NATIONAL RADIO ASTRONOMY OBSERVATORY

NRAO CHEMICAL LAB REPORT NO. 4

TITLE: Chemical Lab Procedures, 1983

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I. Metal Cleaning and Preparation

Generally speaking, oils, greases, general shop dirt, oxide films and the like make up the undesirable film on a piece that is to be plated. Sometimes something unusual such as scotch tape is or has been on a piece, and when this is the case, cleaning may seem a little more difficult.

A solvent or mixture of solvents can be chosen to clean a particular piece. It has been found wise to consider probable degree of polarity or nonpolarity, and probable functional group types of any organic dirt present. For instance, greases are generally nonpolar in nature. Hence, to try to use a polar solvent, e.g. water, is fruitless and undiscerning. A nonpolar solvent would be indicated. On the other hand, for dirt such as scotch tape, a more polar organic solvent such as butyl acetate is much to be preferred.

Generally, a mixture of 5% Olin's Polytergent B-300 plus 10% acetic acid in butyl cellosolve has been used - the detergent helps get rid of nonpolar dirt. Where practicable, this has been done under the influence of ultrasound. Occasionally, an instrument, e.g. a brush, is implemented to get rid of stubborn dirt. Following this, an acetone rinse and then a water rinse is employed.

In the cases of COPPER AND BRASS (but not tellurium copper), where no solder has been used, an alkaline reverse electrocleaning (the piece being made anodic) in a sodium hydroxide-sodium carbonate bath using a current sufficient to produce mild bubbling is often used. Whether or not this is found advantageous, a final 1.5 minute swirl in a 10% by wt. sulfamic acid-10% by vol. acetic acid chemical polishing rinse and solder preparer is used.

TELLURIUM COPPER and SOLDER are negatively affected by alkaline electrocleaning, and this procedure is contraindicated. The acetic-sulfamic rinse is appropriate, however.

Under some circumstances, a high-current reverse electropolishing of copper in mixed phosphoric acids is most useful and beneficial. Electroforms wherein some of the copper but not all has been grown should, if removed from the electroforming bath for processing, be electropolished at 12 amps for 1-2 minutes, rinsed and reentered. This prevents "layer formation" in the electroform.

PHOSPHOR-BRONZE can be electropolished by reverse current (6 ASF) in four parts methanol to one part concentrated nitric acid.

ALUMINUM MANDRELS used in electroforming are cleaned in a special way that will be considered in the section on electroforming.

ALUMINUM can be bright-dipped by immersion for exactly one minute in a 215° sharp mixture of 84 mls. phosphoric acid to 3.3 mls. nitric acid to 12.7 mls. glacial acetic acid. Results are excellent.

0.007" WIRE (COPPER) is chemically cleaned by immersion in 1% nitric acid in glacial acetic acid for 8.5 minutes. This removes about 0.0006" from the diameter of the wire. The wire is then gold-plated to form coils.

