The First Platinum Refiners

THE FRENCH GOLDSMITHS AND THE ARSENIC PROCESS

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Credit must undoubtedly be given to the arsenic process of removing base metals from native platinum, and principally to its practice by Janety, the Master Goldsmith of Paris, in the years just before and during the French Revolution for leading to the first real exploitation of platinum as an industrial metal and for enabling its properties to be fully appreciated.

Surprisingly soon after Ulloa's first announcement of the occurrence of platinum in New Granada, samples of the material reached Western Europe and were examined exhaustively by a number of scientists there. By 1750 many of its striking properties were established and thoughts began to turn towards making use of them, but before this could be done it was necessary for the granular native metal to be converted into malleable sheet.

That it was fusible at an extremely high temperature was demonstrated by Macquer and Baumé in 1758, although only in a minute quantity in the focus of a powerful burning-mirror. But very early on (Baumé announced it formally in 1758) the pioneers found that the material could be welded into coherent malleable form by forging it at a very high temperature, but one well below its melting point, just as is the case with the working of iron.

But with platinum the temperature required is very much higher than that which is sufficient for iron and, while attainable, was then very difficult to hold. Now unfortunately it so happens that the South American native platinum contains a certain percentage of iron and, at these temperatures, this iron oxidises not to the soft oxides of the blacksmith's forge, but to a hard refractory skin of magnetite which effectively prevents welding.

The early workers soon realised this and knew that they had to get rid of the iron before they could weld the metal into ingots. There were two courses open to them. The first was by a dry metallurgical method seeking to extract the iron by a combination of scorification and fluxing at the highest temperature possible; the second was by a wet chemical process by which the platinum was dissolved in aqua regia and then precipitated (of course without the iron) by means of potassium or ammonium chloride. But this wet process was complex, messy and slow in developing, and it was not until 1786 that a commercially manageable process emerged from it in Spain.

The metallurgists were quicker and were in the market with a malleable product at least a year earlier. According to the most detailed account of their activities, they treated the native metal with three or four times its weight of 'white arsenic' (arsenious acid) and a few ounces of 'salt of tartar' or (later) potassium carbonate.

The origin of the use of an arsenic compound as the oxidising agent for the removal of the iron goes back to the discovery by Scheffer in 1751 that the addition of a small quantity of arsenic to platinum induced it to melt at a low temperature. (We know now that the platinum-arsenic eutectic contains 13 per cent of the latter and melts at 597°C.)

His successors were preoccupied with this phenomenon, and were confident that somehow it would help them to the solution of their problem. They were right, because in the course of their scorification process the platinum was liquefied in the presence of reduced arsenic and collected at the bottom of the fusion, where it solidified when the melt was allowed to cool.

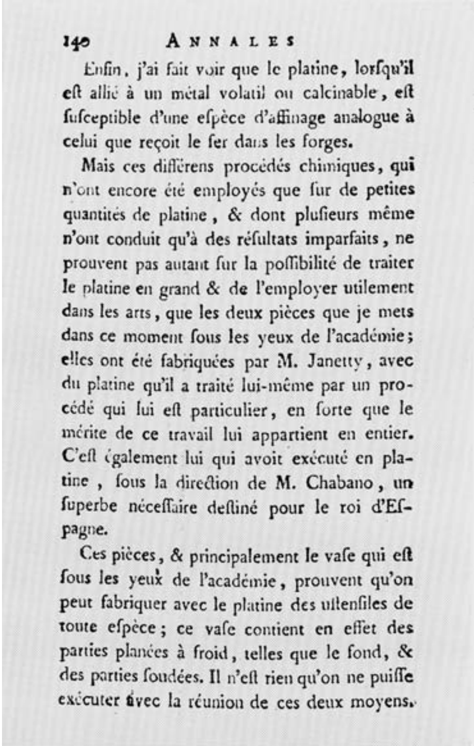
Removal of the Arsenic

Their next problem was to remove the arsenic, which they could do by volatilising it either as metal or as oxide, according to whether air was admitted to the process or not. Here they were severely limited as to the temperature to be employed, since on no account must the metal be permitted to melt; if this happened, the free surface would be reduced so much that the process of oxidation and volatilisation would be prolonged almost indefinitely.

