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The Platinum Decathlon – A Tribute to the Foresight of Antoine Baumé

"So many excellent properties united in a single metal make it desirable that it should be introduced into commerce", Antoine Baumé – "Chymie Experimentale et Raisonnée" (1773)

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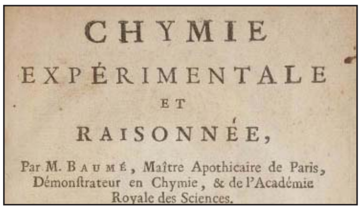
Ten application areas and ten properties of platinum (or its alloys) are selected here to represent a "platinum decathlon". Platinum has a unique combination of properties which make it eminently suitable for many applications from jewellery to anticancer drugs, from high-temperature engineering to a range of catalytic applications. The 18th century French chemist Antoine Baumé foresaw the desirability of platinum's use in industry and its use today in many essential areas bears this out.

Introduction

Platinum (atomic number 78) is an element of the third row of the transition metal series and hence is one of the densest of metals (*ca.* 20 g cm^{-3}) with a high melting point (>1750ºC). It comprises only 1–10 ng g^{-1} of the earth's crust (1) making it a genuinely rare metal, with annual output less than a tenth that of gold. There are only a few locations in the world where platinum has sufficient concentration to make mining economically viable. The largest area of this type is the Bushveld igneous complex in South Africa, identified by Hans Merensky in 1924. In recent times this region has provided approximately three quarters of the world's platinum supply.

The specific properties of platinum have been exploited over the years to create a range of consumer and industrial uses. These are indicated in **Table I** and below we will discuss how the applications have arisen.


CHYMIE
EXPÉRIMENTALE
ET
RAISONNÉE,
Par M. BAUMÉ, Maître Apothicaire de Paris, Démonſtrateur en Chymie, & de l'Académie Royale des Sciences.

"Chymie Experimentale et Raisonnée"

Table I

Properties	Value, units	Applications									
		Jewellery	Biomedical devices	High-temperature engineering	Ammonia oxidation	Sensors and thermocouples	Petrochemicals reforming	Emissions control	Hard disks	Silicones	Anticancer drugs
Melting point	~1770ºC	✓		✓		✓					
Ductility (tensile elongation, annealed, room temperature)	35–40%	✓			✓						
Oxidation resistance: 1200ºC 1600ºC	0.1–0.3 g m^{-2} h^{-1} 1.2 g m^{-2} h^{-1}	✓		✓	✓	✓					
Electrochemical oxidation potential	–1.2 V		✓				✓	✓			
DC corrosion resistance	5–7 mg amp^{-1} $year^{-1}$		✓		✓						
Relative radiopacity	30 × Ti 6.7 × Ni		✓								
Electrical conductivity	9.937 × 10^6 S m^{-1}		✓			✓					
Creep rate: 1000ºC	0.04% h^{-1}			✓							
Coercivity: Pt/Co alloy	*ca.* 10 kOe								✓		
Common oxidation states	0, +2, +4									✓	✓

Ten Application Areas of Platinum

1. Jewellery

The values of rarity and purity, associated with its enduring quality and resistance to tarnishing, mean that platinum has been used for decoration since the 7th century BC, as shown by the Thebes casket (**Figure 1**). More recently, these qualities have made platinum a very popular metal for wedding rings (**Figure 2**) particularly in Asian countries and this has accounted for significant growth in platinum jewellery demand in China as consumer wealth has increased.

Fig. 1. The Casket of Thebes

Fig. 2. Platinum wedding rings (Copyright © J. Fischer & Sohn KG)

Each of the jewellery metals lends itself to particular types of work related to its properties. For example, pure gold can be used to provide large areas of reflective finish but it is too soft (Vickers hardness 25) for constructing many pieces and must necessarily be alloyed with other metals. Platinum is harder (Vickers hardness 45) but must still be alloyed with small amounts of other metals, which can include other platinum group metals, for jewellery use. Whereas platinum cannot be used for large areas of reflective finish, it is particularly suited to creating intricate designs using laser welding (2). The whiteness of platinum is also advantageous in not imparting any colour when setting stones, and it can be used to make very fine settings for holding stones which are not possible using gold.

