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PLATINUM METALS

E. A. Smith

THE PLATINUM METALS

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CUTTING A MOUNT FOR A PLATINUM ORNAMENT

By courtesy of the Goldsmiths' and Silversmiths' Company, Ltd., London

(1462K) [*Frontispiece*

PITMAN'S COMMON COMMODITIES
AND INDUSTRIES

THE PLATINUM METALS

BY

ERNEST A. SMITH
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LONDON
SIR ISAAC PITMAN & SONS, LTD.
PARKER STREET, KINGSWAY, W.C.2
BATH, MELBOURNE, TORONTO, NEW YORK

PRINTED IN GREAT BRITAIN
AT THE PITMAN PRESS, BATH

PREFACE

THE second decade of the twentieth century has brought to the average man a general, if somewhat vague, realization of the importance of the precious metal platinum, and its applications both in science and industry.

The properties and industrial applications of gold and silver, the oldest of the so-called precious metals, have long been known and appreciated. But when the general reader comes to platinum he finds himself to be on less familiar ground.

This is partly accounted for by the fact that platinum, from an industrial standpoint, is a comparatively new metal, and whilst it has long been familiar to the scientist and utilized by him, it is only within quite recent years that it has come more prominently before the general public and its industrial value duly appreciated.

Owing to the great difficulties which had to be overcome in freeing platinum from the other metals with which it is invariably associated in nature, it was many years after its discovery before the metal found any practical application.

Following its subsequent production on a commercial basis, the intensive application of science in industry in recent years has emphasized its value and fundamental importance in chemical and other manufacturing processes, a fact that was brought into prominence during the war period by the urgent demand for platinum for munition purposes.

This demand led to the conservation of platinum by the Government for this purpose, and incidentally caused much more frequent reference to be made to the metal in the technical and general press.

The growing popularity of platinum jewellery during the past two decades has also done much to make the metal more familiar to the general public.

Moreover, the platinum industry had its birth, and has been considerably developed, in Great Britain, and has now assumed an importance which has a very direct bearing upon the progress of the industries in which the metal is utilized.

Considering, therefore, the prominent place that platinum is now taking in modern industry and in scientific research, and is still more destined to take in the future, it may well take its place with gold and silver in a series of books, such as the present, dealing with commodities that are serving useful purposes in many directions and subscribing to the well-being of the community.

The work has been entitled *Platinum Metals* because, whilst it deals primarily with platinum itself, it includes those lesser known metals invariably associated in nature with platinum, and have certain commercial value of their own, and constitute what is commonly known as the Platinum Group, which cannot well be excluded when dealing with the metallurgical treatment of platinum and its industrial applications.

In view of the appeal which it is hoped this series will make to those who are beginning to take an interest in the raw materials and finished products of present-day industries, especial attention has been devoted to the many scientific and industrial applications, not only of the platinum metals in the metallic condition—either alone or alloyed with other metals—but also to the various compounds which have found important uses in photography and for other purposes.

There is no pretence of dealing with the subject of platinum and its allied metals exhaustively in such a small work, but it is hoped that sufficient information has been given to show the causes which have operated in the course of time in "advancing platinum, the once despised by-product of the alluvial gold miner, to the rank of the most precious of the useful metals."

A number of books and treatises duly mentioned in the text have been consulted for data reproduced in these pages, and the author gratefully acknowledges all information derived from these sources.

The author also wishes to express his indebtedness to the several firms who have supplied blocks for the illustrations, and whose names have been given in the text.

Especial thanks are due to the Goldsmiths' and Silversmiths' Company, Ltd., London, for the frontispiece and other photographs illustrative of the working of platinum for jewellery purposes.

ERNEST A. SMITH.

BIRMINGHAM,
1924.

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CHAPTER I

HISTORICAL SUMMARY OF PLATINUM[1]

METALS, on account of their wonderful utility, have from very early times been regarded as one of the most valuable acquisitions of civilized man.

In modern times they have been produced on so vast a scale, and have found such wide application in industry and art, that it is now generally recognized that an adequate supply of useful metals is one of the principal factors in industrial progress.

This being so, it will readily be appreciated that considerable importance attaches to the discovery from time to time of new metals, especially when they are subsequently found to be of value for industrial purposes.

Amongst the metals discovered in more recent times platinum, and its allied metals, must take a prominent place since their importance to civilized man can hardly be over-estimated.

The commercial production of platinum during the Victorian era marks a special epoch in the history of metals, as it was soon found that platinum possessed remarkable chemical and physical properties such as are possessed by no other single metal, and which at

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[1] Many of these historical data are derived from Roscoe & Schorlemmer's *Chemistry*. Vol. ii—The Metals.

once gave it a unique position amongst all the known metals.

As a consequence platinum has come rapidly into prominence during the past few decades, and at the present time it occupies a very conspicuous place amongst the useful metals, and is in such increasing demand that the limited supply available from all the present known sources is quite inadequate to meet industrial requirements.

Platinum belongs to that small group of metals which on account of their permanency were termed precious or noble by the alchemists to distinguish them from the so-called base metals, like lead and copper which are readily corroded by exposure to atmospheric influences. Unlike most of the metals now in common use platinum, as already mentioned, remained unknown until comparatively recent times, consequently a study of its history transfers us at once into a modern era of metallurgical science when chemical and physical science were available to assist in its development.

There is no conclusive evidence that platinum was known to the ancients, even to those familiar with gold, a metal that platinum in many respects resembles; neither is there any evidence that it was known to the alchemists.

What appears to be the first authentic reference in European literature to the heavy white metal that was subsequently christened platinum is a statement by Julius Scalinger in his book *Exercitations Exotericoe de Subtilitate*, published about 1600, wherein he speaks of a white infusible metal found in the mines of Mexico and Darien (Panama).

Since it was subsequently proved that platinum occurs in this district in payable quantities, it appears very probable that this was the metal referred to.

The metal was, however, first definitely mentioned by name by Don Antonio de Ulloa, a Spanish naval officer, who describes it in the account of his travels to South America with a French Astronomical Mission in 1735, and entitled *A Narrative of a Journey to South America.* Although the discovery was made known at the time, a full account of it was not published until 1748, thirteen years later.

In this account Ulloa, to whom the discovery of platinum is now usually attributed, refers to the metal under the name of "platina" as a definite metallic mineral which occurs in the Choco district of Colombia, and is found in admixture with the gold of that district.

Platinum had, however, apparently been known in South America long prior to Ulloa's account of it, as it would appear from modern discovery that the aborigines of the region had observed the white metallic grains mixed with native gold and collected them, and became fairly skilled in the manufacture of simple domestic ornaments from native platinum, such as they had been accustomed to make with native gold. Many such crude works of art have been found in ancient graves in South America, some even composed of platinum overlaid with gold by welding together the two metals.

Platinum received its name in consequence of its white appearance and close resemblance in this respect to silver, the Spaniards having called it *platina del Pinto,* "*platina*" being the diminutive of "*plata*" the Spanish for silver, and Pinto the name of the river in the auriferous sands of which the metal was first found.

Owing to its great weight, and being at that time less valuable than gold, the early Spanish gold-seekers used platinum to counterfeit gold by covering platinum with a thin layer of the then more precious metal.

For this reason the Spanish Government took all possible precautions to prevent the exportation of platinum, and even ordered it to be thrown into the sea.

It would be idle to speculate as to how much of the precious metal, that is so much sought after at the present time, was thus lost in the drastic measures taken to prevent it from being fraudulently used to be covered or alloyed with gold.

In 1741, seven years before the publication of Ulloa's description of the metal, samples of native platinum, said to have been derived from alluvial deposits at Carthagena in Colombia, were brought to England by Charles Wood, an assayer of Jamaica, to whom the credit of the discovery of platinum is sometimes, though erroneously, attributed.

To Wood, however, must be ascribed the credit of having first brought the metal to Europe, but owing to its refractory nature it could not at that time be melted and utilized for industrial purposes, even if a sufficient quantity had been available, and in consequence it did not become generally known.

Indeed, little appears to have been done with Wood's samples until some years later when the crude metal was carefully examined by the well-known chemist William Watson, who regarded it as a semi-metal or metalloid, and described its properties in the *Philosophical Transactions of the Royal Society*, London, in 1750, two years after the appearance of Ulloa's account.[1]

When the crude metal was first introduced into Europe it was compared with gold and was actually brought into the market under the name of "white gold."

Further investigations on crude platinum were carried out in 1752 by Scheffer, assayer of the Stockholm Mint,

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[1] *Treatise on Chemistry*, Roscoe & Schorlemmer. Vol. ii—The Metals.

who obtained his material from the gold-bearing sands of the river Pinto in Colombia. He considerably advanced the knowledge of platinum by showing that it is insoluble in nitric acid or any single acid, but is completely soluble in *aqua regia*, a mixture of nitric and hydrochloric acid. He showed also that it is infusible at the highest temperature attainable in the furnaces then known, but that it is capable of forming fusible alloys with other metals and with arsenic.

A notable contribution to the chemistry of platinum was made in 1757 by Marggarf, one of the best analysts of the day, who showed that platinum is precipitated from its chloride solution by the addition of potassium or ammonium salts, but not by sodium salts. This reaction subsequently proved to be of valuable service in the commercial preparation of the metal and opened up a new era in the metallurgical treatment of crude platinum, and it now forms the basis of all modern methods of extracting and purifying the metal.

Next came the researches on platinum by Macquer and Beaumes which were published in the *Memoirs of the Paris Academy* in 1758. The most important new fact observed by these chemists was that platinum can be fused in the sun's rays focused by a powerful lens or burning glass. This is the first record we have that platinum, in common with all other metals, can be rendered molten if a sufficiently high temperature is employed, and the possibility of melting it was a question of considerable industrial importance.

Another diligent worker on platinum about this time was Count von Sickingen, the representative of the Palatinate at the Court of Paris, who is said to have been the first, in 1772, to prepare a small quantity of the metal and to roll it into foil and draw it into wire, and also to show that when alloyed with a fair excess of silver, platinum is to some extent soluble in nitric acid.

A further valuable addition to the knowledge of platinum was made in 1777 when Bergmann, the renowned Swedish chemist, further investigated Marggarf's reaction and explained more fully the nature of the changes which occur when a solution of platinum is treated with the alkalis.

In 1784 Archard recorded that malleable platinum was obtained by heating an alloy of platinum and arsenic sufficiently strongly to expel the volatile arsenic and leave a malleable mass of platinum, and with metal prepared in this way he manufactured what in all probability was the first platinum crucible. Thus the suitability of platinum vessels for chemical analysis was early recognized.

For some years subsequent to 1787, Janetty and Chabaneau, working silversmiths of Paris, employed this method of preparing sheets of the metal and became celebrated for their platinum work.

The platinum produced by this method, however, was very impure, and spongy ; it failed to withstand high temperatures, and was also unsatisfactory for crucibles to withstand the fusion of alkaline carbonates.

By this time the importance of the reaction discovered by Marggarf, whereby the double chloride of platinum and potassium was obtained on the addition of potassium chloride to a platinum solution, appears to have attracted further attention.

Up to this time, however, no satisfactory method for the manufacture of platinum on a commercial scale appears to have been devised.

It is true that a few platinum crucibles and other laboratory vessels were being manufactured by welding the spongy platinum resulting from the ignition of the platinum-arsenic alloy used by Archard, but the eighteenth century closed without seeing the establishment of a platinum industry.

The crude metal was difficult to obtain and very expensive, as the only known source of platinum was South America, from whence the whole of the metal used in the preceding researches, as well as many of those carried on at a later time, was obtained.

With the dawn of the nineteenth century more serious attempts were made to produce platinum commercially, but progress was slow until the supply of the crude metal was augmented by the discovery of the world renowned deposits in the Ural mountains about the middle of the century.

Knowledge respecting the chemistry of platinum was now sufficiently advanced to furnish the capable investigator with methods of preparation that gave a prospect of success when applied on a large scale, and such investigators were soon forthcoming, and the manufacture of malleable platinum ingots by forging the spongy metal at a white heat marks the next historical step in the development of the metal.

As previously stated, many attempts to render platinum malleable and ductile were made during the latter part of the eighteenth century, but none were commercially satisfactory, and the nineteenth century had dawned before the platinum industry was actually founded as the result of English enterprise.

Charles Knight in 1800 devised a process for the commercial production of the metal which consisted in dissolving the crude metal in *aqua regia,* precipitating the platinum with ammonium chloride, packing the dried precipitate into conical moulds of fireclay and strongly heating to expel the ammonium and chlorine and thus obtain a residue of metallic platinum.

The metal so prepared consisted of a coherent spongy mass which at a white heat could be hammered or welded into a compact malleable ingot that could be worked into sheet and various forms.

Knight published a description of his method in *Tilloch's Philosophical Magazine* for 1803, but it appears that between the years 1800 and 1809, Thomas Cook, a relative of a member of the well-known firm of Messrs. Johnson, Matthey & Co., platinum refiners of London, was also employed in working on platinum, and had discovered (whether independently of Knight is uncertain) a similar method for preparing and consolidating the sponge.[1]

Knight's process was afterwards perfected and elaborated by Dr. Wollaston, who described it in the Bakerian Lecture of the London Royal Society for 1828, and on that account it has from that time been commonly known as " Wollaston's Process."

Although identical in the main features with Knight's method of preparation, Wollaston's process is distinguished from it in several important particulars, mainly in conditions of manipulation in consolidating the platinum sponge that result in the production of a purer and more satisfactory metal, and in consequence Wollaston's was the method by which all malleable platinum was manufactured up to the year 1859 when Hare's and Deville's process of melting the metal, described later, came into use.

The interest aroused in the new metal by the beginning of the nineteenth century led to a series of investigations on crude platinum by the most eminent metallurgists of the day, among whom may be mentioned Berzelius, Vanquelain, and more especially Wollaston, and

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[1] Roscoe & Schorlemmer, *Treatise on Chemistry*. Vol. ii—The Metals.

subsequently by Deville and Debray and George Matthey.

Further examination of the platiniferous grains by these investigators soon displayed the fact that the crude metal was not composed entirely of platinum, but consisted of a complex mixture of several metals which, whilst somewhat similar to platinum, had very distinct and valuable properties of their own.

The result of research not only greatly assisted the development of the technical chemistry of platinum itself, but early led to the discovery and isolation, in a more or less pure state, of the five other metals known as the platinum group, viz., Iridium, Palladium, Rhodium, Ruthenium, and Osmium.

In nature they all occur associated together in what is commonly known as *platinum ore,* and they are on this account usually spoken of as *the platinum metals.*

Platinum ore, or more correctly native platinum, contains all these elements in the metallic state, and they are very rarely found in any other condition.

As will be seen from the following details, all the additional five metals, with the exception of ruthenium, were discovered in the year 1804, a year that will always be memorable in the history of the " platinum metals."

Platinum, chemical symbol, Pt. Platinum was probably first recognized as a new metal in 1735, by Don Antonio de Ulloa, in the alluvial deposits of the river Pinto in the province of Choco, Colombia (South America).

Rhodium, chemical symbol, Rh. This metal was discovered by Wollaston in 1804, and was so named by him from the Greek *ῥόδον,* a rose, in recognition of the beautiful rose colour of aqueous solutions of its salts.

Palladium, chemical symbol, Pd. This metal was also discovered by Wollaston in 1804, and named palladium from the planet Pallas which had been discovered by his friend Olbers in 1802.

Osmium, chemical symbol, Os. Osmium was first identified as a new metal by Tennant in 1804, who derived its name from the Greek ὀσμή, a smell, on account of the odour of its volatile tetroxide.

Iridium, chemical symbol, Ir. Iridium was first identified as a new metal by Tennant in 1804, who suggested its name in recognition of the different colours exhibited by its salts.

Ruthenium, chemical symbol, Ru. The name ruthenium is due to Osann who obtained what he believed to be the oxide of a new metal in 1828, and this was confirmed by Claus in 1845, who retained the name used by Osann.[1] It is a difficult metal to isolate, and this fact probably accounts for its later discovery.

The discovery of these five new metals created considerable interest amongst chemists and metallurgists, but for many years after their isolation very little was accurately known of their special properties owing to the difficulty attending their preparation in a pure state and to their comparative rarety, as the grains of crude platinum as a general rule contain from 70 to 90 per cent of platinum, the remaining 10 or 20 per cent representing the other platinum metals combined.

Platinum being the most plentiful and most important member of the group continued, not unnaturally, to receive most attention, especially in regard to its production on a commercial scale, but the development of metallurgical processes for its extraction was handicapped by the comparative smallness of the supply of raw material, and little progress was made until larger supplies of crude platinum from Russia became available.

During the first few decades of the nineteenth century,

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[1] *Inorganic Chemistry,* J. N. Friend. Vol. ix, Part I.

small but increasing quantities of crude platinum continued to reach the London market and were treated by the so-called Wollaston process.

In 1847 Dr. Robert Hare of Philadelphia, the inventor of the oxy-hydrogen blowpipe, taking advantage of the intense heat produced by the combination of hydrogen and oxygen, demonstrated that the difficult and tedious process of consolidating platinum sponge employed up to that time could be replaced by the simple operation of melting the metal in the oxy-hydrogen blowpipe flame. In this way he melted as much as 2 lb. of platinum sponge at a time.

The introduction of this method of melting the metal may be said to have opened a new epoch in the metallurgy of platinum, which is one of the most difficult metals to melt and had hitherto defied all attempts to liquefy it in large quantities.

This discovery exerted a great influence on the development of the industry, as it produced a more compact metal than was possible by the welding process formerly in use.

By this time the commercial manufacture of platinum had become fairly established, and platinum apparatus, manufactured from metal melted by oxy-hydrogen, was exhibited by Messrs. Johnson, Matthey & Co., at the International Exhibitions in London in 1851 and 1862, and the Paris Exhibition of 1867.

In the year 1859 Hare's process was greatly improved by the well-known French chemists Deville and Debray, who prepared platinum for industrial purposes by melting with oxy-hydrogen either the crude metal, or platinum sponge, in a small furnace constructed of lime as described later in the text.

Deville and Debray in 1861 also devised a "dry" or furnace method of extracting platinum from the crude ore, which consisted of smelting it with lead ore in order to obtain an alloy of lead and the platinum metals from which the latter were separated subsequently by the cupellation process.

The metal produced by the processes of Wollaston and of Deville and Debray was not pure but contained 2 per cent or more of iridium and other platinum metals, but it was malleable and capable of being rolled and otherwise mechanically treated, and was quite suitable for a number of purposes.

The methods of Wollaston and Deville and Debray form the basis of all the methods of extracting and refining platinum at the present time, a fact that proves how securely the foundation of the metallurgy of platinum was laid by these careful and painstaking investigators.

The development of the platinum industry appears to have been slow until about 1876, the price of the metal up to that time having been under £5 per pound. From that year onwards, however, progress was more rapid and the value of the metal, although subject to considerable fluctuations, has steadily increased, until at the present time it is considerably above that of gold.

From the brief historical survey given above it will have been observed that whilst the first fifty years following Ulloa's discovery of platinum furnished comparatively little knowledge respecting the chemical and physical properties of the metal, yet such few facts as were established as the result of investigation during that period played no small part in the subsequent development of the metal.

It will have been observed also that the early metallurgical treatment of platinum is divisible into four well defined stages all of which mark distinct steps forward in the industrial development of the metal.

These stages are—

First. The discovery that platinum could readily be dissolved in a mixture of hydrochloric and nitric acids.

Second. That the metal could be precipitated from solution by means of ammonium chloride.

Third. That this precipitate was decomposed on heating, yielding finely divided metallic platinum that could be welded at a white heat into a solid block capable of being rolled into sheet or drawn into wire.

Fourth. That the finely divided metal produced as above described, after compression into blocks, could be melted and cast into ingots in the same manner as other metals.

The platinum produced in the early days of the industry was far from pure, being contaminated with other platinum metals, and in consequence more serious attention began to be directed to the production of a purer metal in comparatively large quantities, and also to the isolation in a pure state of other metals of the platinum group on a commercial scale.

This became possible when larger quantities of raw material became available not only for commercial purposes but for investigation, and research soon resulted in an extension of knowledge of the chemical and physical properties of all the metals comprising the platinum group.

