CHAPTER XII
ALLOYS AND BUTTONS CONTAINING GOLD AND PLATINUM-GROUP METALS

Material handled. Jewelers' buttons. Dental alloys. Equipment and chemicals. (A) Preliminary treatments. (B) Melting into a button if necessary. (C) Granulating the button or rolling it thin. (D) Dissolving the metal in aqua regia. (E) Recovering iridium from the silver chloride. (F) Recovering dissolved platinum. (G) Recovering gold. (H) Recovering silver if worth while. (I) The Stock Pot. Summary and diagram. Silver-rich buttons. Questions and answers.

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MATERIAL HANDLED

In Chapter XI we refined mixtures of gold and platinum particles, the process consisting of the removal of first one, then another contaminating substance, the platinum particles finally being left clean and in practically their original form.

In this chapter we assume that our gold and platinum metals are already melted and alloyed together, as in the case of certain dental alloys. Such material must be dissolved completely, all the gold and all the platinum going into solution and then being precipitated separately. Both jewelers and dental technicians will handle materials of this kind.

It is assumed that the reader is familiar with earlier chapters of this book, has had experience in dissolving and recovering gold, and has performed the acquaintance experiments in Chapter X. If he has carried through a refining according to Chapter XI, so much the better.

JEWELERS' BUTTONS AND ALLOYS

The jeweler occasionally has materials suitable for refining according to this chapter. Thus, after a few weeks of refining the mixtures described in Chapter XI he will have accumulated a number of old filter papers his paper storage containing particles
of precious metals and considerable dirt. He will reduce this to a button, as described in Chapter XVIII on Low Grade Wastes, which button should be refined according to the procedure shortly to be described.

In past years, when indium and platinum were much more expensive than they are now, platinum alloys containing gold, palladium, nickel, silver, and even other metals, were sometimes made into jewelry. Scrap and old jewelry made of this stock should be handled according to this chapter. White gold of the highest class (see Chapter VII) contains palladium; scrap and old jewelry made of such white gold should also be handled as described here. Chapter IX on "Identifying" tells how to recognize these complex platinum alloys and how to determine whether a white gold does or does not contain palladium.

DENTAL ALLOYS

Precious metals are employed in dentistry in several forms, some of which have already been discussed. Pure gold in the form of foil or adhesive sponge, is used in fillings; the scrap, which is nearly 24-k gold, should be refined according to Chapter V or VI. There are several kinds of dental gold solders and alloys in which gold and silver are the only precious metals present; these also should be refined according to Chapter V or VI. Amalgams and amalgam alloys contain silver, and sometimes (by accident) other precious metals as well; these should be laid aside and treated according to Chapter XVI. Platinum and iridio-platinum pins also are discussed in Chapter XVI, and generally should be treated separately, but if they are included by accident in the material described below, no harm will be done. Finally, we reach the very important modern alloys that are the main concern of this chapter - the wrought gold alloys and the casting gold alloys in which gold and platinum-group metals are present.

Base metals also find large employment in dentistry, and naturally become mixed with the precious metal wastes. Skinner's SCIENCE OF DENTAL MATERIALS, listed in the Appendix, describes their application. Thus aluminum is used in making dental plates; so are stainless steel and some of the chromium alloys. Nickel and tungsten are used in dental pins. Steel is employed for dental instruments, drills, etc. "Technic" alloys, which are not used in the mouth, but only for practice, demonstration, etc., are of two
types first the fusible alloys such as the bismuth-lead-tin alloys which are used in dies and counterdies, some of which melt at temperatures as low as that of boiling water, and second the yellow silver-copper technic alloys that look like gold. The workman should try to exclude these base metals as far as possible from his valuable wastes, as they not only consume time and chemicals, but some of them, like lead and tungsten, complicate the refining even when present in small quantities.

Modern dental gold alloys always contain silver and copper, frequently platinum, palladium, zinc and tin as well. Sometimes iridium, rhodium, nickel, and indium are present in small amounts, and the base metals aluminum, magnesium, manganese and iron have been found.

Much interesting research has been done on dental alloys during the last few years, both by the firms that sell them and by the National Bureau of Standards, with the cooperation of the American Dental Association. If the reader is not already familiar with these investigations, he should at once obtain some of the publications described in Chapter E of the Appendix. A familiarity with these recent researches will be of great usefulness both to the user and the refiner of these alloys.