A common jewellery component is wire. Platinum is formable enough that jewellery manufacturers can melt and cast small ingots before rolling them to rod and hand drawing to wire, allowing the wire to be produced as it is required (3). Platinum wire is a striking example of the ductility of platinum. The platinum can be drawn down to 0.0006 mm diameter for commercial supply. At that final thickness, if the wire was drawn down from a 10 cm long, 1 cm diameter rod, approximately 2777 km of wire could be produced.

2. Biomedical Devices

Biomedical devices are used inside a living body. There is a wide range of such devices, from the complex (pacemakers) (**Figure 3**) to the very simple (bone pins to help broken bones heal correctly), and even replacement parts (artificial knees or hip joints). All of these have a primary requirement that they do not harm the tissues exposed to them.

One problem suffered by *in vivo* devices is that they are exposed to the body's naturally occurring fluids. The environment which these fluids form is not constant; for example, the pH can change with exertion. The fluids also contain a wide variety of ions, including chloride ions, which are known to be very aggressive in corrosion. As a result, biomaterials must be resistant to corrosion in a wide range of environments. If corrosion does occur it will result in metal ions being released into the body. These can be toxic to surrounding tissues, and will also interact with the fluids, potentially forming more dangerous compounds. Thus the corrosion resistance of platinum makes it a good candidate for biomaterials as it is not susceptible to this kind of reaction within the body. As a result platinum has been used increasingly as a biomaterial as the range of devices has been extended.

A given device will also have other properties required by its function. For example, one biomedical device with increasing use is the stent (**Figure 4**). Typically, this consists of a tube or scaffold and a balloon. The stent is inserted into an artery with the tube collapsed and carefully manoeuvred through the artery till it is in the correct position. The balloon is then inflated to expand the tube, then deflated and removed. The tube must be ductile enough to be opened, yet strong enough to remain open once the balloon is removed. It is also highly useful to the surgeon that the stent is radiopaque such that its position can be seen by X-rays to assist positioning. This can either be done through the use of marker rings if the stent itself is made of base metal alloy, or through construction of the stent using a platinum alloy, for example, chromium-platinum (37% iron, 33% platinum, 18% chromium etc.) as supplied by Boston Scientific. Since the first insertion of a stent into a patient in 1986 the design of stents has improved steadily. One problem which has been addressed for coronary stents is that of restenosis (4). This is the growth of smooth muscle cells at the site of the injury (analogous to a scar forming over

