a primary effect on the anti-tumour property, which is very difficult to correlate with any chemical reactivity effects.

In the S 180 test system, complexes with primary amines (R.NH₂; R=alkyl) retain...
### Table III
Activity of Ammine Complexes with Chelated Dicarboxylate Ligands X in [Pt(NH$_3$)$_2$X]

<table>
<thead>
<tr>
<th>Sarcoma 180</th>
<th>Solvent</th>
<th>Dose Range mg/kg</th>
<th>Dose Response</th>
<th>Toxic Level mg/kg</th>
<th>T/C</th>
<th>Dose mg/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>oxalate</td>
<td>DMSO (slurry)</td>
<td>5-20</td>
<td>+</td>
<td>16-20</td>
<td>9</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>WS</td>
<td>12-18</td>
<td>+</td>
<td>17</td>
<td>24</td>
<td>14-16</td>
</tr>
<tr>
<td></td>
<td>W</td>
<td>10-20f</td>
<td>+</td>
<td>10</td>
<td>0</td>
<td>10a</td>
</tr>
<tr>
<td></td>
<td>W</td>
<td>0.5-6d</td>
<td>+</td>
<td>3-4</td>
<td>25</td>
<td>2.5</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>WS</td>
<td>10-60</td>
<td>+</td>
<td>35</td>
<td>7</td>
<td>30</td>
</tr>
<tr>
<td>malonate</td>
<td>W</td>
<td>5-24f</td>
<td>+</td>
<td>24</td>
<td>28</td>
<td>20-24</td>
</tr>
<tr>
<td>methyl malonate</td>
<td>W</td>
<td>1-7d</td>
<td>+</td>
<td>8</td>
<td>12</td>
<td>7</td>
</tr>
<tr>
<td>ethylmalonate</td>
<td>W</td>
<td>10-80</td>
<td>+</td>
<td>65</td>
<td>7</td>
<td>60</td>
</tr>
<tr>
<td>1,1 cyclobutane dicarboxylate</td>
<td>W</td>
<td>30-80</td>
<td>+</td>
<td>&gt;80</td>
<td>17</td>
<td>70-80</td>
</tr>
<tr>
<td>ADJ/PC6 Plasma Cell Tumour</td>
<td>Solvent</td>
<td>Dose Range mg/kg</td>
<td>Dose Response</td>
<td>LD$_{50}$</td>
<td>ID$_{90}$</td>
<td>T.I.</td>
</tr>
<tr>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>malonate</td>
<td>A</td>
<td>1-320</td>
<td>+</td>
<td>225</td>
<td>18.5</td>
<td>12.2</td>
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a 66 per cent survivors only  
d Daily injections for 9 days  
g Multiple injections due to low solubility

*Platinum Metals Rev.*, 1973, 17, (1)
<table>
<thead>
<tr>
<th>Sarcoma 180</th>
<th>Solvent</th>
<th>Dose Range mg/kg</th>
<th>Dose Response</th>
<th>Toxic Level mg/kg</th>
<th>T/C</th>
<th>Dose mg/kg</th>
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<tr>
<td>H₂N</td>
<td>S</td>
<td>4-15</td>
<td>+</td>
<td>~9</td>
<td>3</td>
<td>8</td>
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<tr>
<td>CH₃NH₂</td>
<td>S</td>
<td>10-30</td>
<td>+</td>
<td>12-20°C</td>
<td>14</td>
<td>14°C</td>
</tr>
<tr>
<td>(CH₃)₂NH</td>
<td>S</td>
<td>30-150</td>
<td>+</td>
<td>~100</td>
<td>25</td>
<td>80</td>
</tr>
<tr>
<td>C₂H₅NH₂</td>
<td>S</td>
<td>5-50</td>
<td>+</td>
<td>~40</td>
<td>14</td>
<td>40</td>
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<tr>
<td>(C₆H₅)₂NH</td>
<td>SS</td>
<td>15-60</td>
<td>-</td>
<td>&gt;60</td>
<td>75</td>
<td>60</td>
</tr>
<tr>
<td>HOCl₂H₂NH₂</td>
<td>S</td>
<td>20-225</td>
<td>+</td>
<td>~125</td>
<td>22</td>
<td>125</td>
</tr>
<tr>
<td>i-C₆H₅NH₂</td>
<td>SS</td>
<td>20-50</td>
<td>±</td>
<td>&gt;50</td>
<td>33</td>
<td>30</td>
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<thead>
<tr>
<th>ADJ PC6 Plasma Cell Tumour</th>
<th>Solvent</th>
<th>Dose Range mg/kg</th>
<th>Dose Response</th>
<th>LD₅₀</th>
<th>IDₙ₀</th>
<th>T.I.</th>
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<td>NH₃</td>
<td>A</td>
<td>0.1-40</td>
<td>+</td>
<td>13.0</td>
<td>1.6</td>
<td>8.1</td>
</tr>
<tr>
<td>CH₃NH₂</td>
<td>A</td>
<td>-</td>
<td>-</td>
<td>18.5</td>
<td>18.5</td>
<td>1.0</td>
</tr>
<tr>
<td>CIC₂H₄NH₂</td>
<td>A</td>
<td>+</td>
<td>-</td>
<td>45.0</td>
<td>17.5</td>
<td>2.6</td>
</tr>
<tr>
<td></td>
<td>A</td>
<td>2.5-160</td>
<td>+</td>
<td>56.5</td>
<td>2.6</td>
<td>21.7</td>
</tr>
<tr>
<td></td>
<td>A</td>
<td>3-200</td>
<td>+</td>
<td>141</td>
<td>10.8</td>
<td>13.1</td>
</tr>
<tr>
<td></td>
<td>A</td>
<td>-</td>
<td>-</td>
<td>90</td>
<td>&gt;90</td>
<td>&lt;1.0</td>
</tr>
<tr>
<td></td>
<td>A</td>
<td>-</td>
<td>-</td>
<td>18</td>
<td>&gt;18</td>
<td>&lt;1.0</td>
</tr>
<tr>
<td></td>
<td>A</td>
<td>1-80</td>
<td>+</td>
<td>56.5</td>
<td>2.3</td>
<td>24.6</td>
</tr>
<tr>
<td></td>
<td>A</td>
<td>6-750</td>
<td>+</td>
<td>67</td>
<td>&lt;6</td>
<td>&gt;11.1</td>
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<tr>
<td></td>
<td>A</td>
<td>1-3200</td>
<td>+</td>
<td>480</td>
<td>2.4</td>
<td>200</td>
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<td></td>
<td>A</td>
<td>1-3200</td>
<td>+</td>
<td>&gt;3200</td>
<td>12</td>
<td>&gt;267</td>
</tr>
<tr>
<td></td>
<td>A</td>
<td>5-625</td>
<td>+</td>
<td>&gt;625</td>
<td>18</td>
<td>&gt;35</td>
</tr>
</tbody>
</table>

*Plantinum Metals Rev., 1973, 17, (1)*
Table V

Changes in Activity on Varying A in [PtACl₂]

<table>
<thead>
<tr>
<th>Sarcoma 180</th>
<th>ADJ/PC6 Plasma Cell Tumour</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(For key to columns see Table IV opposite)</td>
</tr>
<tr>
<td>H₃N.CH₂.CH₂.NH₂</td>
<td>S</td>
</tr>
<tr>
<td>ethylenediamine</td>
<td></td>
</tr>
<tr>
<td>H₃N.CH₂.CH₂.NH₂</td>
<td>S</td>
</tr>
<tr>
<td>N-methylethylenediamine</td>
<td></td>
</tr>
<tr>
<td>H₃N.CH₂.CH₂.NH</td>
<td>S</td>
</tr>
<tr>
<td>3CH₂</td>
<td></td>
</tr>
<tr>
<td>N,N'-dimethylethylenediamine</td>
<td></td>
</tr>
<tr>
<td>H₂C.N.CH₂.CH₂.NH₂</td>
<td>SS</td>
</tr>
<tr>
<td>N,N-diethylethylenediamine</td>
<td></td>
</tr>
<tr>
<td>H₂C.N.CH₂.CH₂.NH</td>
<td>SS</td>
</tr>
<tr>
<td>N,N-diethyl-N'-ethylethylenediamine</td>
<td></td>
</tr>
<tr>
<td>H₃N.CH₂.CH₂.NH</td>
<td>SS</td>
</tr>
<tr>
<td>N,N'-diethylethylenediamine</td>
<td></td>
</tr>
<tr>
<td>H₃C₂N.CH₂.CH₂.NH₂</td>
<td>S</td>
</tr>
<tr>
<td>N,N-diethyl-N'-ethylethylenediamine</td>
<td></td>
</tr>
<tr>
<td>H₂N.CH₂.CH₂.CH₂.NH₂</td>
<td>SS</td>
</tr>
<tr>
<td>1,2-propylenediamine</td>
<td></td>
</tr>
<tr>
<td>H₂N.CH₂.CH₂.CH₂.NH₂</td>
<td>SS</td>
</tr>
<tr>
<td>1,3-propylenediamine</td>
<td></td>
</tr>
<tr>
<td>SS</td>
<td>10-30</td>
</tr>
<tr>
<td>1,2-diaminocyclohexane</td>
<td></td>
</tr>
<tr>
<td>SS</td>
<td>20-80</td>
</tr>
<tr>
<td>o-phenylenediamine</td>
<td></td>
</tr>
<tr>
<td>SS</td>
<td>10-30</td>
</tr>
<tr>
<td>o-phenanthroline</td>
<td></td>
</tr>
</tbody>
</table>

ADJ/PC6 Plasma Cell Tumour

(For key to columns see Table IV opposite)

1,2-diaminocyclohexane

| A | 0.3-40 | + | 141 | 2.1 | 6.9 |

o-phenylenediamine

| A | 0.6-80 | + | 48 | 2.4 | 20.4 |

4,5-dimethyl-o-phenylenediamine

| A | 12-1500 | + | 680 | <12 | >56.7 |

*Plantinum Metals Rev., 1973, 17, (1)*
activity, although at an apparently reduced level compared to the parent ammine. With secondary amines \((R\_2\text{NH}; R=\text{CH}_3, \text{C}_2\text{H}_5)\) the response is only marginally apparent. Where the alkyl moiety exceeds two carbon atoms the compounds are highly insoluble and show marginal activity at best, although this may be enhanced when the chlorides are converted to more soluble analogues, such as malonates. Aromatic, heterocyclic and alicyclic amine complexes have shown little or no activity at the levels which have been tested so far. The pyridine complex shows some activity against the Ehrlich ascites tumour \((20)\). In the case of bidentate amines the ethylenediamine complex shows a good response (as reported originally by Rosenberg \((1)\)) but alkyl-substituted ethylenediamine complexes are only marginally active (Table V). Again, the more extensive the alkyl substitution the higher is the dosage required to obtain the optimum effect, although the differences in response are not very distinct. No distinction could be found between the aryl and alkyl compounds 1,2-diaminocyclohexane and \(\text{o-phenylenediamine}\).

In the ADJ/PC6 test system, the primary amine methylamine, \(\text{CH}_3\text{NH}_2\), gave rise to greatly reduced activity but with no change in toxicity. Effects like this have been noted in other cases and indicate that toxicity may not be so closely related to anti-tumour activity as to prevent the existence of other compounds with a low toxicity and a high activity. In fact, the series of compounds with cyclic nitrogen ligands gives good results for this tumour with the ethylenecine, \(\text{CH}_2\text{NH}\), and pyrrolidine, \(\text{CH}_2(\text{CH}_3)\text{NH}\), complexes some two to three times more selective than the parent compound. Again, relatively small changes, such as in morpholine and a substituted ethylenecine, lead to loss of activity. Although ethylenecines are anti-tumour agents in their own right, the molecule is greatly stabilised on coordination and it seems unlikely that ethylenecine itself plays a role in the anti-tumour response. Unfortunately the ethylenecine complex has shown little sign of activity against \(S\_180\).

Complexes with aromatic or alicyclic diamines or with two alicyclic amines give outstanding results against the ADJ/PC6 tumour and some have T.I.s which are very much better than that of the parent compound. The cyclopentamine and cyclohexylamine compounds are the best ever tried against this tumour. Preliminary results for activity of the hexylamine derivative against other tumours (\(S\_180\) \((21)\), Leukemia L-1210 and Walker 256 Carcinosarcoma \((22)\)) are rather disappointing and suggest that the anti-tumour activity is very specific. However, recent data on the cyclopentamine derivative are much more promising \((22)\).

**Activity and Amine Structure**

At present there is no obvious explanation for the variation of activity with amine structure. It does not seem very likely that kinetic effects alone are responsible, and hydrogen bonding interactions between the amine ligands and biological molecules (receptors) may be important in stabilising the receptor-drug complex. Increasing substitution of the hydrogens in \(\text{NH}_2\) by alkyl groups will tend to decrease the hydrogen bonding potential and this could be related to the decrease in activity on alkyl substitution. Membrane interactions may also be important.

A variety of \(X\) ligands were used in conjunction with these amines, and in general where a chloro complex was active the corresponding oxalates and malonates also showed a good response (Table VI). Halide complex activity was in the order \(\text{Cl} > \text{Br} > \text{I}\).

