Fifty Years of Research on the Platinum Metals

By A. R. Powell, F.R.S.

Among the industrial concerns who were quick to appreciate the value of research to their business and future prosperity must be numbered the firm of Johnson Matthey. Before the end of World War I, and just after achieving the centenary of their foundation, the then directors of the company decided to establish a small Research Department and the present writer was invited to organise and develop it.

At this time industrial research in Great Britain was on a very small scale, and it was not until the early nineteen-twenties that a real impetus was given by the initial steps taken by government and industry in collaboration to establish the early Research Associations.

At this time too the output of platinum and its allied metals was by today's standards extremely small and their industrial uses were few. The greater part of the world's supplies still came from Russia, although increasing amounts were becoming available from the Mond process of recovering nickel from the nickel-copper ores of Sudbury, Ontario, and for some years these had been refined by Johnson Matthey.

The production of nitric acid by the oxidation of ammonia over platinum gauze catalysts was yet to be established at Billingham; viscose rayon production by Courtaulds and others, needing platinum alloy spinnerets, was in its infancy, and the use of thermocouples was virtually confined to heat treatment processes and laboratory work. The melting of glass in platinum, originating with Faraday's studies, had not yet been adopted in industry, while the demand for electrical contacts in the platinum metals was chiefly represented by the automobile magneto.

In 1918 the methods used for refining, melting and working platinum differed very little from those used in the middle of the nineteenth century. Repeated precipitation of ammonium chloroplatinate with intermediate calcination and re-dissolution of the

The very early Ajax-Northrup high frequency induction furnace acquired in 1919 for research into the melting of platinum. The problem of suitable crucible material was solved by the use, for the first time, of zircon

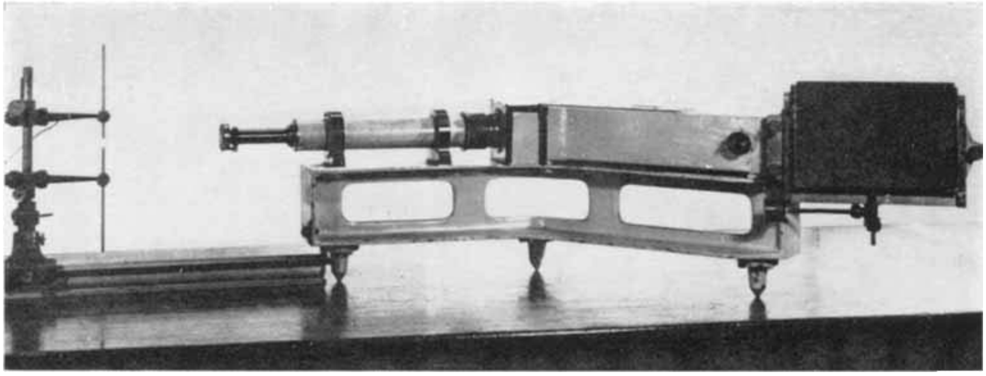
On February 11th, 1918, A. R. Powell, a young man of 23, was invited by the directors of Johnson Matthey to join the company and to establish a Research Department. From small beginnings the department grew over the years, and Mr Powell remained at its head until 1954, when he became Consulting Research Chemist to the company. He retired from active duties in 1960 but is still associated with the laboratories on a consulting basis. He was elected a Fellow of the Royal Society in 1953 for his work on the chemistry of the platinum metals. In this article Mr Powell looks back on fifty years of research in this field and contrasts some of the methods and equipment of the early days with modern research facilities.

crude metal in aqua regia formed the basis of the method for obtaining the pure metal, which was then prepared for working either by melting with an oxy-hydrogen flame in a furnace made from two blocks of calcined marble, or by consolidation of platinum powder by heating and forging into an ingot. Lime-melting was used chiefly for making platinum alloys for electrical contacts and scientific apparatus, while powder metallurgy ingots were used for making pure platinum sheet for crucibles, dishes, electrodes, large vessels for chemical manufacturers and for making pure platinum wire for thermocouples and resistance thermometers.

The Beginning of Induction Melting

With the invention of the Ajax-Northrup high-frequency induction furnace just after the end of the war, Johnson Matthey were attracted to the feasibility of its use for melting platinum and a furnace was purchased late in 1919, the first to be used in this country. The question of what kind of crucible to use for the melting operation was the first major problem put to the young Research Department and was solved in a relatively short time by the use of purified zircon sand which was carefully ground and graded into different grain sizes, which were re-blended in suitable proportions with a temporary binder and water to give a paste which was shaped on a potter's wheel; after drying and

Today the research metallurgists have available to them modern vacuum melting furnaces for investigations on the platinum metals and their alloys



The Hilger medium spectrograph purchased in 1920, initially for the determination of iron in rhodium. Since that time a wide range of spectrographic instruments has been installed

firing at the full heat of an oxy-gas burner, crucibles were produced in which up to 50 melts each of 100 oz of pure platinum were made before failure. These were the first zircon crucibles ever made and they were used for the first melting of platinum on a commercial scale in an electric furnace.