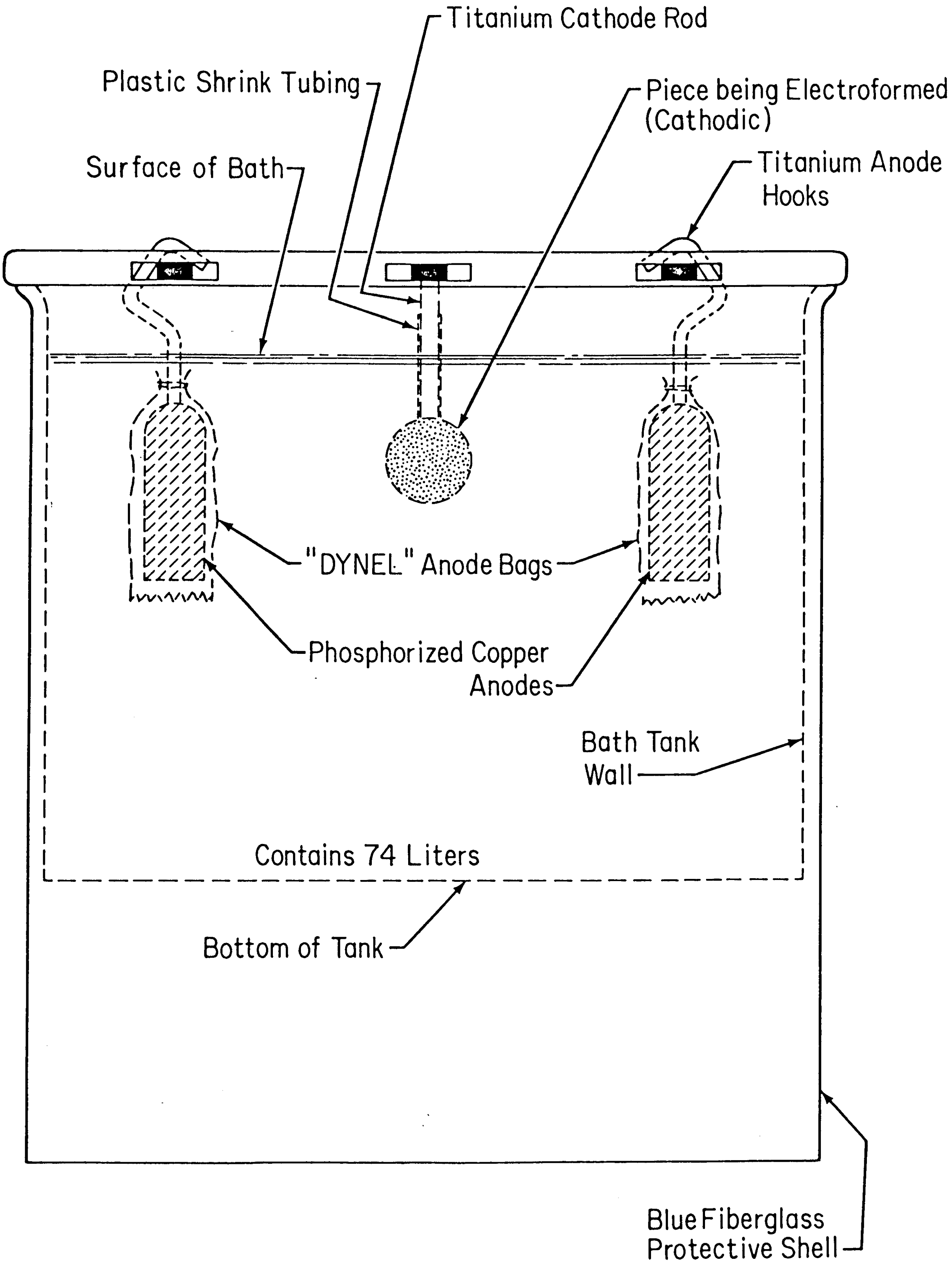


Fig. 1. Large cubath #1 acid-copper-sulfate electroforming bath

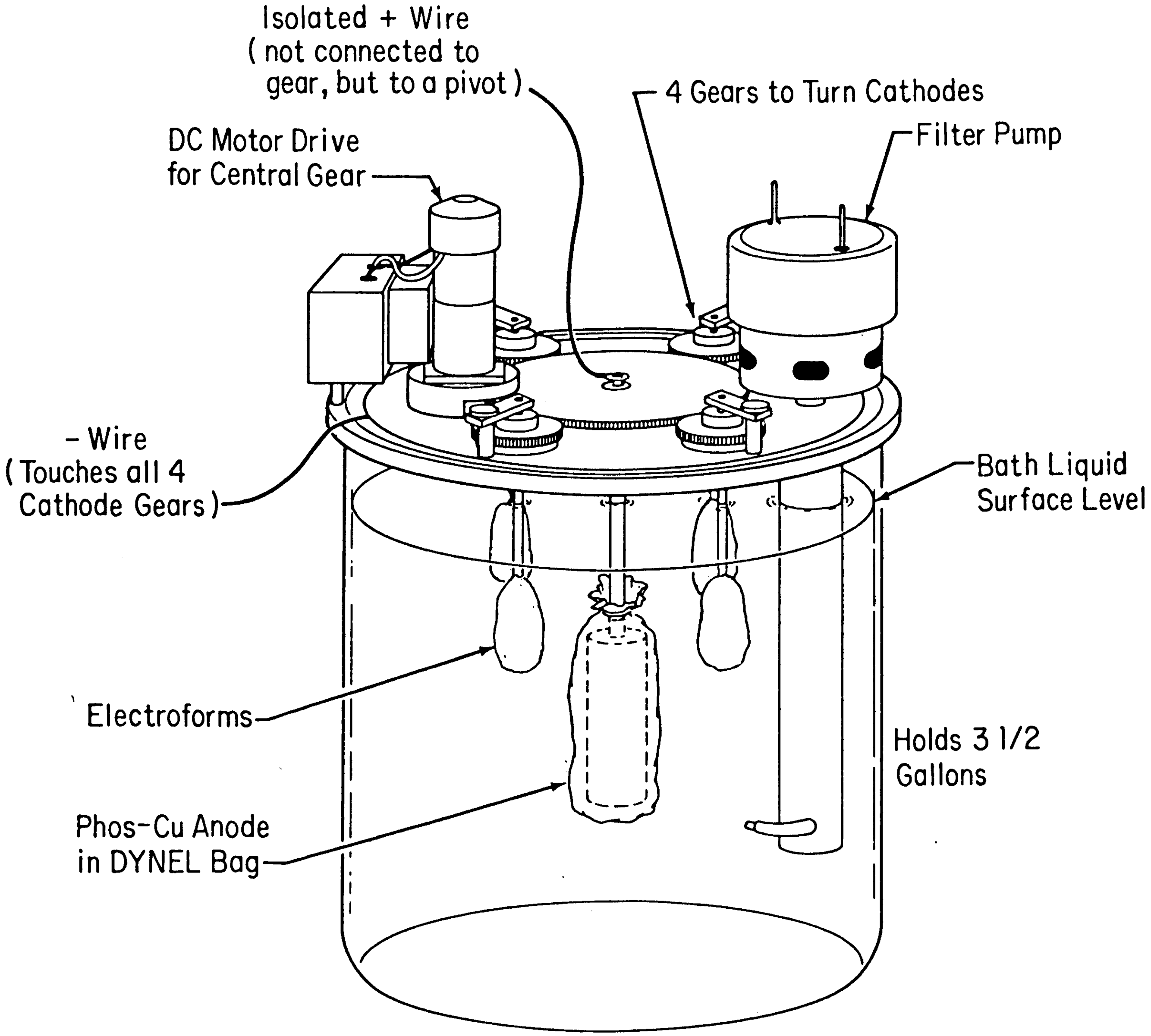
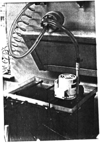


Fig. 2. Small cubath #1 acid-copper-sulfate electroforming bath.



Large cubath #1

Small cubath #1

II. Bath Formulations, Maintenance, Quantitative Analysis, and Operational Parameters

Sel-Rex CuBath #1 Acid Copper Sulfate Electroforming Bath

Discussion: This is a proprietary copper sulfate-sulfuric acid bath with brighteners-levelers, etc. called "hy", "lo", and "D." The anodes used are phosphorized copper, the pH is in the vicinity of 1.0 or less, agitation is vigorous by filtered air, filtration is by an immersible pump with a polyester wound cartridge, operational temperature is room temperature, DC electricity is used at usually 20-30 ASF, unless no sharp edges exist, when perhaps 40 to 50 ASF could be employed. Currently at NRAO, two of these baths are used - one of about 74 liters and referred to as the large cubath, the other of about 3.5 gallons referred to as the small cubath. The large cubath is housed in a typical plastic, rectangular tank, as in Figure 1 and picture 1. The small cubath is in a NRAO shop-fabricated structure, as in Figure 2 and picture 2, and features a central anode and four symmetrically placed rotating cathodes for electroforming.

Deviations from Sel-Rex specifications have been adopted to suit the bath better to NRAO electroforming requirements. Typical Sel-Rex specifications are as follows:

$CuSO_4$ -------- 9 ounces/gallon optimum

H_2SO_4 -------- 23 ounces/gallon optimum

chloride -------- 30 milligrams/liter optimum

copper as metal -------- 2¼ ounces/gallon optimum

sulfuric acid to copper metal ratio -------- about 7/1

Adopted NRAO specifications are as follows, although it is not a critical thing:

$CuSO_4$ -------- 16.4 ounces/gallon

H_2SO_4 -------- 18.0 ounces/gallon

chloride -------- 30 milligrams/liter

sulfuric acid to copper metal ratio -------- about 4½ to 1

Maintenance of Cubath #1: Hull cell tests are performed to determine changes necessary in brightener levels, chloride ion level (adjusted by adding very small amounts of hydrochloric acid), sulfuric acid, phosphoric acid, copper sulfate, and agitation. The 267 ml. Hull cell is usually used, at 2 amps per panel for 5 minute intervals, on brass panels using a corrugated copper anode. Occasionally 10 or 15 minutes is used to determine if the bath will tend to produce "knots."