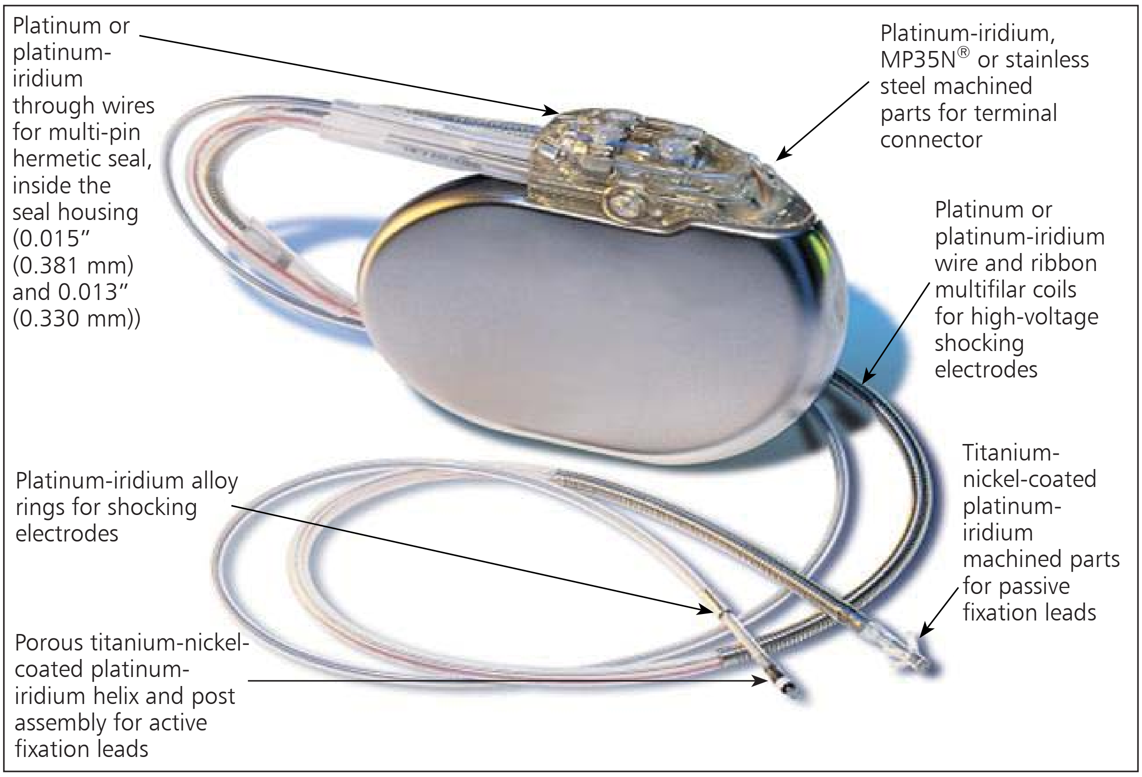


Fig. 3. An implantable cardioverter defibrillator, showing the components that are made from platinum or platinum group metal alloys

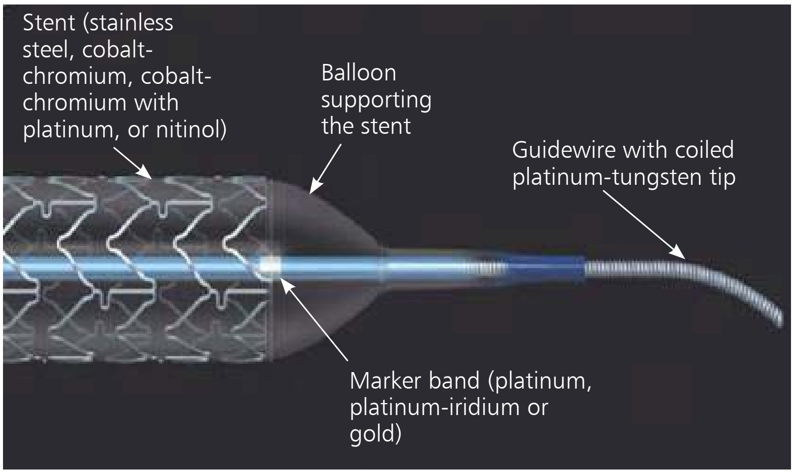


Fig. 4. A balloon-mounted stent used in percutaneous transluminal coronary angioplasty (PTCA, or balloon angioplasty) procedures (Copyright © Abbott Vascular Devices)

an injury) leading to reblocking. Drug-eluting stents, where a drug is released from a biocompatible polymer forming the stent or a coating, can help in reducing restenosis (5). A temporary stent procedure can also be used to unblock arteries in the brain in people suffering strokes. A platinum-titanium stent (for example, as manufactured by Covidien) is guided to where the clot has formed and expanded to allow blood to reach the patient's brain as soon as possible, minimising ischemic damage. The clot seeps into the mesh of the stent and after a few minutes the stent and clot are removed together (6).

A large number of other radiopaque platinum marker rings are also produced for other devices such as catheters to allow the surgeon to follow their progress during an operation.

The corrosion resistance and electrical conductivity of platinum have made it a metal of choice for the electrodes used in both pacemakers and neuromodulators, and the array of electrodes within a cochlear implant. A much older use is as a coating for irradiated iridium wire for localised delivery of radiation for cancer therapy. The tip of the iridium wire is left exposed, and the radiopaque platinum prevents the rest of the wire from affecting the body, allowing radiotherapy to be targeted on specific sites.

Platinum metal is therefore used for treating many conditions from deafness to Parkinson's disease, to heart conditions, to cancer (7).