Relatively few complexes have been tested in which the \(A\) ligands are non-N-donors. As yet none have shown activity against any test tumour. Although there is no justification at present to suggest that these complexes cannot give rise to anti-tumour activity, there does appear to be a clear preference for amine-based systems. Apart from oxygen, the variation of different donors will naturally involve ligands which are for the most part either more strongly labilising neutral groups, such as \(S\)- and \(P\)-donor atom ligands and various \(\pi\)-acceptor systems, or charged ligands which give rise to charged complexes.
Table VI  
Various Amine Complexes Containing Oxalate and Malonate Ligands \([\text{PtA}_2\text{X}]\) or \([\text{PtAX}]\)

<table>
<thead>
<tr>
<th>Sarcoma 180 Complex</th>
<th>Solvent</th>
<th>Dose Range (mg/kg)</th>
<th>Dose Response</th>
<th>Toxic Level (mg/kg)</th>
<th>T/C</th>
<th>Dose (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{H}_2\text{N} \text{C} \text{H}_2 \text{N} \text{C} \text{H}_2 \text{Pt} \text{O} \text{C} \text{O} \text{C} \text{O} )</td>
<td>W</td>
<td>5-80</td>
<td>+</td>
<td>20-30</td>
<td>21</td>
<td>30</td>
</tr>
<tr>
<td>oxalatobis(methylamine)platinum(II)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{H}_2\text{N} \text{C} \text{H}_2 \text{N} \text{C} \text{H}_2 \text{Pt} \text{O} \text{C} \text{O} \text{CH}_3 \text{O} \text{C} \text{O} )</td>
<td>W</td>
<td>80-180</td>
<td>+</td>
<td>&gt;180</td>
<td>20</td>
<td>120-180</td>
</tr>
<tr>
<td>malonatobis(methylamine)platinum(II)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{H}_2\text{N} \text{C} \text{H}_2 \text{N} \text{C} \text{H}_2 \text{Pt} \text{O} \text{C} \text{O} \text{CH}_2 \text{N} \text{C} \text{H}_2 \text{O} \text{C} \text{O} )</td>
<td>W</td>
<td>10-80</td>
<td>±</td>
<td>20-40</td>
<td>21</td>
<td>10</td>
</tr>
<tr>
<td>oxalatobis(ethylamine)platinum(II)</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>(\text{H}_2\text{N} \text{C} \text{H}_2 \text{N} \text{C} \text{H}_2 \text{Pt} \text{O} \text{C} \text{O} \text{CH}_3 \text{O} \text{C} \text{O} )</td>
<td>W</td>
<td>45-90</td>
<td>+</td>
<td>65</td>
<td>9</td>
<td>60</td>
</tr>
<tr>
<td>malonato-1,3-propylenediamineplatinum(II)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{H}_2\text{N} \text{C} \text{H}_2 \text{N} \text{C} \text{H}_2 \text{Pt} \text{O} \text{C} \text{O} \text{CH}_2 \text{N} \text{C} \text{H}_2 \text{O} \text{C} \text{O} )</td>
<td>W</td>
<td>20-80</td>
<td>+</td>
<td>90</td>
<td>28</td>
<td>60-80</td>
</tr>
<tr>
<td>malonato-1,3-propylenediamineplatinum(II)</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>(\text{H}_2\text{N} \text{C} \text{H}_2 \text{N} \text{C} \text{H}_2 \text{Pt} \text{O} \text{C} \text{O} \text{CH}_3 \text{O} \text{C} \text{O} )</td>
<td>W</td>
<td>0.25-16</td>
<td>−</td>
<td>3(e)</td>
<td>75</td>
<td>0.25-2</td>
</tr>
<tr>
<td>oxalatoethylenediamineplatinum(II)</td>
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<td></td>
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<td></td>
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<td>(\text{H}_2\text{N} \text{C} \text{H}_2 \text{N} \text{C} \text{H}_2 \text{Pt} \text{O} \text{C} \text{O} \text{CH}_3 \text{O} \text{C} \text{O} )</td>
<td>W</td>
<td>5-80</td>
<td>+</td>
<td>45-60</td>
<td>18</td>
<td>40</td>
</tr>
<tr>
<td>malonatoethylenediamineplatinum(II)</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{H}_2\text{N} \text{C} \text{H}_2 \text{N} \text{C} \text{H}_2 \text{Pt} \text{O} \text{C} \text{O} \text{CH}_2 \text{N} \text{C} \text{H}_2 \text{O} \text{C} \text{O} )</td>
<td>W</td>
<td>30-90</td>
<td>+</td>
<td>&gt;90</td>
<td>4</td>
<td>90</td>
</tr>
<tr>
<td>methylmalonatoethylenediamineplatinum(II)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{H}_2\text{N} \text{C} \text{H}_2 \text{N} \text{C} \text{H}_2 \text{Pt} \text{O} \text{C} \text{O} \text{CH}_2 \text{N} \text{C} \text{H}_2 \text{O} \text{C} \text{O} )</td>
<td>WS</td>
<td>40-120</td>
<td>±</td>
<td>&gt;120</td>
<td>51</td>
<td>90-120</td>
</tr>
<tr>
<td>ethylmalonatoethylenediamineplatinum(II)</td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

\(e\) Highly toxic – convulsions  
\(i\) Only 50 per cent survivors

*Platinum Metals Rev., 1973, 17, (1)*
Charge Effects

Although platinum(II) substitution reaction rates are largely independent of charge (23), the charge type of the complex appears to play an important role in the anti-tumour property. As yet only neutral species have shown any appreciable activity. Even when the criterion of cis leaving groups of intermediate lability (e.g. Cl) has been satisfied, the charged complexes which have been tested are inactive and relatively non-toxic. This effect would seem to be biophysical in nature and may be related to transport across cell membranes or to the greater efficiency with which charged compounds (which are generally quite water-soluble) are eliminated from the body. Some active neutral complexes (e.g. cis-[Pt(MeNH₂Cl₂][Pten(mal)], [Pt(NH₃₂)₂Memal], [Pt(NH₃₂)₂Etmal]) are considerably more water-soluble than cis-[Pt(NH₃₂)₂Cl₂]. This might be advantageous in clinical studies, although there is some evidence that a higher aqueous solubility results in a higher therapeutic dose due to the increased rate of excretion.

Highly Toxic Compounds

Apart from [Pt(en)ox] (Table VI) these are all aquo species. They appear to act on the neuromuscular system, and cause the animals to undergo periodic but violent convulsions, with death occurring within a few hours. [Pt(en)ox] was the most severe example and this may support the suggestion that enzymatic removal of chelated groups is occurring, since the reactivities of oxalate and water, when coordinated to platinum(II), are not in any way comparable. The high toxicity of these aquo species emphasises how important it is that hydrolysis should not be allowed to occur prior to inoculation.

Other Metal Compounds

Palladium(II) analogues of active platinum(II) complexes have been tested against Sarcoma 180 but only marginal activity was observed. It is likely that the greater reactivity of palladium(II) (its complexes generally react some $10^4$ times faster than comparable platinum(II) species (24)) is responsible for this effect. A few ammine complexes of rhodium(III) and iridium(III) have been tested against S 180, and only mer-[Rh(NH₃₂)₂Cl₂] has shown any signs of promise. G. R. Gale and co-workers have found that a photochemical reaction product of ammonium hexachloroiridate(IV) shows some activity towards Leukemia L 1210, although their suggestion that cis-[Ir(NH₃₂)₂Cl₂] is the effective species seems rather unlikely.

Conclusion

The following physical, chemical and structural parameters appear to be essential for the observance of anti-cancer activity:

1. The complex should be neutral.
2. It should contain a pair of cis leaving groups, the reactivity of which should generally fall within a range of lability approximately centred on that of the chlorides in cis-[Pt(NH₃₂)₂Cl₂]. However, cis leaving groups which are relatively non-labile in vitro (i.e. malonate) can give rise to active compounds.
3. The requirement of cis leaving groups is a necessary but insufficient criterion for observing activity.
4. The other ligands play an important role. They should be relatively inert and neutral. There appears to be a clear preference for amine type systems, although variation of this structure has given complex results and no clear pattern has emerged. However, the activity of compounds such as those containing alicyclic amines (e.g. cyclohexylamine) indicates that some platinum compounds may be highly selective. Continuing synthetic work may uncover many more interesting compounds and should further clarify these outlines of the structure-activity relationships.

The authors acknowledge the cooperation of Dr. B. Rosenberg, Dr. M. L. Tobe and Dr. T. A. Connors in the preparation of this manuscript.
Abbreviations
Solvents: W = water; WS = water slurry
S = saline (0.15 M); SS = saline slurry
B = sodium bromide (0.04 M)
A = arachis oil
DMSO = dimethylsulphoxide
ox-oxalate = oxalate
mal = malonate
en = ethylenediamine
dien = diethylenetriamine
Memal = methylmalonate
Etmal = ethylmalonate

References
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19. B. Rosenberg and J. Davidson, personal communication (U.S. Patent applied for)
21. B. Rosenberg, L. Van Camp and H. Peresie, personal communication
22. T. A. Connors, personal communication

Rustenburg to Expand Platinum Production Again

PROBLEMS OF THE EXHAUST CATALYST DEMAND

The big question facing the platinum producers, particularly Rustenburg, the largest of them, is the extent to which platinum metals will be used in catalytic converters to deal with automobile exhaust emissions. Because the automobile producers hope that the legislation facing them may be eased in its severity or delayed in its application, and because the catalyst technology they may have to rely upon is still being developed, they are naturally reluctant to commit themselves to platinum producers other than in somewhat elastic terms.

The lead time for getting substantial additional production of platinum metals into effect has been seriously eroded by the period of indecision of the automotive industry at large. Rustenburg's problem is compounded by the fact that it serves a large proportion of the world's needs of platinum for established uses, and its customers must not be made to feel that their future security of supplies is threatened by the prospective new use.

Therefore Rustenburg has taken the bold decision, with the attendant risk, of initiating the expansion of production at both the Rustenburg and Union mines to the optimum level as well as opening a new mine in an area where extensive exploration has already been done in anticipation of such a move.

The refineries operated jointly with Johnson Matthey must correspondingly be enlarged to give a total production capability, when fully established, of the order of twice the present output.

H. R. B.
Thick-film Ruthenium Resistor Pastes

NEW COMPOSITIONS FOR SCREEN-PRINTED CIRCUITS

T. H. Lemon
Research Laboratories, Johnson Matthey & Co Limited

New and improved compositions of pastes for ruthenium resistors have been developed at the Johnson Matthey Research Laboratories. Evaluation of the properties of such resistors shows that these materials are suitable both technically and economically for use in circuits designed for the domestic electronics market. This article is based on a paper given at Internepcon 72, Brighton, last October.

During the last few years thick-film hybrid microelectronics has evolved into a technology which is being used in circuits of increasing sophistication and complexity. These advanced applications have required thick-film materials with improved electrical properties capable of functioning reliably under conditions that until recently were considered impracticable for hybrid circuits. At the same time, thick-film hybrid modules are being developed for use in equipment designed primarily for the domestic market. Here the main requirements are for inexpensive compositions which, while producing films with satisfactory electrical performances, can be processed easily under conditions which do not have to be controlled stringently to ensure success. These apparently conflicting demands have in this technology nowhere been more problematical than with thick-film resistor compositions.

It was with these diverse roles in mind that a new range of thick-film resistor pastes has been developed at the Johnson Matthey Research Laboratories. This range sets out to satisfy what was considered to be a number of fundamental requirements. First, the resistor compositions should be versatile. This means, among other things, that the inherent electrical properties of the resistors should display minimal dependences on, for example, the shapes and sizes of printed areas and on the conditions under which these films are processed. Secondly, of course, the pastes should yield, over a wide range, films with high electrical performances—in particular, low temperature coefficient of resistance (TCR), low current noise and good stability in electrical properties when stressed under extreme life-test conditions.

Workers in the Johnson Matthey Research Laboratories had shown earlier that resistor compositions based upon ruthenium dioxide display good electrical properties and produce thick-film resistors acceptable for many applications (1). Ruthenium dioxide, which is stable under normal atmospheric conditions up to $1000\degree C$ (2), has electrical properties which are metallic in nature with a resistivity of about $50\, \mu \text{ohm cm}$ and a TCR value of $+3000\, \text{ppm/deg C}$ (3). The thick-film resistor compositions now developed use a double oxide of niobium and ruthenium together with a glass component suspended in an organic medium. By doping ruthenium dioxide with niobium pentoxide it has been shown that the high positive TCR value intrinsic to ruthenium dioxide may be conveniently attenuated (4).

The glass phase in the resistor paste should be compatible with the conductive species, the substrate material and a number of different electrode compositions. The glass used is a member of the lead borosilicate family.
This decimal counter manufactured by Culton Industries Ltd. includes two sets of 50 ruthenium resistors, which were printed and fired on to 2\(\frac{1}{2}\) in \times 1 in alumina substrates using Johnson Matthey RF resistor pastes prepared under carefully controlled conditions to ensure purity and reproducibility.

The two solid components—the ruthenium—niobium oxide and the glass—are mixed thoroughly by milling before being dispersed in an organic medium. The medium or vehicle imparts the correct rheological or flow properties, making the pastes suitable for

Test patterns used to assess the basic electrical performances of thick-film ruthenium resistors. The resistor compositions are compatible with a variety of electrode materials, such as gold, gold-palladium, gold-platinum, silver, and silver-palladium.
use in automatic and semi-automatic screen-printing machines. The pastes show no solid precipitation after prolonged storage, and pre-rolling is not required before the materials are used.

After drying the films are fired in a belt furnace programmed to a relatively simple profile having a peak temperature of 760°C. On firing, the conductive species and glass component remain chemically inactive; the important reactions occurring in the films are confined to oxidation of organic constituents from the medium and to fusion of the glass. The thickness of the fired films is between 1.2 and 15 μm.

**Fig. 4** Variation of resistance with peak firing temperature for thick-film ruthenium resistors. The throughput time of the firing process was kept constant and the peak firing temperature was shifted by 10 deg C either side of the recommended 760°C.

**Assessment of Performance**

The performances of thick-film ruthenium resistors have been assessed over a range of printing, firing and life-test conditions. Examples of test patterns used to obtain some of this information are shown in Fig. 2. The electrical properties of the printed and fired films are logged automatically and the results are computed to yield mean sheet resistance, coefficient of variation and also sketch histograms of the results.

The histograms displayed in Fig. 3 are for as-fired resistances of 100 tracks from each of the compositions $10^3$, $10^4$, $10^5$, and $10^6$ ohm/sq. Coefficients of variation (standard deviations) less than ±5 per cent may be obtained readily for resistance values within any one batch over the range 30 ohm to 3000 ohm.
Fig. 5  Variation of temperature coefficient of resistance (TCR) with peak firing temperature for thick-film ruthenium resistors. Firing conditions were identical to those of Fig. 4.

