

Refining and Melting Some Platinum Metals

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It is difficult to give a refining outline that may be followed for any and all combinations of the platinum metals; different combinations require different methods of attack. This paper does not pretend to go into all of the reactions of the metals of the platinum group, but will outline the commercial refining of platinum scrap.

TYPICAL PLATINUM SCRAP

As a concrete case, let us take 100 oz. of miscellaneous scrap, made up of jewelry scrap, dental scrap and laboratory ware. This lot will contain some platinum, palladium, iridium, ruthenium, rhodium, gold, silver and copper.

The first problem is to get all of the metals in solution. If the scrap is principally platinum, palladium and gold, a treatment with aqua regia is the course to pursue; but if the scrap contains alloys high in iridium or ruthenium, aqua regia will act too slowly. In the case in hand, we are going to presume that we have scrap high in iridium and ruthenium, and proceed accordingly.

OBTAINING RESIDUE A

Place the scrap, together with six times its weight of granulated test lead, in a solid carbon crucible. This crucible may be placed inside a clay graphite crucible packed with charcoal, to prevent the excessive oxidation of the carbon crucible by the furnace blast. Place a tight cover on the carbon crucible; heat gradually to a good red heat and allow it to soak in the heat for 4 or 5 hr. After the leaded mass is cool, dissolve in dilute nitric acid (1-6) on a steam plate or sand bath. This dissolves practically all of the lead and most of the palladium, silver and copper, together with some of the platinum and rhodium, and leaves the iridium, ruthenium, gold, and most of the rhodium and platinum as a finely divided residue. Siphon off the clear solution and treat the residue with another portion of dilute nitric acid to insure the solution of the lead and copper. The second nitric acid solution is added to the first, and the residue is filtered on suction and washed thoroughly with hot

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water. This is Residue A, and contains gold, iridium, ruthenium, platinum, rhodium, and some palladium.

It is very important to get the iridium, ruthenium and rhodium into a finely divided condition in order to effect their dissolution and purification by the method which will be outlined later. The lead fusion and nitric acid parting serve to accomplish this division.

TREATMENT LEADING TO RESIDUE B

Add sulfuric acid to the filtrate from the lead parting to precipitate the lead; filter and wash with cold dilute sulfuric, discarding lead sulfate. Treat filtrate from the lead sulfate precipitate with hydrochloric acid, to precipitate the bulk of the silver. Filter off silver chloride. The filtrate will contain palladium and copper, and small amounts of platinum and rhodium which may have gone into solution in the dilute nitric acid treatment. To avoid the tedious evaporation often resorted to in reclaiming these metals from a bulky filtrate, add ammonium chloride salt in generous amount and saturate the solution with chlorine gas. This will precipitate all of the platinum and palladium as double ammonium chlorides, which can be filtered off and washed with cold ammonium chloride solution, and finally with alcohol, dried and burned to sponge. This sponge is added to Residue A.

The filtrate, which contains rhodium and copper, is cemented for several days with copper sheets. This cements out the rhodium, which is filtered off and set aside for further treatment. Call this rhodium black.

An optional method for handling the nitric acid solution from the lead parting is to cement immediately on copper sheets. This cements out silver, palladium, platinum and rhodium, and leaves copper and lead in solution. These cements are filtered off and added to residue A. The advantage of this optional method is to avoid the filtering and washing of a very bulky lead sulfate precipitate. On the other hand, this cementation must be continued for several days to be complete.

Residue A is dissolved in a mixture of three parts hydrochloric, one part nitric, one part sulfuric and two parts water. (The reason for the inclusion of sulfuric acid in this mixture will appear later.) The dissolution is carried out in large cylindrical crocks made of Pyrex glass or of porcelain. The crocks should have close-fitting covers, to retard the loss of nitrous oxide and chlorine. Treatment is best carried out on a steam plate; heating to boiling unnecessarily expels the active chlorine. After action has ceased, allow the solution to settle and siphon the clear solution into large porcelain basins. If sufficient acid has been used, a second acid treatment of the residue is unnecessary. The residue is filtered off and washed with hot water. It contains almost all of the

iridium and ruthenium, and some of the rhodium, but practically no platinum, palladium and gold. This residue is dried on a steam plate, and brushed from the filter paper. The paper is incinerated at a low heat, and added to the brushed off residue. This is Residue B.