On the other hand, arsenic oxidises freely at quite a low temperature and the arsenious oxide produced volatilises appreciably at 300°C and freely above 450°C. So if the temperature of the mixed metal were kept at about 500°C and not allowed to approach the melting point of 597°C, the elimination of the arsenic proceeded at a reasonable speed. Before it was complete, the button was tested carefully for magnetism and, if this were still evident, it was crushed to powder and the whole process carried out a second or even a third time until all trace of magnetism and therefore of iron had gone.

Forging and Working

The buttons were next subjected to the highest temperature obtainable and then, after cooling, cleaned in nitric acid followed by boiling with water until free from acid. Several buttons were then placed one upon the other, heated to a white heat, struck with a pestle to make them adhere, and then forged thoroughly on an anvil. This produced a malleable ingot that could be worked to produce both foil and hammered wire.


140 ANNALES

Enfin, j'ai fait voir que le platine, lorſqu'il eſt allié à un métal volatil ou calcinable, eſt ſuſceptible d'une eſpèce d'affinage analogue à celui que reçoit le fer dans les forges.

Mais ces différens procédés chimiques, qui n'ont encore été employés que ſur de petites quantités de platine, & dont pluſieurs même n'ont conduit qu'à des réſultats imparfaits, ne prouvent pas autant ſur la poſſibilité de traiter le platine en grand & de l'employer utilement dans les arts, que les deux pièces que je mets dans ce moment ſous les yeux de l'académie; elles ont été fabriquées par M. Janetty, avec du platine qu'il a traité lui-même par un procédé qui lui eſt particulier, en ſorte que le mérite de ce travail lui appartient en entier. C'eſt également lui qui avoit exécuté en platine, ſous la direction de M. Chabano, un ſuperbe néceſſaire deſtiné pour le roi d'Eſpagne.

Ces pièces, & principalement le vaſe qui eſt ſous les yeux de l'académie, prouvent qu'on peut fabriquer avec le platine des uſtenſiles de toute eſpèce; ce vaſe contient en effet des parties planées à froid, telles que le fond, & des parties ſoudées. Il n'eſt rien qu'on ne puiſſe exécuter avec la réunion de ces deux moyens.

A page from Lavoisier's report to the Academy in 1790 describing Janety's process for refining platinum. In showing two pieces of Janety's fabrication Lavoisier emphasised that there was now no limit to the type of vessel that could be produced in platinum

The first man to experiment with this complicated process was Franz Karl Achard, Professor of Physical Chemistry in the Royal Academy of Science at Berlin, who established the principles and later poured the liquid arsenic-platinum eutectic into the mould of a crucible (1). But the first commercial interest in the process undoubtedly came from some of the goldsmiths serving the French court, who grew up under the conditions of high luxury that applied there in the times of Louis XIV and XV. The first to come into the platinum story are Antoine Joseph Tugot and his former apprentice Jacques Daumy, practising at 58 rue de la Verrerie in Paris. Hoefer, writing in the article on platinum in the *Encyclopedie Moderne*, definitely states that these two men were the first to put platinum to use on a relatively large scale in 1785

(2). Tugot seems to have dropped out, but Daumy carried on the process for several years (3) and became a specialist in cladding copper with a thin sheet of platinum to form a *doublé* metal.

Marc Etienne Janety

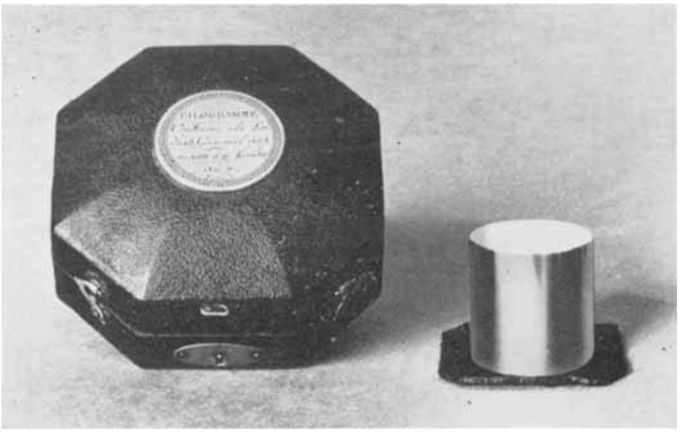
In due course his son succeeded him but it was another whose name ranks highest in the history of the exploitation of the arsenic process and that is the King's Goldsmith, Marc Etienne Janety. This man, a Master Goldsmith of Paris since 1777, began to take an interest in platinum in 1786 (4), and by 1788 he is said to have 'succeeded in making it in large amounts very pure and very malleable' and to have made 'crucibles, snuff boxes, etc.' of it. The report goes on: 'he makes use of arsenic to melt it but he has special methods of removing it afterwards . . . very dangerous since he has several times been seen in an atmosphere full of arsenic fumes'.