In addition to the Hull cell test for brightener determinations, occasional major adjustments or checks are necessary in order to keep the cubath operating at its best. Then quantitative analysis by wet-test methods is called for. The following procedures are used to determine copper metal concentration, sulfuric acid concentration, and chloride ion concentration:

1. COPPER METAL CONCENTRATION: Carefully pipette a 5.0 ml. sample of the bath into a 500 ml. erlenmeyer flask and add 100 ml. distilled water. Add ammonium hydroxide (approximately 2-5 mls.) until solution turns a deep blue. Gently boil until the deep color disappears, using a boileezer, since foaming tends to be vigorous. Add glacial acetic acid until the solution turns acid (5-10 mls., as determined by pH paper test of vapor boiling off). Add 2 mls. more glacial acetic acid. Boil an additional 2 minutes, then cool and add 4 grams potassium iodide (amount not critical as it is used as an indicator). Titrate with 0.1 N sodium thiosulfate solution until the solution turns a pale yellow color. Add 2 mls. starch solution (not critical) and titrate to a white endpoint. The ounces per gallon of copper equals 0.17 times the mls. of thiosulfate.

2. SULFURIC ACID CONCENTRATION: Carefully pipette a 10.0 ml. sample of the bath into a 500 ml. erlenmeyer and add 150 mls. distilled water. Titrate

with a 1.0 N sodium hydroxide solution with rapid mechanical stirring until the first faint sign of a permanent turbidity appears. The ounces per gallon of sulfuric acid equals 0.426 times the mls. of sodium hydroxide solution.

3. CHLORIDE ION CONCENTRATION: (gravimetric determination) Pipette accurately a 100 ml. sample of the bath into a beaker. Add 10 mls. nitric acid and 5 mls. 10% silver nitrate. Boil and stir until the silver chloride is coagulated. Carefully filter through a fine sintered-glass weighing crucible, and thoroughly dry at about 120°C for two hours. Cool and determine the weight by subtracting the tare weight. Mg/1 Cl^- equals wt. AgCl times 0.2474 times 4000.

Modified ASTM Rochelle Copper Cyanide Flash Bath

Composition and Formulation: 4 liters distilled water
add 450 grams sodium cyanide
slowly with stirring add 378 grams CuCN
add 540 grams Rochelle Salts (Na-K Tartrate)
add water to make 9 liters
adjust free cyanide to 0.50 ounces/gallon
(NaCN raises, CuCN lowers)
adjust pH to 10.0 with $NaHCO_3$

Operational Parameters: This depends upon the particular use to which the bath is going to be put. For general purpose use, for example when flashing over brass or tellurium-copper or beryllium-copper, a current density of perhaps 10 or 20 ASF could be used just long enough to cover the part, thus providing compatibility for sulfate-copper or gold which will later be applied.

For flashing zincated aluminum, however, individual current densities and times depend upon the aluminum's type and geometrical configurations. See the table below:

Type Aluminum	Current Density	Time
7075	22 ASF if exceedingly sharp projections on a large piece aren't present.	20-30 secs.
6061	24 ASF subject to same conditions as above	15-30 secs.
2024	24 ASF subject to same conditions as above	30 secs.

Other operational parameters remain constant, regardless of the use to which the bath is put. These are as follows:

Temperature: 40°C
Agitation: magnetic stirring
Filtration: wound polyester cartridge

Quantitative Analysis:

1. Free Cyanide: Pipette a 10.0 ml. sample into a 250 ml. erlenmeyer flask. Add 90 mls. distilled water, also 5 mls. 10% KI solution. Titrate with 0.10 N $AgNO_3$ solution until a faint yellow turbidity persists. NaCN in ounces/gallon equals 0.131 times mls. silver nitrate solution. Normal bath color is a pale, straw yellow. If the bath persists in a blue color, then the free cyanide is about zero. Adjust it!

2. Rochelle Salts: This test is not usually required as it is more practical to decompose and dispose of the bath than to use the time testing and adjusting Rochelle Salts. However, if desired, there is a satisfactory procedure in Metal Finishing Guidebook and Directory.

3. Carbonates: The same as is the case with Rochelle Salts. It should be noted that carbonates come from electrolytic oxidation of cyanide. Carbonate concentration has a lot to do with plate quality. If plate quality becomes poor and pH adjustment or free cyanide adjustment doesn't improve matters much, it is likely the case that carbonate contamination has ruined the bath.

Sel-Rex Aurobond TC Neutral Gold Strike Bath

Discussion: This is a proprietary citrate base gold strike bath meant to place a thin barrier between basis metal and whatever gold would be used for the main gold plating. For instance, a brass feed horn needs, say, 50 microinches of gold plate for corrosion resistance. To seal the brass, a layer of copper is needed. This is put on in the form of a copper cyanide strike. Say that it is desirable to maximize outward appearance. Then a thin layer of copper from the cubath #1 bath would be desired to level and brighten the outward surface. This could not be applied directly to the brass, for it tends to peel off due to compatibility problems, hence the underlying copper cyanide strike to provide a barrier. After the cyanide strike and the sulfate copper layer, gold may be applied. Trouble arises, since at NRAO we use the excellent, but occasionally a little bothersome, Sel-Rex BDT 200 Sulfite Gold Plating Bath. This is not compatible with sulfate copper, hence a gold strike barrier between the BDT and the sulfate copper is required. If this is not done, bad blistering and peeling of the BDT ensues. What is needed is a gold strike compatible with both of these. Hence, the Aurobond TC. It should be noted that, although Aurobond TC contains no free cyanide, it does contain gold cyanide and hence should be handled with caution.

Operational Parameters: Basically, the operation of the bath is very simple. If any difficulty with the bath is experienced, it is usually more advantageous to dispose of the bath than adjust it for adjustments other than temperature and pH. If gold is still present, it should be recovered. Operational parameters are:

Initial Au content--------0.2 troy oz./gal.
pH-----------------------5.5
Temperature---------------50°C (must be up to temperature for maximum "covering power")
Anode--------------------Platinized Titanium
Current density-----------3 to 5 ASF (3 is used due to same power source being used for BDT which runs at 3 ASF)
Plating Time--------------20 to 30 seconds, unless deep recesses, and then 45 seconds is used

Bath Makeup: About one-half gallon distilled water is used for a one-gallon bath. To this is added 181.44 grams "part A" makeup salts, with stirring. Then to a few hundred mils. of warm distilled water is added 10.22 grams "part B" gold salts. This is carefully added to the first solution, with several distilled rinsings. Then the bath is brought up to one gallon. pH can be adjusted to 5.5 if it isn't already there, but this is not usually necessary. If it is, though, proprietary pH adjustment salts are provided by the Sel-Rex people, or use sodium triphosphate to raise pH ... citric acid to lower it.

Sel-Rex BDT 200 Sulfite Gold Plating Bath

Discussion: This is an excellent gold plating bath. It can also be a very annoying bath if not properly understood and carefully maintained. It is self-levelling and produces a very bright, pure, yellow gold (99.9%) plate of moderate hardness (knoop hardness 130 to 190).