The wrought gold alloys and casting alloys which are the main interest of this chapter, are used for a variety of prosthetic purposes, and many formulas have been proposed. Gold is the principal constituent of most of them, especially the yellow ones. The silver content of the wrought gold alloys ranges from about 5% to as much as 15%; this point will be brought up again later. Platinum and palladium together may run from 10% to as much as 25%. Normally iridium is present in small proportions less than 1% and probably got in by accident rather than by design. In the white alloys there is considerable nickel as much as 18%; copper runs from 9% to 15%, more or less, while zinc rarely runs over 1%. The American Dental Association Specifications


2 These specifications were prepared by the National Bureau of Standards, in cooperation with the Dental Association and the manufacturers of dental gold materials. See Chapter E of this volume.
that dental wrought gold alloys should contain at least 75% gold-and-platinum-group metals.

The casting gold alloys are also made up in a wide variety of formulas. They differ from the wrought golds primarily in that the gold content is relatively higher up to 90% and over and the platinum-group metals are lower. The Association Specifications require for soft casting alloys a minimum of 83% gold and platinum group, and for medium and hard casting alloys a 78% minimum.

The dental technician will have a variety of wastes containing these alloys, including scrap, clippings, old dentures, and the stuff swept from the bench where they are fabricated.

For convenience we shall divide these materials into two grades: first grade, consisting of clean buttons, sprues, dentures, clean scrap, and clean old jewelry; while second grade scrap consists of filings and stuff swept from the bench, which contain considerable dirt such as emery, rouge, carborundum, wax, rubber, plaster of paris, in vestment compound, charcoal, and what not.

For the present we shall exclude all amalgams and mercury; these will be taken care of in Chapter XVI.

For the present we shall handle material that contains comparatively little silver. Later in this chapter we shall consider the button in which silver is the major element.

**EQUIPMENT AND CHEMICALS**

These are the same as were employed in Chapter XI. Since in this chapter we dissolve all our metal, we may need some more large vessels, such as a large evaporating dish and one or more large jars or crocks, in addition to those already used.

**BEGINNING WORK**

For your first refining take a very small quantity, say 40 or 50 dwt., in order to gauge the size of vessels that this method calls for. Briefly, the procedures are as follows, most of them being already familiar.

A. Any preliminary treatment that may be useful.
B. Melting into a button if necessary.
C. Granulating this button, or rolling it thin, as preferred.
D. Dissolving the metal in aqua regia.
E. Recovering the iridium from the silver chloride.
F. Recovering platinum from the aqua regia solution, as usual.
G. Recovering gold from the aqua regia solution, as usual.
H. Recovering silver if worth while.
I. Laying aside the remaining solution the Stock Pot for treatment in Chapter XIII.

A. PRELIMINARY TREATMENTS

First grade clean scrap rarely needs any preliminary treatment. But second grade stuff, in which there is much assorted dirt, should be sieved, and probably burned in the frying pan or boiled in caustic, and it may help to take out iron particles with a magnet. Remember that if appreciable quantities of amalgam are present, the material should be treated by methods to be described later Chapter XVI.

Nitric acid, which we used in Chapters III, V, VI and XI to get rid of base metals, is sometimes employed here, but not always, for a variety of reasons. Thus, high grade wrought or casting golds are not attacked by it; therefore nothing would be accomplished by using it. Sometimes it pays to use it on the second grade (dirty) materials, depending upon the kind of dirt present, but usually it is easier to flux the dirt off in the next procedure. A further consideration is the possible presence of palladium. You will recall that palladium, when present in pure form or in certain alloys, is soluble in nitric acid; also a few rare alloys containing platinum will go completely into solution when boiled in nitric acid.

Accordingly, take a sample of your material, and boil it in nitric acid for a few minutes, then test the liquid with stannous chloride testing solution. If it shows that platinum or palladium has gone into solution, omit the treatment with nitric acid.

If you find that nitric acid dissolves only base metals, then treat the whole quantity of material with nitric acid as usual. If the solution contains worth while quantities of silver, put it in your Silver Jar and refine according to Chapter VIII.

If you are in doubt, omit the nitric acid treatment.

B. MELTING THE MATERIAL INTO A BUTTON, IF NECESSARY

Second-grade stuff, especially if it contains much carborundum or emery, is generally melted into a button.
Mix it well with a flux such as crushed borax glass and soda ash, using equal weights of flux and material, and melt in a gold-melting furnace, using a sand crucible. The flux serves to liquefy the dirt, while the metallic particles collect into a button at the bottom of the crucible. If the proportion of emery is high, use more flux. The chapter on Low Grade Wastes gives formulas of other fluxes. Do not use litharge. Let the melt cool in the crucible, which is then broken and the button carefully separated from the slag.