Research eventually culminated in the successful commercial production of the individual platinum metals in a comparatively pure state, and thus eventually placed at the disposal of industry metals possessing remarkable properties of extreme value for special purposes.

As a result the application of platinum and its allied metals has experienced considerable development during the past four or five decades, and there is scarcely an industry that has not benefited directly or indirectly from this expansion.

In connection with the early development of the platinum industry the name of Dr. W. H. Wollaston (1766-1828), a noteworthy name in the chemical history of the period in which he lived, will always take a prominent place since his more thorough system of analysis of the crude metal was largely responsible for the discoveries of the metals of the platinum group, two of which palladium and rhodium he himself isolated.

Moreover, we owe to this able British philosopher much of the more exact knowledge of the peculiar chemical and physical properties which have brought platinum into such an important position in the laboratory both of the experimental chemist and physicist and into the field of industry.

For the more modern production of platinum and its allied metals in a pure state the industry is greatly indebted to P. N. Johnson, F.R.S. (1793-1866), and later to George Matthey, F.R.S. (1825-1913), of the firm of Johnson, Matthey & Co., whose researches in 1879, and subsequent years, played an important part in the general advancement of the practical science of the platinum metals within the last half-century.

Matthey's researches did much to facilitate the production of the platinum group metals in a pure state and at a price comparable with that of the ordinary market qualities.

The more modern methods now in use for the production and manufacture of the platinum metals are more fully dealt with in the chapter dealing with their Metallurgy.

Hitherto the quantity of platinum, and of its allied metals, has been too small to render its application for industrial purposes other than confined, but its usefulness is rapidly extending so that at the present time the demand for the metal far exceeds the supply ; in fact, so far is this the case that substitutes have been introduced in some cases with a view to liberating the precious metal for purposes where its use is of fundamental importance.

The following pages cover a survey of the production of the platinum metals, and their manufacture and application to the manifold uses of modern industry.

It may easily be conceived that a metal indestructible as gold, almost as hard as copper, infusible in the hottest ordinary furnaces, resisting the action of concentrated acids, and at the same time so malleable and highly ductile that it can readily be rolled into sheet, and drawn into wire, must be capable of being applied to a great many useful purposes.

CHAPTER II

OCCURRENCE AND DISTRIBUTION

(i) **Occurrence.** Platinum, like gold, almost invariably occurs in nature in the metallic state and most frequently in old river beds or alluvial deposits, usually known as "placers," in which gold is also present.

In fact, so common is its occurrence in sandy or alluvial deposits that more than 90 per cent of the platinum of commerce is derived from such sources.

These placers have been formed by the erosion of primitive rocks, usually ultrabasic igneous rock such as dunite and serpentine, and the crude platinum is most frequently found in the form either of approximately spherical, or less frequently, flattened grains, steel grey in colour, and in some cases magnetic.

The crude platinum is associated in the placers chiefly with metallic gold, and with heavy mineral substances such as chromite, magnetite, quartz, etc.

The admixture of gold is very variable ranging from 2 to 3 per cent in some districts to as much as 20 to 25 per cent in others.[1] The platinum grains are never pure, containing only from 70 to 90 per cent of platinum, the remainder consisting of the other platinum metals, with iron and other base metals.

As a general rule the size of crude platinum grains is less than that of linseed, although in some cases they are as large as hempseed. Typical water worn grains of crude platinum are shown in Fig. 1. Occasionally large masses or nuggets have been found in the Ural mountains, in Russia, the maximum weight being nearly twenty-two

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[1] Gowland, *Metallurgy of Non-ferrous Metals*.

pounds. An example of a Russian nugget of crude platinum is illustrated in Fig. 2.

Unlike gold, platinum very seldom occurs in a lode formation, but a few instances of such occurrence have been reported in recent years.

Platinum also occurs in nature in combination with arsenic in the mineral sperrylite, an arsenide of platinum ($Pt\ As_2$) in the form of minute octahedral crystals.

FIG. 1

TYPICAL WATER WORN GRAINS OF NATIVE PLATINUM

It occurs in this form more especially in the nickeliferous pyrites or pyrrhotite of Sudbury, in Ontario, Canada, in which ore it was first found, and also in the copper ores of the Rambler Mine, Laramie, Wyoming.

All the other metals of the platinum group are found in alloy with platinum itself, but in addition some of them occur in special native alloys.

Thus, iridium is frequently found alloyed with osmium in greatly varying proportions.

The native alloy, which is found largely in Tasmania, is commonly called "irid-osmine"; but when the percentage of iridium exceeds that of the osmium the alloy is more conveniently known as osm-iridium, and conversely when osmium preponderates, as "irid-osmium."

FIG. 2

EXAMPLE OF NUGGET OF CRUDE PLATINUM FOUND IN THE URALS, RUSSIA

Some platinum, rhodium, ruthenium, and other metals are usually present in minor quantities in the alloy.

Osm-iridium is of considerable value for its iridium content, of which metal it is the chief source of supply.

When occurring in coarse grains of suitable size it is used as a tipping for gold nibs of fountain pens, and is known commercially as " point metal."

Palladium occurs in crude platinum, but also sometimes in a nearly pure state in the form of grains, associated with grains of crude platinum.

Analyses of crude platinum are given on page 25.

(ii) **Distribution of Platinum Metals.** Contrary to popular impression platinum and its allied metals are as widely distributed in nature as gold and other metals, but usually it occurs in such exceedingly minute quantities as either to escape observation or not to pay the cost of extraction.

Whilst the occurrence of native platinum has been reported from many and widely-scattered localities, both of the Eastern and Western Hemispheres, the districts which have produced the metal in sufficient quantity to render its recovery commercially profitable are very few in number and limited in extent.

As an indication of the wideness of the geographical distribution of platinum it may be stated that, apart from the rich deposits in Russia, deposits of the metal more or less promising have been found in California, Oregon, Alaska, Canada, Mexico, Brazil, and other parts of South America, Australia, Tasmania, Dutch East Indies and Papua, Africa, Japan, and other places. Compared, however, with the quantity of platinum obtained from Russia, the quantities of metal from these places are small and add little to the world's annual production.

The great shortage of platinum has, however, led to greater attention being given to the less productive sources, and copper and nickeliferous minerals in particular are being more sedulously sought and more skilfully mined and utilized to-day than ever before, in order to recover to the utmost even the comparatively minute quantity of precious metal they contain.

In some cases, notably in Colombia, increased output has been made possible by the introduction of more modern methods of mining and of ore dressing.

This shortage has also caused energetic prospecting to be made in all hitherto unexplored regions in all parts of the world, and in consequence several fresh occurrences of the metal have been brought to light in recent years, but unfortunately few of these so far have shown signs of yielding the metal in payable quantities.

The most promising new sources of platinum brought to light in recent years appear to be those in which it occurs in minute quantities disseminated in ores of copper, nickel, and other metals, as already indicated, and in the metallurgical treatment of which the precious metals become concentrated and are subsequently recovered in payable quantity in refining the base metal by processes to which reference is made later.

In this way sources of platinum and its allied metals have been discovered in recent years which were long unsuspected. These facts have led to a very minute examination of all classes of ore deposits in the hope that the precious metals that may be present in minute traces in the original materials, may be so concentrated either mechanically or by metallurgical means that they will eventually be separated at a profit.

So far comparatively little prospecting has been done in the vast domain of China, and although little platinum has been reported as occurring in that country it is possible that at some future date, when the country is opened up to mining enterprise, it may prove to be a fruitful source of supply of the metal.

There are also vast unexplored regions in Australia, America, and Africa, which may yet yield payable quantities of the much sought for metal.

The extremely small proportion which the precious metal bears to the worthless sand or rock material with which it is accompanied, constitutes one of the most striking differences between the ores of gold and platinum, and those of all other metals.

Owing, however, to the intrinsic value of gold and of platinum it is possible to profitably treat ores for the extraction of these metals when they contain only a few pennyweight of precious metal per ton of ore.

Thus, the mean return from the gold ores treated by the cyanide process method of extraction on the Rand in South Africa, is less than half an ounce per ton of ore treated, or about one part of gold in 70,000 parts of worthless material.[1]

Auriferous gravels also which do not require to be crushed are sometimes treated at a profit when they contain only two or three grains of gold per ton, or, say, one part of gold in five million.

The same is true of platinum placers, the amount of crude platinum recovered from these being usually only a few grains per cubic yard of material treated.

Beyond the limits of profitable extraction both gold and platinum are very widely disseminated.

On the other hand, the ores of base metals such as copper and lead cannot profitably be treated unless they contain several per cent of metal, and even then low grade ores require to be submitted to some preliminary process of dressing and concentration in order to enrich the material before the metal can be profitably extracted.

(iii) **Sources of Supply of Platinum Metals.** The chief present day sources of supply of platinum and its allied

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[1] T. K. Rose, *Metallurgy of Gold*.

metals may conveniently be treated under two heads, namely; (*a*) The British Empire, and (*b*) Foreign Countries.

(*a*) BRITISH EMPIRE SOURCE OF PLATINUM SUPPLY. It has been pointed out by Sir R. A. S. Redmayne[1] that the British Empire is not so limited in supplies, or in respect of potential resources, of platinum as statistics of production would at first sight lead one to suppose. This is particularly true of Canada, which occupies the third place in the world's production of platinum, Russia and Colombia occupying the first and second respectively.

The only statistics of platinum production that have been published in Canada relate to British Columbia, where platinum has been obtained for many years past from the placer deposits of the Trelameen district.

The output of platinum from gravels in British Columbia is, however, almost negligibly small in comparison with the amount obtained from the nickel-copper "mattes," resulting from the smelting of the ores of the Sudbury district, Ontario. Considerable amounts of platinum and palladium are obtained as a by-product in refining this matte both in Canada, North America, and in England.

Canada's large share in the world's nickel production, and the stability of the nickel mining industry of Ontario, make this an important Imperial resource of platinum.

As regards potential resources mention should be made of the platiniferous copper-nickel deposits of the Insizwa range in the Union of South Africa, and also of the recently reported discovery of platinum in lode formation in the Waterberg district of the Transvaal, which has aroused a great deal of interest, both on account of the unique nature of the find and of the great

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[1] *Chem. Trade Journal,* 15th May, 1920, p. 629. (From report in *The Times.*)

economic possibilities that are opened up to the Union and to the British Empire in general.

The Commonwealth of Australia has furnished very small quantities of platinum, whilst Tasmania is by far the most important osm-iridium producing country in the world, the next in importance being Russia, Colombia, and Papua.

(*b*) FOREIGN SOURCES OF SUPPLY. Since the beginning of the platinum industry Russia has been the largest producer, the output prior to 1914 amounting approximately to 90 per cent of the world's total output, the metal being obtained from placers in the Government of Perm in the central Urals.

The platiniferous area is approximately confined to a length of about 80 miles in the central Ural range, along the eastern slope, the principal centre of the placers being at Goroblagodat, and on the western side at Nizhni Tagilsk.

Colombia, in South America, is the second largest producer of platinum in the world, the metal coming chiefly from the Choco region, near the western frontier of the republic, at altitudes varying from 1,500 ft. upwards.

(iv) **The World's Production of Platinum.** The world's total production of platinum from the establishment of the industry up to the present time has been estimated at approximately 11,000,000 troy ozs., of which Russia has contributed about 90 per cent, Colombia about 7 per cent, and Borneo about 2 per cent, the remainder coming almost entirely and about equally from the United States, Australia, and Canada.[1]

Of the total production, probably about 99 per cent has been obtained from placer deposits.

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[1] *Platinum Metals.* Imperial Mineral Resources Bureau, 1922, p. 17.

Deposits containing osm-iridium are widely distributed in Western Tasmania, from which the world's supply of these metals is mainly obtained.

It is difficult to obtain exact figures of the annual production of crude platinum.

This is particularly so in the case of Russia, "where there appears to have been a tendency for private enterprises to keep their published outputs as low as possible, in order to avoid registration.

"The discrepancy between the official and the actual figures of production in Russia is variously estimated at from 20 to 60 per cent."[1]

"The outstanding features of the world's placer-production of platinum metals during recent years are, first, the serious decline in the Russian output and, second, the considerable increase in that of Colombia.

"The former is accounted for by shortage of labour, difficulties in obtaining renewals and other essential supplies for the dredges by means of which most of the platinum in Russia in recent years has been recovered, and the destruction of many of the dredges during the latter half of the European war period.

"The increase in the Colombian production has been largely due to the stimulus afforded by the increased demand for platinum during, and since, the war and the curtailment of Russian production and exports."

The outputs of platinum from alluvial deposits only in the chief producing countries in 1913 may be taken as representative of the annual production under normal conditions.[2]

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[1] *The Platinum Metals.* Lumb. Imperial Inst. 1920, p. 13.

[2] *Platinum Metals.* Imperial Mineral Resources Bureau. 922, p. 17.

British Empire.	1913. Ozs., Troy	Foreign Countries.	1913. Ozs., Troy.
Canada . . .	18	Russia . . .	157,735
India . . .	58	United States .	483
New South Wales .	442	Colombia . .	15,000
Tasmania . .	1,262	Borneo & Sumatra	183
Total . .	1,780	Total . .	173,401

During the war, and since the armistice, the production of platinum has been very irregular, and although conditions are slowly improving, the worlds output has by no means reached that of pre-war days.

The following are typical analysis of crude platinum from different sources—

ANALYSES OF NATIVE PLATINUM

	Russia Urals[1]	Colombia (S. America)[2]	British Columbia[3]
Platinum . .	76·22–86·50	76·82–86·20	72·07
Iron . . .	6·54–17·30	7·20–7·80	8·59
Palladium . .	0·75–1·94	0·50–1·14	0·19
Rhodium . .	0·96–3·17	1·22–2·50	2·57
Iridium . .	0–0·98	0·85–1·55	1·14
Copper . .	0–0·86	0·60–0·88	3·39
Osm-iridium and Volatile matter	0·50–2·10	0·95–7·98	10·51
Osmium . .	0·–054	–	–
Gold . . .	–	1·00–1·50	–
Sand . . .	–	0·95–4·35	1·69

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[1] Extremes of four analyses: Dana, *A System of Mineralogy*, 1909.

[2] Extremes of three analyses: Deville and Debray, *Ann. Chim. Phys.*, 1859, 56, 385.

[3] Hoffman, Trans. Roy. Soc. Canada, 1887, 5, iii, 17. (References per *Inorganic Chemistry*, J. N. Friend. Vol. ix, Part I.)

CHAPTER III

MINING AND METALLURGICAL TREATMENT OF PLATINUM DEPOSITS

1. **The Mining of Platinum Deposits.** As already mentioned crude platinum in alluvial deposits is found imbedded in strata of clay, sand, and gravel from which it has to be freed as far as possible before it is submitted to the refinery for purification and separation of the several metals it contains.

In placer mining the platiniferous earthy material, usually called "pay-dirt," is exposed to the action of water, by which means the clay is carried off in suspension, and the sand and gravel removed by the force of the current; the platinum, accompanied with gold, if that metal is also present in the placer, on account of their high specific gravity or heaviness, either remain behind in the apparatus employed, or in the case of gold is caught and amalgamated with mercury.

Owing to the great difference existing between the density of platinum and that of siliceous alluvial gravels, it is easily separated from them by washing as indicated, but the methods employed for this purpose, although essentially the same in principle, vary not only with the localities in which the operation is carried on but also in accordance with the nature of the minerals with which the native platinum is associated.

In former times the mining of platinum placers in Russia was entirely carried on by primitive methods with hand labour, but the utilization of dredges has steadily increased, since their introduction in 1896.

It has been pointed out by Perret[1] that "the climatic

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[1] *Trans. Inst. Min. & Met.*, 1911-12, Vol. xxi, pp. 647-690.

and economic conditions of the large territory over which Russian mines are scattered, have caused the adoption for Russian mining of its own special methods, the distinctive features of which are the predominance of muscular force and simplicity of equipment, to admit of local repairs. The reason for the predominance of muscular force is the cheapness of labour in general, and the short Siberian summers."

"There is now, however, a tendency for the adoption of more perfect methods based on mechanical principles, but before discarding entirely the methods which have stood the test of time, Russian engineers wish to make certain of the superiority of new methods, and they realize that the success of any more perfect technical methods largely depends upon the efficient education of the workmen."

PROSPECTING. The first mining operation to be carried on in the extraction of platinum from alluvial deposits, sands of rivers, etc., is detailed prospecting, which has for its object not only the determination of the richness of the deposits but also the reserves of metal they contain. The method of prospecting in use in Russian platinum mining is to place a series of pits or bore-holes in straight lines across the deposits, and naturally the decision as to the right direction of these lines requires the exercise of much judgment and experience, otherwise the richer parts of a deposit may never be found.

The sample gravel removed from the pits is separately washed in a simple form of washing apparatus, termed a "stanok," which removes the sandy material and concentrates the platiniferous grains.

The metal is then weighed to determine the value of the deposit.

The data collected during prospecting, in conjunction with economical conditions, are the deciding factors in choosing the method of exploitation of the deposit.

The method may be open-cast or underground, according to the relative thickness of the overburden of barren material and the pay-dirt, and nature of the ground.

The work is divided as follows—

(1) IN OPEN WORKINGS: (*a*) Stripping, (*b*) Mining of the pay-dirt, (*c*) Washing, (*d*) Removing the tailings or waste material.

(2) IN UNDERGROUND WORKINGS: (*a*) Mining by shafts and drives, (*b*) Washing, (*c*) Removing the tailings.

(*a*) *Stripping.* In Russia the removal of the overburden with few exceptions is carried out by manual labour, the soil being carted away on two-wheeled tipping carts drawn by horses.

In the winter the carting is done by sledges.

In the Urals the stripping is almost exclusively done by workmen who supply their own horses, chiefly in the winter.

In winter, when the excavations freeze, the ground is thawed by wood fires.

Stripping is one of the operations in placer mining which generally demands considerable expenditure, and for that reason attention has more than once been directed to mechanical methods of stripping and excavating, such as steam shovels or excavators, in order to try and reduce the cost of this part of the working of the platinum alluvials.

The equipment of mines with machine stripping requires, however, considerable preliminary expenditure which can only be borne by large mines, and in consequence much of the stripping in alluvial platinum mining is still carried on by hand labour, where dredging operations have not been introduced for the recovery of the precious metal.

(*b*) *Mining of the Pay-dirt.* In mines where dredging is not in use the gravels, after the stripping operations, are mined by open cuts, or, if the overburden of barren material is thick, shafts or drives are employed.

The former method is much preferred, both on account of its relative cheapness, and also because it is possible to obtain a better clean-up of the bed-rock.

Open work mining has everywhere and always been carried out by hand, and no attempts have yet been made to install excavators.

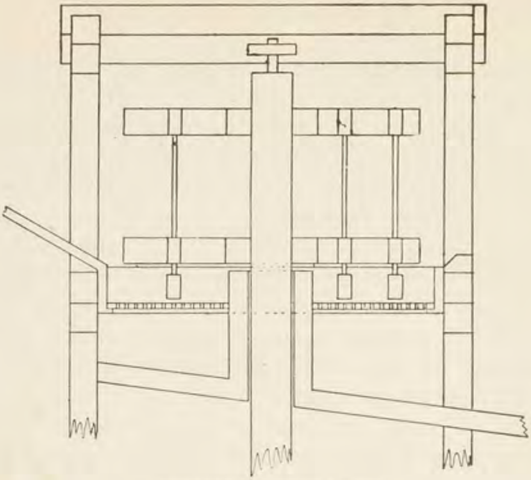
Wages are paid per cube of ground excavated, and when carts are used for the transportation of the material to the washer, this item is included in the contract price.

In cases where the overburden is thick, the gravels are mined by underground workings carried on through shafts sunk vertically from the surface, or by drives or drifts, which consist of underground workings or excavations which are driven horizontally, or nearly so, through the deposit.

When the nature of the placer and ground allow it drives are preferable, as they afford a natural drainage instead of the expensive unwatering equipment required by shafts. The capacity of each separate shaft is not by any means large, and for this reason, in shaft-mining, the pay-dirt is usually mined during winter and stored so that it can be washed in the summer.