3. High-Temperature Engineering

3.1 Glass Fibre Manufacture

Glass fibres are produced by passing molten glass through a 'bushing' (8) (**Figure 5**). This consists of a box with many nozzles in the base. The glass strands produced from these nozzles are collected in a variety of ways depending on the planned application – for example the fibres may be broken by periodic blasts of cold air to produce fibres of a known length, or wound onto reels, or even allowed to settle into a tangled mat (used for fibre glass insulation). The driving force for improvements has been the desire to fit more nozzles into a bushing, requiring the nozzles to have the thinnest walls and be packed as tightly as possible. The application also exerts some high demands on the material. In order for the fibres produced from each nozzle to be the same, the force exerted on each nozzle by the molten glass must remain constant. The material used must therefore be able to retain strength, especially creep strength (avoiding deformation over long time periods under the influence of loads at high temperature) to avoid the base 'bowing'. This results in the middle of the base sinking further than the edges, introducing a curve, and causing the nozzles to point in different directions, altering the forces at each nozzle. Stiffening ribs are often added to help mitigate this. The molten glass is also hot, alkaline and corrosive. The material must resist oxidation and chemical attack, both from the glass, and from impurities within the glass (for example, sulfur).

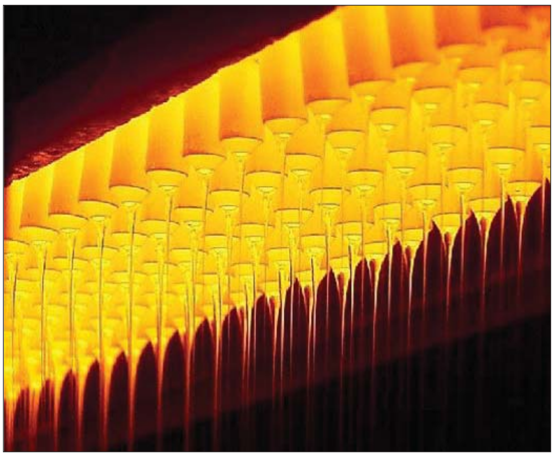


Fig. 5. Molten glass passing through a platinum-rhodium 'bushing', which consists of a box with many nozzles in the base, to create glass fibres (9)

The materials used for this application are platinum-rhodium alloys. These have the strength at high temperatures and general corrosion resistance required by the application. Despite this, the bushings still only have a production life of approximately one year.

The requirement to fit more nozzles onto the base of a bushing has seen an increase in numbers from 51 in the original bushings to 4000 in more recent ones. This has been made possible by improvements in both processing and understanding (9). For example, the addition of rhodium improved the high-temperature properties, but also changed the way the glass wetted the nozzles. This made it possible to remove a countersink previously required to stop the glass flowing over the edges of the nozzle and coating the bushing, thus reducing the nozzle size. The nozzles can be made by either pressing and drilling out the ends, or by cutting holes in the base and welding on the nozzles. In both cases, the main limitation on how close to each other the nozzles can be is the space required for the processing equipment.

The ability of platinum-rhodium alloy to resist corrosion from the glass is also important in maintaining the purity of the glass. In recent years this has become important for the production of the liquid crystal flat screen displays which have become ubiquitous in mobile phones, computers and televisions.

3.2 Turbine Engines

Today's civilian air fleet is propelled primarily by turbofan jet engines. A series of fans and compressors force air into the combustion chamber, where it is mixed with fuel and ignited. The gases expand and produce thrust to power the jet. The gas temperature rises as the gas is compressed throughout the engine, and the efficiency of the engine rises dependent on this gas temperature. As a result, the operating temperature of each stage has been increased over the years, and the materials used have therefore had to be improved to withstand higher and higher temperatures. The final compressor stage is now exposed to temperatures (1500ºC or more) which are above the melting point of the construction alloy used (a nickel-based superalloy) under highly oxidising conditions.

The blades need protection from these temperatures, and this is provided both by internal air cooling and by coatings to prevent the heat from reaching the blade. The coating must also protect the blade from oxidation. A platinum aluminide coating is a well-established technology to provide oxidation resistance (10) (**Figure 6**). Applying such a coating is a multi-stage process – first a platinum coating is applied (both aqueous and spray techniques are used for this) then the coated blade is heated to allow the platinum to diffuse into the nickel-based superalloy blade. The blade is then pack aluminised, which diffuses aluminium into the surface, forming a platinum aluminide layer. The layer greatly improves the oxidation resistance of the blades. As it was formed by diffusing platinum and aluminium into the nickel superalloy, it is well adhered to the surface. The platinum aluminide surface also allows a further ceramic thermal barrier layer to be applied. This ceramic layer helps to protect the blade from the high temperatures, but without the platinum aluminide coating, it would not adhere to the superalloy. The platinum aluminide coating allows the blades to operate continuously for 20,000 hours, and can be stripped and replaced once per blade.