First-grade clean stuff, such as old dentures, may or may not need to be melted into a button. It does no harm in any case, and after a little experience you can tell whether it does any good or not; different kinds of metal call for different treatments.

Thus, if your metal—either first-grade or second-grade material runs more than half platinum, whose melting point is high, ordinary melting will not get it into a homogeneous button; you will want to lower the melting point of the whole mass by adding some brass, or perhaps some copper or zinc. If you have some rolled or filled gold scrap to get rid of, here is a good place to utilize it by melting it in with your second-grade dental wastes.

When breaking the crucible to remove the button, look out for beads or shot metal embedded in the slag; if there are many of these it means that you did not heat long enough, or did not use enough flux, or that your platinum percentage was too high. If properly done, the melting will consolidate all the metallic particles into a button, and all the emery, rouge, plaster of paris, etc. will go into the slag which then can be thrown away.
C. GRANULATING THE METAL, OR ROLLING IT THIN

The next task is to get the metal into such form that acids can work upon it easily. Sometimes the lumps or buttons are so soft that they can be rolled thin as paper. Cut the strips into short lengths and twist them so they will not lie flat in the acid, then anneal. Roll very thin; a few minutes spent at the rolls will save hours in the acid.

But often these metals refuse to roll, and it is easier to granulate them. This is done by remelting the metal and pouring it while molten into a big vessel of water. (See Chapter V.)

If your metal is as much as 12% silver, the silver will cause trouble when you try to dissolve the button in aqua regia. In Chapter VII on green gold we discussed this subject and the reader would do well to refer to this chapter now. So, if you know your metal to contain as much as 12% silver, melt some other metal in with it—gold, or copper, or zinc or brass—sufficient to get the silver content down to say 10% or less.

If you do not know what the percentage of silver is, drop a piece of your metal into a little aqua regia, heat to a boil, and see what happens. If the acids are very slow to act the chances are that it would pay you to melt your metal up with brass, gold, or other metal, in proper quantity to reduce the silver to 10% or less.

Usually it is best to add this extra metal when you are about to granulate the material. But some workers like to add it when making the first melt, just described.

D. DISSOLVING THE METAL IN AQUA REGIA

Place the metal, which by now is rolled thin or granulated, in a casserole and cover it with aqua regia. Mix as follows:

| Nitric acid, full strength | 1 part |
| Hydrochloric acid, full strength | 4 parts |
| Water | 2 parts |

Do not add any sulphuric acid yet.

Use 6 or 8 fluid ounces of the mixture to each Troy ounce of metal; with much platinum you may need more.

Sometimes the acids go to work at once; usually you will have to heat. If possible, set the casserole on a steam bath as that does not cause spattering or require continuous attention. Stir often to dis
lodge the scum of silver chloride. Place an inverted funnel over the dish, to prevent spattering, save acid, and keep out dirt.

Some people like to use an Erlenmeyer flask for this step, because it permits them to see what is going on. The thin Pyrex glass models withstand heat well. The frontispiece shows several Erlenmeyer flasks in operation, and on page 171 the reader will find other illustrations, with catalogue numbers and prices. The refiner may have occasion to use both the narrow-mouthed form and the wide-mouthed; the latter when there is some danger of boiling over. The narrow-mouthed form comes in many sizes, from the tiny 10 cc. size to the 6000 cc. model. The wide-mouthed form is made in three sizes 250, 500, and 1000 cc. Another advantage of these flasks is that the material therein can be stirred easily merely by rotating the flask not too briskly, of course, or it might froth over.

Do not use an evaporating dish for this procedure, as it permits too much acid to evaporate off wastefully.

The length of time required to dissolve the metals depends upon several factors. You can hasten matters by having the pieces very small and thin, by heating, and by stirring often to loosen the coating of silver chloride. Also, the more platinum and the more silver in the metal, the slower the action of the acids.

Silver, especially, makes the process slow. If it runs as high as 12% the slowness is noticeable; if as high as 25% the metal is practically insoluble.

Sometimes it helps matters to pour the solution off into a pitcher, then dump the whole mass of metal into the mortar and grind it hard with the pestle, to loosen the chloride. Then dump it back into the casserole, washing it back with a little water; then cover it again with the aqua regia solution, which will now go to work again with vigor.

Sometimes individual lumps or strips of metal will be much slower to dissolve than the bulk of the material. It may pay to pick out such lumps and lay them aside until they can be melted up and the silver content reduced to 10% or less.