(*c*) *Washing.* The gravel obtained from any placer deposit is next subjected to a washing process whereby the platinum grains are separated from the sandy material.

The gravel is washed by different methods in different districts, but the machines usually employed in Russia



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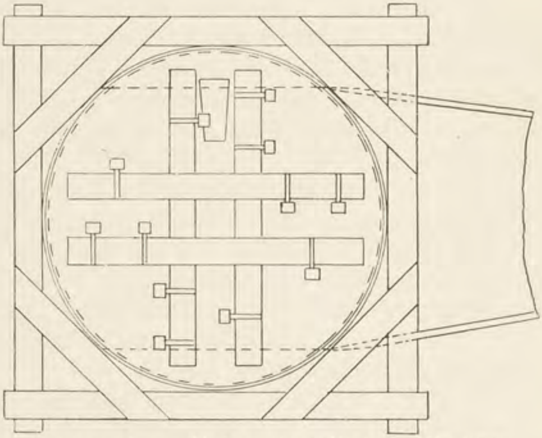

By courtesy of *The Institution of Mining and Metallurgy*

PLAN

FIG. 3

RUSSIAN PAN-WASHER OR "CHASHA"

are the pan-washer or "chasha," and the revolving screen, or "trommel."

Sandy clays are usually treated in a washing pan or chasha, as they cannot be economically disintegrated in a trommel.

The chasha which is shown in elevation and plan in Fig. 3, is similar to the puddling machine used in Australia. The dirt is tipped into this washer and is disintegrated by revolving stirrers, whilst the necessary water plays on to the material in jets from a circular pipe within the mill. The usual speed is eighteen revolutions per minute. In the screen, at the bottom of the washer, is a trap-door through which the coarse gravel can be emptied. The smaller material passes through the holes into the sluice, where the precious metal is caught in riffles in the usual way.

The construction of the revolving screen used in Ural mines only differs from the well-known type used on dredges in being conical and rotates on a horizontal shaft.

The water is introduced by jets at both ends of the trommel.

Another form of washing appartus used in the Urals is the "boronka," shown in elevation and plan in Fig. 4. This apparatus consists of an arc-shaped concave cast-iron screen with $\frac{3}{4}$ in. holes, over which are suspended iron pendulums which, when moving to and fro, mix and disintegrate the material. The finer material passes through the screen into a sluice in which the platinum is caught.

A boronka has a capacity of 12 cub. yards per hour, and is used in small plants in the Urals as an auxiliary washer.

The "sluices" or sluice boxes in which the precious metal from the washers is caught are slightly inclined troughs made of wood, through which the gravel is carried by a stream of water.

The angle or slope of the sluices varies in different localities, but in the Urals the slope is usually from one-eighth to one-twelfth, and as a general rule the length is from 35 ft. to 50 ft. They are provided with wooden riffles which collect and retain the heavy platinum grains. (Perret.)

A clean-up is made once a day, and consists in collecting all the material remaining in the riffles which is then treated in a simple washing apparatus known as a "wash-herd," to remove as much of the remaining sand as possible.

When only the black sand and metal particles remain, the latter are separated from the former by hand, or with brushes.

The miners become very skilled in manipulating this device, and effect a very clean separation.

The concentrate of platinum and black sand is next dried and the latter then removed by means of a magnet.

If gold is present in the concentrate it is removed by the addition of mercury with which it forms an amalgam, whilst the platinum is not affected.

"As platinum does not amalgamate with mercury, the removal of native gold from native platinum is a simple matter, but this very fact results in a loss of much of the latter metal in alluvial workings where platinum occurs in small proportions as compared with the gold and is, in too many cases, allowed to pass away with the waste from the amalgamation. It is impossible to estimate the extent of this loss, but it is a fact that increasing proportions of platinum and the allied metals are being recovered in the refining of bullion obtained from alluvial gold, and that all ordinary refined gold contains platinum and iridium."[1]

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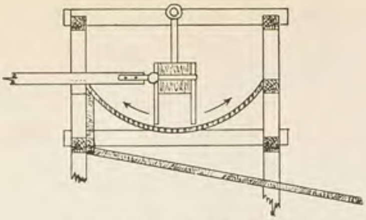
[1] Ref., G. T. Holloway, Article on Platinum, *Thorpe's Dict. of Applied Chemistry*, 1918 Edition, Vol. iv, p. 301.



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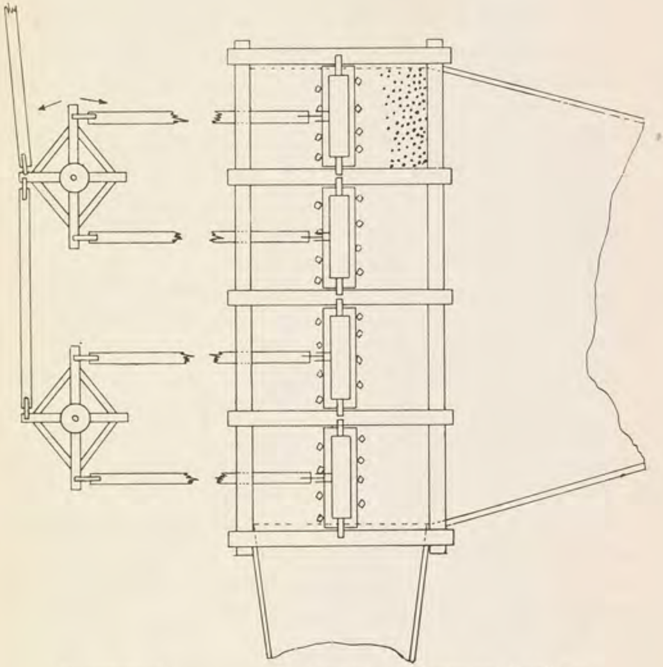


By courtesy of *The Institution of Mining and Metallurgy*

PLAN

FIG. 4

RUSSIAN "BORONKA"

(*d*) *The Disposal of the "Tailings"* or waste sandy material resulting from the treatment of the alluvial is a difficult problem, owing to the large quantities to be dealt with.

The simplest method adopted is to erect the washers on the bank of a river, into which the fine stuff can be dumped, whilst the coarse material is carted away.

This method unfortunately soon results in the silting up of the river, and besides this the fine sands bank up down stream causing all kinds of complications.

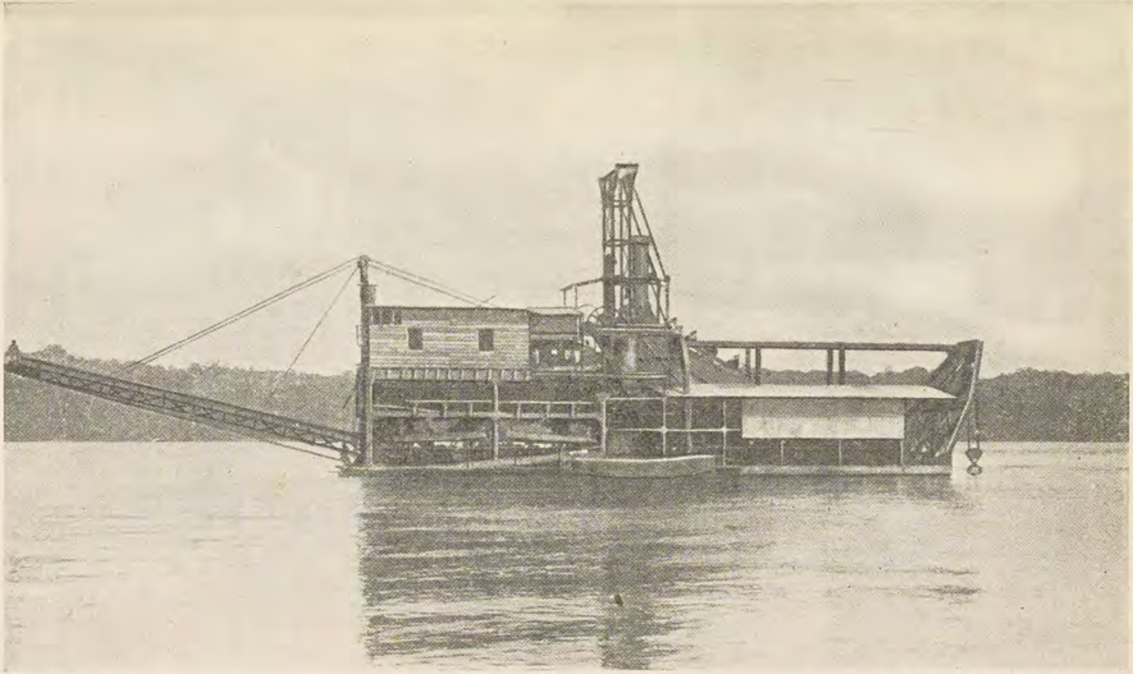
In Siberia the coarse and fine tailings are generally carted away and dumped on waste ground, but when washing from 600 to 650 cub. yards ten horses and fifteen day labourers are required, so that this work becomes expensive, amounting in pre-war days to about 1¾d. per cub. yard.

Consequently, attempts have been made in recent years to install chain and rope hoists and remove the tailings by mechanical means.

DREDGING. The question of the mechanical methods of exploitation of platinum placers began to receive attention nearly thirty years ago, and dredges were introduced into the Russian platinum mining centres in 1896.

Since that time the utilization of dredges has steadily increased, and there is little doubt that the future of both Russian gold and platinum placer mining is largely dependent on the exploitation of the deposits by dredging.

The modern dredge, a typical example of which is illustrated in Fig. 5, consists of a pontoon from which projects a long arm or jib carrying a ladder or endless chain of iron buckets, with a capacity usually of 3 to 15 cub. ft. per bucket.



By courtesy of *Messrs. Fraser & Chalmers*

Fig. 5

DREDGE FOR WORKING ALLUVIAL DEPOSITS

On the pontoon is the machinery for working the chain of buckets, and for moving the dredge as required.

The buckets are so arranged that they scoop up the sand and gravel from the bed of the stream, and deliver it to a revolving screen or trommel, the undersize or finer material from which passes over a succession of sluices and tables which extract the platinum and gold, whilst the exhausted tailings are removed by an inclined elevator, or stacker, often of the endless belt type, at the stern of the pontoon.

As the tailings are usually thrown back into the river the stacker is preferably placed well to the stern of the pontoon so as to prevent the waste material being scraped up a second time.

Such dredges can excavate from 30,000 to 300,000 cub. yards of gravel per month. Dredges in Russia, however, have to work under difficult conditions, owing to the climate and the nature of the ground.

Similar conditions do not exist either in New Zealand or California, and in consequence the Russian industry develops slowly, and during the war period was practically at a standstill. Nevertheless, closer attention has been given to the industry during the past two or three years, and dredges will yet play an important part in the development of the Russian platinum industry. The mining of platinum alluvial by dredging has seen considerable development in Colombia within the past decade. Though based primarily upon the recovery of a very small amount of precious metal in a comparatively large bulk of barren material, the industry has shown itself capable of being conducted at considerable profit.

One of the main causes for this is the comparative simplicity of the dredging operations and the recovery of the precious metal from the material brought up by the dredge.

The labour problem is also quite easily solved, as the crew of a dredge consists of only two or three men, sometimes only one. Another important factor is that the operations of a dredge can easily be controlled, owing to the close record which usually is kept of the time during which the dredge is in operation and of stoppages, so that the maximum amount of active duty can be obtained, and in consequence a close watch of the actual amount of precious metal recovered.[1]

The early attempts to recover platinum by dredging were not altogether satisfactory because the dredging machinery which was used for the purpose was in many cases unsuited for it, both in mechanical construction and in the devices which were intended for the saving of the platinum and any accompanying gold.

It is now, however, appreciated that the variations in the character of deposits in the different districts in which dredges operate are matters of importance, since a type of dredge that has given good results in one region is not necessarily adapted for another, and, as already pointed out, both the platinum and gold deposits of Russia differ materially from those in other parts of the world, and in consequence require special consideration.

It has been stated that before the war only 20 per cent of the Russian annual output of crude platinum was obtained by dredging, the remaining 80 per cent being recovered entirely by hand labour.

At the end of the war none of the Russian dredges were working so far as is known.

Since the establishment of Soviet rule, the production

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[1] See Editorial on "Dredging," *Mining Magazine*. Vol. xiii, 1906, p. 575.

of platinum from the important Tagilsk placers appears to have been obtained entirely by hand labour.

This is probably accounted for by the scarcity and increased cost of the parts necessary for repairing the dredges and the absence of skilled labour in the mining districts to effect the repairs. During the past five years some attempt appears to have been made to restart the dredging industry, but it was reported in the year 1922 that dredging operations in the Russian platinum regions had had to be restricted owing to the difficulty found by Russian engineering firms in executing repairs. The number of plants then at work was only about one-half the usual number.

The dredge production of platinum in the United States of America in 1923 was estimated at approximately 1,000 ozs.,[1] and the estimated output for Colombia as not more than 40,000 ozs.

2. **Extraction of Platinum from its "Ores."** The metallurgical treatment of crude platiniferous material differs in many respects from that adopted for all other metals, mainly on account of the intrinsic value of platinum compared with other metals, and also because of the comparatively small quantity of raw material that is annually available for treatment.

Thus, whilst on the one hand the common metals such as lead, copper, zinc, etc., are extracted from their ores by large scale processes capable of producing many hundreds of tons of metal monthly, and gold and silver ores also are treated in quantities capable of yielding many thousands of ounces of the precious metals monthly ; on the other hand the crude material from which platinum and its allied metals are obtained is only found in sufficient quantity to permit of a few pounds being treated at one time and resulting in the

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[1] Report of the U.S.A. Geo. Survey.

production of only a comparatively few ounces of platinum and its allied metals.

Also, as already mentioned, the monetary value of platinum is now greater than that of any other metal, not excepting gold, consequently the utmost care has to be exercised to prevent loss in treating platiniferous material, since working losses that may be permissible even in the large scale treatment of gold ores, would not be permissible in extracting the six valuable metals that constitute the platinum group.

These important factors have to be borne in mind in devising processes for the economic treatment of crude platinum material.

The fact that platinum cannot be amalgamated with mercury or profitably extracted by alkaline cyanide so largely employed in present-day gold extraction, renders it impossible to treat platiniferous ores similarly to gold ores, even if they occurred to the same extent and were of the same richness as the latter.

Although the crude platinum usually contains from about 70 to 90 per cent of the metal, it may be well to point out at the outset, that the separation and purification of the metals contained in the somewhat complex alloy which constitutes crude platinum, is a long and difficult operation and necessitates not only an extensive knowledge of the chemical properties of the individual metals concerned, but also expert manipulative skill.

The methods of extraction may conveniently be described under two heads: (1) Dry or Smelting Methods; (2) Wet or Chemical Methods.

1. DRY OR SMELTING METHODS OF EXTRACTION. The method originally introduced by Deville and Debray had for its object the preparation of platinum direct from its ores in a furnace, but the method is now seldom used. It did not produce pure platinum,

but its alloys with iridium and rhodium in small proportions.

The ore was smelted with lead oxide and fluxes in order to obtain platiniferous lead, from which the precious metal was subsequently separated by cupellation.

The resulting mass of platinum metals was then remelted in a lime crucible by means of the oxy-hydrogen blowpipe to effect their further purification, and finally cast into a slab to be worked up into sheet, etc.

This dry method of platinum extraction is little practised at the present time for the treatment of the crude platinum grains resulting from the dressing of alluvial material, but smelting processes are by no means obsolete in platinum metallurgy as they are of considerable importance, mainly as concentration processes whereby very small quantities of the platinum metals contained in ores of other metals and in metallurgical products may be concentrated and profitably extracted.

Attention has already been drawn to the fact that gold and silver, and also platinum and its allied metals, are not infrequently associated with ores of copper, copper-nickel, and many other metals, often in such small amounts as to appear of no value to judge from an assay of the original ore, but owing to the concentration of the precious metals that occurs when such ores are smelted, they may be extracted profitably, and within recent years the supply of platinum metals has been augmented to no small extent by the suitable treatment of such ores. In these ores as previously stated, the precious metal is often in a very finely divided state, disseminated throughout the mass and frequently in no larger proportion than 1 part to 70,000 parts or more of barren material.

The final product from the smelting process consists of crude metallic copper, or copper-nickel alloy, with which the precious metals are alloyed, and which is now very generally subjected to electrolytic refining during which operation the precious metals are separated and still further concentrated and finally recovered.

A most notable example of this is the recovery of platinum metals from the extensive deposits of nickel-copper ore that occurs in the Sudbury district of Canada, to which reference has been made.

In this case the ore is first smelted in blast furnaces to produce a crude matte, or artificial sulphide of nickel-copper and iron, which contains the precious metals.

This matte is then either roasted to expel part of the sulphur and the roasted material smelted in a reverberatory furnace to produce a concentrated matte, or the crude matte is concentrated direct by Bessemerizing in a converter, which is a process analogous to the well-known Bessemer process used for the conversion of pig-iron into steel by blowing air through the melted metal.

Bessemerization of copper matte consists in blowing a highly subdivided stream of air under pressure through the molten matte, which is contained in a barrel shaped converter with side blow, whereby sulphur and iron are oxidized, and the matte thereby concentrated.

The purified matte obtained by Bessemerizing, or otherwise, is treated for the production of a nickel-copper alloy which is submitted to electrolytic refining for the purification of the copper and nickel, and final recovery of the platinum metals, etc.

Smelting processes are also used for the concentration and recovery of platinum and other precious metals in the various by-products resulting either from the metallurgical treatment of ores or from the working of the metals in the different stages of manufacture.

The smelting is carried out either in blast or in reverberatory furnaces of moderate size into which a mixture of the platiniferous material, fuel and fluxes, etc., is charged.

The composition of the charge based on the nature of the material to be smelted is determined beforehand, and the quantities of the different ingredients required can then be calculated.

In most cases the material is mixed with lead ores or lead-producing material, and the lead so obtained alloys with the precious metals and collects in the well of the furnace from which it is tapped and cast into bars or pigs.

The platiniferous lead is then subjected to cupellation, whereby the lead is oxidized, leaving a molten residual alloy of the precious metals which is frequently granulated in water and the granules treated with acid to effect their solution. The various precious metals are finally separated by chemical means in the usual way.

2. Wet or Chemical Methods of Extraction. The chemical methods of treating crude platinum at the present time in most refineries are based largely on those devised by Wollaston, Claus, Berzelius, Deville and Debray, and others to which reference has already been made. At the same time it must not be overlooked that the more successful and complete recovery of the individual metals of the platinum group accomplished in present-day metallurgical practice is due in no small measure to new methods of separation introduced by modern chemists and metallurgists, who have made a special study of this complicated group of metals and carried out a considerable amount of research with a view to improving the processes devised by the earlier workers.

Since most of the platinum metals are only of secondary industrial importance compared with platinum itself, primary attention is given to the recovery of the platinum, and the methods of extraction have chiefly been devised to permit of the recovery of this valuable metal as completely and as expeditiously as possible, and also in as high a state of purity as possible.

But commercial platinum always contains a small quantity of other platinum metals, and where a very pure product is required the commercial metal has to be submitted to further refining.

The grains of native platinum sent to the refinery contain the platinum metals not only in widely varying proportions according to the source from which they come, but the material obtained from a single deposit usually consists of different kinds of grains.

Thus in many cases two kinds of metallic grains can be distinguished, namely : (1) dull grains consisting of crude platinum containing from 5 to 10 per cent or more of other members of its group, and (2) brighter grains consisting mainly of osm-iridium.

These two kinds differ very materially in their behaviour towards *aqua regia*, the platinum grains being readily attacked and brought into solution by this reagent, whereas the osm-iridium grains remain undissolved. This different behaviour of the two classes of grains permits at the very outset of a preliminary separation of some of the metals, and gives two distinct products, a solution and an insoluble residue, both of which are treated separately and by different methods.

The wet methods now in use consist essentially in dissolving the crude platinum, crushed as fine as possible, in *aqua regia*—3 vols. of hydrochloric and 1 vol. nitric acids—precipitating the platinum as ammonium platinichloride, heating the precipitate to redness to decompose it, and form spongy platinum, which is compressed into small cakes and then melted, by the oxy-hydrogen blowpipe in a furnace constructed of blocks of lime, or in an electric furnace.