Fig. 6. In a turbine engine, a platinum aluminide coating protects the blade from oxidation

4. Ammonia Oxidation

A major use for platinum wire is in the production of gauzes for nitric acid production in the Ostwald process. This is the oxidation of anhydrous ammonia to nitrogen dioxide over platinum (today generally a 90/10 or 95/5 platinum-rhodium alloy) at high temperature and pressure. The nitrogen dioxide is then reacted with water to make nitric acid. The platinum is in the form of woven or knitted (**Figure 7**) gauze sheets, and several of these sheets are stacked into a pack.

The process is a mature technology, having been patented by Wilhelm Ostwald in 1902. It was based on an 1838 patent by Kuhlman on the oxidation of ammonia over platinum sponge, which was in turn based on a 1789 experiment by Milner who oxidised ammonia over manganese(IV) oxide. The first plant was built in 1906, producing 300 kg of nitric oxide per day. By 1908 this production had been increased tenfold. These initial plants used crimped and coiled platinum strips, but 1909 saw the first use of platinum gauzes. The process became much more popular in 1913 when the Haber process for the production of ammonia was developed, and the two technologies have been linked since then (11).

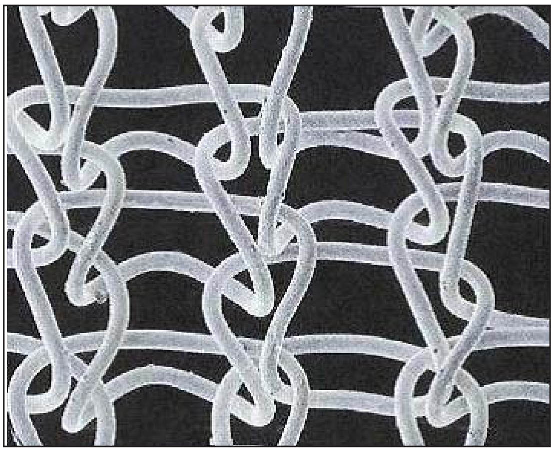


Fig. 7. Nitro-LoK was the second of the knitted gauze products and was developed for those ammonia oxidation plants whose main requirement is strength and flexibility. The extra strength when compared to the traditional knits is achieved by reducing the central loop and creating a more uniform structure, improving the strength by 40%

The conditions for the Ostwald process (a typical example is 300ºC and 9 bar pressure) are very aggressive (12). It therefore requires a very corrosion and oxidation resistant material, which must also catalyse the oxidation. The platinum-rhodium alloy used fulfils these requirements, but even such a resistant material is slowly consumed. The gauzes suffer from oxidation and slow loss of platinum (it is believed that this comes from the formation of a volatile platinum oxide). As a result, the gauzes slowly become less efficient and need replacement. The used gauzes are refined to recycle the platinum and rhodium. A further gauze is fitted downstream in the processing to catch and assist recovery of the lost platinum. Advances in gauze and catalyst design have also been incorporated over the years, such as the addition of palladium to the packs to reduce platinum loss, and the use of knitted rather than woven gauzes to reduce production costs (13).

The Ostwald process is also a key part of the agricultural industry as it supplies the nitrates required for fertilisers.

5. Sensors and Thermocouples

Platinum is used for a wide range of sensor applications. These range from thermocouples to more modern applications such as oxygen sensors in car exhaust systems.

5.1 Oxygen Sensors

Oxygen sensors for car exhaust gas (lambda sensors) (**Figure 8**) are used to help run a gasoline engine more efficiently (14). The oxygen content is related to the amount of unburned fuel remaining in the engine. The sensor consists of a porous platinum coating on both the inside and the outside of a zirconia tube. The tube is closed at one end and placed in the exhaust stream. This exposes the outside to the exhaust and the inside remains exposed to normal air. The exhaust heats the zirconia tube, which becomes an ionic conductor. As the oxygen content in the atmosphere at each platinum sensor is different, there will be a potential difference between them. This difference is monitored, and changes are used to control the fuel flow through the engine to ensure that the gas/fuel mixture allows for complete combustion of the fuel (15).