In 1790 he was honoured by Lavoisier himself introducing to the Academy two pieces of his work, one of which was a coffee pot with, as Lavoisier was careful to point out, 'cold-worked parts such as the bottom and soldered parts . . . by using together these two means there is no limit to what can be made' (5).

In 1792 the Academy asked Berthollet and Pelletier to examine his work to see if it were deserving of public support. Their report was published in the same year and states that he had devoted himself to the work with very great obstinacy and courage, that he had made many sacrifices and exposed himself to great dangers, but eventually had obtained success and produced many articles of platinum for both artistic and scientific use. The authors, echoing Lavoisier, point out that, although platinum had actually been 'melted' by others before Janety, only small objects had been made from it; 'it is therefore to this artist that we owe the bringing of this art to perfection and especially the ways of working it on a large scale.' Full details of his process are then given (6).

The New Metric Standards

Janety continued his work in Paris until about 1794 when, deciding that the position of King's Goldsmith was becoming a little incompatible with the political atmosphere of the times, he retired to Marseilles to set up afresh as a manufacturer of base-metal clock parts. There, in 1795, he was sought out by the new French government, because of his knowledge of the working of platinum, to come back to Paris and prepare the standards of length and weight for the newly established metric system. He came back to Paris in September 1795 and started work in November. The Commission of Weights and Measures gave him 200 marcs (say 1600 ounces) of native platinum and agreed to pay him 15 francs per ounce for the fabrication, with an allowance of 25 per cent for



One of the standard kilograms made by Janety in 1798 in platinum refined by the arsenic process. The label on the case reads 'Kilogramme Conformé a la loi du 18 Germinal An 3, presente le 4 Messidor An 7'

The Campo Formio Medal, struck in platinum in 1798 and showing Napoleon returning triumphantly from the wars in Italy and Austria. This medal required two thousand strokes of the press, indicating considerable hardness, probably due to the presence of iridium, but also great toughness as a result of efficient refining and complete freedom from arsenic

scrap. Between 1795 and 1802 he made four standard metres and four standard kilograms. The final products had all to be carefully standardised against earlier standards made in other metals with different coefficients of expansion. Eventually this process was completed and one of his metres was chosen as the approved actual standard and called the *Metre des Archives.* It and its three fellows are still preserved in Paris (7).

In 1798 a platinum medal commemorating the Treaty of Campo Formio was struck in Paris to a design of the famous medallist Benjamin Duvivier and presented to the Institut. It is still in existence and was shown in 1953 in London at the Wollaston Exhibition. The metal has taken the design perfectly, but there is a fine crack visible on the reverse. It is said to have required two thousand blows of the fly-press, which indicates considerable hardness, no doubt due to the presence in the metal of iridium, but at the same time great toughness as a result of efficient refining and complete freedom from arsenic (8).

In 1810 Janety exhibited a bucket-shaped vessel, seven inches in diameter and five inches deep weighing eighteen ounces and a retort holding a litre, showing that the size and scope of his work was increasing. The chemist d'Arcet in introducing these says: 'You know with what perseverance M. Janety *père* has struggled for more than thirty-three years against the obstacles opposing the reduction of native platinum into malleable platinum. It is only by long labours and by the loss of his health, of his fortune, of his profession, that he has succeeded in conquering them, and the happy results that he has presented to you are without any doubt the fruit of the greatest and most willing sacrifice that has been made in the advancement of an art' (9). In 1812 d'Arcet reports again, and he now refers to 'M. Janety *fils*, pupil and successor to his father', so that we can assume that the latter retired about this time. The objects presented by the son on this occasion were even larger vessels of 22 and 16 litres for the concentration of sulphuric acid, but in the same report we learn that 'M. Janety announces that for more than a year he has ceased to use arsenic in the preparation of his platinum' (10).

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