After thus removing the platinum, the other metals of the platinum group are recovered from the solution and from the insoluble residue.

The following is an outline of the practice which has been adopted in many modern platinum refineries for the recovery of all the metals contained in crude platinum : it is summarized from the excellent description of the metallurgy of platinum by Louis Dupare, given in *Le Platine du Monde* (Geneva, 1920).[1]

The process involves ten main operations as follows—

1. The treatment of the mineral with *aqua regia* with the separation of the insoluble osm-iridium and sand, etc.

2. The precipitation of the platinum as ammonium chloroplatinate and subsequent calcination of the precipitate to produce platinum sponge.

3. The separation of iridium as ammonium chloroiridiate from the mother liquor by long standing and calcination of the precipitate to obtain metallic iridium.

4. The treatment of the mother liquors (after removal of the platinum and iridium as stated) with iron, or with zinc, to separate in the metallic state other metals of the platinum group (together with any small quantities of platinum not previously separated) which are deposited as a fine black precipitate called "first blacks."

Drying and roasting of the "blacks" and treatment with dilute sulphuric acid to remove copper and other base metals.

5. Treatment of the cleaned "blacks" with dilute *aqua regia* to obtain a solution containing palladium

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[1] See also translation by F. Sanbour, A. E. Redding, and G. M. Nelson, Eighteenth Report of State Mineralogist of California, 1922, p. 158.

(with traces of platinum, rhodium, and iridium) and an insoluble residue containing rhodium.

6. After separating the traces of platinum, rhodium, and iridium from the solution from 5 with ammonium chloride, the palladium is separated by means of metallic iron as a black mass which is purified and the metal sold as palladium sponge.

7. The insoluble residue from 5 is fused with barium dioxide, and the fused mass treated with *aqua regia* to effect solution of the rhodium and iridium. These metals are then precipitated with ammonium chloride and finally converted into metallic sponge.

8. The insoluble residue of osm-iridium remaining after the first treatment of the ore with acid, is fused with zinc to effect its decomposition.

The fused product is treated with *aqua regia*, and the acid liquor so obtained is submitted to distillation.

9. The acid liquor is distilled in the presence of steam whereby osmium distills over as osmic acid, and is collected in water, and the osmium subsequently separated as metal.

10. The acid liquor retains the iridium and ruthenium which are separated with ammonium chloride, and finally converted into sponge.

When the metals are required in a very pure state the commercial metal obtained by processes such as that briefly described above is further purified. In most cases several reprecipitations will give metal of the desired purity.

3. **Recovery of Platinum Metals by Electrolytic Refining.** (1) BULLION REFINING. The gold and silver bullion from certain districts contains platinum metals, and the introduction of electrolytic methods of refining within recent years has effected the recovery of the latter in appreciable quantities. Two electrolytic methods of

refining precious metal bullion are in use both of which are necessary, neither being sufficient without the help of the other. They are the Moebius and the Wohlwill processes, called after the names of their inventors.

The former is used for the refining of silver bullion containing small quantities of gold, and known as Dóre bullion, whilst the latter is used for gold bullion.

In the Moebius process the electrolyte consists of a dilute solution of silver nitrate. Silver, copper and some other metals are dissolved at the anodes, and pure silver is deposited at the cathodes which consist of thin rolled sheets of pure silver. The anodes of impure silver are usually 18 in. long, 10 in. wide, and about ½ in. thick ; they are connected with the positive conductor, and are enclosed in linen or cotton bags to catch the gold, platinum metals, and other impurities.

The slime or mud in the bags is removed once or twice a week, treated with sulphuric acid, well washed, then melted and cast into suitable slabs to enable the impure gold thus obtained to be refined electrolytically.

The gold remaining in the slime cannot be made sufficiently pure by the Moebius process to be fit for use in the arts, since it is contaminated with impurities such as lead as well as containing in many cases small proportions of the platinum metals in sufficient quantity to pay for extraction.

The anode mud is accordingly melted down, as stated, and used as the anodes in the Wohlwill process, in which the electrolyte is gold chloride.

In this process, when the electric current is passed through the bath, gold, copper, etc., are dissolved at the anodes and pure gold is deposited in a firmly coherent form at the cathodes, whilst silver and the platinum metals, etc., remain undissolved in the porcelain cells in which the process is conducted.

The slime at the bottom of the cells is removed from time to time, and the silver and platinum metals it contains are recovered by chemical treatment.

The Moebius and Wohlwill processes are now used together, to the exclusion of the usual sulphuric acid refining process, at the United States Mints at Philadelphia, Denver, and San Francisco, and also at the New York Assay Office where commercial refining of bullion is undertaken.

It is estimated that the production of refined platinum in the United States from the refining of bullion amounts annually to about 650 to 700 oz., in addition to palladium and other metals of the platinum group.

(2) COPPER REFINING. The electrolytic refining of crude copper, and of copper-nickel alloys, has made great strides in the past few decades in consequence of the demand for pure copper for electrical work, and its introduction has brought to light the presence of platinum and its allied metals in ores, in which their existence had not previously been suspected.

In this process the copper or other metal to be refined is cast into thick plates to form anodes, which are enveloped in canvas bags.

They are then connected with the positive pole of a dynamo, and suspended in a bath consisting of an acidulated solution of copper sulphate, alternating with thin plates of pure copper as cathodes, connected with the negative pole.

When the current passes copper is deposited on the thin plates, and the acid liberated at the positive pole attacks and dissolves the crude copper, which in turn is deposited in a pure state. The impurities it contains, including the precious metals, either remain dissolved in the bath or, more usually, are left in an insoluble form as a mud, which is retained in the bags.

The methods adopted for the final recovery and refining of the platinum metals contained in the mud are kept secret, but they usually involve chemical separations such as are described above.

As showing the importance of precious metals recovered by this method of refining it may be stated that for some years the chief source of supply of palladium has been the copper-nickel ore of Sudbury, Ontario, from whose matte, the artificial sulphide obtained by smelting the ore, it is recovered.

The important and increasing production of the platinum metals concentrated during the " bessemerization " and final electrolytic treatment of copper ores and, particularly of the matte obtained from the nickel-copper ores of Sudbury, Ontario, and from the arsenical copper-nickel ores, associated with native silver in the Cobalt district of Ontario, has already been mentioned.

These and other metallurgical operations in which the precious metals become naturally concentrated in a product requiring final electrolytic purification or acid treatment are, as pointed out by the late G. T. Holloway,[1] the only ones from which any substantial increase in the output of platinum metals can be expected, but they are sufficiently promising to deserve special attention from both metallurgist and chemist. No trustworthy information is available as to the exact procedure, but it appears to be confined mainly to the treatment of the anode mud obtained during the final electrolytic purification of the crude metals or the residue left by the acid or other treatment of the matte.

The " mud " or residue contains the gold, silver, and platinum metals together with traces of other metals, and is melted down and refined by ordinary chemical processes, such as those described previously.

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[1] Platinum—*Thorpe's Dict. of Applied Chem.*, 1918.

4. **Melting Platinum.** The spongy platinum prepared as above described is broken up by rubbing, then sifted, damped with water and strongly compressed in a steel mould by means of a piston operated by a fly press, or by repeated blows with a heavy hammer. If the quantity of sponge is large it is usually compressed into a number of small cakes of convenient size to facilitate compression and melting.

With the exception of a few details of improvement in the method of construction the present-day furnace used for melting platinum, whether in the form of sponge or scrap metal, differs very little from that originally used by Deville and Debray.

The furnace, which is usually about 8 to 12 in. square, is constructed of two blocks of lime bound together with a casing of stout sheet iron, as shown in Fig. 6.

In the upper block there is an opening for the admission of the blowpipe flame.

The lower block contains the cavity in which the platinum is melted, and on one side of its upper edge there is a narrow groove through which the molten metal is poured.

The furnace rests on an iron plate, provided with a handle, so arranged that it can readily be tilted when the platinum has to be poured. Oxy-coal gas is usually employed in commercial practice instead of oxy-hydrogen.

The blowpipe or " torch " in use with this furnace consists of a double metal tube ; the inner one conveys oxygen and the outer one conveys hydrogen or coal-gas to the furnace, and the combustion of the hydrogen in the oxygen creates the most intense heat, which is capable of melting a considerable quantity of platinum at a time.

With quantities much above 50 oz. it is necessary to

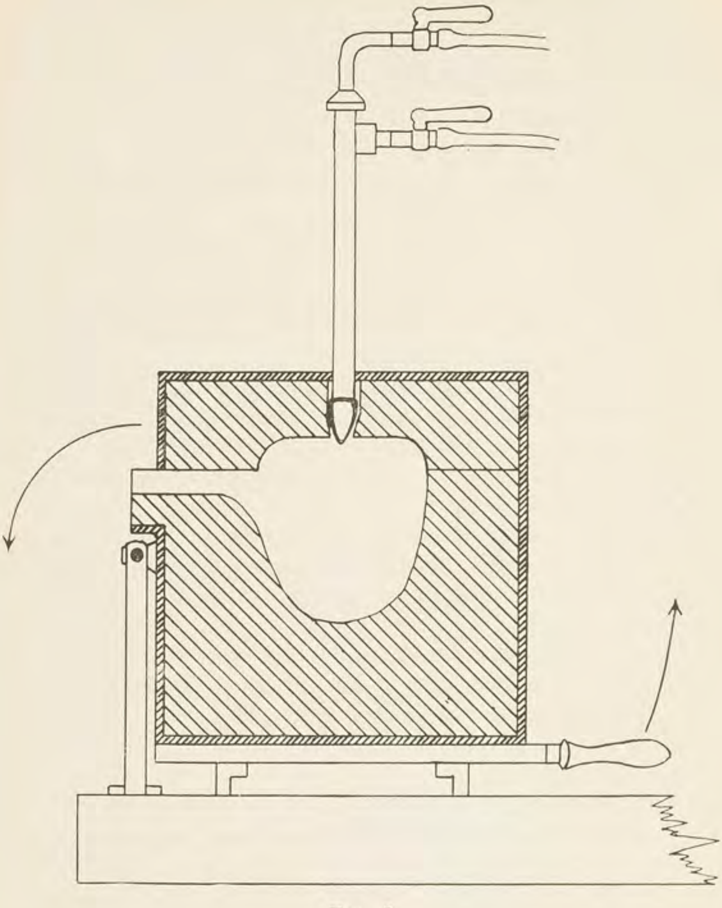

Fig. 6

PLATINUM MELTING FURNACE (OXY-HYDROGEN)

use two blowpipes so that the required heat may be maintained.

During the operation of melting the blowpipe is very liable to become overheated through the intense heat produced, and to avoid this it is usual to enclose it in an outer jacket or tube (not shown in the illustration) through which cold water is allowed to flow continuously thus keeping the blowpipe and jet as cool as possible.

Lime, in the form of limestone blocks or of dolomite, the double carbonate of lime and magnesium, is most frequently used for the furnaces, but within recent years other very infusible materials have been suggested.

Lime is so bad a conductor of heat that a small basin made of this substance less than an inch in thickness may be filled with molten platinum without the temperature of the exterior surface being raised much above 150° C.

During the operation of melting, the metal is not only rendered fluid, but is also refined, any osmium present being expelled in the form of tetroxide vapour, whilst silicon is removed in the state of calcium silicate, which, forming a fusible slag, is ultimately absorbed by the walls of the furnace.

Other impurities are in like manner removed by volatilization or converted into oxides and fluxed off by the material of the furnace.

The moulds into which the molten platinum is cast are usually made of compressed carbon blocks, as metal moulds would readily be destroyed owing to the high temperature of the fluid metal.

The property of absorbing gases possessed by the platinum metals constitutes a source of trouble in melting them.

For example, in melting platinum, if the composition of the mixed gas used for melting is incorrect, gas may be dissolved by the molten metal and, since the solid metal is a much poorer solvent than the molten, it will be set free on solidification, causing the metal to " spit " in the same manner as does solidifying silver, which has likewise absorbed oxygen when in the molten condition.

Generally, however, the gas has not the opportunity to escape in this way, and is partly entrapped in the platinum bar as small gas inclusions.

These often do not appear until the bar is rolled down to thin sheet and annealed, when the surface is found to be covered with numerous gas blisters.

A bar that is much gassed swells badly on solidifying and is remelted forthwith, but the manufacturer's trouble chiefly comes when insufficient gas is trapped to cause swelling and only reveals itself in the form of a few blisters scattered over the surface when the bar has been rolled down to sheet.

It will be obvious from these remarks that great care must be taken to have the correct proportions of coal-gas or hydrogen and oxygen in melting the platinum metals.

Electric Melting of Platinum. During the past few years increasing attention has been given to the melting of platinum in electrically-heated furnaces, and a number of these are now in use in platinum refineries.

One of the furnaces of this type most frequently used for platinum and precious metal melting, is the Ajax-Northrup high-frequency induction furnace made by the Ajax-Wyatt Electric Furnace Co.

The equipment of an Ajax-Northrup plant consists essentially of a high frequency converter to change currents of commercial frequency into high frequency current, and of the furnace proper.

The smaller sets, such as are used for platinum, are usually single phase and the larger sets three phase.

The furnace itself consists of the inductor coil of water-cooled copper tube surrounding a loose fitting cylindrical tube of electrical insulating material. Into this tube the crucible is placed and a heat insulating refractory material is put around and beneath the crucible, between it and the insulating tube.

When the required heat is attained, the crucible can either be withdrawn from the furnace, or else can be left in position, and the whole furnace tilted; when melting platinum the latter method is adopted.

Witchers and Jordan[1] found that platinum melted in lime in the Ajax-Northrup high-frequency induction furnace, with free access of air and without excessive superheating, was of satisfactory purity as determined by the thermoelectric tests, although spectrographic tests usually gave evidence of the presence of calcium.

Melts of platinum in magnesia in the induction furnace were seriously contaminated with magnesium when a graphite or tungsten shell was used outside the refractory liner.

Consideration of the qualities required in a refractory material for general use in melting metals of the platinum group and their alloys led to the belief that thorium or zirconium oxide should be more satisfactory than lime or magnesium, and tests with magnesia in the induction furnace were discontinued.

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[1] Trans. *American Electro-Chem. Soc.* Vol. xliii., 1923, p. 393.

CHAPTER IV

GENERAL PROPERTIES OF THE PLATINUM METALS

In some respects the metals comprising the platinum group are similar in their general behaviour, and their physical and chemical properties may for convenience be considered collectively.

The first noticeable feature about these metals is that they are remarkably alike in colour, and in having high melting points, and high specific gravities.

Also, with the exception of palladium, they are all very difficult to get into solution.

In general appearance the metals of the platinum group are all silver-white lustrous metals capable of receiving a high polish, and remaining bright in dry air.

Each of the platinum metals, however, possesses its own characteristic tint, slight though it may be in some cases, that distinguishes it from other members of the group, but the individual tint is only apparent by repeatedly reflecting the light from surface to surface of the metal.

The distinguishing colours—tints of the individual platinum metals are tabulated on page 59, but it must be admitted that when the metals are in the usual commercial forms of sheet or wire it is extremely difficult to distinguish between them by appearance only.

In these circumstances it is almost invariably necessary to confirm by some chemical test.

The two most frequent metals of the group met with in general use are platinum and palladium, and these are readily distinguished by applying a drop of *aqua regia* which has only slow action on platinum and leaves no stain, whilst palladium is readily attacked and produces a brownish coloration.

The platinum metals are included amongst the heaviest substances known, the specific gravities falling into two distinct groups, namely, the lighter metals constituting the ruthenium group, and the heavier metals the osmium group.

The first group includes palladium, rhodium, and ruthenium with specific gravities ranging between 11·3 and 12·0, whilst those of platinum, iridium, and osmium, which constitute the second group, range from 21·5 to 23·0.

The density of the metals of the first group, although very close to one another, are widely different from those of the second group ; and it will be observed from the following figures that the specific gravities fall, with increasing atomic weights, thus—

GROUP I.			GROUP II.		
Metal.	Specific Gravity.	Atomic Weight. O=16.	Metal.	Specific Gravity.	Atomic Weight. O=16.
Ruthenium	12·0	101·7	Osmium .	23·0	190·9
Rhodium .	11·5	102·9	Iridium .	22·4	193·1
Palladium .	11·3	106·7	Platinum .	21·5	195·2

As is always the case with metals the density varies according to the physical condition, thus the specific gravity of cast platinum is 21·5, and that of fully annealed pure platinum wire is 21·43, whilst the same wire hardened by mechanical treatment has a specific gravity of 21·39.

The above figures must therefore be regarded as relative only. It will be observed that ruthenium is the lightest metal of the group, and osmium is the heaviest, and in fact is the heaviest substance known.

The platinum metals are amongst the most permanent substances known, being unacted upon by air or by oxygen at ordinary temperatures, and it is to this fact that they largely owe their industrial value.

With the exception of osmium, which burns when strongly heated, forming the tetroxide, they are scarcely oxidized by oxygen at any temperature. The first to be affected on heating are palladium and ruthenium, both of which become superficially oxidized.

All members of the group are very difficult to melt, and are in consequence frequently classed as refractory metals, but they are fusible in the oxy-hydrogen flame, or the electric furnace, with the exception of osmium, which after fusion almost at once volatilizes as tetroxide.

The most easily fusible of the metals is palladium, which melts at 1,550° C. which is about the temperature required to melt wrought iron.

The melting point of platinum is somewhat higher, but it may be boiled at the temperature produced by the oxy-hydrogen flame. Ruthenium and rhodium come next in order of fusibility, the latter metal being just fusible by the oxy-hydrogen flame, whilst iridium and osmium have still higher melting points, the latter metal, according to Moissan, being melted and slowly distilled in the electric furnace.

The melting points of the platinum metals recorded by different observers vary considerably, due to the use of impure metal, but the table on page 59 gives the most recent and probably the most accurate determinations, compared with melting points of silver, copper and gold.

Platinum and palladium, especially the latter metal, absorb oxygen when molten and " spit " in a similar manner to silver when the gas is expelled on solidification.

This phenomenon is also observed in other metals of the platinum group but to a lesser extent.

With regard to working properties, platinum and palladium are very malleable and ductile metals, and are prepared commercially in the form of thin sheet and wire, and may readily be stamped and spun. Palladium is, however, slightly less workable than platinum. Both these metals may be welded at a temperature approaching a white heat.

In common with all other metals platinum and palladium are hardened by mechanical treatment but may be softened by annealing or heating to a suitable temperature. Thus, pure platinum is softened at about 650° C., whilst hard or commercial platinum requires to be heated to about 1,000° C. for about ten minutes. Palladium is softened at a bright red heat.

All the other metals of the group are brittle at ordinary temperatures, but iridium and rhodium are malleable to a certain extent at a red heat.

Platinum has a very low electrical conductivity, and its coefficient of expansion is lower than that of any other metal, and is the same as that of glass. These properties render it extremely useful in the electrical industry as shown later.

The platinum metals are further characterized by their resistance to the action of acids and most chemical agents.

With the exception of palladium, which readily dissolves in hot nitric acid, these metals, when in compact form, are unacted upon by ordinary acids.

Aqua regia converts osmium into the tetroxide ; it dissolves platinum with the formation of tetrachloride ($\mathrm{Pt\ Cl_4}$), and slowly acts upon ruthenium, but is without action upon rhodium and iridium. The two latter metals are rendered soluble by fusion in a fine state of division with potassium hydrogen sulphate.

When in a state of very fine division several of the platinum metals are less resistant to attack by acids, and this fact constitutes one of the difficulties met with in their separation and refining.

Platinum, and certain of its allied metals, when alloyed with a large proportion of silver or with some other metals, is dissolved to a considerable extent in nitric acid.

When alloyed with zinc, and the excess of zinc dissolved in hydrochloric acid, some of the platinum metals are left in the form of a finely-divided metallic residue which is explosive.

Thus explosive platinum, ruthenium, and rhodium are obtained in this manner. The exact cause of this phenomenon is not known.

