The Growing Industrial Use of the Platinum Metals

A QUARTER CENTURY OF TECHNOLOGICAL PROGRESS

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For the last twenty-five years Platinum Metals Review has recorded and, by the world-wide dissemination of relevant scientific and technical information, assisted in a remarkable growth in the industrial application of the platinum metals. This period has witnessed more new developments in the use of these metals than occurred in the whole of their previously known history, since they were first recognised nearly three centuries earlier.

When this journal was first published in 1957 the total world production of the platinum metals, including that from the Soviet Union, was estimated to be about 1,320,000 troy ounces. For the next three years or so this rate of production remained reasonably steady but subsequently increased, reaching 6,385,900 troy ounces by 1977. Now, in spite of the general recession, it is believed that total world production has increased to over 7 million troy ounces, and may even be approaching 8 million.

Established Uses for the Metals

A major part of this increase can be accounted for by the growth of applications which were established prior to this period, and to later developments that were associated with them. For example, a world-wide increase in the need for nitrate fertilisers over the last two decades has required a considerable increase in the use of rhodium-platinum catalyst gauzes for the oxidation of ammonia with air during the manufacture of nitric acid. In the period under review, processes that use noble metal catchment gauzes have been developed to recover much of the rhodium-platinum which was previously lost from the catalyst gauzes during use. In addition rhodium-platinum catalysts have been utilised for the economical control of the nitrogen oxides formerly emitted from nitric acid plants as a characteristic brown plume.

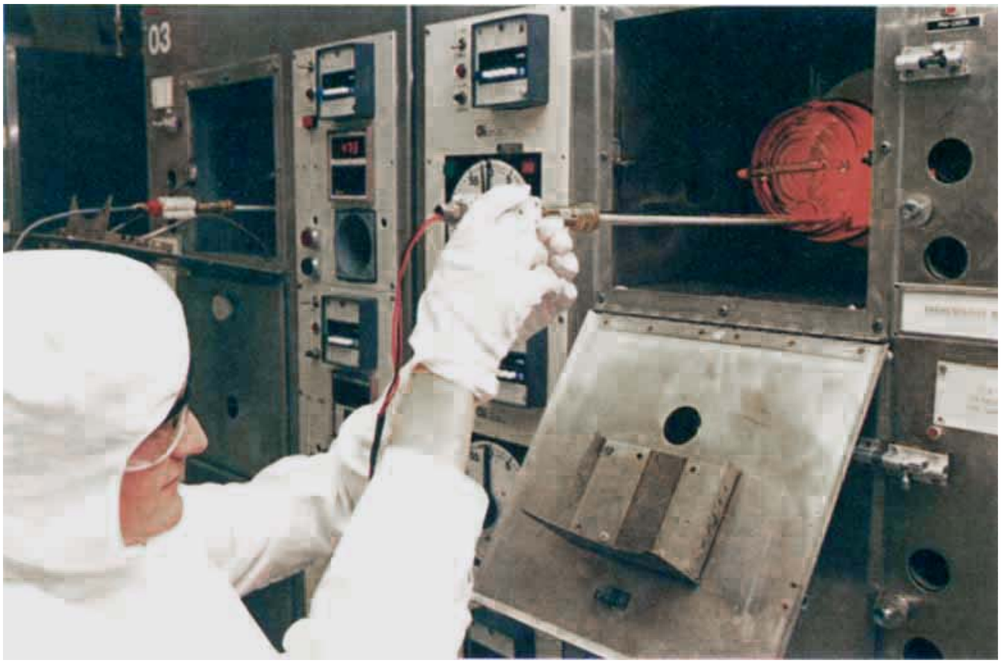
Again, there has been a great extension in the use of platinum alloys in glass making generally, while the increasing use of glass fibre for heat and sound insulation and in woven form for a growing number of fibre-reinforced products has resulted, of course, in a greater demand for the high-temperature alloys from which the fibre manufacturing equipment is constructed. More recently the development of fibre-optics for telecommunication purposes has depended upon the use of special high-purity platinum equipment for the production of the fibre.