5.2 Thermocouples

A thermocouple consists of two wires of different metals (**Figure 9**). When any metal is subjected to a thermal gradient it will generate a voltage (the Seebeck effect). If two dissimilar metals are joined together, a potential difference will exist between them. Using a third metal to complete the circuit allows this potential to be measured, and compared to the voltage generated at a known temperature. This then allows the temperature of the joint between the

Fig. 8. Oxygen sensors for car exhaust gas (lambda sensors) monitor oxygen levels in the exhaust gases and provide feedback to the electronic engine management system which controls the air to fuel ratio (Copyright © Robert Bosch GmbH)

Fig. 9. A thermocouple consists of two wires of different metals joined together at one end to enable the temperature of the joint between the two metals to be calculated

two metals to be calculated. Platinum and platinum-rhodium alloys are used for three high temperature standard grades of thermocouple (16). Grade B links a 30% rhodium-platinum wire with a 6% rhodium-platinum wire, and is used at temperatures up to 1800ºC. Type R links a 13% rhodium-platinum alloy with pure platinum and is effective to 1600ºC. Type S joins a 10% rhodium-platinum wire to pure platinum and is also used to 1600ºC. Type S thermocouples are also used as the standard of calibration for the melting point of gold.

6. Petrochemical Reforming

The major uses of petroleum products, both as fuels (motor, aviation and heating) and petrochemicals (solvents, polymers and plastics) require low molecular weight hydrocarbons. However, naturally occurring deposits contain a significant amount of heavier compounds that are unsuitable for these applications. During the refining of crude oil these heavier materials must be converted to the valuable lighter fractions by cracking and reforming processes. Platinum catalysts, which were first introduced by Universal Oil Products (UOP Ltd) in 1949, play a key role in these reforming processes (17). The catalysts offer a combination of the hydrogen transfer properties of platinum with the acid catalysis provided by the alumina support treated with chloride. This allows the isomerisation of alkanes to cyclic and branched structures and an increase in aromatic content that improves the octane rating. Over the years, improvements to the catalysts have involved the addition of promoters such as tin or rhenium and the thrifting of the platinum loading (18). Nonetheless, despite the recovery of platinum from used catalysts, the increase in demand for fuels in the corresponding period has required the steady increase in the amount of platinum used in this way.

The ability of platinum to catalyse hydrogenation/dehydrogenation processes also plays a role in the production of alkenes for polymerisation. In particular, processes to exploit the increasing amounts of shale-derived gas are of current interest. The dehydrogenation of propane to propene, the monomer of polypropylene, is one such process. Dow Texas Operations have recently announced that a 750,000 metric tonnes per annum propene plant, will be operational from 2015 using platinum catalysts as part of Honeywell UOP's Oleflex™ technology (**Figure 10**).

Fig. 10. The UOP Oleflex™ Process produces polymer grade propylene from a propane feedstock (Photo courtesy of UOP, A Honeywell Company)

7. Emissions Control

The ability of platinum to promote the oxidation of coal gas was identified by Sir Humphry Davy in the very earliest days in the study of catalysis (1817). This ability to promote the oxidation of hydrocarbons and carbon monoxide, while also allowing the reduction of nitric oxides to nitrogen, underlies the modern application of platinum in automobile exhaust catalysts (three-way catalysts) (**Figure 11**). This has become the largest use of platinum in the present day. Since the introduction of the first catalysts in the 1970s, there has been continual improvement due to the use of different promoters and support materials, with thrifting of platinum levels and substitution with palladium. The complex chemistry of reactions required has resulted in complex formulations for the catalyst coatings, with the support materials in the form of a coating on ceramic also playing an important part. Continuing challenges are provided by the progressive tightening of legislative limits around the world. Examples include the need for better performance at low temperatures, such as those occurring at start up of the engine, and