10^6 ohm. Similar analytical treatments of TCR values for a given resistor composition show that tracking within 10 ppm/deg C is achieved.

The results in Fig. 3 were obtained for resistor compositions processed on a firing schedule having a peak temperature of 760°C. However, if that firing cycle is now altered, only minor shifts are produced in resistivity levels of the fired films and the reproducibilities of results remain unimpaired, as seen in Fig. 4.

The small changes in resistance with peak firing temperature are accompanied by equal minor shifts in TCR values, as seen in Fig. 5.

These resistor compositions therefore can accommodate quite a large degree of latitude in firing conditions without producing significant changes in the basic electrical properties of the films. Nor is it necessary to limit the shape of resistor track to obtain the intrinsic resistance value for these materials.

The aspect ratio (i.e. ratio of resistor length to width) can be varied an hundredfold without producing a dramatic change in the inherent electrical properties of a given composition. Some examples of various aspect ratios can be seen among the test patterns shown in Fig. 2. If the aspect ratio is kept constant, the track resistance of a given composition retains a consistent value over a wide range of resistor sizes (5).

Fig. 6  Electrical noise values for 5 mm square ruthenium resistors printed and fired with three different electrode materials. For this resistor size the zero level of db/decade occurs at 3 × 10^6 ohm/sq.
The electrical noise values of ruthenium resistors are low and display a characteristic dependence upon the size of resistor track (6). Furthermore, keeping the aspect ratio constant, the noise levels are found to be independent of electrode material, as shown in Fig. 6.

**Surface Characteristics**

The surface characteristics of fired resistor tracks have been assessed both by profilometer and by scanning electron microscopy. The surfaces of printed and fired ruthenium resistors are smooth, having centre line average (CLA) values of between 0.3 and 1.0 μm. It would seem on this evidence that the surface features make these materials ideal candidates for use in trimmers and in hand-controlled potentiometers. Evaluations of resistor tracks under test conditions employed for potentiometric devices have justified these expectations.

Printed and fired resistor tracks have each been subjected to 400,000 wiper sweeps and in each case the track resistance, track linearity and contact resistance variation (CRV) have been measured before and after testing. Track resistances changed by less than 0.5 per cent from original values, and track linearities retained a constant value.
throughout the test at around \( \pm 1 \) per cent. CRV values under these test conditions remained well below 3 per cent of the track resistance.

The bulk properties of ruthenium resistors have been life-tested under both static and dynamic conditions. In the former case, samples were subjected to damp heat and dry heat environments under conditions of no electrical load.

First as shown in Fig. 7, under damp heat conditions, resistance changes are within \( \pm 0.05 \) per cent of original value after 56 days exposure to 90 per cent relative humidity at 40°C. This meets the conditions outlined in British Standard BS2011: Methods for the Environmental Testing of Electronic Components and Electronic Equipment.

Under dry heat conditions, as shown in Fig. 8, and again with no potential applied to the samples, drifts in resistance values of approximately \( \pm 0.5 \) per cent are found after nearly 10,000 hours at 150°C.

With a power dissipation in each resistor of 7.75 W/cm² (50 W/in²), the drifts in resistance for these compositions are small—around \( \pm 1 \) per cent of the original value after a test period approaching 10,000 hours (Fig. 9). Under the d.c. load conditions imposed on the high ohmic samples, \( 10^{4} \) Ω/sq and \( 10^{6} \) Ω/sq, were exposed to voltages equivalent to 1000 V/in and 3250 V/in, respectively. It can be seen from Fig. 9 that these materials are capable of operating reliably under conditions of high voltage stress such as are found in, for example, domestic television sets.

Available Compositions

What is therefore available at present is a range of ruthenium resistor compositions having TCR values generally better than \( \pm 100 \) ppm/deg C; the materials are capable of operating reliably under the severe conditions now employed to test printed and fired components in hybrid circuits. It has also been shown that these resistor pastes may be readily processed under a variety of conditions which little affect the inherent electrical properties of the system.

The adaptability and versatility of these materials have been demonstrated in practice and examples are shown in Figs. 1 and 10. Figure 1 shows a prototype thick-film decimal counter in which the perforated substrates carry 50 resistors with values from \( 10^{3} \) Ω to \( 10^{6} \) Ω, and on the underside 20 thick-film capacitors each of 200 pF. Connections from one surface to the other are made by lead-throughs and form convenient mounting areas for the 30 diodes required by the circuit. The counter is
This circuit using Johnson Matthey thick-film ruthenium resistor compositions was designed by Pye Dynamics for incorporation into an automobile tachometer manufactured by Smiths Industries Ltd. Ruthenium resistors in such an application combine superior electrical performance with low cost.

These resistor compositions will be developed to cover the full range 30 ohm/sq to $10^7$ ohm/sq, thus offering engineers even further flexibility in designing passive thick-film circuits. An extensive evaluation programme is being conducted to establish the response of ruthenium resistors to laser trimming and the effect that this has on the long-term stabilities of these materials. Indeed, the electrical performances of ruthenium resistors are under constant surveillance to meet readily the progressive demands of thick-film hybrid circuit design.

**Conclusions**

In conclusion, therefore, this high-grade thick-film ruthenium resistor system satisfies the advanced requirements of sophisticated hybrid circuits and can be used with economic justification in modules designed primarily for the highly competitive domestic market.

These thick-film ruthenium resistor compositions are at present available over the range 30 ohm/sq to $10^6$ ohm/sq. Eventually these resistor compositions will be developed to cover the full range 30 ohm/sq to $10^7$ ohm/sq, thus offering engineers even further flexibility in designing passive thick-film circuits. An extensive evaluation programme is being conducted to establish the response of ruthenium resistors to laser trimming and the effect that this has on the long-term stabilities of these materials. Indeed, the electrical performances of ruthenium resistors are under constant surveillance to meet readily the progressive demands of thick-film hybrid circuit design.

**References**

4. British Patent 1,210,493
Ordering in Platinum Group Metal Alloys

R. S. Irani
Materials Science Laboratory, University of Sussex, Brighton, England

The ordering of the interesting family of alloys based on the platinum group metals has been hitherto somewhat neglected, partly due to problems of specimen preparation. Techniques used in metallographic studies on these alloys are described. Understanding of the properties of these alloys may lead to wider practical applications of them.

Platinum group metals form the basis of a number of binary alloys which exhibit an order/disorder transformation. Such a transition involves rearrangement of atomic species from a random solid solution to a regular distribution of the atoms on specific lattice points below a sharply defined temperature $T_c$. Figure 1 shows the unit cell for the two different states in the case of the cobalt-platinum system, by way of example. The latter is an example of an alloy undergoing a (cubic)$_n$-(non-cubic)$_n$ transition, unlike the alloy FePd$_3$ which transforms from a (cubic)$_6$-(cubic)$_6$ superlattice. A fuller list of superlattice alloys based on the platinum group metals is included in the table. As can be seen, platinum features very frequently as a binary constituent.

Metallography of Platinum Group Metal Alloys

In the past, a great deal of difficulty has been experienced in obtaining samples of platinum group metal alloys suitable for examination by either optical or electron microscopy. This is because of the inert nature of the alloys and only when highly corrosive reagents are employed is etching at all feasible. Mechanical grinding can be performed in the usual way, for instance by means of diamond-dust abrasives. Etching of samples has been facilitated by the ion-bombardment method (1) in which energetic argon ions collide with the specimen surface, thereby transferring their momentum to the surface atoms of the sample. By a series of interatomic collisions this process selectively removes metal atoms; those with the lowest binding energy are ejected faster than other atoms. Both CuPt (2) and CuAu (3) have been successfully etched via this approach. However, electropolishing (either for bulk samples or for thin-foil preparation) is generally far

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* $D=$ disordered; $O=$ ordered.

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Fig. 1 Example of unit cell of a binary alloy before and after the disorder/order transformation. 1a Disordered cell of CoPt. 1b. Ordered cell of CoPt.
Superlattice Alloys Based on the Platinum Group Metals

<table>
<thead>
<tr>
<th>Ordered Structure Type</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetragonal (L1₀-type)</td>
<td>CdPt, CoPt, Cu₅Pd, FePd, FePt, MnPt, NiPt</td>
</tr>
<tr>
<td>Face-centred cubic (L₁₂-type)</td>
<td>CoPt₃, Cu₄Pt, FePd₃, FePt₃, Fe₃Pt, MnPt₃, Ni₃Pt</td>
</tr>
<tr>
<td>Body-centred cubic (B₂-type)</td>
<td>BePd, CuPd, FeRh, RhSc, RhTi</td>
</tr>
<tr>
<td>Rhombohedral (L₁₁-type)</td>
<td>Cu₅Pt (unique)</td>
</tr>
<tr>
<td>Close-packed hexagonal (DO₁₁-type)</td>
<td>Pt₂U</td>
</tr>
</tbody>
</table>

more difficult than for most alloys and a breakthrough was achieved by Reiswig (4) who employed alternating current conditions at a precise voltage to electropolish Os-Ir alloys. The a.c. prevents passivation and, because of self-rectification, permits some metal removal to take place. Although no superlattices exist in these Os-Ir alloys, the technique developed by Reiswig enabled Johnson (5) to apply it to a number of other noble metals and alloys and it is very likely that most, if not all, platinum group metal-based ordered alloys can be successfully polished in this manner. For instance, Corke (6) has already applied the method for thinning samples of CuPt for electron microscopy.

Recently, the corrosion resistance of these alloys has been beneficially employed to polish bulk samples by means of thermal polishing, for instance of CuPt (7), and an extension of the technique can easily be made to other ordered alloys, e.g. MnPt, FePd, etc. Essentially the method involves polishing the specimen up to 1 μm by diamond paste and then relieving the polishing stresses by suitable heat-treatment, such that the damaged surface layer is evaporated and a strain-free surface results. For this technique to be successful the superlattice must be non-cubic, as polarised light is used to detect the anisotropic nature of the ordered morphologies.

Techniques of Observation

Apart from optical microscopy (with or without polarised light), transmission electron microscopy has also been employed to study ordered structures. Although thin foil production is still a major obstacle, the increasing use of 1 MeV electron microscopes has somewhat eased the situation, since thicker foils (up to four times as thick as on 100 keV microscopes) can now be readily examined. Moreover, the very high atomic numbers of the platinum group metals mean that radiation damage effects under the highly energetic electron beam are reduced. Unfortunately, the advantages outlined above are sometimes outweighed in platinum group metal alloys containing other transition elements, since the foils interact with the electron beam, hence restricting electron microscopy analysis to replica work. However, over the last few years a further boost to the examination of superlattice structures within the platinum group metal-based alloys has been the development of field-ion microscopy. This technique has been limited to only the most strongly bound metals or alloys, i.e. ones with a high melting point, and thus is particularly relevant to the systems tabulated since platinum group metal-based alloys certainly provide this necessity.

Ordered Morphologies

To date, very few of the systems listed in the table have been metallographically studied. However, one particular superstructure which has been examined in great depth is CoPt on account of its commercial importance as a permanent magnet material. Newkirk et al. (8)
Fig. 2 The microstructure of the alloys depends upon the temperature of annealing. 2a (upper) High temperature domain structure in CoPt for annealing near $T_c$ (Neukirch et al. (8)). 2b (lower) Grain boundary domains in CoPt for low temperature annealing grow with prolonged annealing (8).

have observed a range of completely different ordered microstructures depending on the annealing temperature. At temperatures close to $T_c$ the structure has a lamellar morphology within the originally disordered grains, with the ordered plates growing along (110) matrix planes (Fig. 2a), while at low annealing temperatures irregular ordered domains form at grain boundaries (Fig. 2b) and grow steadily with prolonged annealing. These metallographic observations were coupled with X-ray diffraction studies and from the overall analysis Newkirk (8) was able to conclude that ordering in CoPt proceeds via the nucleation and growth of discrete ordered domains in a disordered matrix, i.e. a Gibbsian Type I phase change is involved. According to Southworth (9) who carried out a field-ion microscope study of the same alloy, a much more complex ordering mechanism is involved than that suggested by Newkirk, and only near $T_c$ is a nucleation-and-growth mechanism found to operate. The lamellar structure, referred to above and also observed in other systems such as Cu$_3$Pd (10), is in fact the result of internal deformation manifesting itself in the form of twinning. The deformation arises owing to stresses generated during the ordering process, on account of a lattice mismatch between the growing non-cubic ordered domain and the cubic disordered matrix. Surface shear is invariably observed on a pre-polished sample and occasionally the shear has been large enough to be quantitatively measured via interferometry, for instance as in Fe$_3$Pt (11) and CuPt (Fig. 3).

Ordered Platinum Group Metal Systems

Apart from giving rise to surface shear, a further implication of the (cubic)$_0$→(non-cubic)$_o$ transformation is the tremendous increase (over 100 per cent rise relative to the disordered value) in the strength of the alloy during the ordering cycle. Typical precipitation-hardening ageing curves are obtained, as illustrated in Fig. 4 for the CoPt stoichiometry, although of course what “precipitates” here is a phase of a different structure (a tetragonal lattice is replacing a f.c.c. lattice) but of the same composition, since the reaction occurs in a single-phase region of the equilibrium diagram. One important point worth noting is that the maximum hardness always occurs when the alloy is not fully ordered. Therefore the nucleation-and-growth model fits this observation particularly well, as one can interpret.
the high strength in terms of a domain-size hardening effect (analogous to the Hall-Petch grain-size theory). Similar behaviour of order-hardening has also been noted for CuPt (12) and Cu₄Pd (10).