One of the most interesting general properties of the platinum group of metals is their capacity for dissolving oxygen and other gases, for this probably accounts for their great activity as catalytic agents, a term which is given to substances which exert a powerful influence in promoting a chemical change without themselves being affected. Such agents play a very great part in chemical phenomena and have fitly been compared with the oil which contributes so much to the smooth working of an engine without actually supplying any of the driving power. A little oil makes a big difference, and a catalytic agent similarly facilitates chemical changes out of all proportions to its quantity.

Both platinum and palladium, in a finely divided state, have proved to be of the highest value in many technical operations, and are used as catalysts in several chemical processes described later.

All the platinum metals, under suitable conditions, combine with oxygen and chlorine, and with other elements to form salts, some of which are of considerable industrial value, and are dealt with on page 107.

The characteristic physical properties of the individual metals of the platinum group are given in the following table.

COMPARATIVE COLOURS OF THE PLATINUM METALS.

Metal.	Usual Description.
Platinum . .	Silver white.
Palladium . .	Silver white.
Iridium . .	Between Silver and tin, slight grey tint.
Rhodium . .	Resembles Aluminium, faint bluish tinge.
Ruthenium .	Closely resembles platinum.
Osmium . .	Tin-white with decided greyish-blue tint.
Silver . . .	Standard of metallic whiteness.
Gold . . .	Yellow.
Copper . .	Red.

PHYSICAL CONSTANTS OF THE PLATINUM METALS.

Metal.	Melting Point.[1]		Specific Gravity.	Brinell Hardness (annealed).	Erichsen cupping, value in mm.
	° C.	° F.			
Platinum . .	1,755	3,191	21·5	47	12·2
Palladium .	1,550	2,822	11·3	49	12·0
Iridium . .	2,350	4,262	22·4	172	—
Rhodium . .	1,950	3,542	11·5	139	—
Ruthenium about	2,450	4,442	12·0	220 ?	—
Osmium	2,600 2,700	4,712 4,892	23·0	—	—
Silver . .	962	1,762	10·5	50	12·9
Gold . .	1,064	1,948	19·3	45	13·0
Copper . .	1,084	1,985	8·9	55	11·8

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[1] F. E. Carter, *Amer. Electro-Chem. Soc.*, 1923, p. 277.

CHAPTER V

USES OF THE PLATINUM METALS

As previously pointed out, platinum itself is technically the most important metal of the "platinum group," the other metals associated with platinum being found in much smaller quantities, and do not possess the valuable combined properties of platinum. Moreover, they have only a very limited industrial application, and when used it is generally in the form of alloys.

The great industrial value of platinum is indicated by the many important uses to which it is put in manufacture and art, in both of which fields its unique properties have made it indispensable.

Platinum is principally used in the chemical, electrical, dental, and jewellery industries, and also for a number of miscellaneous purposes; its numerous industrial applications may therefore conveniently be considered under these five heads.

The earliest commercial application of platinum consisted in the conversion of the metal into coinage in 1828, when platinum was cheaper than gold. In that year the Russian Government, during the reign of Nicholas I, instituted platinum coinage, which consisted of 3-rouble, 6-rouble, and 12-rouble pieces, weighing respectively 0·3355 oz., 0·6710 oz., and 1·342 oz. A 6-rouble piece is illustrated in Fig. 7.

In those days the modern methods of refining and of melting were unknown, the metal required for the coinage was therefore prepared by the old method of consolidating platinum sponge at a white heat until the mass was brought to a perfectly malleable state, and the metal then sent to the Russian Mint to be converted into coin as stated. Owing, however, to the difficulties of manufacture, fluctuation in price, etc., the use of platinum for coinage was discontinued in 1845.

(1) **Uses of Platinum in the Chemical Industry.** In the chemical industry platinum is extensively used, both in manufacturing processes and in the laboratory, since it combines a high melting point with great resistance to attack by reagents—whether acid or alkaline—and is in consequence well suited for the manufacture of plant in which chemical reactions have to be performed, and of chemical laboratory apparatus. In fact it may truly be said that platinum has played a very important part in the development of the chemical industry, especially during the past two or three decades.

FIG. 7

RUSSIAN PLATINUM COINS (1828-1845)

Its use for the manufacture of chemical plant has, however, of necessity had to be restricted owing to the scarcity of the metal and its consequent high price, but for many years large basins and stills of platinum have been extensively used in the final stages of sulphuric acid manufacture by the old chamber process in which the acid is made in towers or chambers and is first concentrated in large lead pans, and then if a final concentration is necessary to bring it up to the standard of commercial requirements platinum stills have usually been installed.

As early as 1809 Messrs. Johnson, Matthey & Co., Ltd., the well-known platinum refiners of London, manufactured a platinum still for the concentration of sulphuric acid which weighed 424 oz.

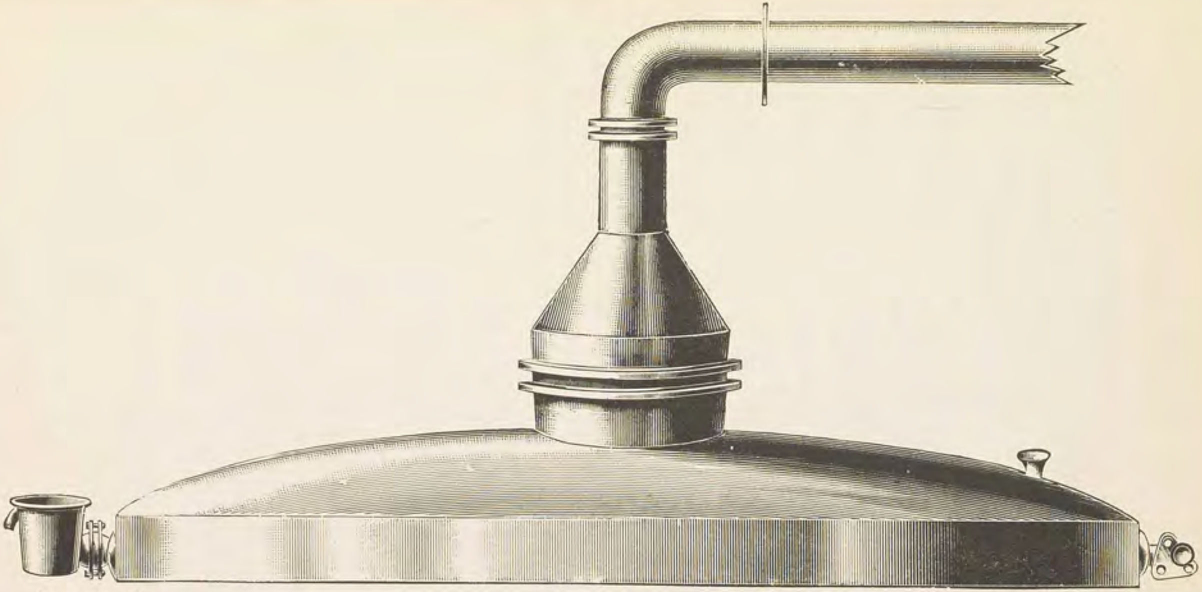
The most generally adopted and universally approved form of platinum apparatus for the concentration of sulphuric acid is that shown in Fig. 8, which is known as the " double delplace " form. This particular form of apparatus was first introduced by Messrs. Johnson, Matthey & Co., Ltd., in 1875, and since that time the firm have supplied some hundreds throughout the world.

The ordinary standard size of this apparatus weighs, complete with all appurtenances, including cooler, 2,000 oz. troy (60 kilos). The plant is capable of producing 10 tons (10,000 kilos) of sulphuric acid of 94 per cent strength in twenty-four hours under ordinary working conditions, or about one-half this quantity if concentration is continued to produce acid of 97·5 per cent.

In some cases the acid is concentrated in shallow round platinum pans, weighing from 600 to 700 oz. (18 to 22 kilos) and cooled in some simple form of platinum refrigerator, the weight of which varies proportionately to cooling capacity.

Since concentrated sulphuric acid has a certain amount of solvent action on platinum, it is the usual practice when constructing plant of this metal to line or coat it internally with gold, so as to form a protective coating that will more readily resist the attack of the acid.

For this purpose a compound plate of the two metals



By courtesy of *Johnson, Matthey & Co., Ltd.*

FIG. 8

PLATINUM APPARATUS FOR CONCENTRATION OF SULPHURIC ACID "DOUBLE DELPLACE" FORM is made by welding or soldering a thick sheet of gold on to one of platinum, and the compound plate thus formed is then rolled to the desired thickness. A gold-lined platinum still was exhibited by Johnson and Matthey at the Paris Exhibition of 1858.

Of late years platinum has largely been replaced by gold in sulphuric acid concentration, and more recently by silica glass, or where the presence of traces of iron is unimportant by vessels of special resistant alloys, such as those of iron-silicon, and nickel-chromium, etc.

In constructing platinum plant the various pieces are joined either by autogenous soldering in a similar manner to lead "burning," or by the use of gold solder.

Sulphuric acid is now, however, largely manufactured by the contact process, invented by Messel in 1875, which is founded on the production of sulphur trioxide, when a mixture of sulphur dioxide and oxygen is passed through a series of iron tubes containing platinized asbestos in which the platinum exists in a very finely divided form.

Combination begins at 300° C. and then proceeds without any further external heating being required, as a considerable amount of heat is evolved in the reaction.

The sulphur trioxide thus formed is absorbed by being passed into strong sulphuric acid, to which a corresponding quantity of water is added at the same time, and a very pure concentrated acid is thus produced.

The temperature at which the process is conducted is of considerable importance, since the reaction will only occur very slowly if the temperature be too low.

On the other hand, if the temperature is too high the change can never become even approximately complete, hence an intermediate temperature must therefore be chosen, and it is found that the best temperature to maintain in the apparatus is about 400° to 425° C.[1]

There are several kinds of platinum " contact mass " used in this method of sulphuric acid manufacture, the two most commonly used having asbestos or magnesium sulphate bases.

The so-called mass is made by soaking the base in a solution of platinum chloride and afterwards heating it, whereby the chloride is decomposed and very fine particles of metallic platinum remain more or less completely distributed throughout the mass. Some " contact mass " contains from 7 to 8 per cent by weight of platinum, whilst certain manufacturers make a mass containing as little as 0·2 per cent.

This finely divided condition of the platinum is necessary since the success of the contact process depends on the catalytic property of platinum in a heated condition, reference to which has been made above.

" In the grillo process, now used in this country, the finely divided platinum is suspended, not in asbestos but in a porous soluble salt such as anhydrous magnesium sulphate, obtained by heating the hydrated sulphate.

" This salt is very feathery and highly porous, and has the advantage of being soluble. Consequently, if the platinum becomes ' poisoned ' (i.e. contaminated by impurity such as arsenic) and inefficient, the salt is taken from the contact plant, placed in vessels and treated with water. The salt is dissolved away and the platinum black is left. It is then possible to wash the platinum with hydrochloric acid and other reagents, which remove the impurities."[2] If necessary the

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[1] *Metals and Metallic Compounds*, U. R. Evans, 1923. Vol. iii, p. 255.

[2] N. R. Evans, *loc. cit.*

platinum can then be dissolved in *aqua regia* and reprecipitated without serious loss.

The contact process is found to be more economical for the manufacture of concentrated sulphuric acid than the old chamber method in which a gaseous catalyst (viz., oxide of nitrogen) is used, and many tons of acid were made by the former process for munition purposes during the war period.

Many other catalyzers have been employed with success, but none result in so complete a conversion of the sulphur dioxide into trioxide, and, even when they are employed, the aid of spongy platinum is generally required for the completion of the reaction.

Thus in the Mannheim process which, although originating in Germany, has largely been used in the United States, the first stage of the oxidation of dioxide to trioxide is carried out at a high temperature with iron oxide as catalyst.

A 60 per cent conversion is thus obtained, and the gases are then cooled and purified, and caused to react further at a lower temperature by means of a platinum catalyst.[1]

Another important technical operation which depends upon the action of a platinum catalyst is the manufacture of nitric acid from ammonia, but in such plants platinum gauze of very fine mesh is used as the catalyzer, instead of platinum sponge.

The process consists in passing a mixture of ammonia gas and air over heated platinum gauze, whereby the ammonia is decomposed into its elements, and the liberated nitrogen oxidized. The reaction is exothermic, or heat producing, and when once the plant is in operation, the heat evolved is sufficient to maintain the temperature of the gauze for the continuance of the process.

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[1] U. R. Evans, *Metals and Metallic Compounds*. Vol. iii, p. 258.

In many plants the principle of heat exchange has been adopted with success, the hot emergent gases being used to preheat the gases entering the plant.

In the usual method for the commercial production of nitric acid the nitrate of soda found in nature has been the crude material from which most of the world's supplies have hitherto been obtained, but the supply of this salt is falling short of requirements and Professor B. Dunstan has recently pointed out[1] that a serious demand might be made on platinum in the future to furnish the catalyzer required in converting ammonia into nitric acid by a process of oxidation such as that outlined above.

Finely divided platinum is also used in the manufacture of acetic acid, one of the processes for making this acid consisting in the rapid oxidation of alcohol by means of spongy platinum, platinum black, or platinized asbestos.

If platinum in any of these finely divided forms is heated in contact with a mixture of air and alcoholic vapour, the formation and condensation of acetic acid and water takes place at once. The process is very effective and gives a pure product, but the first cost of the platinum seems to prevent its being used on an extensive working scale.

From the foregoing remarks it will be seen that platinum is now taking a very prominent place in the chemical industry as a catalyzer, and in view of the success that has attended its introduction for this purpose there is little doubt that it is destined to take a still more prominent place in this capacity in the future, provided a sufficient quantity of the metal is available at a reasonable price.

This will only be rendered possible by conserving the

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[1] Queensland Gov. *Mins. Journ.* Vol. xxii, 1921, p. 96.

present supplies of the metal for industries of fundamental importance to the well-being of the community, and restricting the use of platinum for purely ornamental purposes.

Amongst other uses of platinum in the chemical industry, may be mentioned platinum hydro caps, now being used in certain processes of artificial silk manufacture.

In the realm of metallurgy platinum vessels or boilers are used in the nitric acid refining process of separating or " parting " gold from silver.

In this process the granules of silver-gold alloy, obtained by pouring the metal into water, and containing about one-third their weight of gold, are treated with nitric acid in platinum vessels, each heated over its own fire, when the silver is dissolved, leaving the gold as an insoluble residue.

Owing to the increased price of platinum, however, many refineries have now introduced boilers consisting of large porcelain or stoneware vessels set in tanks, in which water is kept boiling by injected steam. Like the platinum boilers, they are fitted with suitable hoods for carrying off the nitrous fumes to a condensing arrangement.

In the early days of the electro-chemistry industry when platinum was comparatively cheap, platinum electrodes were commonly used.

Now, however, owing to the increased price of platinum, they are only used in exceptional cases having been replaced, wherever possible, by electrodes of carbon or of Acheson graphite, or by other metals.

In the electrolytic production of perborate, persulphuric acid, perchlorates, etc., platinum anodes are still used, as a suitable substitute has not yet been found.

Platinum has long found extensive use in chemical laboratory apparatus. At the beginning of the nineteenth century, however, vessels made of platinum were still so scarce and costly that very few chemists could boast of possessing such apparatus.

It was not until the method of rendering platinum workable on a commercial scale was developed that wire, foil, crucibles, and other articles made of the metal came into more general use, and began to be regarded as an essential part of a chemical laboratory equipment.

The past quarter of a century has seen wonderful strides in chemical experimentation and analysis, and the demand for platinum apparatus has grown enormously during that period.

In addition to the enormous number of crucibles, of various shapes and sizes, for use in every class of chemical laboratory, chemists now require a host of other platinum utensils such as dishes and trays, spatulas, tubes, distilling apparatus, electrodes for electro-chemical analysis, etc.

It would be difficult to over-estimate the effects which the use of platinum apparatus has had upon the progress of the sciences and indirectly on industry.

Great credit is due to many of the early investigators who achieved wonderful results in spite of the limited amount of platinum apparatus available, and who frequently worked under very unfavourable conditions such as would not exist in a well-equipped modern laboratory provided with many appliances that the modern chemist has been in the habit of using and regards as indispensable.

As conspicuous instances of successful investigations in more modern times which depended on the use of platinum apparatus, mention may be made of the important work of the renowned French chemist, Moissan, who in 1886 succeeded in isolating fluorine, and the proof by Mme. Curie and Mlle. Gleditsch, that the action of radium emanation on solutions of copper does not produce any lithium, as was supposed by Ramsay to be the case.[1]

The discovery of Moissan was a great achievement, as hitherto the exceedingly active element fluorine had baffled all attempts to isolate it.

Moissan's success depended upon the discovery that a solution of the acid potassium fluoride in anhydrous hydrofluoric acid is an electrolyte, and that by the passage of an electric current through this solution, fluorine is disengaged at the anode, or positive electrode, and hydrogen is evolved at the cathode.

The reaction was performed in a U-tube made of an alloy of platinum and iridium, a material which is less acted upon by the liberated fluorine than platinum alone.

The apparatus had two side tubes which could either be closed with a screw cap or connected to platinum delivery tubes by means of the union.

The two limbs of the tube were closed by means of stoppers made of fluor spar, which could be securely screwed into the tube. These served to insulate the electrodes, which were constructed of the same platinum-iridium alloy.

The use of platinum crucibles in the chemical analysis of rocks is indispensable, since by far the greater number of the silicates of which the rocks are formed are insoluble in water and in acids, and require to be decomposed by other means.

For analysis the rock constituents require to be brought into a soluble mass, and this necessitates fusions being made in a metallic crucible and the use of fluxes, whereby soluble compounds are formed.

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[1] Platinum; the most precious of the metals. H. F. Keller, *Journ. of Franklin Inst.* Vol. clxxiv, 1912, p. 542.

Crucibles of gold and silver cannot be used because they will not resist high temperatures, and for various reasons crucibles made of other metals, such as nickel, although used in some few cases, are not generally suitable.

It is only since platinum crucibles were introduced that it has become possible to accurately determine the composition of rocks, and an enormous amount of scientific information of extreme value not only to the geologist but also to other branches of knowledge has been obtained, especially in recent years, by the use of this simple piece of apparatus.

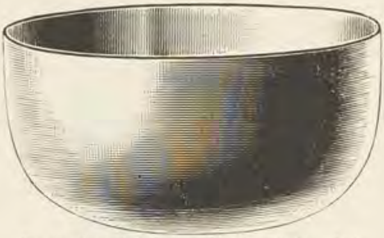
By courtesy of Johnson, Matthey & Co., Ltd.

FIG. 9

CRUCIBLE AND LID

At the present time a relatively large amount of platinum is actually consumed annually in the production of various kinds of apparatus used in the chemical laboratory, but a large proportion of this metal is not destroyed, and with care in use will last a very long time, and when no longer fit for further use it can be melted and used again for the manufacture of similar apparatus.

It has been estimated that about 10 per cent of the whole world's supply of platinum is utilized in the production of laboratory apparatus of one kind or another.



By courtesy of Johnson, Matthey & Co., Ltd.

Fig. 10

BASIN

Owing to the comparative softness of pure platinum, much of the chemical apparatus is made with platinum alloyed with iridium in order to harden it and increase its resistance to abrasives, and the attacks of chemicals.

Much of the platinum apparatus used by chemists contains about 2 per cent of iridium, and such metal is known commercially as "hard platinum" as distinguished from ordinary refined platinum, and it is more expensive than the latter.

Some typical examples of the various platinum vessels more commonly used in chemical laboratories, manufactured by Messrs. Johnson, Matthey & Co., are illustrated on pages 71-77.

Figs. 9 and 10 illustrate the ordinary type of platinum crucible and basin, both of which pieces of apparatus are probably more extensively used in the laboratory than any others.

The weight of the crucibles, which are spun or stamped from sheet metal, varies usually from about 9 to 125 grammes (i.e. 0·3 to 4 oz. troy), and they have a capacity of 10 to 125 cub. centimetres.

The covers are frequently made of special shape so that when inverted they may be used as a capsule, and thus economize the use of platinum.

For special purposes crucibles are made of iridio-platinum containing from 10 to 30 per cent of iridium.