The measurement and control of temperature by means of platinum alloy thermocouples and resistance thermometers may be considered to be one of the traditional uses for these metals, first for laboratory work and metal heat treatment but later for steel production and a wide variety of high temperature industrial processes. In recent years thick film platinum resistance temperature detectors have been produced using a variety of techniques, including sophisticated developments of the screen printing process used for the decoration of pottery and advanced by the requirements of the microelectronics industry. These temperature detectors can be manufactured by automatic processes at a low cost, and are both accurate and durable, and thus have potential for domestic and industrial applications.

In the electrical and electronic industries the

The oxidation of ammonia during the production of nitric acid is one of the most important chemical processes undertaken on a large industrial scale. The reaction, which is one of the most efficient known, is carried out in the presence of a rhodium-platinum catalyst, this usually being a woven gauze. Here new catalyst gauzes are being installed in an ammonia oxidation plant

The use of platinum for the manufacture of crucibles was established some time before the end of the eighteenth century, and such crucibles, together with other apparatus fabricated in platinum, became an essential requirement for accurate chemical analysis. Now, almost three hundred years later, modern analytical techniques still demand the use of crucibles made from the platinum metals. Here samples of steelmaking slag are being prepared for X-ray fluorescence analysis by fusion with a lithium tetraborate flux. The crucibles are 5 per cent gold-platinum, a material that is not readily wetted by the flux. As a result, when the glassy samples are poured from the crucible very little is retained and cleaning is largely unnecessary



The production of semiconductor materials requires the most careful control of both raw materials and manufacturing conditions, including processing temperatures. The measurement and control of high temperature electrical resistance furnaces is accomplished best by the use of platinum metals thermocouples, and here, at the laboratories of National Semiconductor Limited, the temperature profile inside the tube of a diffusion furnace at about 1200°C is being established by means of a profiling thermocouple unit. This consists of hot junctions placed to monitor to high accuracies the temperature at specific points in the hot zone of the furnace

In order to maximise the reaction, the surface area of catalysts for the control of noxious emissions must be as large as is practicable. Alumina pellets have a high surface area but tend to obstruct the passage of gases through them. In contrast, ceramic or metal honeycomb supports, with an alumina washcoat on the surfaces, allow the free passage of gases, are lighter in weight and do not suffer from attrition. Uncoated and coated supports are illustrated here, together with a partial section through a unit mounted in a steel container

uses of the platinum metals, in many different forms, are numerous and changing as the industries seek greater reliability and cost effectiveness, as well as new products. Platinum metals in one form or another serve as contacts in high and low voltage applications while both thin- and thick-film technologies make use of the properties of platinum metal compositions developed for specific purposes. Palladium and some of its alloys are widely used as conductor materials, while thick film ruthenium oxide systems are used as the basis of resistors.

Prior to 1957 platinum had been used in the oil industry for a few highly successful years. In 1949 supported platinum catalysts were first introduced for the up-grading of low octane petroleum naphthas to the high quality gasoline required for motor vehicles and piston engined aircraft, and this application grew rapidly in importance as the concept was proved and accepted. With a fuller understanding of the processes, and continuing research and development, the amount of platinum required in the catalyst has been significantly reduced, a recent major development being the introduction of bimetallic catalysts. Of course, the platinum catalyst is not destroyed during the reforming process, but it loses its activity over a period of time unless it is regenerated. This may be done in situ or after removal from the reactor. A further, and more economic, innovation involves the continuous withdrawal of very small batches of catalyst which are restored to fresh quality and returned to the system.

Newer Uses for the Platinum Metals

In recent years there has been an increasing demand for the platinum metals for applications that were non-existent, and in some cases probably undreamed of, twenty-five years ago. The Table shows the estimated annual consumption in the United States of America over the five year period from 1979 to 1983 of the principal platinum metals, the figures being based upon the report "Supply and Use Patterns for the Platinum-Group Metals" prepared by a distinguished panel set up to consider trends in the use of these metals with the object of providing background information to guide those involved in fixing the size of the U.S. national stockpile. (This most important work was reviewed recently, see *Platinum Metals Rev.*, 1980, **24**, (4), 143).