Some of the problems that can arise? Peeling and blistering, patches of black, pink appearance on high current areas, "lint" on plated wire, organic cellophane-like pieces floating in bath, etc. Below is a trouble-shooting chart to demonstrate what to do to treat a symptom and what causes the symptom:

SYMPTOM	CAUSE	TREATMENT
peeling or blistering of gold	lack of compatibility with underlying layer	plate a layer of metal in between from a bath that is compatible with both.
patches of black	incomplete cleaning and/or low pH	adjust pH to 9.5 and clean part a little better
pink appearance on high current areas	gold level in bath is too low or current is too high	recalculate current. If current is okay, analyze gold content and make necessary additions
lint	gradual buildup with time	filter bath
cellophane-like pieces floating in bath	probably electrolytic oxidation-reduction reaction of organics in bath and/or salt buildup	filter bath
yellow color of bath	pH too low	adjust bath w. 20% NaOH

Operational Parameters: See the chart below. The temperature recommended by the Sel-Rex people is 35-55°C. We use 40° to minimize tendency of blistering of copper-aluminum layer due to thermal expansion differences.

Gold content	0.7 to 2.0 recommended oz./gal. If less than 0.5, problems begin to manifest themselves, e.g. pink in high current area.
pH	9.5 (adjust up w. 20% NaOH, down ONLY IF ABSOLUTELY NECESSARY w. 5% H_2SO_4 very carefully, as gold tends to precipitate out due to some sulfite-forming sulfurous acid, reducing some gold to the metal.
Filtration	batch filter, don't continuous filter. Bath reacts with Tygon tubing
Specific gravity	8°-35° Baumé (preferably lower end).
Anode	Platinized Titanium.
Current density	3 ASF.
Plating rate	0.0001" in 13 minutes @ 3 ASF or 1 troy ounce Au in 250 amp minutes.

Quantitative Analysis of BDT 200 Bath: This consists of a gold metal determination, modifying the procedure used for gold metal determination of a cyanide-gold bath.

The modified procedure is as follows:

1. Accurately pipette 10.0 mls. gold bath into a 250 ml. erlenmeyer. In a hood, add 15 mls. conc. HCl, and evaporate with stirring to a syrup (DON'T ALLOW TO BOIL DRY). Since some sulfurous acid is generated, some of the gold will come out as finely divided metal. Add 5 mls. HNO_3 to the syrup and 15 mls. HCl. Boil to a syrup again. Add another 15 mls. HCl, boil to a syrup again. Repeat one more time. This drives off nitrogenous compounds. Add 150 mls. distilled to final syrup. Add 25 mls. of 20% KI and 2 mls. 1% starch indicator solution. Titrate w. 0.01 N sodium thiosulfate to colorless endpoint, using good lab procedure. Record number of milliliters thiosulfate used.

2. Now, to standardize the thiosulfate solution used, weigh out 0.0500 gram fine gold wire. Dissolve in minimum aqua regia necessary, then go through a boiling down and three HCl additions with boiling down, as above. Titrate and record this number. Then, the gold in the bath can be calculated thusly:

troy oz. Au/gallon of bath =

(0.608/mls. thiosulfate for 0.0500 gms. Au) x mls. for sample

For example, if titration of bath took 48 mls. thiosulfate and standardizing took 37 mls. for the 0.0500 grams wire, then

tr. oz./gal. = (0.608/37) x 48 = 0.79 oz./gal. Au in bath

General-Purpose Alkaline Electrocleaning Bath

Discussion: This bath is a convenient method of insuring cleanness of a part to be plated. Both the alkaline cleaning principle and the vigorous bubbling of oxygen improves the platability of a piece in many instances. A few metals should not be cleaned by this process, however. Some examples are: soldered pieces, tellurium-copper pieces, beryllium-copper and aluminum.

In the cleaning process, since the pieces to be cleaned are made anodic, some metal goes into solution. The bath's life can be extended considerably, however, by occasional small additions of sodium sulfide solution, although not in excess. A good indicator of how much to add is to note the decrease in the characteristic blue color, caused by copper ion. Don't quite totally eliminate the blue color. Copper is precipitated out as the black sulfide, which is taken out of the bath by the constant filtration (polyester wound cartridge).

Bath Composition: 200 gms. Na_2CO_3 + 200 gms. NaOH + 100 gms. sodium gluconate + 2 mls. Polytergent B-300 are combined with water to make 8 liters.

Operational Parameters: There are not critical parameters with this bath. Typically, they run as follows:

Temperature------------------------50°C
Agitation--------------------------Vigorous
Filtration-------------------------Constant
Current density--------------------50-75 ASF reverse
Cathode (piece being anodic)-------stainless steel or other insoluble material

Occasionally the current used or the time of cleaning is too great. This may roughen up corners and edges, even blackening them to an extent. If dimensions or surface smoothness are not too critical, the part often can be salvaged by rinsing and then soaking in sulfamic-acetic acids solution, which tends to eliminate the black and brighten and smooth the surface.

III. General Plating Procedures

Most often, pieces which are received in the plating lab consist of the following metals: copper, brass, tellurium-copper, beryllium-copper, oxygen-free-high-conductivity (OFHC) copper. Barring use of the alkaline electrocleaning bath, these metals are generally plated in the same manner, using the same bath combinations. General plating procedure is as follows:

1. Solvent clean
2. Where applicable, alkaline electroclean
3. Rinse with tap water
4. Sulfamic-acetic acids solution rinse 1.5 minutes with swirling
5. Copper cyanide strike for sealing and compatibility
6. Acid-copper sulfate "level" for 4 minutes @ 30 ASF (if dimensions not unusually critical)
7. Sulfamic-acetic acids solution rinse another 1.5 minutes with swirling
8. Aurobond TC-strike for compatibility
9. BDT 200 plate to desired microinches (usually 50; however, 25 if dimensions are critical, or 100 if high durability required)
10. Water-rinse, acetone-rinse, air-dry.