A common feature amongst a host of platinum group metal-based superlattices is their magnetic behaviour. This has been concisely reviewed by Kouvel (13). The concept of a transient “two-phase” (ordered + disordered) structure of a partially ordered alloy (mentioned above), has been employed to interpret why CoPt is one of the hardest permanent magnet materials known (Hc = 3500–4700 Oe). Although not on the same scale as that of CoPt, partial ordering within FePd also drastically raises its coercive field from the disordered value of 2 to 260 Oe (14). Recently, evidence of small areas within CoPt consisting of a magnetic domain structure characteristic of materials with low magnetisation and very strong anisotropy has been obtained (15).

The Fe-Pt alloys too have been widely studied, particularly around the Fe₆Pt stoichiometry, on account of the Invar effect (negative or zero coefficient of thermal expansion), which is caused by large saturation magnetostrections and is in fact greater than that found in Fe-Ni alloys (16). A reference must also be made to the ordered equiatomic FeRh composition where an abrupt transition (first order) occurs between antiferromagnetic and ferromagnetic states, at about 350 K. This is particularly interesting since the transition is between two completely contrasting magnetic states.

**Conclusions**

It appears that very few platinum group metal-based ordered alloys have been studied

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**Fig. 3 Multiple-beam interferogram showing surface shear in the binary alloy CuPt (2)**

**Fig. 4 Precipitation hardening-aging curves for (a) 42 per cent CoPt and (b) 48 per cent CoPt alloys show how the hardness of the alloys depends upon the annealing time**
in any great detail with the notable exception of CoPt (17), which has been extensively used in spite of the high cost of the alloy. In fact, cost considerations and perhaps specimen preparation problems have retarded a wider application of this family of alloys, although occasionally they have formed the basis of an experimental study on account of certain unique features, such as the investigation of CuPt, which is the only known ordered alloy with a rhombohedral super-lattice.

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The Surface Tension of Molten Glass
A MODIFIED DIPPING CYLINDER METHOD

The detachment method of measuring surface tension was first employed by Wilhelmy in 1863 and was later developed by du Noüy into a commercial instrument. This typically consists of a horizontal iridium-platinum ring attached to one arm of a balance. The ring is then immersed in the liquid. The force required to pull the ring from the surface of the liquid is then measured and is proportional to surface tension.

Du Noüy's method has been applied successfully to the measurement of the surface tension of glass, with the important difference that the ring has evolved into a shallow cylinder. Hitherto some form of balance has been retained with attendant difficulty of usage. This objection has now been overcome by R. L. Tiede of Owens Corning Fiberglas Corp., who measures the pull on the cylinder with a load cell (Am. Ceram. Soc. Bull., 1972, 51, (6), 539-541). Not only is the new apparatus much quicker and easier to use but it is capable of giving results reproducible to within ± 1 per cent.

The glass, usually about 300 g, is melted in an electrically heated platinum alloy container. The cylinder is attached by a thin wire to the load cell which is slowly raised and lowered by a reversible electric motor. Initially the cylinder is suspended just above the surface of the glass, and a chart recorder, to which the load cell is connected, is adjusted for zero and full scale deflection as appropriate to the type of glass being studied. The cylinder is now lowered until its entire circumference is in contact with the glass; it is then withdrawn from the melt, allowing a characteristic trace to be plotted up to the point of separation from the surface.

The maximum value of the downward force experienced by the cylinder is obtained by calculation from this trace. The surface tension is then obtained by substituting this value into an equation relating surface tension to the dimensions of the cylinder, the downward force and the density of the glass.

The apparatus is sufficiently versatile to permit the rapid determination of surface tension at different temperatures and also to measure viscosity and electrical conductivity before the glass is finally drained from the furnace.

A. D. M. K.
Platinum the Pathfinder

AN EXAMPLE OF OCCAM’S RAZOR AT WORK

By W. D. Mogerman

A half-dozen centuries ago, the celebrated English philosopher William of Occam invented a mental paring device which he applied to the excessive verbiage and fruitless hypotheses of contemporaries with such rigour that his invention became known as “Occam’s Razor”. Although William’s entire attitude was a refreshing novelty at the time, it probably did not add to his popularity. Nevertheless, many thoughtful men of the day evidently agreed with him that if the rising sun of new thirteenth-century learning was really going to illuminate anything—for example, if the marvellous ideas and revelations of his fellow-friar, Roger Bacon, were ever to enlighten mankind—then “Beings ought not to be multiplied except out of necessity”. The cutting edge of this maxim was a relentless search for the fewest Beings or hypotheses necessary and sufficient to clarify a given observation or experiment. More than that, said William, merely cluttered up the mind and led back to the confusion and darkness of former ages.

Now even when correct, indiscriminate applications of Occam’s Razor are not the best way to get elected to public office; and many men have applied it incorrectly over the years. But on the whole the stern old philosopher’s criterion has served us exceedingly well since he died in 1349. It has probably served us better in science than in philosophy or politics, which are pretty much as he left them so long ago. Our present excursion will therefore be restricted to the relatively safe area where indisputable

“This beautiful, magnificent and valuable metal... is a very remarkable metal in many points, besides its known special uses,” said Michael Faraday in the course of his famous lecture on platinum delivered to the members of the Royal Institution in 1861. The published researches of Faraday and of those who followed him in developing our knowledge of electrical phenomena show how greatly they relied upon platinum to provide a means of carrying, making and breaking current. Reliable platinum crucibles played a fundamental part in obtaining analytical data for the infant science of chemistry; platinum boilers permitted the concentration of sulphuric acid in the pioneer days of chemical industry. The development of the electric telegraph, of the incandescent lamp, and later of the thermionic valve, all involved the use of platinum, as did the early internal combustion engines, first for igniter tubes and subsequently for magneto contacts.
changes have occurred. Many significant advances have clearly been made over the years by isolating a laboratory phenomenon as well as may be and concentrating one’s attack on the factors that appear to be authentically inherent. The essential factors are usually difficult enough to handle without wittingly or unwittingly introducing spurious novelties. Unessential Beings must still be shunned at every turn, whether these arise from mental preconceptions or from defective apparatus. It was surely reasons of this latter kind that caused Michael Faraday to speak of platinum as “this beautiful, magnificent, and valuable metal” (1).

**Inherent Beings Only, Please**

Now it must be realised that such warm and somewhat emotional language was not characteristic of the mild and reserved Faraday, who understood and appreciated the unique values of every element as well as any scientist going—and probably better than most. Nevertheless, it is also clear that the self-educated genius did not speak in this way of the various other metallic elements he knew so well. He spoke from retirement at the age of 71, and was probably thinking of the numerous occasions on which platinum had served him—and his extraordinary employer, Sir Humphry Davy—by eliminating unnecessary Beings that might have been introduced through corrosion, fusion or loss of strength at high temperatures, cracks formed during fabrication, evaporation losses, electrolytic decomposition, or other trouble-making instabilities. His mind may have turned back to the early days at the Royal Institution, when venturesome joint investigations with Sir Humphry, made in fragile apparatus, put them into separate bandages more than once. He may have been thinking also of the catalytic powers of platinum, which this prolific pair discovered independently of other workers.

Faraday was by no means the first investigator to use platinum apparatus for important experimental work, but he provided a rare example of one whose decisive and life-long operations on a small scale have led straight to the founding of great modern industries which now produce and use many metals and other materials on extremely large scales indeed.

It is well known that he showed little or no interest in pursuing commercial exploitation of his own discoveries. Of course, the inner workings of such a mind are inexplicable by definition. A genius is not nearly as simple as others say he is. The stunning directness of Faraday’s final attack on a problem was undoubtedly part of his essential nature, and
would have been so if he had never heard of Occam. But like many lesser men, he often reconnoitred the ramparts in silence for a long time before he launched the victorious attack which later seems so simple when described in his writings. The greatly-gifted pioneers are probably all natural wielders of the “Razor”, and not to be claimed as conscious disciples of Occam. But as such admirable examples of mother wit at work cannot fail to benefit all, let us consider a few as space permits.

Little Acorns That Flourished

During Friedrich Wöhler's first attempts to isolate aluminium in 1827 he heated a mixture of potassium and aluminium chloride in a ceramic crucible. The reaction was so violent that the cover had to be wired shut. Some tiny spangles of metal were observed after the melt was cooled and leached, but there was generally not enough aluminium to yield conclusive results. Wöhler then turned to more promising paths (including the one that led to the synthesis of urea in 1828), and stayed on them for 18 years. In 1845 he finally got around to testing a suggestion about milder aluminium reduction that had been first made to him by Liebig in 1836. (In those days many investigators did not rush to mobilise their hormones or elevate their hackles until a threat to priority arose.)

Liebig's suggestion was to moderate the violence of the reaction by passing aluminium chloride vapour over hot potassium. Wöhler tried this in glassware and found that his tubes were shattered every time. He then turned to platinum containers and for the first time obtained globules of aluminium large enough to be used for the determination of the chemical and physical properties of the new metal.

Here platinum tubes openly helped Wöhler make an important discovery, but they were probably doing good by stealth also—to the reported properties of aluminium. This was shown a few years later by the able French scientist whom Faraday called “my friend Deville of Paris”. Henri Deville took up the work and was able to prove that Wöhler's product contained some platinum. He proceeded to produce larger amounts of purer aluminium by improving on Wöhler's method.

But the really substantial amounts that ultimately converted aluminium from an expensive curiosity into the great modern industry it is today waited for a plentiful supply of cheap electricity for the processing of fused ores. The trail leads directly back to Faraday. For years he laboured to “turn magnetism into electricity”, as he put it. He was finally successful in an endeavour that many before him had considered vain. For example, the famous Dr Thomas Young, whose authority at the Royal Institution stood much higher than Faraday's at that time, misapplied Occam's Razor to that idea and thought he had thereby shelved it as effectively as the idea of perpetual motion. In his otherwise excellent treatise on Natural Philosophy (1800), the very able Dr Young declared: “There is no reason to imagine any immediate connexion between magnetism and electricity.” A giant of science is likely to make an error in proportion to his size. A full score of years passed before Oersted revealed the truth by means of a simple observation that shook the scientific world and led to great things for Faraday.

Early Batteries and Lamps

It is difficult for us now, lapped in the wealth of modern knowledge, to realise the grinding poverty of basic information during the early days. After voltaic electricity appeared it was not at all obvious to investigators that all kinds of electricity were qualitatively alike. Men such as Wollaston and Faraday devoted much time to ascertaining that currents derived from different sources—frictional, voltaic, animal, or what-not—were identical in their effects. Faraday moved on to develop his new ideas on generation only after satisfying himself on
that score. Volta had used pairs of silver and zinc (or copper) rods in his famous "Couronne de Tasses", but this pristine device was soon found to be associated with rapid deterioration of the zinc. The necessary role of this wastage and its full significance for associated materials were not immediately realised, not even by Davy in his classical work on the cathodic protection of ship's bottoms. The search for greater durability in voltaic piles led to the use of precious metals. As early as 1803 the German scientist J. W. Ritter claimed that he had constructed a cell with accumulator virtues by using gold and silver plates, but this was shown to be an error. However, the trend toward use of the noble metals continued to find favour. Faraday and others turned to platinum and amalgamated zinc plates for some early batteries. The favourable results encouraged him to inquire, "Is there not, then, great reason to hope and believe that, by a closer experimental investigation of the principles which govern the development and action of this subtile agent, we shall be able to increase the power of our batteries or invent new instruments which shall a thousandfold surpass in energy those which we at present possess?" (2).

The affirmative answer to this question Faraday provided himself through his subsequent work on electromagnetism. The bar magnet which he used to determine whether a magnet really would turn around a fixed conductor was loaded at the bottom end with platinum and floated in mercury. The magnet did revolve as he had hoped, and it literally started the whole world turning. In a short time, flowing electricity in great quantities became available for those prepared to use it. There was an embarrassment of such riches before the many problems of distribution and convenient consumption were solved.

The new generators could supply current cheaply based on coal. The carbon arc light was soon developed for outdoor uses. The next acknowledged problem was "to subdivide the current" so that it might be safely brought indoors, even into the ordinary household. As John Tyndall, Faraday's successor at the Royal Institution, put it almost a century ago, "It is Faraday's spark which now shines upon our coasts (in lighthouses), and promises to illuminate our streets, halls, quays, squares, warehouses, and perhaps at no distant day, our homes" (3). All of these places are now copiously lighted.
and otherwise treated by electrical means—the end result of more than a century of slow work with the aid of Occam’s Razor. A good many unnecessary Beings multiplied by the first workers had to be discarded before success was achieved. The deteriorating rigours of high temperature incandescence caused some early lamp investigators like Sylvanus P. Thompson and Werner Siemens to give up the search, although they had been very successful in related work.

Other men turned to the use of platinum group metals, with or without the aid of vacua. Sir William Grove, Warren de la Rue, Sir Joseph Swan, Thomas A. Edison and Auer von Welsbach were among the inventors of proven ability who used platinum metals or alloys in their early efforts with incandescent lamp filaments.

Of course, these very able men also used platinum in other ways during their extensive careers, especially Grove in his pioneer fuel cell of 1839 and Edison in various detection devices, but we are now speaking only of their successful efforts to establish a great new electrical lamp industry.

After some years, the path led to the use of carbon in vacuum, and finally to the coiled filaments of ductile tungsten in the gas-filled lamps of today. But the familiar pathfinder served well until displaced by cheaper new materials.

On the other hand, platinum has been called to replace cheaper materials where it turned out that much more was needed than a durable hot filament. For example, coated platinum filaments replace tungsten in electron microscopes where the advantages of low emission temperature and slow evaporation rate, uniform field of illumination with little drift, as well as a small electron source are wanted.

There remain any number of instances where the highest general reliability is the only possible criterion, and is often taken for granted by users. The naval writer, Dudley Pope, has described what it meant to the daring men who subdued the Graf Spee during the “Battle of the River Plate” to have electrical bridges of an iridium-platinum alloy unfailingly ready to ignite the cordite in their guns (4).

If one decides to oppose the superior 11-inch armament of a German pocket battleship with the 8-inch guns of British cruisers, it is clearly desirable that the smaller guns go off every time.