EXTRACTING THE GOLD

The aqua regia solution, obtained above, contains platinum, palladium, gold, rhodium, and small amounts of iridium and ruthenium. This solution is evaporated on sand baths to expel nitric acid. The presence of sulfuric acid in the solution serves to expel nitric acid in one evaporation and keeps the solution from evaporating to a dry salt, which might cake hard and crack the basins. It converts any lead that may be present to lead sulfate. After this solution has evaporated to a sirupy consistency, it is cooled and the salt is dissolved in a generous quantity of cold dilute hydrochloric acid (1-10). The solutions are then heated to boiling to dissolve the last traces of salt. The solutions are transferred to a large crock and allowed to settle until clear; settling overnight is good practice. The clear solution is siphoned into another crock, the residue is filtered off and the filtrate added to the clear solution in the crock. The residue will contain silver chloride, lead sulfate and some baked-out gold.

The baked-out gold may be quickly extracted by treating the residue with concentrated hydrochloric acid and careful additions of dilute sodium chlorate solution. Stir vigorously while adding the sodium chlorate solution, in order to avoid explosions. After the gold has dissolved, the solution should be filtered and the filtrate added to the main solution in the crock. The main solution is now saturated with sulfur dioxide gas, which precipitates all the gold as finely divided metallic gold. The gold is filtered off and leached thoroughly with hot hydrochloric acid, to dissolve occluded platinum metals. This leach is added to the filtrate. The gold is then washed successively with hot water, aqua ammonia, and again hot water. These washings are discarded; the gold is dried and melted.

OBTAINING PLATINUM SPONGE

The filtrate from the gold precipitation contains platinum, palladium, rhodium, and some iridium. It is thoroughly saturated for several hours with chlorine gas to counteract the reducing action of the sulfur dioxide treatment and to oxidize the platinum metals in the solution to their highest valency. The solution is now put into basins and evaporated to smaller volume, or until there is no perceptible odor of chlorine gas but there is a strong odor of hydrochloric acid. A small quantity of alcohol is stirred into the hot solution; this serves to reduce the chlorides

of iridium and palladium to a lower valency and to hold them in solution while the platinum is being precipitated. Precipitate the platinum from a hot solution with hot concentrated ammonium chloride solution. Using both solutions hot will give an immediate crystalline precipitation of orange-colored platinum ammonium chloride, which is easy to filter and wash. (The color of the platinum ammonium chloride salt varies from light yellow to orange according to the heat of the reacting solutions.) Filter off the platinum ammonium chloride on suction filters, wash with half and half cold water and ammonium chloride solution, and finally wash with alcohol, dry and burn. A slow, careful burning of the platinum salt is necessary, to prevent loss of platinum as the ammonium chloride sublimates off. Burning under a cover, with the introduction of hydrogen, will aid in avoiding the loss of platinum. This gives a quite pure platinum sponge, but if higher purity is desired, a second crystallization of the platinum may be made.

We might say, at this point, that all of these ammonium chloride precipitations of the platinum metals are somewhat fractional. The precipitated metal always contains small amounts of the other platinum metals, and requires a second crystallization if high purity is desired; and secondly, all of the filtrates contain traces of the metal being precipitated, and must be worked for recoveries.