Finally all the metal will seem to be dissolved, and you will have left only the powdery residue of silver chloride. Here, however, we meet a new consideration a point that has not come up before. If your original material contained iridium, the iridium will now remain undissolved as a metallic dark powder, mixed with the silver chloride.
This fact that when these alloys are dissolved in aqua regia the iridium remains undissolved was not appreciated by most early workers, but careful research at the National Bureau of Standards and elsewhere has established the fact that iridium does have this peculiarity. And if the platinum content is high, sometimes some of the platinum also will remain with the silver chloride. This may or may not complicate your task, however, first because dental alloys normally contain little if any iridium, and second because the platinum content is rarely high. The iridium residue has a dark color, and as you become more experienced you can tell by its appearance whether the silver chloride does or does not contain enough value to justify its further treatment. Assuming for the moment that our material might contain a good amount of iridium, we would proceed as follows:

E. RECOVERING IRIDIUM FROM THE SILVER CHLORIDE RESIDUE

When the aqua regia has dissolved all the metal that will dissolve, dilute it with its own volume of hot water, let it stand a little while; then pour or siphon off the solution do not filter it yet leaving the residue in the dish. Wash the residue and add the washings to the main solution. This main solution contains the gold, platinum, and palladium, and the base metals. Add a little sulphuric acid to it at this point, an ounce or less to each quart of solution, stirring well and adding the acid slowly. This precipitates any lead that might be present, and also facilitates the removal later of the excess nitric acid. Set the solution aside to settle, while we turn our attention to the residue in the dish.

Take a small sample, say as much as can be taken on the tip of the porcelain spoon, place it in a small beaker or tiny porcelain casserole, and add chemically pure ammonia diluted with hot water. Ammonia dissolves silver chloride, leaving iridium or platinum undissolved as a fine heavy dark residue, so fine that it may be almost

3 See William H. Swanger's paper on ANALYSIS OF DENTAL GOLD ALLOYS, Scientific Paper of the Bureau of Standards No. 532, of August 11, 1926. Also see Raleigh Gilchrist's NEW PROCEDURE FOR THE ANALYSIS OF DENTAL GOLD ALLOYS, Journal of Research of the National Bureau of Standards, Vol. 20, June 1938, pages 745-771. These papers, which are devoted primarily to the analysis of these alloys, rather than to their refining, are mentioned again in Chapter E of the Appendix.
indefinite. Rotate the little vessel and whirl all the powder into the
center, and it will be easier to see.

Frequently there is a light-weight light-colored residue, insoluble
in ammonia, that is merely flakes of glass or porcelain scaled off
the dishes and acid bottles. This is plainly of no value, and should
not deceive a careful observer.

You may find that no precious-metal residue remains; if so your
silver chloride is of small value and may be placed in the Silver Jar
or with other silver residues. But if the ammonia test reveals ap-
preciable quantities of iridium, then the whole quantity of silver
chloride must be dissolved out.

This procedure is similar to procedure 4 in Chapter XI, where you
dissolved the silver chloride from the platinum filings, using either
cyanide or ammonia. If you are not already familiar with this pro-
cedure, go over it again now. Simply cover the material with water to
which cyanide or ammonia is added, and heat. Most workers prefer
ammonia for this task, rather than cyanide, because it is safer and be-
cause the silver may be recovered therefrom more conveniently.

Sometimes this treatment reveals pieces of metal that have not
been acted upon sufficiently by the aqua regia, and which must be
returned for further treatment, but after you have had a little ex-
perience this will not occur.

The residue that remains after all the silver chloride is dissolved
will consist of the fine dark iridium powder, which may contain
some platinum, and almost always there will be the light flakes of
porcelain or glass from the vessels. Wash it well and catch it in a
filter paper. The disposal of this powder will depend upon the
needs of the worker. If the iridium is to be used in making up
new alloys, the flakes of porcelain or glass should be removed with
hydrofluoric acid according to the method given in Chapter XVI.
If not, let the residue dry and then sell it to a professional refiner
who gives credit for iridium.

F. RECOVERING PLATINUM FROM THE AQUA REGIA

Returning now to the aqua regia solution that contains dissolved
gold, platinum, palladium, and base metals: we shall recover first
the platinum, then the gold, according to methods that were used
in Chapter XI. Turn back now to Chapter XI, procedure 6, and
proceed exactly as there described.
You will note that the first step is to consider any sediment that may be present; sometimes there is much sediment, sometimes very little, and it can be removed now or later, as desired. The next step is to drive off excess nitric acid, dilute with water, filter if not perfectly clear, and recover platinum with ammonium chloride, exactly as in procedures 6, 7 and 8 in Chapter XI.

G. RECOVERING GOLD

This is accomplished precisely as in procedures 9 and 10, Chapter XI.