By courtesy of Johnson, Matthey & Co., Ltd.

FIG. 11

COMBUSTION BOAT

Platinum dishes are supplied with or without lips and without handles, as shown, or with one or two handles as desired for special purposes.

The weight varies usually from 15 to 200 grammes (i.e. 0·5 to 6·5 oz. troy), whilst the capacity varies from 30 to 600 cub. centimetres.

Owing to the high price of platinum, alloys of gold and platinum, and of gold and palladium have been introduced during the past decade for the manufacture of chemical apparatus.

In order to avoid contamination when handling platinum apparatus whilst hot, platinum-tipped iron crucible tongs are very frequently employed.

For certain classes of combustion analysis, and for similar operations, the platinum boats shown in Fig. 11

are used ; these usually weigh from 5 to 6 grammes, or approximately 0·2 oz. troy.

Other platinum apparatus used in the chemical laboratory consists of triangles made of stout wire on which to support platinum crucibles during heating, and filter cones made of perforated sheet metal, Fig. 12, which are used as a support to filter paper during filtering operations. Also platinum tips or nozzles for blowpipes (Fig. 13), and spatulas (Fig. 14).

FIG. 12
FILTER CONE

FIG. 13
NOZZLE

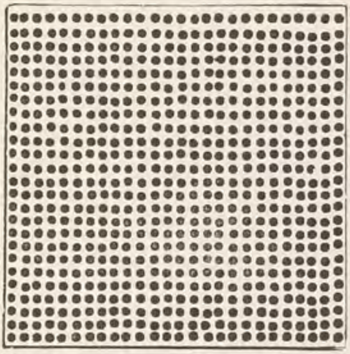
FIG. 14
SPATULA

Within recent years platinum has found increasing use in the form of perforated sheet, Fig. 15, wire gauze, Fig. 16, and stout wire in apparatus for the electrolytic methods of analysis for the quantitative estimation of metals by the process of electrolysis.

As is well known this process is based upon the fact that when solutions of certain metallic salts are submitted to the action of an electric current of suitable strength, the metals are precipitated upon the negative electrode in the form of coherent films or deposits.

The operation is, in fact, an electro-plating process, where the article to be coated or " plated " is a weighed piece of platinum, and the metal with which it is coated is the metal that is to be estimated.

The apparatus required for electro analysis consists essentially of two platinum electrodes. That which is to serve as the cathode, and receive the deposited metal, is usually made in the form either of a cylinder or cone, which in either case is riveted or welded to a stout platinum wire, as shown in Fig. 17.



By courtesy of Johnson, Matthey & Co., Ltd.

FIG. 15

PERFORATED SHEET

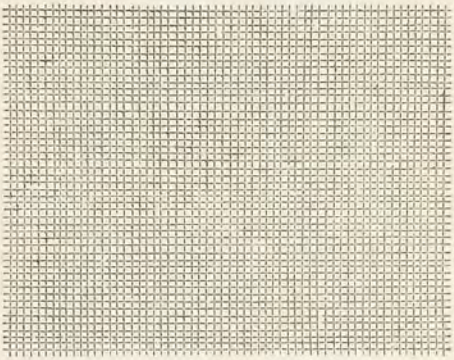
Other forms of cathode are also in use, and not infrequently a platinum basin is made to serve the purpose.

The anode is conveniently made of thick platinum wire bent into some such form as that shown in Fig. 18, or welded to a disc of platinum as shown in Fig. 19.

The forms of both cathode and anode used in electrolytic methods of analysis are, however, very varied, each manipulator having his own particular design, but those shown may be regarded as typical of those generally used.

Platinum is more suitable as an anode material than any other substance as it is not readily attacked, but in a chloride solution the pure metal is perceptibly corroded, and on this account anodes of platinum-iridium alloy are used and are found to be quite satisfactory.

Electrodes exposed to severe chemical attack are not infrequently made of platinum alloyed with from 10 to 15 per cent of iridium.



By courtesy of *Johnson, Matthey & Co., Ltd.*

FIG. 16

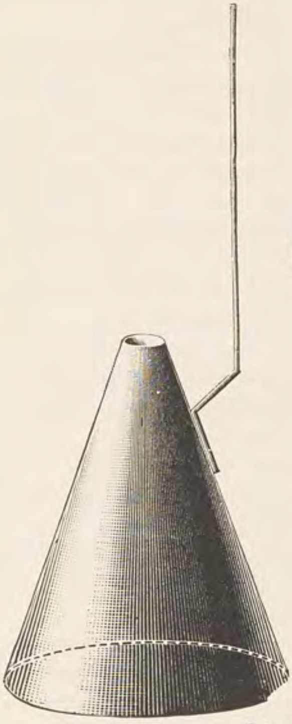
WIRE GAUZE

Since the introduction of rapidly rotating cathodes in 1898, electrodes consisting of cylinders of perforated sheet or wire gauze have been very largely used for the electrolytic analysis of certain metals.

The advantage that wire gauze electrodes possess over those made of platinum foil in the form of cylinders or cones as shown, consists in a uniform distribution of the current upon the inside and outside.

Fig. 18

Fig. 19



By courtesy of *Johnson, Matthey & Co., Ltd.*

Fig. 17

ELECTROLYTIC ANALYSIS APPARATUS

Of late years electrodes of other metals, in some cases plated with platinum, have been introduced as substitutes for platinum, but few of these have proved to be as satisfactory for the purpose as platinum itself.

Platinum apparatus for gold assaying was introduced by Messrs. Johnson, Matthey & Co., about 1855, and is still in use in all the principal mints and assay offices throughout the world.

This consists of a number of short platinum tubes, or thimble-like cups, contained in a shallow tray made of stout wire of the same metal. The object of the apparatus is to treat simultaneously a number of gold samples which have to be subjected to the action of nitric acid to dissolve out the silver they contain. For this purpose each assay sample is placed in a separate thimble, and the tray immersed in hot dilute nitric acid, whereby the silver is dissolved out leaving a residue of gold which is finally weighed.

This apparatus has proved to be of considerable service in mints and hall-marking assay offices where several hundred gold assays have frequently to be dealt with per diem.

Another important use of platinum is the manufacture of weights for use in chemical, physical, and assay laboratories.

The weights used, almost exclusively, by chemists and physists, are those of the French or metric system, the gramme being taken as the unit.

From 1 gramme upwards the weights are usually made of brass, but the smaller weights of 0·5 gramme downwards are commonly flat, and made from platinum sheet, being square in shape with one corner turned up to facilitate their being lifted by a small brass forceps.

The untarnishable nature of platinum ensures a constancy in weight, and this metal is in consequence invariably used for all sets of weights where great accuracy is necessary.

2. **Uses of Platinum in the Electrical Industry.** Platinum, on account of its high melting point and resistance to oxidation and corrosion, and other useful properties, has taken a very prominent part in the modern development of the electrical industry. One of its earliest applications in this connection was in the form of wire for the lead-in wires of incandescent lamps which at one time were made solely of this metal.

Attention has already been drawn to the great similarity between the coefficient of expansion of platinum and that of glass which permits of the metal being sealed through glass to form a perfectly air-tight joint, and in consequence formerly it was considered to be the only metal suitable to connect the inside filament of incandescent lamps with the outside copper wire through glass and thus convey the electric current to the filament.

None of the cheap metals are so satisfactory for this purpose, and until comparatively recently platinum was the only metal employed, but now it has been largely replaced by wires of nickel steel, which have a low coefficient of expansion and have been found to be very suitable as a substitute.

This gradual substitution of cheaper metal for platinum has been brought about partly on account of improvements in the lamps themselves, and also by the ever increasing price of platinum.

Platinum is, however, still largely used in the construction of physical apparatus in which it is necessary to effect electrical contact through glass.

Formerly platinum was used in the construction of the well-known " Groves " battery, the electric cell that took so prominent a part in the pioneer scientific work of Michael Faraday. Its use in the construction of battery cells has now, however, been discontinued.

The great electrical resistance of platinum, which is about seven times greater than that of copper, has been taken advantage of in the construction of electrical resistance furnaces for which purpose it is very suitable when its high melting point and freedom from oxidation are also taken into consideration.

As is well known, when a current of electricity is passed through a metallic wire, the wire becomes hot, the energy of the electric current being converted into heat. No chemical change occurs in the wire, and after it has been allowed to cool it is in all respects the same as it was before the current was passed through it, although long continued use results in a certain amount of deterioration.

Before the introduction of electrical resistances made of base metals such as nickel-chrome alloys, the electrical furnaces for laboratory and experimental purposes were generally wound with platinum wire and, in consequence, were costly to manufacture and to repair.

Furnaces designed with a view to reducing the cost to reasonable limits, whilst at the same time retaining all the useful features of furnaces wound with platinum, have now been placed on the market and are in extensive use, but for many scientific investigations the platinum electric resistance furnace is still preferred.

In these furnaces the platinum resistance is completely embedded in the walls of the furnace which are usually made of some suitable fireclay.

They are designed to work up to temperatures of about 1,200° C. "In the older pattern of laboratory furnace a helix of platinum wire was wound on a porcelain tube.

" This had the disadvantage that the wire, if thin enough to use current at the ordinary voltage, quickly burnt out, whilst at high temperatures the porcelain was liable to disintegrate and crack, owing to the very local character of the heating.

"This difficulty is overcome in the Heraeus furnace by using a ribbon of thin platinum foil in place of wire.

"The temperature of the foil is never greatly different from that of the tube, and local overheating is avoided.

"The helix should be wound so closely that adjacent turns are separated by the shortest possible distance, and they are kept in place by an asbestos ribbon.

"The tube of highly refractory porcelain and the foil are enclosed in a thick insulating layer of magnesia and an outer casing of asbestos bound together by metal bands.

"The external appearance of such a furnace adapted for use in a horizontal, vertical, or inclined position is shown in Fig. 20.

"A platinum resistance furnace of this type may be heated for a short time to 1,300°-1,400° C., but continued heating at the latter temperature causes destruction of the porcelain tube ; it is therefore inadvisable to use this pattern of furnace for temperatures above 1,200° C."[1]

The furnace is supported on trunnions and mounted on a trestle frame as shown in the illustration, which is about one-fourth the usual size.

Amongst the many uses to which these electrical resistance furnaces may be put are the determination of the recalescence points of steel ; the annealing of specimens of metals and alloys for microscopic examination ; the demagnetization of steel rods, etc.

The standard of electrical resistance adopted in this country consists of an alloy of platinum and silver

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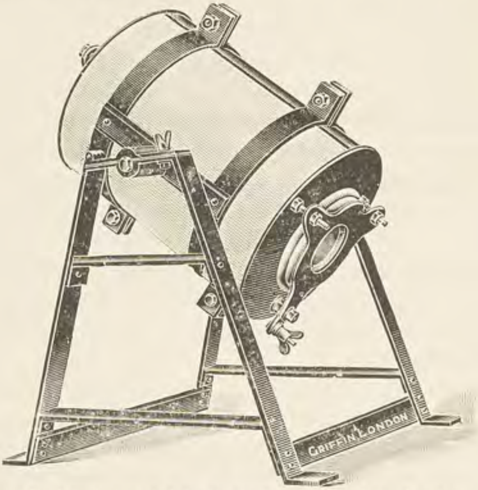
[1] C. H. Desch, *Metallography*, 3rd Edit., 1922, p. 97.

containing 33 per cent of the former metal and 67 of the latter.

Another important use of platinum in the electrical industry is for the contact points or spark plugs of internal combustion engines.



By permission of John J. Griffin & Sons, Ltd., London

FIG. 20

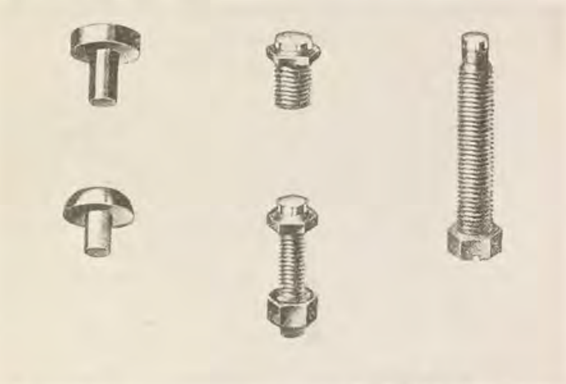
PLATINUM WOUND ELECTRIC TUBE FURNACE

The so-called platinum used for this purpose consists of an alloy of that metal and iridium, the proportion of the latter ranging from 15 to 50 per cent for different classes of work, and averaging about 20 per cent.

For contact points in all forms of electrical apparatus the platinum is used in the form of rivets, which may be made entirely of solid iridio-platinum or of thick discs of this alloy welded to base metal rivets or screws.

The rivets are supplied in a large variety of styles and sizes suitable for contact points in all forms of electrical apparatus, a typical form of solid platinum rivet by Baker & Co., New Jersey, being illustrated in Fig. 21.

In cases where it is permissible to make a portion of the head of the rivet of base metal, the head is reduced in thickness and a solid iridio-platinum disc of uniform thickness, which forms the contact surface, is welded to the base metal.



By courtesy of *Baker & Co., New Jersey*

FIG. 21

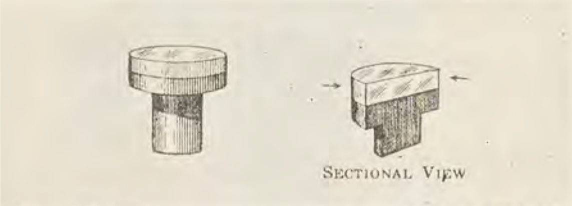
PLATINUM RIVETS

For contact purposes in connection with automobile and flying machine magnetos, starting and lighting devices, etc., the solid iridio-platinum discs are welded to screws, as shown in Fig. 22.

For stationary, marine and automobile, gas, gasoline, and oil engines, especially where the " make-and-break " type of ignition is employed, the contact points are made of iridio-platinum of extreme hardness, and are solid semi-spherical pieces varying from 0·09 in. to about 0·19 in. in diameter, and from 0·075 in. to 0·125 in. in thickness.[1]

The sparking points are attached to the terminal electrodes by soldering or by electrical welding.

The increasing price of platinum has led to the introduction of substitutes, such as tungsten and nickel for contact points, but none of these have proved to be so satisfactory as iridio-platinum for the purpose. The substitutes are prone to oxidize and their life is comparatively short. For certain classes of contact points, however, they are increasing in use, owing to their cheapness.



By courtesy of *Messrs. Baker & Co.*

FIG. 22

COMPOSITE RIVETS AND CONTACTS

"Fine platinum wire has, for many years, had world-wide use as fuse-wire in the construction and operation of the detonating caps of explosives, both in warfare and industrial developments. Many miles of it are used annually and lost from the available supply, but it has no competitor in this particular field.

"Fine platinum wire is also the accepted standard

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[1] Data Concerning Platinum, Baker & Co., Newark, New Jersey.

for protective fuses in electric circuits of small current capacity.

"The fact that this metal does not oxidize at any temperature greatly increases the surety of the interruption of the electric circuit only at the predetermined point.

"For telephonic and telegraphic circuits it is admirably adapted, as the small section of metal required renders the cost insignificant."[1]

Platinum also finds extensive use in the electrical industry in the construction of thermo-couples for pyrometers, the instruments now so largely used for the determination of high temperatures.

Since about the year 1830 physicists have advocated the use of thermo-junctions for the measurements of high temperatures, but it was not until Professor Le Chatelier in 1887 placed at the disposal of metallurgists an admirable thermo-junction that the problem could be considered to be really satisfactorily settled.

Professor Le Chatelier's thermo-couple at first consisted of a platinum wire simply twisted with, or soldered to, another wire of platinum containing 10 per cent of iridium.

When this thermo-junction is heated a current of electricity is generated, and the current passes to a galvanometer or other suitable electrical measuring instrument of high resistance, the amount of whose deflections are proportional to the heat applied to the thermo-junction.

Subsequently an alloy of platinum with 10 or 15 per cent of rhodium was introduced in place of the platinum-iridium alloy, it having been found as the result of experience that the use of the rhodium alloy gives greater

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[1] Ref., Data Concerning Platinum, Baker & Co., Inc., New Jersey.

constancy in continuous use, particularly at high temperatures, with, however, a slight decrease in the sensitiveness of the junction. The pyrometer is calibrated by exposing the thermo-junction to certain known temperatures, such as the solidifying points of salts or metals, or of certain alloys. The choice of couple will depend on the range of temperature required to be covered during the observation, and as a general rule it may be taken that couples of platinum and platinum-iridium alloy may be used for temperatures up to 1,400° C., whilst platinum and platinum-rhodium couples should be used if it is required to go up to temperature of 1,500° or even to 1,600° C.

When accurate measurements are required it is necessary for short intervals to introduce a cold-junction, that is to say, arrangements are made to keep the junction of the pyrometer wires and the galvanometer leads to a constant or known temperature.

For this purpose they are always kept at a temperature of 0° C. by being placed in a glass tube, which is itself plunged into a mass of melting ice.

Since the introduction of these platinum-metal couples enormous strides have been made in pyrometry especially in its application to industrial requirements, and it has followed naturally that investigations have been made with a view to discovering suitable substitutes for the very high priced platinum metals. This has resulted in the introduction of a number of so-called base-metal couples, chiefly nickel-chromium alloys.

But whilst base-metal couples have found extensive use in many industries, the platinum metal couples meet with fairly extensive adoption in scientific work, and for all technical purposes where reliability in temperature measurement is of fundamental importance.

Apart from research work, they are used in actual practice for the determination of furnace temperatures, controlling the heating of particular steel forgings, such for example as the varieties of gun steel, also for the control of annealing or tempering operations, or for any purpose in which exact temperatures are required.

But the measurement of the difference of potential produced when a junction of two metals is heated is not the only way in which platinum has been made serviceable in the measurement of high temperatures. It has long been known that variations of temperature may be determined by measuring the increased electrical resistance of a heated conductor, and a new era in the measurement of heat began in 1872 when Sir William Siemens showed that electrical resistance might be used practically in pyrometry.

In this type of instrument a coil of platinum wire is used, and its resistance to an electric current at the ordinary temperature is balanced by the use of a standard resistance.

On heating the platinum coil its resistance will be increased, and this increase of resistance can be measured and translated into terms of temperature.

Siemens' instrument was, however, liable to changes of zero, but it was shown by Professor Callendar, in 1887, that with certain precautions the electrical-resistance pyrometer may be rendered very trustworthy.

Callendar winds the platinum wire on a plate of mica, excludes reducing gases by enclosing the coil in a tube of doubly-glazed porcelain, and uses a zero method for measuring the resistances with the galvanometer.

Platinum has also rendered considerable service to mankind in its use for cathodes and anticathodes in so-called X-ray tubes, which are now so largely used for medical purposes.

As is well known the term X-rays is given to peculiar invisible rays which are given off by a discharge of electricity through especially constructed vacuum tubes.

The existence of these rays was discovered by Prof. Röntgen in 1895, whilst investigating the phenomena of cathode rays, produced by the discharge of electricity through a rarefied gas from metal electrodes, sealed inside the ends of a long glass tube from which the air has been removed more or less completely.

In the course of this investigation Röntgen observed that a covered photographic plate, which was lying by chance near the apparatus, was affected just as though exposed to ordinary light. He concluded that the effect must be due to some unknown form of radiation ; and the uncertainty of their character led him to apply the term " X-rays."[1]

The X-rays differ from cathode rays in that they pass through many solid substances with comparatively little absorption.

Metals and compounds of heavy metals (e.g., lead, glass) are opaque to the rays ; but non-metallic substances are comparatively transparent.

Thus Röntgen observed that the flesh of the hand is transparent, and more so than the bones.

Consequently, if the hand be laid on a photographic plate (protected, if necessary, from ordinary light by being enclosed in an opaque paper envelope) and held in the path of the rays, a " negative " or " radiograph " is obtained which shows clearly the details of the bones.

A modern type of tube now used frequently for producing X-rays, manufactured by the well-known firm of Cuthbert Andrews of London, is illustrated in Fig. 23.