**Future Directions**

The production of molecular beams, so important for and so characteristic of work in modern physics, requires a high temperature source able to eject particles by evaporation, usually in a vacuum vessel that is rapidly rotated. A source that will not make adventitious contributions of its own is wanted. For such purposes the German scientist Otto Stern used a platinum wire coated with a silver layer, which supplied the pure and volatile molecular beam in this instance. On the other hand, the low temperature pioneers Sir James Dewar and Kamerlingh Onnes both made use of platinum wires in their cryogenic resistance studies which ultimately led to the discovery of superconductivity by Onnes, with all of its mighty potentialities.

It is, of course, much too early to foresee what practical advantages will one day derive from two such remarkable phenomena at opposite ends of the temperature scale. Much close work with Occam’s Razor lies ahead before the full truth stands forth. But perhaps one may be forgiven the observation that these two new areas have chosen a material pathfinder that others before them have found uniquely useful and reliable.

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ABSTRACTS
of current literature on the platinum metals and their alloys

PROPERTIES

Thermal Expansion of Platinum from 293 to 1900K
An expression for the linear thermal expansion of Pt from 293–1900K is given to the T^2 term.

The Determination of the Thermal Expansion of Platinum by X-Ray Diffraction
X-ray diffractometry of electrically heated Pt ribbon and of Pt powder gave the same values of linear thermal expansion, which agreed with those of Kirby and Rothrock found by optical comparator (1968). Pt strip is a reliable standard for X-ray studies of low X-ray absorption materials, e.g. glass-ceramics.

A Thermodynamic Study of Solid Pd-Pt Alloys
The vapour pressure of Pd over Pd-Pt alloys was measured by torsion-effusion. The enthalpy of formation of these alloys was found by calorimetry. The thermodynamic results provided additional evidence for the existence of short-range order in the Pd-Pt system.

Absorption of Hydrogen by Palladium-Platinum Alloys under High Pressures of Hydrogen Gas
The effects of absorption of H on the electrical resistance of Pd-Pt alloys was studied up to 24,000 atm at 25°C. With increasing Pt concentration, there is a gradual but continuous modification of the relationship between H content and the chemical potential of H, and for any given reference pressure, H solubility is always a decreasing function of Pt concentration.

Long-range Order and Ordering Kinetics in CoPt,
H. BERG and J. B. COHEN, Metall. Trans., 1972, 3 (7), 1797-1805
X-ray study of the formation of a Cu3Au-type L12 superlattice in CoPt3 shows it is first order and follows Rothstein’s equation; a two-phase region exists at 668–685°C (Tc). CoPt3 tolerates less long-range order (S=0.64) than Cu3Au before disordering. Domain growth is similar to grain growth.

Identification of the Superconducting Phases in the Molybdenum-Platinum System
X-ray, metallographic, magnetic and calorimetric analyses of 0-50 at. % Pt-Mo alloys were used to characterise the superconductivity of each phase. Maximum Tc (7.5K) occurs in the partially ordered hexagonal DO19-type phase (>50 at. % Pt) not the A15-type as previously thought.

Quenching Effects in Au-Pd Alloys Studied by Electrical Resistivity
The specific resistivity of 0-50 at. % Pd–Au alloys was measured from 25°C up to the melting point. Quenched-in defects were followed by electrical resistivity measurements during isothermal ageing. Literature studies conclude that SRO exists in Ag-Pd, Au-Pd and Cu-Pd and increases the electrical resistivity. Quenched-in vacancies provide low temperature atomic mobility for establishment of SRO. Compositional dependence of vacancy parameters is minimal.

On the Short-range Order Formation in Gold-Palladium Alloys
H. HAAS and K. LÜCKE, Scripta Metall., 1972, 6 (8), 715-720
The changes in resistivity during isothermal annealing at different temperatures are compared for quenched 10 at. % Pd–Au and Ag–Au. All the alloys showed increased resistivity due to short-range order formation. Differences in behaviour between Pd–Au and Ag–Au are explained by a repulsion between vacancies and Pd atoms but
not Ag atoms causing greater ordering of Ag-Au by the same number of diffusional jumps.

Influence of the Size of Domains on the Properties of Copper-Palladium Alloys
The direction of rotation of the periodic antiphase domain boundary within every C-domain of ordered Cu-Pd is the same. Long-range ordering occurs quickly within them when the rate of cooling is 100 deg C/day but growth of the domains requires prolonged treatment with cooling at 2 deg C/day. The domain boundaries are substantial obstacles to electron conduction. Domain size affects the mechanical properties of the alloy. Breaking down the domains increases the yield point and reduces the creep.

On the Compound Pd₄AlCu and Its Alloys with Silver
The phase diagram of the Pd₄AlCu–Ag system is given showing polymorphous transformations of Pd₄AlCu at 335°C and 825°C.

On the Phase Diagram of Pd-In-Sn and of Some Related Alloys
I. KOSOVINC, M. EL-BORAGY and K. SCHUBERT, "Metall.," 1972, 26, (9), 917–920
The various structures occurring in the Pd-In-Sn and related systems were examined by the powder technique of X-ray diffraction.

Superconductivity in the Palladium-Hydrogen and Palladium-Nickel-Hydrogen Systems
Loading 0–5 at. % Ni-Pd with H₂ by electrolysis of 0.1N H₂SO₄, followed by controlled desorption leaving H₂/Pd > 0.81, causes a broad superconductivity transition starting at up to 5.5K for higher H concentrations.

Weldability of a Corrosion-resistant Titanium-Palladium Alloy
A. BENEŠ and K. ŠTUPEL, Zvaranie, 1972, 21, (2), 38–46
The weldability of 0.05–0.2 and of 0.7 % Pd-Ti hot-rolled sheet was compared to that of pure Ti by mechanical and corrosion tests and metallography. O₁₇ N₁₇ H₁ etc. from the Ar atmosphere diffuse faster into Ti-Pd than into Ti causing greater hardness of the alloys. α Alloys form in the weld and transition zones. The alloys have higher corrosion resistance and a finer structure.

Optical Properties of Iridium at 77 and 295 K
Refractive index and absorption coefficient of Ir were measured at 77 and 295K in the spectral range 15–0.302 μm (0.08–4.08 eV). A two-band conduction model for optical properties in the infrared range was considered. Interband electron transfer occurs at >0.4 eV and causes peaks of the light conduction of 0.44, 1.0, 1.6 and 2.8 eV.

Phase Diagram of the Zirconium-Osmium System in the 50–100 at.% Osmium Region
X-ray and microstructural analyses of 50–100 at.% Os-Zr alloys show the existence of the eutectic compounds ZrOs₈ (a = 5.20Å, c = 8.53Å), which melts congruently at 2660°C, and ZrOs (CsCl-type structure, a = 3.26Å), which melts incongruently at 2040°C. A phase diagram is given.

Electronic Specific Heat of Iron-Rhodium and Iron-Rhodium-Iridium Alloys
The electronic specific heat of Fe₃₀₀–Rh₁₀₀–x Irₓ (x = 1.5, 3.0, 5.0, 6.5), Fe₄₀₀–Rh₂₉₄–x Irₓ and Fe₄₀₀–Rh₂₉₄–x Rhₓ was measured. The coefficient of the linear term, γAF, in the specific heat of antiferromagnetic alloys contains a large magnetic contribution which is attributed to the small fraction of Fe atoms occupying Rh sites of nearly zero exchange field. Measured γAF values fail to confirm the simple electronic nature of the first-order antiferromagnetic-ferromagnetic transition assumed in current theory.

Interaction of the Intermetallic Compounds RuTi-RuHf
The permanent inter solubility of RuTi and RuHf was established by physico-chemical analysis.

Absolute Thermoelectric Power of Chromium-Ruthenium Alloys
The variation with temperature of the absolute thermoelectric power of 0–8.3 at. % Ru-Cr alloys, between 350 and 1000K, shows large anomalies due to the paramagnetic-antiferromagnetic transition. The relative size of the anomaly can be roughly correlated to that shown by the resistivity; it increases with Ru concentration up to 3.0 at. % and then decreases.
Electrical Conductivity and Thermal Conductivity of Rhenium, Osmium, Iridium and Some of Their Alloys with Thorium and Lanthanum over a Wide Range of Temperature


The electrical and thermal conductivities of Re, Os, Ir and of Re-Th, Os-Th and Ir-La alloys were studied as a function of temperature up to 1700°C. The alloys had a higher resistivity and lower thermal conductivity than the metals. Typical variations from 125 to 1325°C were 50–100 Ω cm and 0.5–0.2 W/cm·deg C.

CHEMICAL COMPOUNDS

Proposed Mode of Action of Antitumour Platinum Compounds Based upon Studies with cis-Dichloro([G-3H]-dipyrindine)-platinum(II)


Studies of cis-dichloro([G-3H]-dipyrindine)-platinum(II) suggest that its antitumour and antimitotic properties depend on the dissociation of one or both Cl atoms from the Pt atom to give a cationic, aquated species which forms an acid-resistant bond with intact cells and with DNA.

Effect of cis-Platinum(II) Diaminodichloride on Bone Marrow


Injecting mice with the antitumour agent cis-Pt(II) diaminodichloride has the same effect on mitotic index and cell counts as do low doses of X-irradiation.

Inhibition of Leucine Aminopeptidase and Malate Dehydrogenase by Aquoplatinum(II) Complexes


Leucine aminopeptidase, elevated levels of which are found in certain tumours, and malate dehydrogenase are inhibited by Rb₂PtBr₃ solutions. The active species is shown to be PtBr₅(H₂O)²⁺.

Anisotropic Thermopower in the Quasi-One-Dimensional Conductor K₂Pt(CN)₄Br₃·3H₂O


The thermopower of K₂Pt(CN)₄Br₃·3H₂O is small, anisotropic, temperature dependent above 150K, and increasing below that, and negative, indicating conduction by negative carriers.

Studies of Palladium and Platinum Triphenylphosphine Complexes with Carbon Monoxide at High Pressures


Infrared spectroscopy of M(PPh₃)ₓ (M=Pd, x = 4; M=Pt, x = 3, 4) under high pressures of CO indicated all members of the series M(CO)ₓPPh₃xF (PPh₃)(x=1–4, according to temperature).

Mean Palladium- and Platinum Bond Energies in Complexes of the Divalent and Tetravalent Metals


The mean energies of Pd- and Pt-halogen bonds in complexes were evaluated using a Born-Haber cycle and the relative values found to be Pd-Cl > Pt-Cl > Pt-Br and M(II) — X > M(IV) — X.

Methods for Studying Oxygen-Platinum Metals Interactions

A. OLIVEI, J. Less-common Metals, 1972, 29, (1), 11–23

The thermodynamic properties of the volatile products of O₂-Pt metal reactions were studied by 'pumping' of O₂ by a hot Pt metal filament, and by mass spectrometric analysis of flash desorbed oxidation products and measurement of the rate of evaporation of gases effusing from a Langmuir cell. The quasi-equilibrium approach was applied to the reactions.

New Nitrido and Oxo Complexes of Ruthenium

D. PAWSON and W. P. GRIFFITH, Chem. & Ind., 1972, (15, Aug. 5), 609

The first complexes to contain a terminal Ru==N bond, Cs₅[RuNX₃] (X=Cl, Br), were prepared by adding RuO₂ in CCl₄ to aqueous NaN₃ (Ru : N₃⁻ = 1 : 2) at 0°C in the presence of excess HX and Cs⁺. New ruthenyl complexes trans-C₅₃[RuO₂X₂], (X=Br, CN, 1/2O₂⁺) were prepared by reacting RuO₂ in CCl₄ with the acid and Cs⁺; cooling was essential. The tetrathio dine and pyridine analogues were similarly prepared. All the complexes are diamagnetic.

ELECTROCHEMISTRY

Hydrogen Evolution at Platinum Electrodes in Molten Potassium Bisulphate


The hydrogen evolution reaction at bright Pt electrodes in molten KH₂SO₄ was studied at 270–430°C by steady-state and transient methods. At low potentials the atom-atom combination step is rate determining. At high potentials the ion-atom electrochemical desorption step is rate determining. The two regions are separated by a
transition region in which hysteresis is observed. The absorption isotherm for H atoms shows two-dimensional condensation.

Electrolytic Separation Factors on Platinum under Non-steady State Conditions


A new method was used to study the non-steady state separation factor of hydrogen and deuterium on Pt. The measurement of the separation factor on Pt as a function of frequency can be interpreted only in terms of a progressive weakening of the Pt-H bond with increasing coverage. The discharge of H⁺ on D must also be much faster than that of D⁺ on H.

The Oxygen Film on Platinum Electrodes and the Electro-oxidation of Acetate Ions


Recent literature is reviewed and a consistent and mathematical model is presented to account for the various phenomena observed during the electrolysis of aqueous acetate solutions at Pt electrodes. The complex interaction of a number of competing reactions is discussed, with particular emphasis on oxygen film formation on the Pt surface and its influence on the various acetate ion oxidation reactions.

Effect of the Conditions of Deposition on the Structure and Properties of Rhodium Electrode Catalysts


The structure, H₂ adsorption and catalytic activity of Rh/Rh electrodes in nitrobenzene depend on the surface area of the support and current density during electrodeposition.

Adsorption of Hydrogen by Skeleton Iridium-Ruthenium Electrode Catalysts in 1N Sulphuric Acid Solution


The capacity for H₂ adsorption by skeleton Ir-Ru electrodes is considered.

Electrodeposition and Surface Coatings

Epitaxy at Low Temperatures by Vapour Deposition of Pd, Pt, Rh and Ir Observed by Field Ion Microscopy


The minimum substrate temperatures required for the formation of vapour-deposited epitaxial layers of Pd, Pt, Rh and Ir on either Ir or Rh are respectively 50, 100, 180 and 300K, thus indicating that the minimum temperature increases with the binding energy of the deposited metal. Conditions for epitaxy in these metals are discussed.