RESIDUE C

The filtrate from the platinum ammonium chloride precipitation is reoxidized by saturating with chlorine gas, and a little more ammonium chloride salt is added. This precipitates all of the palladium and iridium, and any platinum which did not previously precipitate, as a red double ammonium chloride salt, and leaves whatever rhodium is present in the filtrate. This filtrate is cemented on zinc and the cement is added to Residue B. The precipitated salt is filtered on suction, and washed with a saturated solution of ammonium chloride. It is then washed into a suitable vessel, using a wash bottle and water, and is treated with an excess of concentrated aqua ammonia; no heat is used in this treatment. The aqua ammonia dissolves palladic ammonium chloride to a colorless solution. The undissolved residue contains any platinum and iridium which may be present, together with traces of occluded palladium and base-metal hydroxides. This residue is filtered off and burned, and is called Residue C.

PRECIPITATING PALLADIUM

The ammoniacal palladium solution is diluted by twice its volume of cold water; hydrochloric acid is added to precipitate the yellow salt of palladosamine chloride. This is filtered on suction, washed with cold

dilute hydrochloric acid, and finally with alcohol, dried and burned under hydrogen to palladium sponge. The filtrate from the palladium precipitate is again chlorinated, any salt separating out is filtered off and the filtrate finally cemented with zinc. This cement is added to Residue C and reworked.

A suggested method for reworking cement together with Residue C, which should carry only small amounts of platinum, palladium and iridium, is as follows: Burn, dissolve in dilute aqua regia, filter off the residue, which is iridium. Add this residue to Residue B. The filtrate is evaporated to dryness, taken up in dilute nitric acid and all the palladium present precipitated in hot solution with mercuric cyanide. The white palladium cyanide is filtered off, washed with hot dilute nitric acid, and burned to palladium sponge. The filtrate from the palladium cyanide precipitate is evaporated three times with hydrochloric acid, and the platinum precipitated with ammonium chloride solution, filtered off and burned to platinum sponge. The filtrate from this platinum precipitation, which may contain iridium, and possibly rhodium, is treated, while hot, with hydrogen sulfide gas; the sulfide precipitation is filtered off, burned and added to Residue B.

REWORKING RESIDUE B

Residue B and rhodium black are combined; this combination contains the iridium, ruthenium and rhodium, and traces of other metals. It is intimately mixed with its own weight of sodium nitrate and 10 times its weight of sodium peroxide. This mixture is fused in an iron pot; the fusion should be carried on quietly for several hours, stirred with an iron rod, and finally poured on to an iron plate. The cooled mass is treated with water and the solution, together with the suspended oxides, is transferred to a glass retort of convenient size; chlorine gas is bubbled through the cold solution in the retort for about one-half hour, then, while the chlorine is continued, heat is gradually applied to the retort. The ruthenium will distill off as a volatile oxide, and is collected in a series of three Wolff bottles containing concentrated hydrochloric acid. Care must be taken that the solution in the retort remains alkaline; otherwise the ruthenium will be precipitated in the retort from an acid hypochlorite solution, and therefore will not entirely distill off as it should. The ruthenium chloride solutions from the Wolff bottles are united and evaporated to small volume; ammonium chloride salt is added and chlorine gas run in until ruthenium ammonium chloride salt is precipitated. This salt is filtered off and washed with alcohol; dried and burned, under hydrogen, to prevent formation of volatile ruthenium oxides. (Freshly precipitated ruthenium sponge is soluble in sodium hypochlorite solution, if the sodium hypochlorite solution is kept alkaline

by the addition of sodium hydroxide.) The solution and residue remaining in the retort are decanted into a basin and boiled with a slight addition of alcohol. This precipitates the iridium and rhodium, and leaves the platinum in the filtrate. The platinum may be recovered by making the filtrate acid with hydrochloric, and cementing on zinc and reworking in the usual manner.

The iridium and rhodium are filtered off and washed with dilute hypochlorite solution; the filter paper and contents are transferred to a beaker and boiled with concentrated hydrochloric acid. This dissolves the iridium and rhodium. The solution is diluted and the filter paper residue is filtered off and discarded. There should be no metallic residue. If there is, another caustic fusion is indicated. Concentrate the iridium-rhodium solution to small volume, add ammonium chloride salt, saturate with chlorine gas and filter off the iridium ammonium chloride which is precipitated. Wash with a saturated solution of ammonium chloride. To free the iridium salt from traces of occluded rhodium, dissolve the salt in hot water, concentrate and reprecipitate iridium with ammonium chloride and chlorine gas, filter and wash with ammonium chloride, and finally with alcohol. This salt should be dried carefully and burned to iridium sponge, and finally burned at a high temperature and reduced under hydrogen.