The cathode is a concave aluminium disc, and the anode is a round piece of platinum foil placed at the

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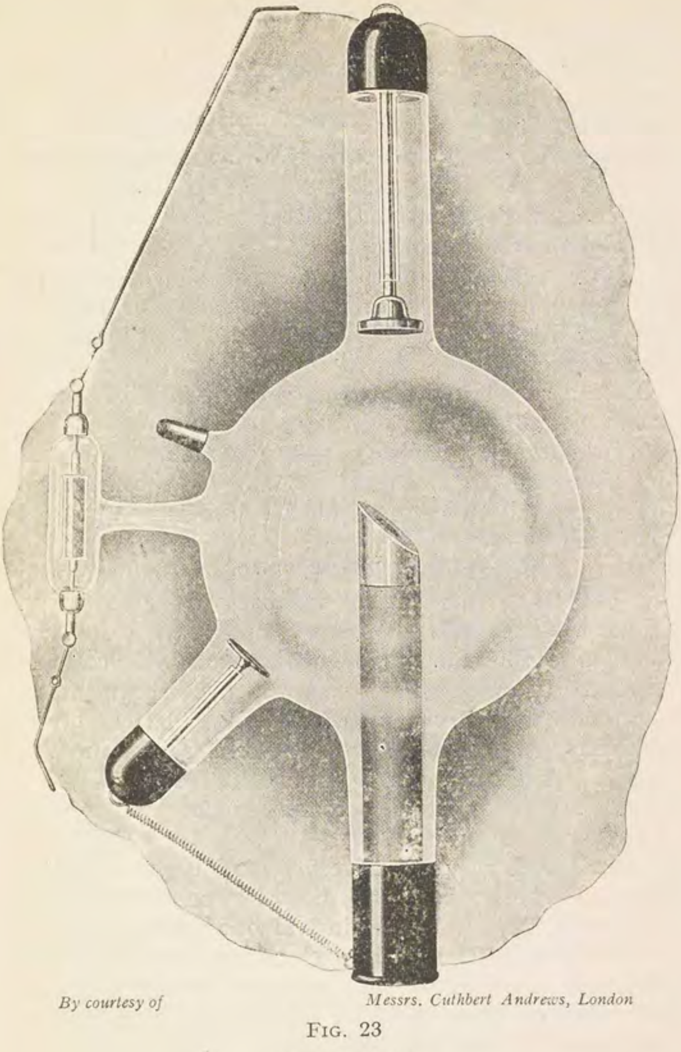
[1] Gregory & Hadley, *A Classbook of Physics*, 1917, p. 478.



By courtesy of *Messrs. Cuthbert Andrews, London*

FIG. 23

X-RAY TUBE

centre of curvature of the cathode and inclined at an angle of 45° to its axis.

On passing an electrical discharge of high voltage through the tube, the cathode rays are concentrated upon a point on the surface of the anode, termed the target, and the X-rays originate from the point where this bombardment occurs.

The construction of the tubes varies in accordance with requirements, but the anticathode, or positive pole of the tube, usually consists of a comparatively thin copper tube, closed at its lower end, to which is affixed a substantial platinum target, whilst in certain cases the anticathodes are of pure platinum.

During the past few years the use of metallic tungsten for the actual target of the X-ray tube has become much more general on account of the increasing price of platinum.

But in the opinion of Messrs. Cuthbert Andrews, who are experts in this class of apparatus, tungsten in an X-ray tube has only one positive merit, viz., it does not burn so readily under the bombardment by the cathode stream. In every other respect (in their judgment), a platinum target is preferable. The latter gives, generally, a constant, steady-working instrument; whereas tungsten tends to form a harder tube, which works unevenly, and becomes much more easily discoloured during use.

Tungsten is very expensive, very difficult to work, and has no intrinsic value as metal; whereas platinum represents always a certain value according to the current price. They strongly advocate a tube with a platinum target to use with moderate currents, leaving the tungsten tubes to those workers who need heavy discharges or ultra-long exposures.

With few exceptions Andrews' tubes are fitted with a device for lowering at will the vacuum or internal resistance of the tube.

The "Osmosis" regulator used for this purpose consists of a tube of palladium or platinum, sealed into the wall of the X-ray tube and closed at its outer end. This metal tube has the property, when heated, of allowing hydrogen to pass through its substance, and then into the X-ray tube, the vacuum of which is consequently lowered.

The various forms of X-ray instruments are intended for all classes of radiographic and therapeutic work, and are now in very general use at all the leading hospitals.

In connection with this work, a double salt consisting of platinum-barium and platino-cyanide is used as a screen as described later.

In recent years, platinum has also been found preferable to other metals for the electron-emitting electrode of the tri-electrode vacuum tube used in wireless telegraphy and telephony.

"In radio-telegraphy in order that signals may be sent from a transmitting station, some method must be supplied to regulate the flow of electric current in the transmitter so as to form the dots and dashes of the telegraphic code. This is done by means of a key, which is a conveniently operated switch by which the current in the transmitting circuit is established and interrupted.

"In hand keys it is customary to make the contacts of platinum, or some alloy thereof, for the flash or spark at the contacts when the circuit is broken will volatilize a softer metal with consequent burning and sticking of the contacts."[1]

Platinum is used in the construction of apparatus employed in the physical laboratory for the study of

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[1] Stone, *Elements of Radiotelegraphy*, pp. 121-122.

electricity, heat, spectroscopy, and the recently discovered radiations referred to above, but its use in the physical laboratory is less extensive than in chemical laboratory equipment.

As much of this physical apparatus is made of glass and is provided with attachments of platinum wire and plates, advantage is taken in its construction of the similarity in the coefficient of expansion of glass and of platinum.

CHAPTER VI

USES OF THE PLATINUM METALS—(*contd.*)

3. Uses of Platinum in the Dental Industry. Platinum has many valuable properties that commend its use for dental purposes. In the mouth it is not affected by oral secretion, and its high melting point make it especially valuable in bridge work, continuous gum work, and as a matrix metal where high fusing porcelains are used for inlays.

As early as 1820 it was introduced in France for a base in continuous gum work, and in more recent times it has been largely used for this purpose in the form of an alloy with silver under the name of "dental alloy."

Until the high price of platinum restricted its use, two qualities of this alloy were in general use in England, the best quality consisting usually of two parts of silver to one part of platinum, and the second quality consisting of three parts of silver and one part of platinum, but the composition varied slightly with different makers.

With the rapid rise in price of platinum less of this metal was added until alloys containing less than 5 per cent of platinum were to be found on the market.

Later an alloy known as "palladium alloy" was introduced, and was essentially dental alloy in which the platinum was replaced by palladium, but the increasing price of the platinum metals has caused both these alloys to be withdrawn almost entirely from the market for dental purposes.

Dental alloy is, however, still used to a limited extent in place of platinum in the manufacture of certain classes of jewellery, and for soldering platinum.

Platinum in the form of wire is largely used in the manufacture of artificial teeth as it happens to have practically the same coefficient of expansion as the enamel material used in the making of such teeth.

Its low rate of expansibility under increased temperature, and its very high fusing point and non-oxidizability make it most useful for pins for artificial teeth, and for continuous gum work, and no satisfactory substitute for it has been found for these purposes.

The platinum wire for dental pins is usually alloyed with from 2 to 3 per cent of copper to harden it, but within recent years, consequent on the high price of platinum, the percentage of copper in some cases has been considerably above this.

As substitutes for the comparatively pure platinum for dental pins alloys of gold-silver-platinum, containing from 10 to 20 per cent of the latter metal, have been introduced during the past few years, and some of these have proved to be very satisfactory in practice.

Originally platinum was introduced into the dental industry as a cheap substitute for gold, the metal at that time being much lower in price than gold, but, with the ever-increasing price of platinum and of the platinum metals, the tendency has been to revert to 18 carat and 16 carat gold for much of the dental work for which dental alloy and other platinum alloys were until recently used, because their cost was below that of the gold alloys.

The addition of platinum increases the strength and elasticity of gold, and in consequence, gold alloys containing from 2 to 20 per cent are used by dentists for bands and base plates.

Platinum in the form of very thin foil is used as a tooth-filling material in the same way as pure gold foil.

Platinum foil, however, is not so pliable and soft as

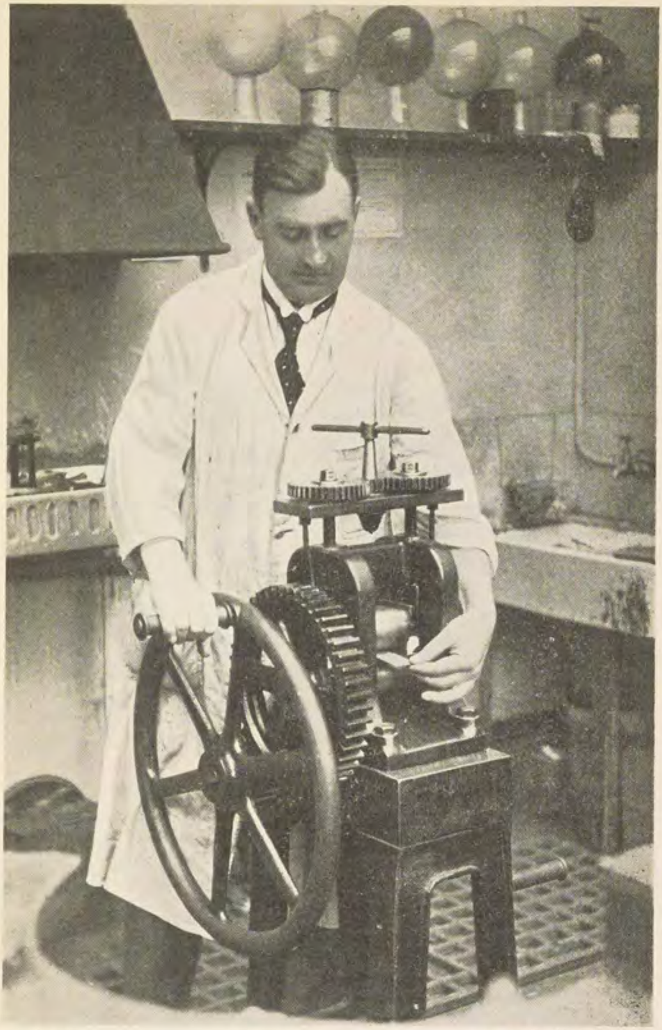

Photo *C. & M. Wilkinson*

FIG. 24

ROLLING PLATINUM SHEET FOR JEWELLERY PURPOSES

By courtesy of Goldsmiths' & Silversmiths' Company, London gold to work, and does not weld so readily ; in order, therefore, to make the leaves of platinum adhere when pressed together the surface is usually covered with a thin film of pure gold by electro-deposition. The foil must be thoroughly annealed when used in order to make it soft and work more readily. Fillings of platinum have the advantage of being almost white when finished.

Fig. 25
DIAMOND BOW BROOCH

Platinized gold foils also are used, which consist of gold foils coated with a thin layer of platinum.

The resistance of platinum to the action of iodine, sulphuric acid, etc., make it a valuable metal for root canal fillers, needles, and points of hypodermic syringes, etc.

The shortage of platinum during the war period led to the introduction of gold-palladium alloys for dental purposes, some of which were placed on the American market under trade names such as rhotanium, palau, etc.

The alloys usually contain from 90 to 60 per cent of gold and, according to Fahrenwald,[1] certain of them have been in the hands of operating dentists for some time and have proved to be equally as good as platinum for many purposes.

They have been used for pins and baked into porcelain teeth, and as thin foil and heavy sheet for other types of construction, all with the most satisfactory results.

The extent to which platinum may be replaced in this manner is limited, however, by the amount of palladium available.

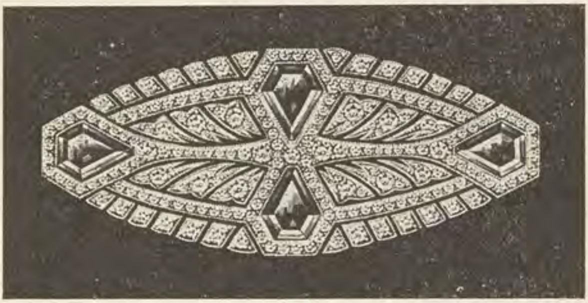

FIG. 26

EMERALD AND DIAMOND BROOCH

4. **Uses of Platinum in the Jewellery Industry.** The use of platinum for the manufacture of jewellery is of comparatively recent origin, but since its introduction for this purpose during the last two decades its use has very rapidly extended, so that in spite of the high price of the metal at the present time it is estimated that something like one-third of the total output of platinum is used in the jewellery industry.

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[1] F. A. Fahrenwald, *Journal of Ind. and Eng. Chemistry.* Vol. ix, 1917, p. 590.

So far as the working properties of platinum are concerned, it is an ideal metal for the use of the goldsmith and jeweller, as it lends itself readily to manipulation and can easily be hammered into intricate designs, or spun and stamped to any desired shape.

A typical form of rolling mill for rolling platinum for jewellery purposes is shown in Fig. 24.

FIG. 27

DIAMOND BROOCH

The strength and general working properties of platinum enable the jeweller to construct designs of gossamer daintiness without sacrifice of security, as valuable gems may be held firmly though so little metal is required, that only a very small part of the gem surface is hidden. The characteristic colour of platinum enhances the beauty of most stones, especially of diamonds.

In the modern application of platinum as a basis for gem setting some very fine examples of the jeweller's art may be seen in every large city.

The cutting of a mount on a platinum ornament is illustrated in the frontispiece, and typical examples of modern platinum jewellery are shown in Figs. 25, 26, 27, 28, 29, and 30, which illustrate work executed by the Goldsmiths' and Silversmiths' Co., Ltd., of Regent Street, London.

Within recent years the various parts required by the manufacturer of jewellery, which were formerly made entirely by hand, have been stamped by machinery and only require to be assembled and soldered together.

Examples of such platinum stampings by Messrs. Blackmore, Howard & Metherell, Ltd., of Hatton Garden, London, are illustrated in Fig. 31.

Platinum is also combined with various carat golds in the form of striped and double sheets. Sheets of this description are very effectively used for cigarette cases and similar articles.

" A large amount of platinum has for some years been used in the United States for jewellery, although in some cases this is merely a plating over some inferior metal.

" Normally, in that country, jeweller's ' platinum ' contains an average of 10 per cent of iridium, but for certain work the proportion may be as high as 15 per

FIG. 28
DIAMOND BRACELET

Fig. 29

DIAMOND BOW BROOCH

cent. In this, as also in the electrical industry, iridium is principally employed as a hardening element."[1]

Within the past few years the use of an alloy of palladium with platinum, in place of iridio-platinum, has been practised to an undue extent in America, despite the timely protests that have been made against it.

The admixture has run from 25 per cent up to even 35 per cent, and as palladium was not long since worth but 56 dollars an ounce, whilst "hard platinum" (with 10 per cent of iridium) was worth 124 dollars an ounce, this would bring down the value of platinum with 25 per cent of palladium to but 102 dollars an ounce.[2]

Then the great difference in specific gravity

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[1] Imp. Min. Res. Bureau, *Platinum*, p. 11.

[2] G. F. Kunz, *Watchmaker, Jeweller, Silversmith, and Optician*, Jan., 1924, p. 127.

between the two metals must be considered, platinum (with iridium) being about 21, whilst palladium is less than 12, giving the combination 75 per cent platinum and 25 per cent palladium a specific gravity of 19·50, almost exactly that of gold. Another most important consideration is that several acids which platinum resists will attack and tarnish palladium. Thus, the usual *aqua regia* test applied to platinum, without producing any stain, will at once give a brown coloration with the palladium alloy.

The State of New York has a law which requires that if an article be stamped, or even described as platinum on the label or invoice, all parts that appear to be platinum must assay at least 925 parts per 1,000 of *platinum group metals.* So long as palladium is cheaper, as well as being a much lighter metal than platinum, it will be evident that the law is too indefinite, and lends itself to abuse as indicated above.

Since platinum has been used in the United Kingdom for jewellery purposes the recognized trade standard of quality

FIG. 30
DIAMOND EXPANDING
WATCH BRACELET

decided upon in 1912 has been 995 parts of pure platinum per 1,000, but in 1922 it became necessary for the London Wholesale Jewellers' and Allied Trades' Association, Ltd., to direct the attention of the trade to the fact that there was a quantity of " platinum " on the market which did not conform to the recognized trade standard.

At a recent public meeting of goldsmiths, called to discuss standard trade descriptions, a recommendation was passed that the term " platinum alloy " shall not in future be recognized as a trade description.

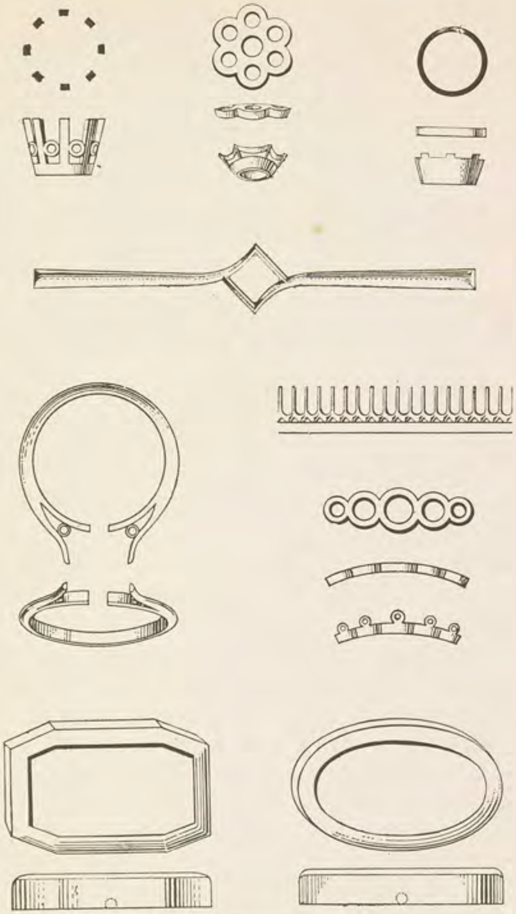
Reputable firms usually put a mark on their productions indicating that pure platinum is used in the articles, but something more than this simple marked assurance appears to be needed between the retailer and his customer, and it is contended that it is here that a hall-mark would be infinitely more satisfactory.

Hall-marking of Platinum. The high esteem in which platinum is held for the mounting of expensive jewellery has raised the question whether it is not entitled under the changed circumstances to the hall-mark of the Government Assay Office in the same way as other precious metals. The question of a hall-mark for platinum has come into greater prominence during the past few months.

On the 6th March, 1924, the Prime Warden and Wardens of the Worshipful Company of Goldsmiths, London, relative to this question, received a deputation of representatives of the jewellery trade, the organizations represented including amongst their members the leading firms in the trade in London and Birmingham.

The deputation pointed out that they were in favour of the standardization of platinum both in the interests of the trade and of the public.

They further submitted that the placing on the market



By courtesy of Blackmore, Howard & Metherell, Ltd., London.

FIG. 31

STAMPED PLATINUM PARTS

of articles alleged to be made of platinum but which were in fact made of platinum alloy or of platinized gold, seriously affected the trade.

They further contended that, if platinum were standardized at not less than 950 per 1,000 purity, the dishonest trader could be dealt with if he invoiced as platinum a metal containing a lower percentage of pure platinum, and they asked the Goldsmiths' Company to promote legislation to standardize platinum at 950 per 1,000 and to assay and mark any platinum articles which might be sent to the Company for that purpose which reached that standard.

The deputation pointed out that there were no insuperable difficulties in the way of assaying and marking of platinum as was shown by the example of France.

The deputation were assured that the Company would give the most careful consideration to the views that had been expressed.[1]

Three marks of guarantee were created by the French Government in 1913 for the stamping of works of goldsmithing and jewellery, composed wholly or in part of platinum. These marks consisted of (1) a dog's head for articles of national manufacture destined for sale in France ; (2) the head of a young girl for objects for exportation ; and (3) a mask for imported goods.

French hall-marked platinum is 950 quality, but the average quality used by Paris goldsmiths is 970.

It is also of interest to know that Switzerland, in 1914, adopted 950 parts of platinum per 1,000 as the minimum standard for articles to be officially controlled, and instituted a hall-mark of a chamois head for all platinum articles found to be of the required standard.