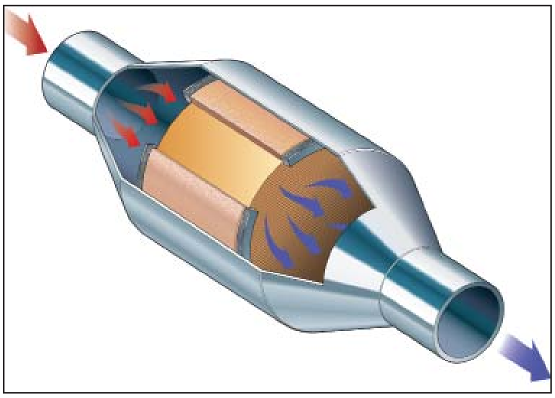


Fig. 11. A three-way catalyst system which simultaneously promotes the oxidation of hydrocarbons and carbon monoxide, while also allowing the reduction of nitric oxides to nitrogen

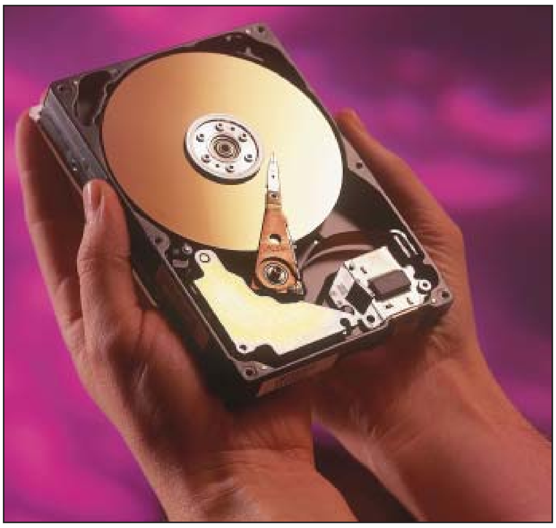


Fig. 12. Platinum-cobalt based alloy in a hard disk drive

better control of nitrous oxide, which is a powerful greenhouse gas (19).

In addition to gasoline engines, the technology has now been developed for diesel engines. The exhaust gas from diesel engines contains higher levels of oxygen and more particulate carbon (soot) than gasoline emissions so a different approach is required. Particulate matter is removed by a diesel particulate filter (DPF) which is periodically regenerated by a high temperature excursion. Hydrocarbons and carbon monoxide are oxidised with a diesel oxidation catalyst (DOC) while reduction of nitrogen oxides requires the addition of a reductant, usually ammonia formed from urea injected into the exhaust stream, and a selective reduction catalyst (SCR) (20). The legislation to control these pollutants has now been extended from light vehicles to heavy-duty trucks and is being increasingly introduced to stationary diesel engines. The geographical spread of regulation along with the tightening of limits in mature markets provides the demand for continued developments in this area.

8. Hard Disks

While for many applications it is the properties of the pure element that lead to the use of platinum, its alloys also show useful properties that have brought about significant applications. One such is the use of platinum-cobalt based alloys as magnetic recording media (21) (**Figure 12**). Nanoparticulate grains of these materials create small magnetic domains with high perpendicular anisotropy and high magnetic coercivity, i.e. they are 'hard' magnetic materials providing permanent magnets. This has led them to being chosen as the materials of choice for magnetic data storage devices such as hard disks. In maximising the efficiency of data storage, it is important that the magnetisation is not influenced by the magnetisation of neighbouring domains and other local fields (degrading the data). Therefore, high coercivity is necessary to allow domain size to be reduced. In addition, other techniques, such as perpendicular recording and the use of ruthenium interlayers providing 'antiferromagnetically-coupled media', have also allowed a reduction in domain size, leading to data capacity increasing by 50% per year or more. In the future, new modifications to the technology such as heat-assisted magnetic recording or patterned media will allow further increases to data levels of up to 100 terabits per square inch (22). With this potential it is unlikely that other data storage methods such as the use of semiconductor materials will match the economy of hard disks, allowing them to remain as the preferred mass market data storage devices for some time to come.

9. Silicone Manufacture

Despite the fact that platinum metal is relatively inert, once dissolved (using chloride media) it displays a rich variety of coordination chemistry leading to uses in catalysis and biomedical applications (23).