The filtrate contains rhodium. It is cemented on zinc or copper; the cement is dried, not burned, and the paper only incinerated. The rhodium cement is fused with sodium acid sulfate. This fusion dissolves the rhodium and leaves any platinum and iridium undissolved. The fusion is taken up in very dilute sulfuric acid, and rhodium is recemented on zinc.

SUGGESTIONS FOR REFINING

1. As previously stated, the order of procedure may be varied according to the composition of the alloy in hand. For instance, with an alloy high in palladium, we recommend the separation of palladium previous to the separation of platinum.

2. In all cases where gold is present, we recommend the removal of gold first, to avoid its inclusion in the precipitations of the platinum metals. The precipitation of gold with sulfur dioxide gas is quantitative, and yields gold of very high purity. The presence of free hydrochloric and sulfuric acids in the solution during the gold precipitation serves to prevent precipitation of platinum and base metals with the gold.

3. Solutions from which precious metals have been extracted should not be thrown away without a very careful test for platinum metals, as solutions that are in a reduced condition, especially amine solutions, do not react to the usual tests for the presence of platinum metals. Oxidation with chlorine gas, followed by cementation on zinc, may be resorted

to; or saturation with hydrogen sulfide gas; or, best of all, a sample of the solution may be evaporated to dryness, the evaporated salt carefully burned and the residue extracted with aqua regia and tested.

4. Chlorine gas will prove a valuable reagent in platinum refining. Its rapid oxidation of metals in solution, and its use in conjunction with ammonium chloride to obtain complete precipitation of the platinum metals, are of prime importance.

MELTING AND WORKING PLATINUM METALS

Platinum metals are commercially melted by means of the oxyhydrogen torch. The size of the torch should be suited to the amount of the metal to be melted. If much melting is to be done, the torch should be fitted with a platinum-iridium tip to prevent base metals from dropping into the melt. Either oxygen and hydrogen, or oxygen and city gas are suitable fuels for this purpose. If city gas is used for large melts, it is advisable to put the gas under pressure by means of a gas booster. Some melting is being done in the electric induction furnace, but the bulk of the melting has been with the torch.

Crucible

The crucible and cover are made of dry, high-burned lime. A good method of preparing the lime block is to granulate dry lime and press it into a cylindrical block, by means of a hydraulic press, using a pressure of about 150 tons to the square inch. After removal from the press, the lime block is fitted into a light sheet-iron casing, which offers a means of holding the block and of fastening it to the pouring stand. The block is then cut out to form a wide, shallow crucible. A similar lime block is pressed for the cover. This is cut out to form an arched roof, and has a hole in the middle of the top for the introduction of the melting torch, and suitable rim vents for the passage of spent gases.

Up to 400 oz. of platinum may be melted at one time in a lime crucible cut from a lime block 9 in. in diameter and 5 in. high, outside dimensions.

For the purpose of pressing this block, a steel plunger and cylindrical steel mold with walls 1 in. thick are used. The cylinder is split vertically into halves, and made slightly elliptical at the parting lines, to facilitate its removal from the lime block.

The lime block should be used immediately, or it will absorb moisture and crack upon the application of heat.

Crucibles made from zirconium oxide are successfully used for platinum melts, but are not as beneficial to the platinum as lime crucibles. Melting in lime has a purifying effect on platinum, for the lime acts as a cupel and tends to absorb small base-metal impurities. In cleaning

up after a melt, the lime may be dissolved away in hydrochloric acid. On the other hand, a zirconia crucible does not absorb moisture as lime does, and may be used repeatedly from day to day, but it does not have the cupelling action of lime and is more difficult to dissolve away.