The First Spectrograph

Investigations on the accurate measurement of high temperatures with platinum:rhodium-platinum thermocouples in 1920 showed that many couples gradually altered in calibration during long use. The presence of iron in the rhodium used for alloying was suspected but chemical methods of analysis did not yield convincing results. In that year the company therefore purchased its first spectrograph—one of the first batch produced by Adam Hilger—and the determination and thence the elimination of the iron impurity were quickly achieved.

The remarkable improvement in purity of rhodium produced by the new process incited a thorough investigation of the older processes of refining all the platinum metals and during the next four years the Research Department was engaged on this work. New methods for refining ruthenium, osmium and iridium to spectrographic purity were first developed and attention then turned to a study of platinum refining. A number of improvements were made to the processes, and the resulting platinum had an α value of 0.003922, higher than that of any platinum available commercially at the time and indicating a very high degree of purity.

At about this time the Research Laboratory made its first move, taking over two more rooms in the Hatton Garden premises, and increasing its small staff. Among these were E. C. Deering—later to become a director and eventually chairman of the company—and E. R. Box, later to become general manager of the company's factories in the Stoke-on-Trent area.

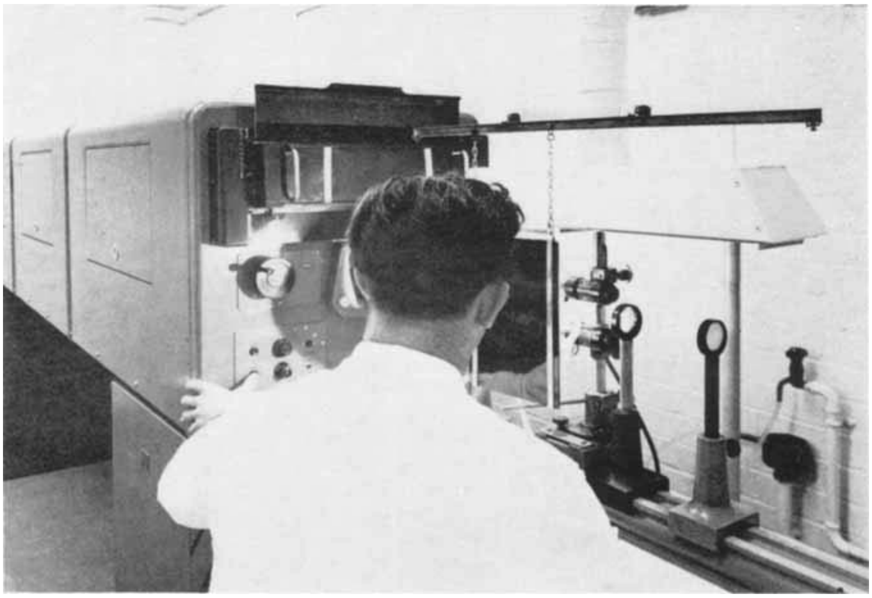
Refining of South African Platinum

The next major problem to be tackled by the Research Department was the treatment of the South African platinum ores. During the years 1924 to 1928 large deposits of platinum-bearing rocks had been discovered all over the Transvaal, but containing payable amounts of platinum only in certain areas mainly in the neighbourhoods of Lydenburg, Potgietersrust and Rustenburg. In these ores the platinum metals were associated with the sulphides of nickel, copper and iron and to that extent resembled those of the Sudbury district in Canada, but were much poorer in copper and nickel and much richer in the platinum metals. Considerable technical problems arose in devising suitable methods of treatment, while the proportion of values recovered compared very unfavourably with that obtained in the working of alluvial deposits. Large samples of the concentrates were therefore sent by the mining companies concerned to the Krupp Grusonwerk at Magdeburg, to various American refiners, to the Chemical and Metallurgical Corporation at Runcorn and to Johnson Matthey.

In 1926 work started in the Research Laboratory to develop a process for treating these sulphide concentrates, and by the following year a successful and economic route had been worked out by a team comprising E. C. Deering, E. R. Box and the writer. This was the only workable process developed, and led to Johnson Matthey becoming the sole refiner of South African platinum.