H. RECOVERING SILVER IF WORTH WHILE

This is accomplished as in Chapter VIII.

I. THE STOCK POT

Here again we follow the procedure of Chapter XI. The solution from which you recovered the gold and most of the platinum still contains all the palladium, as well as a little platinum. This constitutes what is called the Stock Pot, and it is laid aside for further treatment in Chapter XIII.

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SUMMARY AND DIAGRAM

The following diagram will summarize this chapter, and will be useful to the worker who is already familiar with the various procedures. It is helpful to compare it with the scheme given at the end of Chapter XI.
SILVER-RICH BUTTONS

As we intimated earlier in this chapter, if an alloy containing both gold and platinum-group metals should also contain much silver, it will require somewhat different treatment. If the silver content is as high as 15%, the button will be very difficult to dissolve in aqua regia. The best plan, in such cases, is to add enough gold (or copper or brass or zinc) to reduce the silver content to 10% or less, then to proceed according to the method just given.

However, it occasionally happens that an alloy contains so much silver, and so little gold and platinum-group metals, that the above expedient will be unsuitable. If you can so manipulate your materials as to avoid the formation of buttons of this type, do so, as they are not easy to refine.

You will recall in Chapter X, that when a button containing much silver and only a little platinum is treated with nitric acid, more or less platinum goes into solution. If the platinum content is low, it will all dissolve; if the platinum content is high, part of it will dissolve, and part of the silver will remain in the residue. In other words, nitric acid does not effect a separation. And it is not easy to recover the platinum from the nitric acid solution.
The way out is to dissolve such buttons in sulphuric acid not full strength acid, but acid containing about one part water to three parts acid. (Pour the acid into the water, slowly, and stir well.) This can be done when the gold-platinum content is not over 25%. The process is similar in principle to the inquartation described in Chapter VI, where a silver-gold alloy was refined by means of sulphuric acid; and the same precautions should be observed.

After the sulphuric acid has acted all it will, pour it off into a large jar of water, leaving the residue in the vessel. The liquid in the large jar will contain sulphate of silver (and sulphates of base metals), and the silver can be recovered as in Chapter VIII. The residue will contain gold, platinum, and possibly some silver that was not reached by the acid. Collect it and wash well, then treat it with aqua regia exactly as you treated the gold-platinum alloys that constitute the main topic of this chapter.

If you should, by inadvertence, dissolve a silver-platinum alloy in nitric acid, and find that a worthwhile quantity of platinum has gone into solution as platinum nitrate, do this: to the nitric solution, which contains platinum, silver, and perhaps other metals, add enough hydrochloric acid to precipitate all the silver as silver chloride. Filter, and handle the silver chloride as described in Chapter VIII. The solution will contain platinum dissolved in a sort of aqua regia in which the proportion of nitric acid is unusually high. Evaporate as usual to expel the nitric acid, then recover the platinum with ammonium chloride, as usual.

QUESTIONS AND ANSWERS

Q. Is it essential to add sulphuric acid to the aqua regia solution? I have a friend who does this work, and he says he never uses it.

A. No, the sulphuric acid is not necessary. Many expert workers never use it at all, even when lead is present, maintaining that it tends to make the solution so strongly acid that the precipitation of gold is hindered. On the other hand, one of the largest and best refiners of dental wastes uses considerably more sulphuric acid than is suggested in this book. See REFINING AND MELTING SOME PLATINUM METALS, by J. O. Whiteley and C. Dietz, of the Dentists' Supply Co. Laboratories, published by Mining and Metallurgy, March, 1928.

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Q. After precipitating the orange powder, I set the jar aside overnight and next morning there was a crust of green granular stuff all over the orange powder, and some was floating on the liquid. What shall I do?
A. The green crystals are probably a nickel or copper salt, crystallized out when the solution cooled. You may be able to get rid of some of the crystals by fishing them out with the porcelain spoon. Dissolve the rest in a little hot water, stirring well; then before they have time to form again capture your orange powder in a filter paper, and proceed as usual. This happens often when your material contains much nickel or copper.

Q. My material contains considerable palladium, but very little platinum, and no indium to my knowledge. When I add the ammonium chloride in Procedure F, I get hardly enough orange powder to show on a filter paper. Can I omit this treatment?

A. Yes. If you know that your solution contains very little platinum you can omit the ammonium chloride, and proceed immediately to take down the gold. Whatever platinum is present will be recovered when you refine the Stock Pot in the next chapter.

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If you have not already done so, we suggest that you read the group of Questions and Answers at the end of Chapter XI.