IV. Special Plating Procedures (Includes Electroforming)

A number of different, special plating procedures are called for, often on a daily basis. A number of these are listed below:

1. Plating stainless steel
2. Plating and electroforming on aluminum types 7075, 2024, and 6061
3. Plating internal surfaces
4. Plating inner and outer conductors of coaxials

These will be considered one at a time below:

1. Plating stainless steel: A significant improvement has been made in this particular area. Formerly, nickel metal was plated onto the steel and then

a flash of cyanide copper and then acid sulfate copper followed by any gold that might be plated thereon. Recently in the book GOLD PLATING TECHNOLOGY by F. H. Reid and W. Goldie, a suitable copper strike was found that would most satisfactorily replace the usual nickel strike. This is very fortunate, since nickel is considered a "lossy" material in the frequency ranges in which it has been employed by NRAO. Here is a description of the makeup and use of this strike:

0.375 grams $CuSO_4 \cdot 5H_2O$
370 mls. concentrated HCl
add distilled water to 1 liter

copper anode
10 ASF
2 minutes plating time
room temperature
vigorous agitation

2. Plating and electroforming on aluminum types 7075, 2024 and 6061: Zincating solutions are currently used to prepare aluminum for copper plating. In the future, phosphoric acid anodized aluminum receiving copper plate directly may be attempted, but for now here is the general procedure:

1. Acetone clean the mandrel using a gentle bristled "acid brush."
2. Rinse off with acetone from a squeeze bottle.
3. Water rinse before acetone can dry, possibly leaving an organic residue.

4. Immerse with swirling into an alkaline cleaning dip consistin of 44 grams Na_2CO_3 + 44 grams Na_3PO_4 per 1/2 gallon solution for 6-7 minutes at room temperature
5. Water rinse
6. Amchem nitric deoxidizer #4 dip with swirling 10 seconds
7. Carefully and thoroughly water rinse
8. Zincate, and where appropriate, double zincate, as will be described below under each specific aluminum type
9. Quickly but thoroughly water rinse
10. Copper cyanide flash as described under each aluminum type
11. Acid copper sulfate plate 4 minutes @ 20 ASF
12. Water rinse
13. Sulfamic-acetic acids rinse with swirling 1.5 minutes
14. Water rinse
15. Aurobond TC flash @ 3 ASF 20-45 seconds, depending upon geometry of piece
16. Water rinse
17. BDT 200 plate 50-100 microinches
18. Water rinse
19. Aurobond TC flash 15-30 seconds for compatibility
20. Water rinse
21. Electroform in acid-sulfate-copper @ 20 ASF for first day and 30 ASF thereafter

Zincating solutions and procedures are listed below for each type of aluminum used:

Aluminum	Zincate Solution Composition	
6061	525 gms. NaOH + 100 gms. ZnO + 10 gms. Rochelle salts + $FeCl_3 \cdot 6H_2O$, 1 gm. per liter solution.	zincate 20 seconds, then dissolve in Deoxidizer, rinse, then zincate again for 20 seconds. Plate in cyanide copper @ 24 ASF 15-30 seconds.
2024	Same composition as for 6061.	Zincate only once for 25-30 seconds. Plate in cyanide copper @ 24 ASF 30 seconds.
7075	525 gms. NaOH + 100 gms. ZnO per liter solution.	Zincate 45 seconds. Plate @ 22 ASF for 15-30 seconds.

3. Plating internal surfaces: When a piece has external and internal surfaces to be plated, shielding of the electric field occurs so that little plating goes on the internal surfaces, if special plating procedures are not followed. This can be a little tricky, as was found out when some offset

shorts were to be gold plated. Below is a rough example of what the pieces were shaped like:

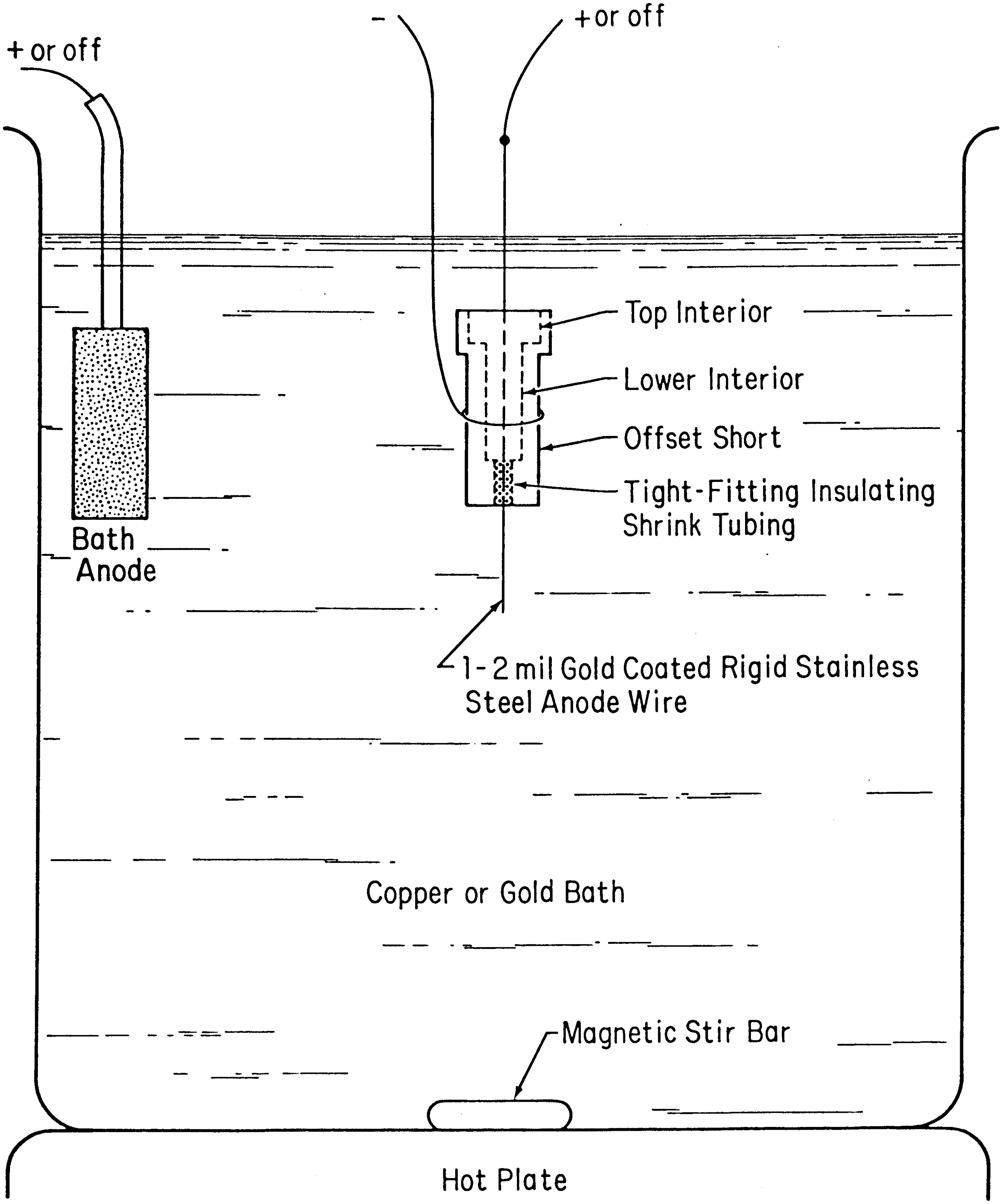


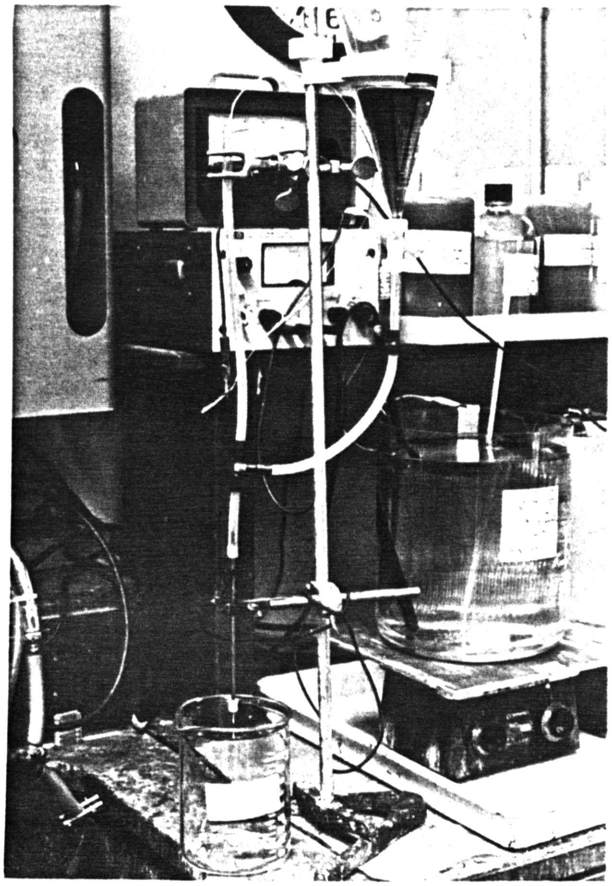
Fig. 3. Differentiating and current determinations of interior and exterior plating surfaces of offset shorts.

The areas to be plated can be broken down into two areas - the external surface area and the internal surface area. It all sounds rather simple, and first plating attempts were based upon this. Results? The internal surface plate was badly "burned." Why? Reconsider Figure 3. A rigid stainless steel wire was copper plated and then a mil or so of gold was plated onto it to provide a rigid, but unreactive, anode. A sleeve of shrink tubing at the anode's base where it passed through the short prevented electrical shorting. Thus, to plate the external surface, the wire holding the short was made cathodic, and the internal SS wire was not hooked up. Copper and gold was thus plated on the exterior. To plate the interior, the stainless steel was made anodic and the piece was made cathodic, thus plating the interior. But here is where the problem came in. Notice that the top interior surface was considerably further away from the stainless anode than the lower interior surface. Hence, more current passed through the lower interior surface. If the upper and lower interior surface areas are added together to figure total interior surface area, the calculated total current is right, but the current densities are such that perhaps instead of the 3 ASF desired for gold, for instance, the top gets only 0.5 ASF, whereas the lower gets, say, 8 ASF, and thus burns. On the other hand, it is a better approximation, but is not totally accurate, if the top interior surface area is totally discounted. Hence, the skilled plater is successful if he properly estimates an effective total surface area that suffices to prevent burning in the high current density areas, but that closely approximates the minimum necessary plating thickness desired.

4. <u>Plating inner and outer conductors of coaxials</u>: Basically, the normal plating procedures are followed. Both conductors are plated to a certain

conductivity rather than to a certain thickness of plate, however. The conductivity measuring device was designed by Dr. S. Weinreb specifically for measuring the conductivity of such pieces. The points of the probe measure off 1 cm. The reading is in milliohms.

The outer conductor is different in another way, also. It requires a special plating setup, since NO PLATE WHATSOEVER IS ALLOWABLE ON THE EXTERIOR OF THE STAINLESS COAXIAL OUTER CONDUCTOR. Consider the setup currently in use, below:



V. Waste Disposal

At this point, NRAO is making strong effort to improve in its methods of disposing of toxic wastes. This is not totally simple, since quantities of waste are really rather minimal, and equipment for waste disposal is typically built for large-scale operations. Some waste disposal techniques were applied in the past for the most toxic chemicals, e.g. cyanides, but much material of a lesser toxicity was not treated. Outlined below is the procedure currently applied in general:

GENERAL FORMAT OF WASTE DISPOSAL:

1. Remove specific toxic agents of a serious nature, according to their own individually required procedure (e.g. Cr^{+6}, CN^-, Pb, etc.).

2. Remove additional metals, e.g. Cu, Al, Sn, etc., by plating out or precipitation.

3. Neutralize remaining liquor.

4. Wash remaining solution down drain with sufficient water to reduce concentration of dissolved solids, e.g. sulfates, etc. of alkali metals and alkaline earths, to below 500 mg/l.

If the waste is a volatile organic compound, burning is preferred in a hood for safety. If burning isn't reasonably possible, boiling it in the hood to vaporize out into the atmosphere is attempted.

SPECIFIC PROCEDURES EMPLOYED:

1. For hexavalent chromium, acidify to pH 3.0 to 3.5 w. HCl. Add saturated sodium bisulfite solution until all orange color is replaced by dark green color. Set 5-10 minutes. Add concentrated caustic soda to precipitate out the chromium as the sesquioxide, Cr_2O_3, pH 8.0-8.5. Stir thoroughly. DO ALL STEPS IN HOOD!

2. Cyanide disposal depends upon quantity to some degree. If only VERY SMALL quantities are to be disposed of (yes, this is done routinely in quantitative testing of gold, by the way), in a hood, with heating, the cyanide can be acidified with excess acid, thus generating hydrocyanic acid which is driven off into the atmosphere to be whisked away.by the heating. For moderate to large

quantities, however, a different procedure is called for. Adjust the cyanide waste solution to a pH greater than 11.0. Slowly, with agitation in an oversized container, and in a hood, add sodium or calcium hypochlorite in excess. Allow "mash" to sit 10-15 minutes to thoroughly oxidize cyanide to the much less toxic cyanate. Reduce the pH SLOWLY, and IN THE HOOD, recognizing that much heat is being liberated and the reaction could become somewhat out of control if normal precaution and common sense isn't applied. Add citric acid monohydrate crystals, with agitation. Allow to sit for 1/2 hour. Proceed to step 2 of general format, above.