It will be seen that the greatest single use for platinum in the U.S.A., amounting to over 57 per cent of the estimated annual consumption, is for emission control catalysts for internal combustion engines. The possible harmful effects of such emissions and the suggested use of catalysts to limit them were reported as early as 1925, but the full dangers were not appreciated and at that time the technology necessary to eliminate or control them did not exist. Immediately prior to the inception of *Platinum Metals Review* a growing concern about many forms of industrial pollution was apparent, and in particular instances platinum catalysts were already finding limited use for their control; indeed the first two issues both noted their commercial use for oxidising hydrocarbon and organic compounds discharged from process ovens. In the last two decades there has been great progress in this utilisation of platinum metals for many forms of pollution control, and the Journal has always acquainted readers with the latest advances. During this time legislation to limit pollution in the United States, Japan and in some other parts of the world, has been enacted and vehicle emission control catalysts developed. Initially regulations required a reduction in the carbon monoxide and hydrocarbons, and this is currently achieved by the use of platinum catalysts to promote their oxidation to carbon dioxide and water. Nitrogen oxides cannot be made harmless by oxidation, but advanced control systems containing platinum catalysts promoted with rhodium achieve this objective by a reduction process.

In addition to the many applications for pollution control, the chemical process industry is continually developing new uses for platinum metals catalysts. These, supported on charcoals and aluminas, have become established over the last twenty-five years as an active, selective and

Estimated Annual Consumption in the U.S.A. 1979 to 1983				
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Application	Platinum	Palladium	Rhodium	Ruthenium
Emission control catalysts for vehicles	756,000	170,000	36,000	—
Catalysts for chemical processing	130,000	240,000	18,000	22,000
Electrical and electronic uses	127,000	356,000	15,000	43,000
Jewellery	100,000	18,000	6,000	6,000
Glass and glass fibre manufacture	70,000	—	16,000	—
Catalysts for ammonia oxidation	56,000	1,000	5,000	—
Dental and medical applications	34,000	125,000	—	—
Catalysts for petroleum processing	25,000	8,700	600	150
Fuel cells	16,000	—	—	—

cost effective means of hydrogenating and dehydrogenating chemical intermediates in the manufacture of plastics, man-made fibres, rubbers, pesticides, dye-stuffs and pharmaceuticals, and in the purification of gas streams.

The recent increases in fuel and feedstock prices have put mounting pressures on the chemical industry to conserve resources. Homogeneous platinum metals catalysts are finding growing favour because their improved selectivity gives higher yields, and they operate at lower temperatures and pressures than base metal homogeneous catalysts. A good example of their application is the low pressure oxo process to produce aldehydes such as butyraldehyde using a soluble rhodium complex as catalyst.

The success of these new processes confirms that in so many respects this is undoubtedly the age of the platinum metals catalyst.

It is interesting that during the last twenty-five years there has been greater progress in the understanding and exploitation of the chemical and electrochemical properties of the platinum metals than the metallurgical. For instance, work on the mechanism of the electrochemical protection of base metals by coatings of platinum has led to the widespread development of systems for the protection of marine structures and oil well casings and pipe-lines against corrosion, although it should perhaps be noted that the principles of cathodic protection had been understood as early as 1824. The use of platinum supported on titanium as anodes for this purpose dates from the late 1950s and with advances in the technology platinised titanium became the most important anode material for the cathodic protection of ships, with tantalum and niobium also finding application as a support. In addition, metallic anodes are employed in industrial electrolytic cells for the manufacture of chemicals, particularly for the production of chlorine and sodium hydroxide from brine. Initially the noble metal was platinum or iridium-platinum but now dimensionally stable anodes of titanium coated with ruthenium oxide are most frequently employed.

The electrochemical properties of the platinum metals are also finding growing applications in medical detection and stimulation devices, while their application in fuel cells for the direct conversion of chemical energy into electrical power—first reported in the literature as early as 1839—has been advanced by the need for light weight power sources for space projects. Fuel cells combine high thermal efficiency with low environmental pollution, and multi-megawatt generator systems may now be close to commercial success in the United States of America and Japan.