Electroplating Investigations

As the hopes of an increasing output of platinum metals from South Africa began to materialise in the late nineteen-twenties attention was turned to investigating possible new uses for the metals. One of the first problems tackled was the development of commercial electrolytes particularly for plating with rhodium and platinum, the main contributor to this work being E. C. Davies, who had joined us in 1929. Amminonitrite baths had been proposed in the United States for plating thin deposits of rhodium on articles of cheap jewellery to produce a silver-like finish but these proved to be inefficient during prolonged use. Baths based on rhodium sulphate or phosphate, or mixtures of these compounds, were then developed both in this country and in the United States. The sulphate bath produced by Johnson Matthey by a new process proved very satisfactory not only for depositing thin bright films of rhodium but also for building up heavy deposits on relatively large and complicated surfaces. Since the latter years of the last century it was known that thin platinum deposits could be obtained from a complex amminophosphate bath but these required much burnishing to give a satisfactory finish. A new bath based on sodium hexahydroxyplatinate developed in the Research Laboratory was found capable of plating bright fairly thick platinum deposits and this was used for this purpose for many years. Recently, however, it has been replaced by a more stable bath based on a sulphatonitrite derivative of platinum.



One of the modern spectrographs, a 3.4 metre Ebert grating instrument, which facilitates the detection and accurate determination of trace impurities in the platinum metals

Research on the electrodeposition of the platinum metals began in 1929 with very simple equipment. Today research in this field is aided by precise electrical control equipment

A process for palladium plating was also developed but no success was achieved in attempts to deposit iridium and ruthenium.

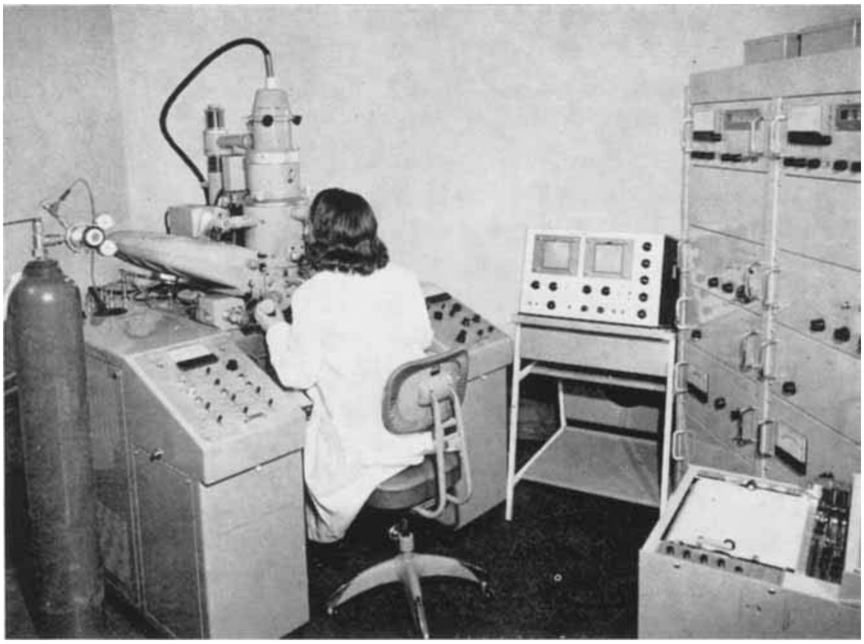
Another move took place in 1929 to more roomy laboratories, and about this time several staff changes also occurred. E. C. Deering left the Research Department to become manager of the platinum refineries erected at Brimsdown, F. E. Kerridge arrived to assist with ceramic research activities, while a little later H. E. Bennett joined us from the National Physical Laboratory to strengthen the metallurgical section. A few years later F. M. Lever joined the chemical section, while in 1938 J. C. Chaston came to us as head of the metallurgical section.

Alloys for Spinnerets

Artificial silk made by the viscose process used iridium-platinum spinnerets in its early days but with increasing scarcity of iridium and rising prices for platinum attention was turned to the use of hard platinum-gold alloys. As a result of a later re-investigation in the laboratory of the platinum-gold system by J. C. Chaston, A. S. Darling and R. A. Mintern the optimum composition for this alloy and the correct conditions for working and heat-treatment to obtain the desired structure and hardness were established. Later it was found possible to reduce the cost of the alloy and improve its properties by adding a small proportion of palladium. In later years this was replaced by a small addition of rhodium.