VI. Whisker Formation

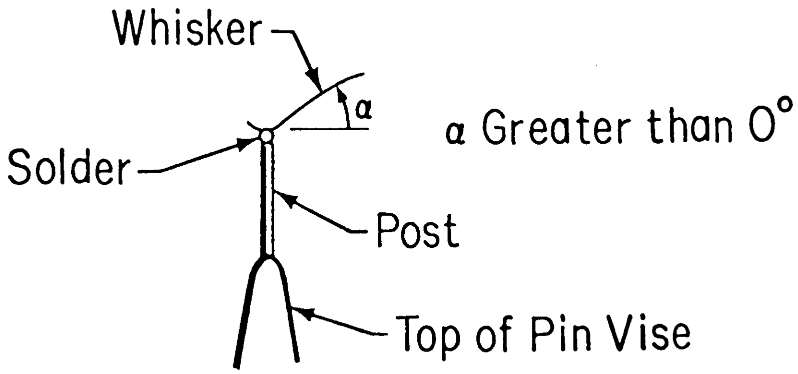
Whisker formation is constantly changing to thinner and thinner whiskers for hopefully better mixers and multipliers. The current accepted whisker is formed from .0005" phosphor-bronze wire. Current attempts to change this to 0.00025 or so inches are being made, employing 0.0005" wire which is electropolished down, using 4 pts. methanol-1 part nitric acid for 10 minutes @ 6 ASF.

The University of Virginia Semiconductor Device Lab under direction of Dr. R. Mattauch is the location of much of the whiskering equipment used by NRAO. Diagrams follow which indicate the setups and settings for proper whisker formation. Etching of the whisker seems to be by a number of mechanisms. Perhaps among these are chemical etching, electrical etching, facilitated by heating and oxidation. At any rate, success is achieved, albeit with a somewhat large labor-per-whisker expenditure.

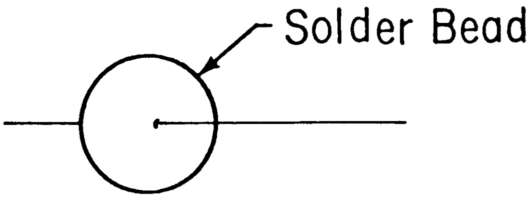
The etchant solution currently used is a 4% by weight sulfamic acid solution. Care must be exercised that a lot of detritus isn't present in the 5 ml. etching bath.

STEPS IN FORMING A WHISKER:

1. Cut approximately 1/2" sections of 0.0005" phosphor-bronze wire using the delicate scissors assigned to the job.
2. Insert a 20-gauge nickel post into the apparatus meant for the purpose.
3. Making sure the post top is flat and all junk, e.g. any solder is scraped off with a scalpel.
4. Carefully put a tiny droplet of "tix" flux just on the top of the post.
5. Using the foot-operated soldering device, put a tiny bead of solder on the top of the post.
6. Moisten the top of the solder with some more flux.
7. Holding a piece of whisker wire at one end with sharp tweezers, solder the other end of the wire to the top of the post, being sure not to crimp, flatten, etc. the whisker wire. Make sure it is attached and firmly centered. (Fig. 4)
8. Remove the posted whisker carefully with tweezers and ultrasonically clean it in methanol for a few seconds.
9. Store for further manipulation in a plastic box with a slab of styrofoam to safeguard whisker. Make 1-2 dozen at a time.
10. Mount post in whiskering device. Twist micrometer until whisker tip is immersed 2 to 5 smallest units on the micrometer dial. (Fig. 5)
11. Point, observing pattern on oscilloscope carefully, as in diagrams. (Fig.
12. Rinse in water, hydrofluoric acid 50%, water.
13. Check for point shape. If good, put aside for plating. If not good, repeat steps 10, 11, 12 and check again, until desired point is obtained or whisker is used up. (Fig. 7)
14. Plate at 8 ma for 20 to 25 seconds in Autronex-N gold bath at UVA, entering and exiting whisker in such a way as not to burn it. (Figs. 8 and 9)



Check through microscope to make sure that top of post looks l below:



Carefully straighten wire upwards to the vertical as below:

Ultrasonically clean flux, etc. with methanol

Fig. 4. "Posting" whisker stock wire on.