LABORATORY APPARATUS AND TECHNIQUE

A Multiconductor Feedthrough for Very Low Temperature Applications


A multiconductor electrical feedthrough for use down to 4.2K consists of a Pt tube containing a ceramic spacer for the Pt wires. Jena 16111 red stripe glass powder is melted around the wires to form a seal.

JOINING

Ceramic-Metal Reaction Welding


When bonding ceramics with metals, either noble metal-ceramic oxide bonding occurs by the formation of a liquid-like intermediate phase (for Au, Pt, Pd) with maintenance of a sharp discontinuity at the interface, or bonding of oxides to other transition metals, e.g. Fe, Co, Ni, occurs by diffusion. Both mechanisms occur below the melting point of any component, in any compatible atmosphere, under little pressure and without deformation.

Bonding of Metals to Ceramics and Glasses


Pt, Fe, Ni, Cu, Al, and Pb were bonded to glasses and ceramics by heating to ~0.9Tₘ(metal) under pressures of from <0.1N/m² for Pt to 10MN/m² for Al and Pb.

HETEROGENEOUS CATALYSIS

Bimetallic Pays off in 3-year Run

C. THOMPSON and W. E. LEMEN, Oil Gas J., 1972, 70, (36, Sept. 4), 80–81

At Mohawk Petroleum Corp., California, a bimetallic platforming catalyst showed excellent stability during three years’ operation with no yield decline, change in H₂ purity or shutdown for regeneration.

Japanese Discover Unique Low-pressure Reforming Catalyst

Oil Gas J., 1972, 70, (37, Sept. 11), 73

Asahi Chemical Industry Co. has discovered that
catalytic behaviour of the system. $\text{H}_2$ adsorption is greater on platinised pyrolytic graphite than on unplatinised. Adsorption energies of $\text{H}_2$ on platinised and on smooth Pt differ. Likewise the specific catalytic activity of Pt deposits for dissociation and ionisation of $\text{H}_2$ and for $\text{HCOOH}$ oxidation is greater than that of smooth Pt, especially for supports with low amounts of Pt.

Removal of Odours by Catalytic Incineration

R. A. SEABLES, Environmental Pollution Management, 1972, 2, (7), 280-283

Malodorous effluent gases from a wide variety of industries can be treated effectively and economically by the Honeycat system which uses a Pt/ceramic honeycomb catalyst for incineration at low temperatures.

On the Effect of the Conditions of Prepara-

The new catalyst over 42 cycle runs.

cation on the Properties of Platinum/Alumina

B. B. ZHARKOV, G. N. MASLYANSKII, N. E. BUYANOVA, V. L. KRYAK, T. M. KLIMENKO, and A. E. RUBINO

Zn. Prikladnoi Khim., 1972, 45, (7), 1434-1438

Addition of $\text{CH}_3\text{COOH}$ to aqueous $\text{H}_2\text{PtCl}_6$ being used to prepare $\text{Pt/Al}_2\text{O}_3$ alters the adsorption characteristics of the $\text{H}_2\text{PtCl}_6$ on the $\text{Al}_2\text{O}_3$ so that the dispersion of Pt is changed and so is activity for reduction. Thermal stability of the catalysts drops as the amount of added $\text{CH}_3\text{COOH}$ increases.

Small Angle X-ray Scattering Investigation of Platinum Metal Dispersions on Alumina Catalysts


Metal particle diameters and distributions in Pt/$\text{Al}_2\text{O}_3$ catalysts were investigated by small angle X-ray scattering. Scattering by pores of the support was eliminated by controlled adsorption of $\text{CH}_3\text{I}$ and $\text{C}_2\text{H}_4\text{I}$. The Guinier and Porod radii were calculated. The diameters increased on ageing. Clusters of very small Pt particles were indicated.

Carbon Molecular Sieve Supports for Metal Catalysts. I. Preparation of the System

Platinum Supported on Polyfurfuryl Alcohol Carbon. II. Selective Hydrogenation of Hydrocarbons over Platinum Supported on Polyfurfuryl Alcohol Carbon

J. L. SCHMITT and P. L. WALKER, Carbon, 1971, 9, (6), 791-796; 1972, 10, (1), 87-92

I. Carbonised polyfurfuryl alcohol (PFA) will behave as a 4 $\AA$ molecular sieve when in large particles, or a 5 $\AA$ sieve after grinding or when an activated C filler is added to the partially-polymerised PFA, causing microcracks to form during carbonisation. These cracks act as diffusion pathways and hasten equilibrium. Varying PFA: filler ratio gives different adsorption properties.
Pt is added to the PFA before curing as almost all the adsorption is by the PFA, not the filler. I. A composite C molecular sieve–Pt catalyst was prepared and shown to act as a 5 Å sieve with slit-shaped pores or pore constrictions. Using a continuous flow technique, shape selectivity was demonstrated for the competitive hydrogenations of 3-methyl-1-butene with both 1-butene and cyclopentene. No selectivity was observed in the 1-butene:isobutene system.

**Catalytic Isomerisation of Normal Nonane**


Isomerisation of n-nonane over 0.27 wt.%Pd/Al₂O₃–B₂O₃ gives mainly methyloctanes with more branching at high conversions. Hydrocracking is favoured >425°C. A carbonium ion mechanism is proposed.

**Isomerisation of n-Pentane on Type Y Zeolites Containing Palladium**


Isomerisation of n-pentane at 380°C, 15–20 atm on Pd/Y in the presence of H₂ reaches 57% or 90% of equilibrium yield. Reaction kinetics and procedure can be described by an equation of the form \( r = k \cdot P_{C,H₄}/P_B \) and by the tendency to isomerise to paraffins via olefins.

**Catalytic Properties of Palladised Zeolites for Hydrogenation of Dimethylphenylcarbinol**


Liquid-phase hydrogenation of dimethylphenylcarbinols over 0.1–5.0 wt.%Pd/zeolites showed that total and specific catalytic activities are related to the amount of Pd and the type of zeolites. Low Pd% samples behave like Pt, high Pd% samples like Pd. Reduction occurred principally at the acetylenic bond.

**Olefin Hydrogenation Catalysed by Supported and Unsupported Mixed Metals**


The hydrogenation activities of Pd-Au catalysts as alloy microspheres and as the mixed metals dispersed on α-Al₂O₃ were studied, and details are given of their comparative performance in some typical hydrogenation reactions.

**The Exchange with Deuterium and Deuteration of Benzene on Evaporated Palladium-Gold Alloy Films**


At Pd <60 at.% the activity of Pd-Au films falls to zero for C₆H₆ deuteration and is decreased for C₆H₆-D exchange, indicating a dissociative mechanism. In p-xylene hydrogenation, ‘rollover’ probability seems insensitive to Au content.

**Electronic Substituent Effects on the Adsorption and Hydrogenation of the Olefinic Bond on Palladium**


The electronic substituent effects on the rate of hydrogenation of 2-aryl-3-methyl-2-butenes and substituted 3,4-dihydro-1,2-dimethylbenzenes, using Pd/C as a catalyst, are small. The transition state is similar to the initial state. Adsorption involves a α-olefin complex.

**Resin-bound Transition Metal Complexes**


Resin-bonded homogeneous Rh catalysts exhibit superior lifetimes and ease of product separation and also maintain high concentrations of unsaturated complex provided chelation is prevented.

**Polymer Supported Rhodium(I) Hydrogenation Catalysts: Factors Controlling Substrate Selectivity**


An analysis is given of parameters causing selectivity in olefin reduction in the presence of a Rh(1) catalyst attached to a divinylbenzenestyrene copolymer bead by a phosphine link. The catalyst can be used repeatedly.

**Electron Spectroscopy for Chemical Analysis (ESCA) Studies on Catalysts. Rhodium on Charcoal**


ESCA studies of Rh foil, Rh/C and Rh₂O₃ showed that catalytic activity depends on surface oxide concentration.

**Hydrogenation of Hydrocarbons on Rhodium Catalysts**


On hydrogenation in MeOH solution over Rh/BaSO₄ and Rh black, 1-hexene gave 2-hexene and n-hexane and cyclohexene yielded cyclohexene and C₆H₆; PhC≡CH selectively gave styrene and then PhEt.

**The Hydroisomerisation of n-Butenes. 2. The Reaction of 1-Butene over Mercury-poisoned Rhodium-Silica Catalysts**


As Hg adsorption is increased, the rates of
hydrogenation and exchange of 1-butene over Rh/SiO₂ decrease uniformly but isomerisation is unaffected up to 6%H₂ > 80%, suggesting the first two occur on the metal and the last on the support, after migration.

Hydrogenation of Aniline in the Liquid Phase. VI. Hydrogenation of Aniline with Ruthenium-Palladium and Ruthenium-Platinum Alloy Catalysts Supported on Activated Carbon
Ru and Pd catalysts have low activity for PhNH₂ hydrogenation whereas Ru-Pd shows activity which passes through a maximum for PhNH₂ at 25 at.%Ru and for C₆H₄ at 75%Ru. Ru-Pt has greater activity than pure Pt for PhNH₂ hydrogenation but for C₆H₄ it is less.

Selective Hydrogenation of Carbonyl Groups of α,β-Unsaturated Aldehydes in the Presence of Iridium Catalysts
α,β-Unsaturated aldehydes such as furylacrolein, crotonic and cinnamic aldehydes and citral are reduced quantitatively in the presence of Ir catalysts to the corresponding unsaturated alcohols. Allyl alcohol is the main product of hydrogenation of acrolein.

Novel Procedures for the Preparation of Platinum and Other Metals in Forms Having Abnormally High Catalytic Activity
Pt, Pd and Ru catalysts prepared by reacting a solid metal halide with sodium naphthalide, etc., have very small crystallite size, unusual chemical and electrostatic properties and extremely high catalytic activity for the oxidation of organic compounds by O₂. They can be rendered non-pyrophoric without loss of activity.

Investigation of Hydrogen Adsorption on ‘Boride’ Catalysts of the Platinum Group Metals
The phase composition of Pt, Pd and Rh borides were compared with those of Pt, Pd and Rh blacks by X-radiography. There is little difference between borides and blacks in capacity to adsorb H₂ or in specific surface area. Heats of adsorption of H₂ and metal–H bond energies were calculated from charging curve data. Heat of adsorption is proportional to amount and stage of charging.

Investigation of the Hydrogenation of p-Carboxybenzaldehyde in the Presence of Pd, Ru and Rh Catalysts
Hydrogenation of p-carboxybenzaldehyde over 0.5%Pd/C, 5%Rh/C and 5%Ru/C is zero order with respect to the substrate and first order with respect to H₂. There is subsequent hydrogenolysis on Pd/C at the C-OH bond to form carbonyls. Hydrogenolysis is very slow on Rh/C but on Ru/C there is selective formation of p-carboxybenzyl alcohol.

New Hydrosilylation Catalysts: Platinum and Rhodium Complexes with Polymeric Ligands
Pt and Rh complexes coordination-bonded to organic polymers catalyse hydrosilylation, giving high yields under mild conditions, the activity being dependent on the nature of the ligand. These catalysts can be easily recovered from the reaction system and recycled.

Palladium-catalysed Vinylic Hydrogen Substitution Reactions with Aryl, Benzyl, and Styryl Halides
A vinylic H of an olefinic compound is replaced by the aryl, benzyl or styryl group of a halide by reaction at 100°C in the presence of a hindered amine and finely divided Pd metal formed by in situ reduction of PdAc.

HOMOGENEOUS CATALYSIS
Palladium(II)-catalysed Exchange and Isomerisation Reactions. III. Allylic Ester Isomerisation in Acetic Acid Catalysed by Palladium(II) Chloride
In the presence of Pd(II) salts in CH₃COOH, unsymmetrical allylic esters will undergo either simultaneous exchange and isomerisation—a reaction of first order in [LiOAc] which takes place by acetoxypalladation-deacyloxy palladation; or isomerisation without exchange—a zero order reaction in [LiOAc] involving an acetoxonium-type intermediate.

IV. The Exchange of Vinylic Chloride with Radioactive Lithium Chloride Catalysed by Palladium(II) Chloride in Acetic Acid
The kinetics and stereochemistry of the Pd-catalysed exchange of vinyl chloride with LiCl
are examined. It probably proceeds at rate =
\[ k[Li,Pd,Cl]\_2[vinyl chloride][LiCl]/[LiCl] \] and
by means of a rapid pre-equilibrium step to form
a \( \pi \) complex which is attacked by \( Cl^\text{-} \) to give a
chloropalladation adduct; dechloropalladation
completes the exchange.

V. The Exchange of Allylic Trifluoroacetates
with Lithium Chloride Catalysed by Palladium(II) Chloride in Acetic Acid
P. M. HENRY, Inorg. Chem., 1972, 11, (8),
1876-1879
The most probable rate expression and mechanism
for the exchange of allylic trifluoroacetates with
Lithium Chloride Catalysed by Palladium(II)
higher Pd(I\text{I}) concentrations is doubted.

Oxidation of Olefins by Palladium(II). IV.
Effect of Palladium(II) Chloride Concentration
on Rate in Aqueous Solution
4437-4440
The rates of oxidation of \( \text{C}_2\text{H}_4 \) and \( \text{C}_3\text{H}_6 \) in a
solution where \([\text{PdCl}_2]^\text{2-}\) = 0.01-0.2 M and
[NaCl] = 0.2-0.5 M were found to fit the expression:
\[ -d[\text{olefin}]/dt=k[\text{PdCl}_2]^\text{2-}[\text{olefin}]/[\text{H}^\text{+}][\text{Cl}^-]^\text{2} ] \]
A second term introduced by Moiseev for these
higher Pd(II) concentrations is doubted.