High Temperature Properties

About this time fibre glass was being developed and an extensive research was undertaken to find the most suitable platinum alloy for making the forehearths or bushings required to produce the glass fibres. These bushings operated at temperatures in the region of 1400°C, where appreciable loss of platinum may occur by volatilisation. The most satisfactory alloy for this purpose was found to be rhodium-platinum, all other alloys being less satisfactory because of oxidation of the alloying metal, excessive loss by volatilisation, or hot-shortness of the welds. Heated electrically at 1450°C in a brick flue allowing a continuous uprising current of air, both platinum and 10 per cent rhodium-platinum alloy lost 10 per cent of their weight in six weeks, most of the precious metal lost condensing on the brick nearest the hot metal in the form of continuously growing crystals while the remainder collected on the cooler brick surfaces as a black powdery deposit containing about 3 per cent of oxygen; there was little difference in the amount of metal lost by the pure platinum and the rhodium alloy, and the condensate from the alloy contained about the same percentage of rhodium as the original alloy. In a steam



The study of the distribution and identification of phases in an alloy system was formerly a lengthy and tedious process. The electron probe micro-analyser makes it possible to establish the structure of an alloy accurately and rapidly

atmosphere, as used in making glass fibres, metal loss by evaporation over the same period was very small. These experiments showed that volatilisation of platinum at high temperatures was due to the presence of oxygen and was not appreciably diminished by alloying with rhodium; the alloy, however, had the greater mechanical strength when hot.

The knowledge gained in these experiments on the behaviour of platinum at high temperatures was later put to good use in designing wire-wound furnaces to operate up to 1600°C.

The long standing question of finding an adequate and permanent home for the Research Laboratories was finally settled in 1938, when a completely new building, with ample space for expansion, was erected at Wembley. A great deal of new equipment was acquired to enlarge the scope of the work, and the department was able to embark on a great many more research projects.

With the rapid development in the early forties of the immersion thermocouple in the steel industry it was found that in continuous use the wires, especially the pure platinum wire, tended to become brittle. This was established in the laboratories to be due to the presence of sulphur-bearing oil in the protective sheaths. This caused the formation of silicon sulphide vapour which lost its silicon to the platinum and so liberated sulphur to continue the reaction.

A great deal of effort also went into the whole field of thermocouples, both on the score of refinements in methods of calibration and in the development of new alloy combinations such as iridium-platinum against gold-palladium for accurate measurement in the medium temperature range.

Many investigations were also made during and after the war years on the properties, and particularly the creep properties, of a number of binary and ternary platinum alloys.

In 1954 the writer was succeeded as Research Manager by Dr J. C. Chaston but continued to function as the company's Consulting Research Chemist.

Constitutional work carried out included the investigation of the gold-platinum diagram already mentioned (an essential foundation

Research into the mechanism of chemical reactions involving platinum group metal catalysts, and into the variables that need to be controlled, is carried out in apparatus of this type

led to the study of their potential uses in the field of homogeneous catalysis.

The company's activities on the heterogeneous catalysis front were greatly expanded to meet the rapidly growing demand for such catalysts from the chemical industry and are now in the charge of Dr G. C. Bond who joined the department in 1962.

In 1965 the services of Dr Chaston were lost by his retirement, and he was succeeded as Research Manager by Dr Lever.

for the development of improved spinneret alloys), the ruthenium-palladium system and in more recent years parts of the molybdenum-platinum system (of importance to the life and performance of platinum-clad molybdenum in the glass industry) and also parts of the ternary gold-rhodium-platinum system.

Other projects in the metallurgical field included the development of new contact alloys, and considerable work on the equiatomic per cent cobalt-platinum alloy that has such outstanding properties as a permanent magnet material.

In the chemical section of the department, considerable improvements in the methods of analysis of the platinum metals aided the refining activities of the company, and work on complexes of the platinum metals, particularly that by Dr F. M. Lever on the ammino-compounds of ruthenium, and later work by the writer and others on the hydrido-compounds of rhodium and organometallic compounds of all the platinum metals,

A project of interest to the glass industry, recently completed and published in this journal, concerned the wetting properties of a number of platinum alloys in contact with molten glass, while a further major study—also reported on in this issue of *Platinum Metals Review* by Dr Darling and his colleagues—has been the successful search for a dispersion-hardened platinum that would retain greatly enhanced strength properties at very high temperatures.

To look back over a continuous span of half a century of association with research on such fascinating metals as those comprising the platinum group is both a sobering and stimulating experience given probably to few men. Progress in research facilities—particularly in instrumentation—has of course been enormous by comparison with the limited resources available in 1918, but the costs of research have naturally risen proportionately and one needs today to give long and careful thought to the selection of new projects and their likely benefits.