The availability of the d-orbitals of transition metals provides the opportunity for the formation of coordination bonds with a wide variety of donor groups. The reactivity of the ligands themselves is then modified leading to the potential for the formation of new bonds. This leads to homogeneous catalysis processes where, in contrast to heterogeneous catalysis, every atom of the metal is capable of acting as a catalytic centre. This property of platinum is used in the preparation of a wide variety of silicone polymers by the reaction known as hydrosilation. Typical catalysts range from simple salts such as potassium hexachloroplatinate(IV) to complexes such as Karstedt catalyst, **Figure 13**. Alkenes are inserted into silane precursors, $R_nSi\text{-}X_{(4-n)}$ (for example, X = H) see **Figure 14** (24, 25).

Silicone polymers have widespread application as easy-release surfaces and coatings. The different catalysts in combination with inhibitors can be used to control the initiation of the polymerisation, assisting in achieving great control over the properties of the final polymer. The catalyst (a few parts per million) remains embedded in the polymer and so this one of the few areas of application where recycling of platinum does not occur.

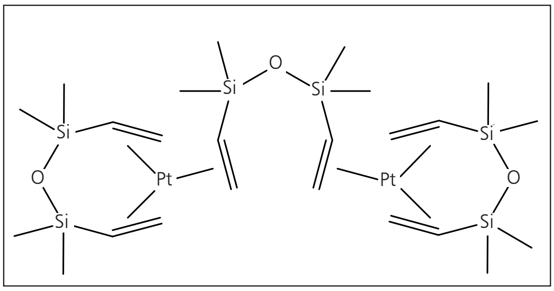


Fig. 13. Karstedt catalyst

10. Anticancer Drugs

As one of the heavier transition metals the exchange reactions of ligands bound to platinum are slow compared to many metals, but this is not always an undesirable feature. In order to influence the function of cells in the body, limited reactivity is required to allow distribution of the chemical within the body, and in many cases strong bonding to reactive sites is necessary to bring about therapeutic benefit. It is just these properties that have resulted in platinum giving rise to some of the most effective anticancer agents of modern times. The first in this series of compounds, cisplatin (**Figure 15**), is a remarkably simple compound first synthesised by Peyrone in 1844. However, it wasn't until the late 1970s that cisplatin was licensed for cancer treatment. Since then it has had a major impact on the treatment of testicular and ovarian cancer and is used widely in combination with other chemotherapeutic agents and other treatment modalities to benefit cancer patients (26). Other platinum drugs that have been licensed include carboplatin and oxaliplatin (**Figure 16**), extending the use of platinum agents to a wider group of tumours (27).

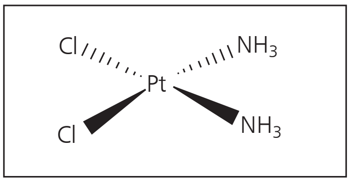


Fig. 15. cis-Diamminedichloroplatinum(II) – known as cisplatin

Sustainability

The increasing demand for platinum in a wide range of applications, some of which we have illustrated above, has in recent times been met by increased mine output. However, due to its high value in scrap, platinum has always been recycled where possible, for example, nitric acid gauzes, glass fibre bushings and reforming catalysts. In recent years, networks have been established for the recycling of automotive emission catalysts and this is playing an ever increasing role in the global platinum market. With the growth in the use of exhaust catalysts in developing countries and applications to a wider variety of engines, this can only increase. Although economic mineral resources of platinum are limited, it is clear that the market mechanisms exist to maintain supplies of platinum that will allow its unique benefits to be widely exploited now and in the future.

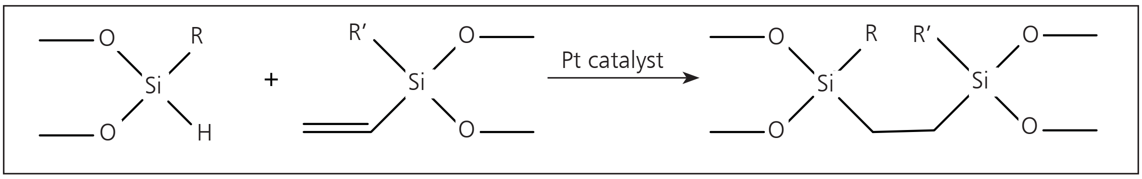


Fig. 14. Use of platinum catalysis in the preparation of silicone materials

Fig. 16. Platinum anticancer drugs

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