At this C.W. Hüls plant, at Marl, West Germany, a special rhodium co-ordination compound manufactured by Johnson Matthey Chemicals is used as a homogeneous catalyst for the low pressure hydroformylation of propylene to n- and iso-butyraldehydes by a process licensed jointly by Johnson Matthey, Davy McKee and Union Carbide. This plant has a design capacity of 250,000 tonnes per year of the more valuable n-butyraldehyde. Worldwide 13 plants with an annual capacity for butyraldehydes of 1·1 million tonnes are operating or under construction

Cisplatin, the first generation platinum anti-tumour drug is manufactured by Johnson Matthey Incorporated under the most carefully controlled, clinical conditions. Early trials on a number of newer platinum compounds suggest that some may offer therapeutic advantages particularly in terms of reduced toxicity

In the same time new electroplating baths for depositing ruthenium, palladium and rhodium have been introduced and applications occur in the electrical and electronics field. Molten salt electrolytes are now used for a number of specific platinum metals plating applications, a notable example being the production of platinum aluminide coatings for the protection of gas turbine components.

Perhaps the most outstanding achievement in the metallurgy of the platinum metals during this period has been the development and successful production of dispersion strengthened platinum and a number of its alloys. These materials contain a uniform distribution of extremely fine refractory precipitate dispersed throughout the mass and the mechanically worked material develops a highly fibrous recrystallation structure on annealing and is unusually stable. In this condition it is many times more resistant to creep failure at elevated temperatures—thus when under stress at 1400°C dispersion strengthened pure platinum can endure for at least twice as long as an alloy of platinum with 40 per cent rhodium, which is generally accepted as the strongest commercially available high-temperature alloy. Such materials can be used with advantage for the construction of equipment required to operate in air at very high temperatures; for example, ZGS rhodium-platinum and ZGS platinum have found widespread use in the production of optical and fibre glass where their high strength and resistance to contamination have resulted in considerable process improvements.

Another metallurgical advance offering new applications potential is the development of platinum-enriched superalloys. The strongest conventional superalloys have relatively poor corrosion resistance, particularly in sulphidising atmospheres and the addition of platinum metals can significantly improve their performance in this respect.

While hardly an industrial application, the present use of *cis*-dichlorodiammineplatinum(II) in cancer therapy is the result of outstanding research and development following the discovery in about 1964 that certain inorganic complexes of platinum exhibited interesting biological effects. The present drug has made a significant contribution to the survival of patients suffering from ovarian and testicular tumours. Phase 1 clinical trials are now being undertaken on a number of newer platinum compounds, and it now seems possible that a second generation drug will result. A short article outlining current work in this important field is presented later in this issue.

An Assured Future for the Platinum Metals

Whatever may be the achievements of the past quarter of a century, however, it is certain that tomorrow's world will be very different from today's. Undoubtedly, solutions will have been found for at least some of the practical problems that at present beset the world, for there is now a greater awareness of the need to apply basic knowledge to this end. The history of platinum has shown it to be a most useful pioneer material, playing an often crucial role in research investigations, or during the establishment of a commercial process, and it is reasonable to expect this trend to continue. If any prophesy is safe it is that catalysts for removing carbon monoxide, hydrocarbons and nitrogen oxides from the exhaust gases of internal combustion engines will have been overtaken by other major uses of the platinum metals in the year 2007. In the motor industry, by then catalysts may be incorporated in the combustion chamber to control pollution at source or new types of motive power may be in use, possibly electrically powered from fuel cells or external combustion engines such as the Stirling engine using a noble metal catalyst to burn the fuel cleanly and efficiently. Whether the largest use will be then for solar energy conversion or storage, in high strength superalloys, in advanced electronics systems, or for one of the many potential applications at present being investigated in academic and industrial research establishments, or even for some yet unconsidered purpose, will become clear only with the passage of time.