Synthesis and Catalytic Properties of \( \pi \)-Allyl
Complexes of Palladium(II) in the Oligomerisation
of Butadiene-1,3
A. S. BEREN'TYUM, I. V. KALECHITS, L. G. KORABLEVA,
I. P. LAVER'EV, M. L. KHIKHELD, and L. P.
Khim., 1972, (8), 1841-1843
A series of mono- and binuclear \( \pi \)-allyl Pd(II)
complexes with O-, N- and S-containing ligands
were synthesised. Pyrazine-2,3-dicarboxylic acid
in the presence of Pd(II) complexes and mono-
ethyl ether anions forms the linear trimer
butadiene-1,3,5-dodecatetraene-1,3,6,10.
A method of transferring Pd(II) complexes in a
catalytically active form in the oligomerisation of
butadiene-1,3 is proposed to account for the effect
of aprotic dipolar solvents.

Catalytic Oligomerisation of Butadiene on
Rh(1) Complexes
P. S. CHERKII, M. L. KHIDEKEL', I. V. KALECHITS,
O. N. EREMEMKO, G. I. KARYAKINA and A. S.
Khim., 1972, (7), 1579-1583
LRh(CO)\text{Cl}_2 complexes, where L is benztiazole,
acridine, imidazole or benzimidazole, were
synthesised and used in \( \text{C}_2\text{H}_4\text{OH}, \text{CH}_3\text{OH} \) or
CH\text{3}OCH\text{3} to catalyse butadiene conversion to a
mixture of 4-vinylcyclohexene, 1,5-cyclo-
octadiene and 1,4-trans-polybutadiene; in DMF
only 4-vinylcyclohexene is produced. Solutions
of binuclear Rh(1) complexes in DMF with
4-vinylcyclohexene form 1,5-cyclooctadiene
complexed with \( n \)-phenylenediene and 1,3,7-octatriene
in the presence of benzidine complexes. This is
connected with the doublet mechanism of the
two active centres of the complexed catalyst.

Rhodium(1)-catalysed Dismutation of Electron-rich Olefins: Rhodium(1) Carbene
Complexes as Intermediates
D. J. CARDIN, M. J. DOYLE and M. F. LAPPERT,
928
Dismutation of two electron-rich olefins, \( \text{C}_3\text{H}_4 \)
and \( \text{C}_4\text{Y}_4 \), proceeds only in the presence of an
additive, in particular a Rh(1) complex, by the
formation of catalytically active intermediate
carbene complexes.

Hydrogen Transfer Reactions. 28. Chiral
Tertiary Phosphine-induced Asymmetric
Induction in the Homogeneous Hydro-
genation of Olefins with Rhodium-Phosphine
Complexes
L. HORNEN and H. SIEGEL, Phosphorus, 1972, 1, (5),
209-216
The products of hydrogenation of \( \alpha \)-substituted
styrnes, catalysed by reaction products of di-\( \mu \)-
chlorobis(1,5-hexadiene)dirhodium and chiral
phoshines, are optically active with \( 2-19\% \)
induction of chirality and their configurations are
related to those of the phosphines. Na ethylate
increases the hydrogenation rate.

Rhodium Complex Catalysed Hydroisilylation
of Carbonyl Compounds
\( \text{PPh}_3\text{RhCl} \) catalyses the hydroisilylation of
carbonyl compounds under mild conditions giving
high yields. \( \text{PPh}_3\text{RhH(SiEt)_3Cl} \) is an
intermediate.

Homogeneous Hydrogenation Using Hydro-
gen Peroxide-activated Iridium Complexes
F. VAN RANTWIJK, T. G. SPEK and H. VAN BEKKUM,
Rec. Trav. Chim. Pays-Bas, 1972, 91, (8), 1057-
1068
Chlorotris(triphenylphosphine)Ir(I) and trans-
carbonylcychlorobis(triphenylphosphine)Ir(I)
were treated with \( \text{H}_2\text{O}_2 \) to yield catalysts for homogene-
ous hydrogenation. Activation appears to involve
selective oxidation of one triphenylphosphine
ligand. Hydrogenation of terminal or cis-
substituted olefinic double bonds, catalysed by
both complexes, is accompanied by extensive
isomerisation.

Some Aspects of the Polymerisation of
Cycloolefins by Group VIII Metal Catalysts
L. PORRI, R. ROSSI, P. DIVERTI and A. LUCHERINI,
1972, POLY 54
\[ ([\text{Cyclooctene}]_2\text{IrX})_2, \quad ([\text{C}_6\text{H}_{12}\text{RuX}_2])_2 \quad (X=\text{Cl}, \text{Br}) \]
OCOF₂₅ (CO)Cl and H₃IrCl₄, 6H₂O are all very active for the polymerisation of norbornene, via ring-opening, but not of cyclopentene and cyclooctene, although the Ir catalysts give copolymers of norbornene with cyclopentene and cyclooctene and the Ru catalysts become active for cyclopentene polymerisation after H₃ treatment. Metallurgy is suggested as the mode of action.

The Oxidation of 2-Propanol by Ruthenium Tetroxide


The kinetics of the oxidation of 2-propanol by RuO₄ in aqueous solutions of HClO₄ were studied, and show two separate mechanisms to apply. At moderate acid concentrations (1-6.5 M HClO₄) the rate determining step involves hydride abstraction, whilst at very high acid concentrations it is carbonium ion formation.

Investigation of the Homogeneous Hydrogenation of Acetylene and Ethylene Compounds in the Presence of RuCl₃(PPh₃)₃


Acetylenic bonds of hexyne-1 were reduced stereospecifically to form the hexene-1. Disubstituted acetylenes were reduced stereospecifically to form cis-ethylenes.

FUEL CELLS

Precious Metal Anodes: State of the Art

E. W. Dreyman, Mater. Protection Performance, 1972, 11, (9), 17-20

The characteristics and applications of Pb-Pt, Pt on Ti, Pt on Nb, Pt on Ta, and Ru oxides on Ti as impressed current anodes are reviewed.

GLASS TECHNOLOGY

Sintering of Ag-Pd in the Presence of a Reactive Glass


Fired size versus time plots for 20 wt. %Pd-Ag show that sintering occurs by grain boundary diffusion in the powder alone and by solution precipitation in the presence of up to 9 vol. % glass.

Plastic Flow and Fracture of Metallic Glass


Studies of the plastic flow and fracture of three Pd₉₆, Auₑ₄, Sb₃₆, c-based alloys show that they are brittle and fracture intergranularly in the fully crystalline state but that plastic flow precedes shear-initiated fracture in the glassy and microcrystalline states.

ELECTRICAL AND ELECTRONIC ENGINEERING

Oxidation of Platinum Group Metal Contacts by the Mechanochemical Reaction

S. Shimosato, J. Japan Inst. Metals, 1972, 36, (6), 610-616

The oxidation of Pt, Pd and Rh contacts was studied by contact resistance measurement, observation and E.P.M.A. Contact resistance increases markedly after operation in purified air, due to mechanochemical oxidation, but this is inhibited in unpurified air by the adsorption of H₂O and organic vapours on the contact.

Internal Stresses and Interdiffusion of Ti-Pd-Au Films Studied by X-ray Diffraction Techniques

S. S. Lau and R. C. Sun, Thin Solid Films, 1972, 10, (2), 273-282

The effect of ageing at 284-425°C on the mechanical and structural properties of three layer Ti/Pd/Au electrical conductor films was studied. Stresses in Au film on Pd/Ti are independent of the substrate ceramic and are lower than those of Au films deposited directly on the Ti bonding layer. During ageing substantial interdiffusion between Au and Pd occurs, the diffusion rate of Pd being greater than that of Au.

Rh-doped LiNbO₃ as an Improved New Material for Reversible Holographic Storage


The use of Rh as a new dopant for LiNbO₃ for hologram production is described. Doping with Rh introduces a new absorption band peaking at ~4860Å, and greatly improves the recording sensitivity, diffraction efficiency, erasing sensitivity and the persistence of holograms.

ThO₂ on Ir Cathodes for Electron Bombarded Semiconductor Devices


ThO₂ on Ir was shown to be superior to standard oxide cathodes as an electron emitter for electron bombarded semiconductor devices. Quadrupole and Auger measurements showed little reduction of ThO₂ by Ir and negligible evaporation products. ThO₂ on Ir is resistant to air and to poisoning and can be reactivated fully.

Preparation, Structure and Electrical Properties of Thick Ruthenium Dioxide Films


Electron microscopy, electrical conductivity and
X-ray diffraction studies carried out on thick polycrystalline RuO₂ films, obtained by decomposition of RuCl₃, show that below 700°C the conductivity and lattice constant depend on Cl content but above 800°C the conductivity depends only on temperature and has a positive coefficient. The films are shown to be Cl-doped oxide.

TEMPERATURE MEASUREMENT

The Movable-junction Stationary-lead Thermocouple


Two types of movable-junction Pt : 10%Rh-Pt research thermocouples have been developed, one to measure temperature and low gradients accurately from 0-1100°C and the other to determine the immersion characteristics of each thermoelement of a couple.

A Method for the Control and Measurement of Wire Temperature in Preparatory Anneals on Standard Pt/Pt-10Rh Thermocouples


A method is described for annealing Pt : 10% Rh-Pt thermocouples at 0-1450°C (particularly at 450°C) by means of a 60Hz heating current and simultaneously measuring and controlling the temperature to ±10°C using the d.c. thermal e.m.f.

NEW PATENTS

METALS AND ALLOYS

Lead Alloys

BADISCHBE ANILIN- & SODA-FABRIK A.G.

British Patent 1,293,031

The corrosion resistance of Pb alloys is improved by adding 0.05-0.2% Pd.

Nitrogen-free Platinum Powders

E. I. DU PONT DE NEMOURS & CO.

U.S. Patent 3,667,935

N₂-free Pt powders are prepared by precipitation from an aqueous PtCl₄ solution with Zn and HCl. This N₂-free Pt powder is relatively coarse and can be used in the production of various electrical circuit structures.

Dental Alloy

AURIUM RESEARCH CORP.

U.S. Patent 3,667,936

An alloy for dental frames which are to carry ceramic coverings contains 8-50% Pd, 3-12% In and the remainder mostly Au or Au and Ag.

CHEMICAL COMPOUNDS

Production of Platinum and Palladium Complexes

PHILLIPS PETROLEUM CO. U.S. Patent 3,671,560

Elementary Pd or Pt is reacted directly with a trisubstituted phosphine to give a zerovalent complex with 4 phosphine groups, e.g. Pd(PPh₃)₄.

Rhodium-Tellurium Oxide

SOLVAY & CIE.

French Appl. 2,099,648

A new compound of Rh and Te has the formula Rh₂TeO₄. It crystallises as a trirutile tetragonal system. It can be used as a semiconductor, catalyst, electrode material etc. The tungsten analogue Rh₂WO₄ has similar properties (French Appl. 2,099,649). French Appl. 2,099,647 is more general and covers the A₃BO₄ compounds where A is Co, Cr, Fe, Mn, Al, Ga, Ir, Rh or V and B is Te, W, Mo, Re. Pt group metal-Te oxides as electrochemical electrodes are covered by French Appl. 2,099,650.

ELECTROCHEMISTRY

MATSUSHITA ELECTRIC INDUSTRIAL CO. LTD.

British Patent 1,284,279

The catalyst for an electrode of an electrochemical cell is made by reducing a mixed solution of a U compound and an active catalyst metal compound of a Pt group metal to produce a U-containing active catalyst metal.

Electrolysis Electrode Coating

P.P.G. INDUSTRIES INC.

U.S. Patent 3,663,414

An anode for the electrolysis of an aqueous solution includes an electroconductive base member, typically Ti, and an electroconductive coating or surface including an inner layer of a Pt group metal and an outer layer of a Pt group metal oxide.

Electrochemical Electrodes

SOLVAY & CIE.

U.S. Patent 3,668,005

Electrochemical electrodes are made by coating a base with RuO₂. The base electrode, consisting of Ti, Ta, etc., is first etched and coated with an oxidisable substance, such as an oil, grease or hydrocarbon. The coated surface is then exposed to RuO₂ which oxidises the coating and deposits RuO₂.

Electrode for a Conducting Cell

E. SLEVÖGT

German Offen. 2,061,976

A cell for measuring electrical conductivity is provided with an electrode made with a Pd skeleton or of compressed Pd powder.
Electrolysis Electrodes
METALLGESELLSCHAFT A.G.
German Offen. 2,100,652
Electrolysis electrodes are made from a graphite body coated with a Pt group metal or metal oxide and fixed with a chemically resistant layer, e.g. TiO₂.

ELECTRODEPOSITION AND SURFACE COATINGS

Pt Thin-film Metallisation Method
TEXAS INSTRUMENTS INC. U.S. Patent 3,657,029
Pt thin-film metallisation layers are selectively etched with aqua regia using a Cr or Ti film as the mask. For example, an integrated circuit structure is metallised with successive layers of Ti, Pt, Au and a metal selected from Mo, W, Re and corrosion-resistant alloys.

Rhodium-Platinum Electroplating
SEL-REX CORP. U.S. Patent 3,671,408
A Rh-Pt alloy is electrodeposited from a bath containing, per litre, 0.1-15g Rh as sulphate, 0.04-2.4g Pt as the 'P salt', Pt(NH₃)₂(NO₃)₂, and at least 20g sulphamic acid.

Coated Electrodes
BADISCH ANILIN- & SODA-FABRIK A.G.
U.S. Patent 3,672,990
Adherent coatings on electrodes are produced using a mixture of SiO₂, GeO₂ and/or SnO₂ and a Pt group metal or compound. The mixture is applied to the metal and fired. SiO₂ and ruthenium acetylacetonate can be used on Zr sheet.

Palladium Electroplating Bath
DEUTSCHE GOLD- & SILBER-SCHEIDEANSTALT
German Offen. 2,105,626
Bright, crack-free coatings are electrodeposited from a bath containing Pd(NO₃)₂, H₂SO₄ and PdSO₄.

HETEROGENEOUS CATALYSIS

Hydrosilane Preparation
DOW CORNING CORP. British Patent 1,285,167
Hydrosilanes are produced by the hydrogenation of disilanes in the presence of a 'transition metal catalyst'. This term is defined as Pd/C, Ru/C, Rh/C and complexes such as Pd and Pt chloride-phosphine complexes.