It is not advisable to melt platinum in ordinary clay, graphite or silica crucibles, because the melted platinum is likely to take up carbon or silicon from the crucible wall and to become brittle.

Melting Procedure

Before the introduction of the metal, the lime crucible should be thoroughly preheated with the torch flame to drive the occluded gases out of the lime. If this preheating is not done, and platinum is melted in the raw crucible, the molten metal will spit considerably in the crucible, on account of gases released from the lime which bubble up through the metal. For this reason, the second melting in a lime crucible is generally quieter than the first.

After the crucible is properly preheated, the cover is raised and the metal introduced. The torch flame is applied through the cover and the flame regulated to carry a slight excess of oxygen. An oxidizing flame is necessary, to keep the platinum from absorbing calcium and also to give a solid casting, free from gas porosity.

The melt may be stirred with a solid carbon rod, for, due to the oxidizing flame, the melt does not take up any carbon. Chemically pure platinum may be melted and stirred in this fashion.

The metal should be quiet before it is poured. A little experience in melting platinum will indicate the proper pouring condition. A well poured ingot will show a down pipe at the top. If there are blowholes in the ingot, a remelting is indicated; in fact, one or more remeltings can do no harm.

Ingot Molds

Melted platinum may be poured into ingot molds made of hard carbon (Acheson graphite slabs, which are machined in halves and clamped together). For wire bars, an ingot 1 in. square by 12 in. long is a convenient size. For plate bars, a flatter ingot is poured. If the ingot mold is given a slight taper, an ingot may be removed by simply inverting the mold.

In this fashion may be melted pure platinum, pure palladium, and alloys of platinum and iridium; platinum and rhodium; platinum, palladium and gold; palladium and gold, etc. On the other hand, platinum alloys high in ruthenium or osmium might better be melted in an electric induction furnace, due to the tendency of ruthenium and osmium to volatilize in an oxidizing atmosphere, and also due to the tendency of

these alloys to absorb gases from the torch flame, which are difficult to expel and which make it difficult to get a sound casting.

Working

The wire bar ingot is heated to a white heat (1200° to 1300° C.) and hot forged under a power hammer. This hot forging tends to compact the metal, close up minute porousness, and to work out the pipe. After forging, the bar is cold rolled and swaged, or drawn to finished size. For drawing through steel dies, platinum may be lubricated by passing it through a box filled with dry powdered soap. For drawing through diamond dies, castor oil or other suitable wet lubricants may be used.

Flat ingots intended for plate are generally given a light cut in a planer, to remove surface imperfections, and then cold rolled to plate or sheet. A preliminary hot forging of plate ingots can do no harm.

If blisters show up in the plate stock, on annealing, a remelt is indicated.

Annealing

Platinum and platinum alloys should be annealed at suitable intervals during the working. The annealing may be done in a muffle furnace with an oxidizing atmosphere; that is, a free access of air. The metal should not be allowed to come in contact with the open flame, particularly if it is a reducing flame, for some of the alloys have a tendency to pick up contamination from the flame, which causes crystalline fractures.

DISCUSSION

E. WICHERS, Washington, D. C.—Reference is made to the sharpness of separation of iridium and platinum in the lead fusion. Ordinarily that is very sharp indeed if the lead is pure, but we have found that the presence of small amounts of zinc in the whole mixture will cause appreciable amounts of iridium to go into solution.

G. F. KUNZ, New York, N. Y.—Do you not have great difficulty with the lead anyway, and also the copper? If the copper is electrolytic, the alloys, I think, are much better than if commercial copper is alloyed. But lead seems to be a very difficult thing to handle and it does carry traces of different metals.

E. WICHERS.—In this case I do not think it is so much a question of zinc in the lead as that zinc may be in the platinum sponge. Frequently the metals are thrown out of solution by means of zinc. If this sponge is then separated by a lead fusion enough zinc is retained to cause serious trouble.