In concluding this section it may be stated that a

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[1] Report in *Watchmaker, Jeweller, Silversmith, and Optician*, April, 1924, p. 573.

number of so-called " white golds " have been introduced in recent years as substitutes for platinum for jewellery purposes. These are alloys of gold with either palladium or nickel to produce a whitening effect, together with zinc and sometimes silver and copper.

The alloys are usually of 18 carat quality and can be hall-marked, although not showing the distinctive yellow colour usual to that quality of gold. The nickel alloys very closely resemble platinum in colour, but are harder to work.

The palladium alloys are softer to work but do not in most cases so closely resemble platinum, and are more costly.

Miscellaneous Uses of Platinum. Amongst the miscellaneous uses of platinum one of the most important is the alloy of platinum 90, and iridium 10, prepared by Messrs. Johnson, Matthey & Co., in 1870, for the Comité International des Poids et Mesures, and chosen after exhaustive trials as the material for the standard metre (The Etalon), kept in Paris, which, in theory, is the standard of the metric system now universally employed in chemical and physical work.

This alloy was first shown by them at the Vienna Exhibition in 1873, and all the standard metres and kilos for international use were subsequently prepared of this alloy and supplied by this firm to the International Committee of Weights and Measures.

The weight of platinum employed in the manufacture of these standards was 250 kilos (about 8,000 oz. troy).

Subsequently Geo. Matthey recommended the alloy containing 15 per cent of iridium for standard measures of length, made in the tubular form, and the 20 per cent alloy for standard weights.

These iridio-platinum tubes were prepared for measuring the coefficient of expansion of the International

Geodesic Rule and Thermometric Metre, after experimental work carried out at the Ecole Normale, Paris.

Other miscellaneous uses for platinum are tubes for gas engines (Fig. 32), and tips for lightning rods. These latter are in the form of a cone and are either made hollow, thus enabling them readily to be brazed to the end of the lightning rod, or made solid with threaded shanks so that they can be screwed direct into the top of the lightning rod. An example of the former, the most usual kind, is shown in Fig. 33.

By courtesy of *Johnson, Matthey & Co., Ltd.*

FIG. 32
GAS ENGINE
TUBE

FIG. 33
LIGHTNING
CONDUCTOR
POINT

FIG. 34
CAUTERY
POINT

Platinum finds use in medicine in the form of cautery tips, typical examples of which are illustrated in Figs. 34 and 35.

Reference may also be made to the use of finely divided platinum in the manufacture of reflecting surfaces by the process known as " sputtering."[1] This method came into

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[1] *The Making of Reflecting Surfaces,* Physical and Optical Soc., London, 26th Nov., 1920.

use during the war period for the " silvering " of glass mirrors for special purposes which were required to retain their surface brightness without tarnishing under atmospheric influences.

For this purpose advantage is taken of the electric discharge of platinum particles from a platinum anode in vacuum.

These particles are deposited on the glass to be converted into a mirror by placing it in the path of the particles whereby the whole surface becomes covered with a film of extremely finely divided platinum.

Upon heating the glass nearly to softening point the film is made to adhere and form a bright metallic surface which has been found to be very permanent and free from tarnish, even after long exposure.

FIG. 35
CAUTERY POINT

Platinum also finds use as iridio-platinum for points in the construction of theodolites for which purpose it seems to be very much in favour for certain classes of surveying work.

5. **Industrial Platinum Compounds.** Several salts of platinum find important uses, two of the most important being the preparation of printing paper for platinotype photographs, and the other the preparation of Barium platino-cyanide for screens in X-ray photography.

" When photographic paper is sensitized with a solution of ferric oxalate mixed with potassium platino-chloride and exposed to light, the ferric oxalate is reduced to the ferrous form and the platinum salt to metallic platinum, the ferrous oxalate on treatment with a solution of potassium oxalate then being totally dissolved.

" When the sensitized paper is exposed to light under a negative the platinum is reduced to metal and becomes fixed on the paper, but where the light cannot penetrate there is no reduction of the ferric salt to the ferrous condition, and the platinum salt remains soluble and is washed out of the paper with water."[1]

The platinotype process was invented some forty years ago by William Willis, whose death has only recently been recorded at the age of 82.

There are modifications of this process, all based on the reactions of ferric and ferrous oxalate, potassium oxalate, and potassium-platinum chloride, but they are modifications in detail only. The principle on which the platinotype paper of to-day works, is essentially the same as that on which was based the first paper put on the market by the inventor.

Platinum salts are of special value in the production of photographic paper as the impressions yielded by them is of superior quality and permanence.

In X-ray photography platinum is used in the form of barium platino-cyanide which has the property of becoming fluorescent, and converts the X-rays and the ultra-violet light rays into visible radiations.

This platinum compound is applied as a coating to a projecting screen, on which the shadows made by the rays are outlined. The term "fluorescent screen" is usually employed to denote the platino-cyanide screen used in visual examination in X-ray work. The screen consists of a perfectly even coating of very fine crystals of the barium-platino cyanide spread over a flat surface such as a sheet of parchment tightly stretched across a wooden frame.

Various salts are used for the electro deposition of platinum in the same manner as the electroplating of gold and silver.

The principal compounds of platinum from the point

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[1] B. Dunstan, *Queensland Government Mining Journal*, 1921, Vol. xxii, p. 96.

of view of the electroplater are platinichloric acid, previously referred to, which is very soluble in water, platinic chloride ($\mathrm{Pt\ Cl_4}$), potassium chloro-platinate, $\mathrm{K_2(Pt\ Cl_6)}$, and the corresponding ammonium compound $\mathrm{(NH_4)_2\ (Pt\ Cl_6)}$, usually known as ammonium platini-chloride.

According to Barclay and Harrison[1] the most generally reliable solution for the electro-deposition of platinum for decorative purposes, where a comparatively thin coating is sufficient, is that introduced by Roseleur, and made up as follows—

Metallic platinum	1 oz.	31·2 gr,
Ammonium phosphate	12 oz.	375·0 gr.
Sodium phosphate ($\mathrm{Na_2\,HPO_4}$)	4 lb.	2 kg.
Water	1 Imp. gall.	5 litres

The platinum is dissolved in *aqua regia*, and the solution repeatedly evaporated down with the addition of a little hydrochloric acid to expel nitric acid.

The crystals obtained are dissolved in distilled water, the platinum precipitated by the addition of the ammonium phosphate solution, and then the sodium salt added with constant stirring until the precipitate dissolves and a clear solution results. After boiling to expel any free ammonia and to improve its working qualities and then adding water to make up for loss by evaporation, the solution is ready for use.

This bath, in common with most others used for platinum deposition, is worked hot with a voltage of about 4 volts.

The electro-deposition of platinum is not, however, so readily effected as in the case of gold and silver, the difficulties met with being connected with the fact that a freshly deposited film of platinum is always in a state of tension, a state of affairs which is usually ascribed to

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[1] *Electro-plating*, 1912, p. 338.

the hydrogen occluded by the metal; on account of this tension the deposit readily begins to peel off when the surface is bent or coiled.[1] The most adherent deposits appear to be obtained in a warm bath as stated.

In some cases it is advisable first to apply a coating of copper or gold; then to deposit the platinum upon that.

Platinum plated on copper is used for scale pans, etc.

Platinum plating is used by the makers of chemical balances in Germany, but the details of the process employed do not appear to have been made public.

Platinum, in common with gold and silver, is used in the ceramic arts for decoration of earthenware, but owing to its price its use has had to be restricted to special decoration where its characteristic colour enhances the design.

For this purpose platinic chloride, either in the liquid or dry powdered form, free from acid, is used.

A fluid mixture is prepared by adding the platinic chloride to an oily menstruum. This may be painted, printed, or otherwise transferred to the glazed surface, and on firing a brilliant grey or black deposit of platinum is left which usually does not require burnishing. This method is analogous to that by which the so-called gold and silver lustres are obtained.

The platinizing of porcelain or of glass produces a metallic film of the brilliancy of silver, but is much more permanent than that produced with silver.

The platinum salt is mixed up into a workable pigment with fat, turpentine, oil of lavender, etc., and applied with camel hair pencils in the ordinary way.

Within recent years a chemical preparation containing a proportion of platinum held in suspension in liquid

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[1] U. R. Evans, *Metals and Metallic Compounds*. Vol. iii, p. 254.

has come into use. Thus, " Platinum enters into the composition of the preparation known in pottery as ' Liquid Silver ' or ' Liquid Platinum,' the explanation for its use being the impossibility of obtaining the desired resultant shade in pottery decorations by use of silver, which would blacken in the kiln fire.

" Platinum especially prepared has been found to give a perfect silver resultant effect in such work."[1]

This preparation is ready for use and is merely painted on the ware after it has passed through the kiln, it has a more or less brilliant glossy appearance without requiring to be polished or burnished.

All the compounds which platinum forms with non-metals are decomposed by heat, and as a general rule also by reducing agents.

Iridium also may be introduced into glazes as an oxide, and gives a colour varying from grey to black.

Rhodium chloride is also added to certain preparations of " liquid gold " to heighten the colour of the film of gold that remains after firing the wares on which it is used.

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[1] Johnson, Matthey & Co., Ltd. *Wembley Exhibition Catalogue*, p. 17.

CHAPTER VII

THE PLATINUM INDUSTRY, AND PRICES OF METALS

1. **The Platinum Industry.** The development of the platinum industry has been summarized in the report on " Platinum Metals," issued by the Imperial Mineral Resources Bureau (1922, p. 18), as follows—

" From about 1870 to 1890 the output of Russian crude platinum was refined in London by Messrs. Johnson, Matthey & Co., and in Paris by Des Moutis, Quennessen & Co.

" Then from 1890 to 1909 the Russian material was refined mainly in England and France by the above firms, but also to a small extent in Germany, the latter country having now come into the field, the chief representative being the firm of Heraeus & Co., of Hanau."

" In 1909 the Société Anonyme d' Industrie du Platine, an organization established in 1898, and already owning a number of plantiniferous areas in the Urals, in addition to possessing a refinery in Paris, contracted with the owners of the important Shuvalov and Demidov placer deposits for the purchase of the whole of their output of unrefined platinum metals at a price arranged on a sliding scale up to 1915, thus acquiring control of the greater portion of the Russian platinum export business."

As a result the British buyer as a rule became largely dependent upon Paris for his supplies and was forced to pay a higher rate than he had done previously.

" Now, however, the French contracts have terminated ; and, having regard to the heavy *ad valorem* export duty, and the embargo on exports of crude platinum, imposed in Russia during the war period, it would appear unlikely that they will be renewed, or that Russian producers will be permitted to enter into similar agreements in the future."

" It has been officially stated that during the period of twenty-five years, 1889 to 1913, only about 1·8 per cent of the Russian output was retained for domestic use, the remainder being distributed as follows—

" To France, 70 per cent ; to Germany, 29 per cent ; to the United Kingdom, 1 per cent."[1]

This 1 per cent, however, represents the quantity of crude platinum exported and directly consigned to the United Kingdom, the bulk of her supplies for refining being received through Paris as previously stated.

No figures appear to be available giving the exact amount of Russian crude platinum annually refined in the United Kingdom in recent years.

" Early in 1914, the Russian Imperial Government imposed a 30 per cent *ad valorem* duty on crude platinum, the value of the metal to be fixed by the Council of Ministers.

" The tax was apparently imposed with the expectation that it would lead to a greatly increased amount of platinum being refined in Russia, where, in 1912, only three platinum refineries existed, these handling only about 2 per cent of the entire domestic production of crude platinum. The tax appears to have failed of its purpose and only to have stimulated the production of platinum in Colombia and other countries.

" Soon after the commencement of the war an embargo was placed on the exportation of crude platinum in quantities valued above 500 roubles, equivalent to £53 13s., at the rate of 2s. 1¾d. per rouble then ruling. But even this did not result in the establishment of

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[1] Imp. Min. Res. Bureau, *Platinum Metals*, 1922, p. 18.

refineries, its only effects being to embarrass foreign purchasing companies and firms who were under contracts to customers, and to cause an accumulation of stocks in Russia.

" In 1915, however, it was reported that the Nikolai-Pavdinsk Company had completed a platinum refinery at Ekaterinburg, which would be under Government control.

" In March, 1916, this refinery commenced the treatment of crude platinum."

" In the year 1917, it was reported that no dredges were working and that it would take a considerable time to put them into condition for future operation.

" All the platinum produced in Russia in that year was recovered by crude hand methods. By an order which became effective on 1st February, 1917, the importation of drawn and spun platinum into Russia was prohibited."

The whole situation of the platinum industry in Russia in recent years is, however, somewhat obscure as very little reliable information is available.

It would appear, however, that the platinum industry was nationalized by the Soviet Government in 1918, and the crude platinum that was won at that time was without any organization.

Afterwards Koltchak's army was in possession of the platinum mining areas from 1918, and under his regime the properties were handed back to the old owners.

The Soviet people, however, again obtained possession on his retirement in 1921, and the Ural Platinum Trust was appointed by the Soviet Government at Moscow, linking up all the platinum properties of Russia, and giving them the authority to utilize the dredges which had been left on the properties by the old owners, without any compensation to those former owners at present.

In 1922 the Anglo-Ural Platinum Trust Company was formed for the purpose of financing and developing the platinum industry when the Russian Government returns the mines and plant as private property, and to try by regular and consistent exploitation to regain the position which the platinum industry held in pre-war days.

The purpose of this company, which is a private one and distinct from the Platinum Trust organized under the Soviet Government, is to work certain Russian platinum mines, and also to refine and market the products. It is, however, susceptible of very wide development, as the powers reserved under the Articles of Association are extremely liberal.

The personalities of the leading directors, all of whom are persons well known in this country and in Russia as largely interested in the platinum industry, offer a guarantee of the best results.

Until the Imperialist war in the year 1914, the world market only knew one real furnisher of platinum, viz., Russia, which country might be considered as holding a monopoly in this industry, but from the foregoing remarks it will be evident that the supplies of crude platinum that have hitherto been available from Russia, and upon which British and Continental refiners have relied so much in the past, are not likely to be forthcoming to the same extent in the very near future as in the past, especially in view of the fact that the deposits are steadily decreasing in their metal content.

Attention is therefore being given to the possibilities of increasing supplies from other sources.

More intensive mining operations in Colombia and elsewhere have resulted in augmented output from placer deposits, and the introduction of electrolytic methods of refining of both precious and base metals is giving an increased output of platinum metals from such sources.

Although the quantity of precious metal recovered from these latter sources is very small in individual cases, yet in the aggregate it is by no means inconsiderable.

It is to such sources that the future must look for supplies to help in replacing the shortage in the Russian platinum output, and with this object in view all promising deposits in all parts of the world are being carefully examined, whether alluvial material or platiniferous base metal ores such as those occurring in Sudbury, Ontario.

For some years the average annual consumption of platinum for industrial purposes has been considerably greater than the production.

The deficiency is made up by old platinum which constantly comes into the market, partly owing to the high price of the metal.

2. **The Price of Platinum Metals.** (1) PLATINUM. When platinum was first produced it had little market value, as its useful industrial properties were not then appreciated.

In the year 1869, when more or less systematic production began, the value of the crude metal was stated to be under 8s. 6d. a troy ounce, but from that year onwards the value, although subject to considerable fluctuations, has steadily increased, and during the past few decades there have been very considerable advances in the value of the precious metal.

Prior to 1896 the market price of refined platinum remained fairly steady between 30s. and 40s. an ounce for many years, but subsequently it rose until it reached 90s. an ounce in 1905, and then advanced rapidly until it was quoted at as much as 160s. an ounce in 1906, the maximum price up to that time.

This great increase in price led to greater activity on the part of the producers in the Urals, because the entire output for a number of years subsequently was bought at fixed prices by the dealers in platinum, as already mentioned.

The average price in 1907 was 140s. an ounce, whilst in the following year, 1908, it fell to 85s. an ounce.

During the next ten years, including the war period, the price of refined platinum rose considerably, the average price in 1909 being 89s., and rising to more than four times this sum in ten years, the average price in 1918 being no less than 388s. an ounce.

Since the armistice the platinum market has been unstable in view of the shortage of supplies, and in consequence the fluctuations in price have been considerable, as shown by the following figures—

PRICE OF REFINED PLATINUM IN THE LONDON METAL MARKET

FOR THE YEARS 1919-1923 INCLUSIVE

Year.	Price in Shillings.		Lowest.
	Highest.	Average.	
1919	—	442s.	—
1920	760s.	600s.	Dec. 440s.
1921	Sept. 430s.	401s.	Jan.--Apr. 380s.
1922	Sept. 520s.	452s.	Feb. 390s.
1923	Mar. 580s.	512s.	Feb. 460s.
1924	Jan. to March	560s. to 580s.	—

As previously mentioned, Russia, in the year 1915, endeavoured to create a local platinum refining industry by imposing an *ad valorem* export duty of 30 per cent on crude metal, but, judging by the reports which have been published, the endeavour was not attended with success.

The present-day tendency appears to be for the price of the refined metal to remain in the neighbourhood of the maximum price hitherto obtained, its present value being about 600s. an ounce, which is more than six times that of gold. This increased value of platinum is due to its scarcity caused by the present condition of affairs in Russia, and the great demand for jewellery made therefrom.

Colombia, which is increasing its output annually, in 1919 put on a platinum export tax of 5 per cent *ad valorem*, and no doubt this will have some effect in preventing any tendency to the lowering of prices.

PALLADIUM. Prior to the war there was little demand for palladium, in fact the supply exceeded the demand, but owing to the great shortage of platinum during and since the war attention was given to palladium as a substitute for some purposes, and in consequence the market value increased.

At the end of 1918 palladium was quoted at 500s. an ounce nominal, and this price was maintained during 1919.

Early in 1920 the price advanced to 800s., this continuing until early in March, when the price eased to 600s. nominal. In July the price fell to 400s., rising again to about 600s. in September, and then declining at the end of the year to 500s. in November, and still lower to 440s. in December.

At the end of 1921 " raw " palladium was quoted at 260s. to 280s.

Since that time the demand for the metal has steadily continued, and the price has been well maintained, the quotations during 1923 fluctuating between 305s. and 360s.

IRIDIUM, for which there is a good demand, varies considerably in price from time to time, quotations for

1923 varying approximately between 1,000s. and 1,300s., so that it is nominally twice as valuable as platinum.

OSM-IRIDIUM. The application of osm-iridium to industrial uses has been extended in recent years, and the demand for this natural alloy, especially for the coarse-grained variety produced in Tasmania, increased considerably after 1917, with a consequent notable advance in the price offered.

The demand for osm-iridium has recently become greatly reduced, and the price has dropped to less than half the average for 1920.

Immediately before the Armistice was signed in 1918, the price paid for crude osm-iridium in the Tasmanian markets was as high as £37 7s. 6d. an ounce.

The price fell considerably afterwards, but stood at a much higher average during 1920, the average local price being £38·38 compared with £23·73, the average for 1919.

The great demand, and consequent high price offered, for Tasmanian osm-iridium are due to the scarcity in other countries of " point metal " for use in the tipping of gold nibs for fountain pens, for which purpose the Tasmanian mineral is admirably adapted.

The price of point-metal osm-iridium is greatly in excess of that obtained for the ordinary fine-grained material, but the actual value cannot be definitely arrived at, as it is determined by negotiation between seller and buyer and not by current rates for crude metal.

The ultimate value of the material of fine grain-size is governed by fluctuations of the platinum market, which, in turn, was until recently controlled by a group of financiers in Paris. So long as the demand for point-metal continues, the industry in Tasmania remains in a flourishing condition, but it was reported in 1921 that, in consequence of a fall in price to about £30 an ounce in June, 1921, and to as low as £18 an ounce by August of that year, many miners were giving up the quest for osm-iridium.

Other Platinum Metals. No prices of osmium, rhodium, or ruthenium are quoted on the London market. As there is little demand for these metals, their sale in common with palladium and iridium is a matter of negotiation, and is regulated by the quantity and quality required.

The average price of rhodium in recent years appears to have been about 400s. an ounce, whilst that of ruthenium has been in the neighbourhood of 200s. to 300s. an ounce.

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