Allyl Carboxylate Production
FARBWERKE HOECHST A.G.
British Patent 1,286,443
In the production of allyl carboxylates propylene, O₂ and a carboxylic acid are reacted together in the presence of a supported mixture of Pd and Bi and optionally a Group I or II salt. Other Pt metals can be used with or instead of Pd.

Polymers Containing Phosphorus
BRITISH PETROLEUM CO. LTD.
British Patent 1,287,566
Vinyl phosphate monomers are used, e.g. with styrene, to produce polymers containing phosphine groups. These can complex Pd, Ir and other metals to give solid catalysts.

Semiconducting Films
T. YAMAOKI British Patent 1,290,491
Surfaces are coated with semiconducting films of materials formed in the gas phase in the presence of catalysts. These include Pt, Pd and Pt-Si alloys. Pt gauze is used in the silane-NH₃ reaction to form a Si₃N₄ film.

Hydrocarbon Conversion
UNIVERSAL OIL PRODUCTS CO.
British Patent 1,291,047
Cyclic hydrocarbons are converted to paraffins using a Rh and/or Ru catalyst supported on a refractory oxide and promoted with a halogen. Convenient catalysts may be produced by impregnating Al₂O₃ with Ru or Rh chloride solution and then drying and calcining.

Hydrocarbon Conversion Catalyst
UNIVERSAL OIL PRODUCTS CO.
U.S. Patent 3,660,309
A more resistant hydrocarbon conversion catalyst consists of a Pt group metal and Ge on a mixture of Al₂O₃ and aluminosilicate. Pt itself is the preferred metal of the group.
Bimetallic Reforming Catalyst
MOBIL OIL CORP. U.S. Patent 3,661,768
An improved start-up procedure for a bimetallic reforming catalyst containing Pt involves reducing the catalyst, previously purged of O₂, with moisture-saturated H₂ gas until a temperature of 485°C is reached, then sulphiding the reduced catalyst and charging naphtha in contact with it.

Exhaust Gas Oxidation
W. R. GRACE & CO. U.S. Patent 3,661,806
The exhaust gas oxidation catalyst, which may be a Pt group metal, is dispersed on an inorganic matrix of specified pore size and distribution.

Paraffin Dehydrogenation
SHELL OIL CO. U.S. Patent 3,662,019
Paraffins are dehydrogenated to olefins over a Pt group metal catalyst containing at least one Group IIB and VIIIB metal, e.g. Pt with Cd, Zn, or Re.

Platinum Catalyst
FARBENTABRIKEN BAYER A.G. U.S. Patent 3,663,166
A catalyst for hydroxylamine production is prepared by hydrolysing a Pt compound, such as K₂PtCl₆, at pH 4.5–9.0 so that hydrated Pt oxide is deposited on a support such as graphite.

Ethylene Oxide Production
STA. ITALIANA RESINE S.P.A. U.S. Patent 3,663,455
C₂H₄ is oxidised to ethylene oxide in the presence of a catalyst containing 7–30% Ag and 0.01–1% Pt, Pd or Au (based on the weight of Ag).

Hydrogenation of Arylaldehydes
UNIVERSAL OIL PRODUCTS CO. U.S. Patent 3,663,626
A continuous process for the hydrogenation of aryl aldehydes to the corresponding alcohols is effected in contact with a catalyst composite of Pt and an alkali metal component.

Multireaction Reforming
STANDARD OIL CO. U.S. Patent 3,664,949
Petroleum feedstocks are reformed in several reactors each containing a Pt group metal, such as Pt, on a mordenite support.

Light Alkane Disproportionation
CHEVRON RESEARCH CO. U.S. Patent 3,668,268
Light alkanes are disproportionated to produce higher hydrocarbons by heating in the presence of a molecular sieve carrying a Group VIII noble metal, e.g. Pd/mordenite.

Paraffin Disproportionation
ATLANTIC RICHFIELD CO. U.S. Patent 3,668,269
Paraffins are disproportionated to yield higher and lower hydrocarbons in the presence of a Pt group metal deposited on an acidic mixture of aluminosilicate and inorganic oxide. In an example Pt is deposited on a faujasite-SiO₂-Al₂O₃ mixture.

Ethylene Hydrogenation Catalysts
E. I. DU PONT DE NEMOURS & CO. U.S. Patent 3,663,181
Orthorhombic Pt metal oxides of the type PtₓMO₉, where M is Mn, Fe, Co, Ni, Cu, Zn, Mg or Cd, are catalysts for the hydrogenation of C₂H₄.

Ethylene Oxide Production
The oxidation of hydroxybenzyl alcohols to salicylaldehydes is catalysed by Pt and promoted by Cd, Ce, In or La.

Exhaust Gas Combustion Catalyst
H. BERGER German Offen. 2,058,264
An active ICE exhaust gas catalyst consists of a finely divided carrier impregnated with catalyst and then shaped, fired, etc. The fine state of division is produced by colloid milling. Pt metals on Mg-Al silicates form suitable compositions.

HOMOGENEOUS CATALYSIS
Acetic Acid Production
AJINOMOTO CO. INC. British Patent 1,286,224
CH₃COOH is produced by heating methyl formate and CO in the presence of a Rh catalyst and a halogen promoter. A wide variety of inorganic and organic Rh salts can be used.

Cyano-substituted Silicon Compounds
UNION CARBIDE CORP. British Patent 1,290,549
HCN adds on to unsaturated groups in siloxanes in the presence of Ni, Pd or Pt zerovalent complexes [e.g. Pd(PPh₃)₄] to form cyano-substituted Si compounds.

Organic Isocyanate Production
OLIN MATHIESON CHEMICAL CORP. U.S. Patent 3,657,308
The production of isocyanates by the reduction of organic nitro compounds is catalysed by a Pt group metal complex of a Lewis base, such as
pyridine or isoquinoline, in the presence of an organic carbonate.

Hydrosilation Catalysts
TORAY INDUSTRIES INC. U.S. Patent 3,658,866
Hydrosilation reactions are catalysed by zero-valent Pd complexes of P, As or Sb ligands, e.g. triphenyl phosphine or trimethyl arsine.

Aldehyde Production
UNION OIL CO. OF CALIFORNIA U.S. Patent 3,660,441
Higher aldehydes are produced from lower aldehydes and acids in the presence of Pt group metal complexes, e.g. an Ir(PPh₃)₂ complex.

Isocyanate Production
OLIN MATHIESON CHEMICAL CORP. U.S. Patent 3,660,458
Organic isocyanates are produced by reacting an organic azo and/or azoxy compound with CO in the presence of a p.g.m. catalyst, e.g. PdCl₂.

Hydroformylation Catalyst
BRITISH PETROLEUM CO. LTD. U.S. Patent 3,660,493
Hydroformylation reactions are catalysed by a complex of Rh(1) carboxylate, e.g. a Rh acetate-PPh₃ complex.

Cyclic Hydrocarboxylation Process
UNION OIL CO. OF CALIFORNIA U.S. Patent 3,668,249
Straight chain acids, anhydrides or esters are produced by the hydrocarboxylation of olefins over Pt group metal catalyst, e.g. a Pd-P complex.

Vinyl Chloride Production
ESSO RESEARCH & ENGINEERING CO. U.S. Patent 3,670,037
Monohalogenated olefins such as vinyl chloride are produced from an olefin, hydrogen halide and source of O₂ in the presence of a Pd catalyst, e.g. PdCl₂.

Rhodium Complexes
JOHNSON MATTHEY & CO. LTD. German Offen. 1,793,616
Catalysts for hydrogenation, hydroformylation, and/or carbonylation reactions are Rh complexes or complex anions of formula RhX(YR₃)ₙ or

\[
(XₙSn)Rh_m
\]

Where X is a halide or pseudohalide, Y is P₃, As or Sb, R is the same or different hydrocarbon groups and n-m = 1 or 3.

FUEL CELLS
Fuel Cell Catalysts
ROBERT BOSCH G.m.b.H. British Patent 1,285,861
A new catalyst for fuel cells is a mixture of Pt or Pt alloy and at least one metal sulphide in an electrically conducting matrix. In one example Pt, Ag₃S and an Au powder matrix are used.

Fuel Cells
MATSUSHITA ELECTRIC INDUSTRIAL CO. LTD. British Patent 1,288,986
A fuel cell electrode consists of a mixture of Ni, Sb and a Pt group metal, e.g. Pd.

Fuel Cell Electrodes
ROBERT BOSCH G.m.b.H. British Patent 1,292,791
A fuel cell electrode has a skeletal structure supporting a mixed catalyst containing P, S, Se or Te and Pt or one of its alloys, e.g. Pt and P.

CATHODIC PROTECTION
Electrodes for Electrolytic or Cathodic Anti-corrosion Protection
SOCIÉTÉ D'ÉTUDES CONTRE LA CORROSION British Patent 1,284,198
A robust electrode for anti-corrosion protection of marine structures and craft comprises one or more tubes of Ta or Ti with a Pt or Rh coating. The electrode is held in grooves of an insulating base by a sealant which penetrates perforations in the metal.

CHEMICAL TECHNOLOGY
Iridium in Uranium Dioxide
U.K. ATOMIC ENERGY AUTHORITY British Patent 1,283,608
A fine, uniform dispersion of a refractory metal in UO₂ fuel inhibits grain growth and release of fission gases. An Ir compound in an HNO₃ solution of uranyl nitrate is decomposed to metal; NH₄⁺ ions are added to precipitate ammonium diuranate. This is then calcined and reduced to UO₂ containing finely dispersed Ir.
**Noble Metal Photographic Nuclei**

*Eastman Kodak Co.*  
*British Patent 1,290,618*

Nuclei for reduction centres in Ag emulsions are produced by reducing a Pt, Pd, Au, Rh and/or Ru salt with a borohydride.

**Hydrogen Separation**

*Johnson Matthey & Co. Ltd.*  
*British Patent 1,292,025*

H₂ is separated from other gases by passage through a discontinuous and/or porous Pd or Pd alloy film deposited on an imperforate tube or membrane substrate made of Ni, Fe, V, Ta or Nb or their alloys.

**Platinum Group Metal-Quinone Complexes**

*Fuji Photo Film Co. Ltd.*  
*U.S. Patent 3,656,961*

A direct positive, photographic Ag halide emulsion contains a soluble salt or a condensed polycyclic quinone complex of a Group VIII metal. The metal is especially Rh, Ir, Ru, Pd, Os, Co or Pt; phenanthraquinone is a suitable quinone.

**Glass Technology**

**Optical Coatings for Glass**

*Carl-Zeiss-Stiftung*  
*British Patent 1,289,498*

An approximately frequency-independent inhibition of radiation is achieved with coatings on glass. These consist of finely divided Pd or PdO in an oxide matrix. TiO₂ containing 18.1% Pd is one example of the coating.

**Pt-Rh-Au Alloy**

*Johnson Matthey & Co. Ltd.*  
*U.S. Patent 3,672,880*

Because of their low wettability by glass, corrosion resistance and high temperature strength, alloys comprising 72–90 wt.% Pt, 9–25% Rh and 1–3% Au are suitable for use as containers with perforated bushing plates for glass fibre manufacture.

**Glass Industry Equipment**

*Johnson Matthey & Co. Ltd.*  
*U.S. Patent 3,657,784*

Stirrers, crucibles, spinning dies and related glass industry equipment made from a refractory metal are flame-sprayed with an O₂ getter and a MgO barrier layer before cladding with an outer layer of a Pt group metal alloy. The volume between the barrier layer and the outer cladding is evacuated. A suitable getter is Zr metal.

**Electrical and Electronic Engineering**

**Schottky Barrier Diodes**

*Western Electric Co.*  
*British Patent 1,286,307*

Schottky barrier diodes are formed using a metal silicide on Si, e.g. Rh, Pt or Pd silicide.

**Contacts on Semiconductors**

*General Electric Co.*  
*British Patent 1,286,834*

Contacts on semiconductors are made from layers of (a) Ti, V, Cr or Al, (b) Pd, (c) Ni and (d) Au, Ag, Sn and/or Pd.

**Field Effect Transistors**

*Texas Instruments Ltd.*  
*British Patent 1,290,419*

Gate electrodes and conductors on field effect transistors are made from Pt (Si semiconductor) or Au (GaAs semiconductor).

**Platinum Alloy Semiconductor Electrodes**

*Nippon Electric Co. Ltd.*  
*U.S. Patent 3,658,489*

The use of pure Pt for semiconductor electrodes leads to difficulties in the masking and etching stages. An alloy that is easier to etch contains Pt with 1–20 at.% Ni.

**Low Current Electrical Contact**

*W. C. Heraeus G.m.b.H.*  
*U.S. Patent 3,672,850*

Ru is vapour deposited in a vacuum directly on to a springy magnetic contact carrier made of Fe-Ni alloy. It forms crystal columns.

**Temperature Measurement**

**Marking Metallic Materials**

*Johnson Matthey & Co. Ltd.*  
*British Patent 1,280,454*

Metal strip, rod or wire, especially Pt alloy thermocouple wire, is coded at intervals by a system of depressions or projections on the surface, including one larger 'marker' to show the direction the code should be read. The marks are inconspicuous but cannot be removed without damaging the wire.

**Sheathed Thermocouple**

*Johnson Matthey & Co. Ltd.*  
*British Patent 1,280,674*

Changes in Pt alloy thermoelectric properties due to the migration of a constituent of one limb to the other limb, especially in the form of the volatile oxide, are minimised by sheathing a thermocouple in a material containing none or less of that constituent than either limb contains and by maintaining a low oxidising potential by including a 'getter', e.g. Ti, Zr or Ta and/or by filling the sheath with an inert gas.

**Platinum Coatings**

*Johnson Matthey & Co. Ltd.*  
*French Patent 2,084,651*

Articles for use at high temperatures consist of a refractory metal core (Nb, Ta, Cr, etc.) coated with a MgO barrier layer and then a Pt group metal or alloy. The articles may be used in thermocouple assemblies.