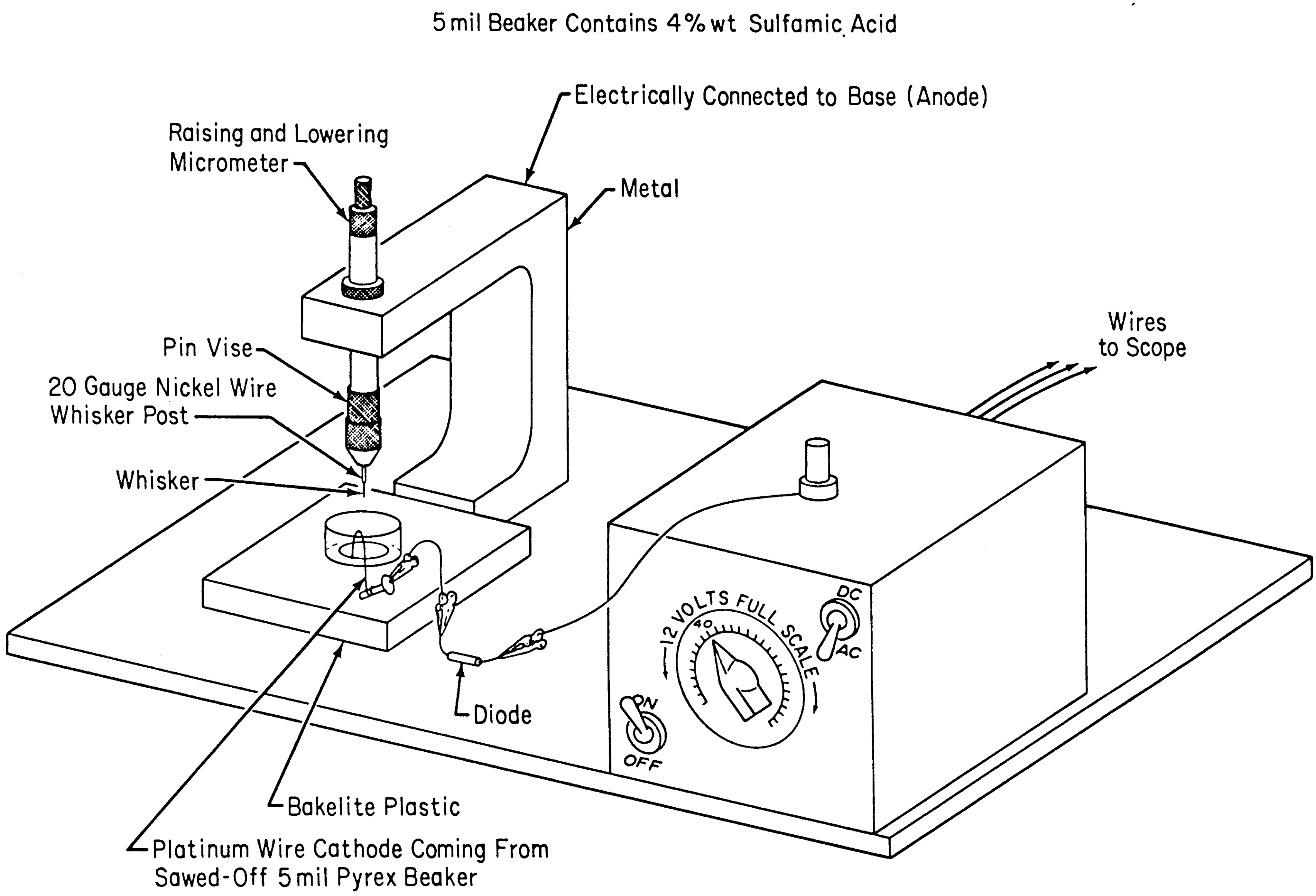


Fig. 5. Pointing Apparatus

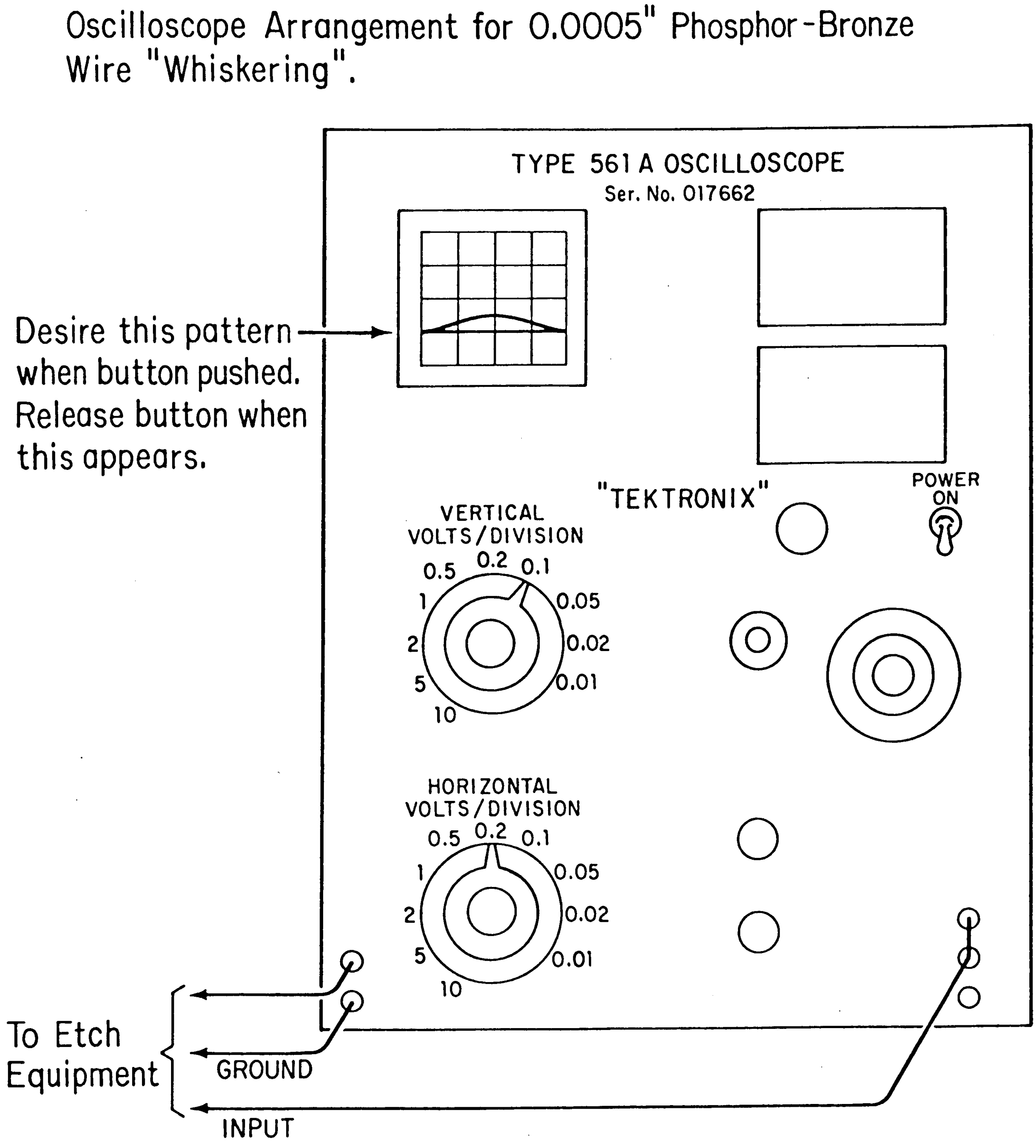
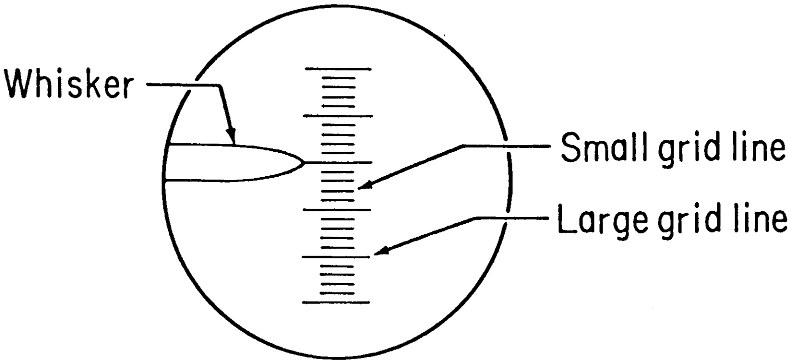
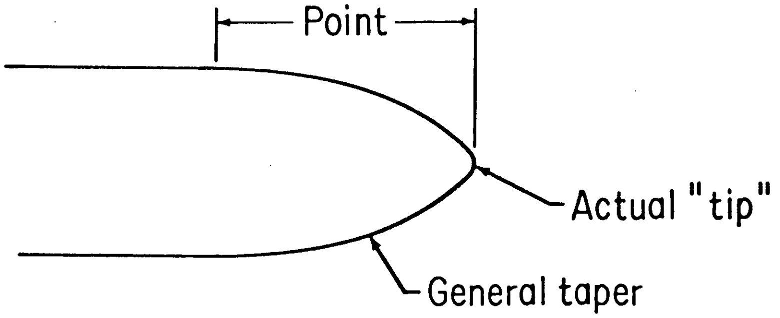


Fig. 6. Device to "measure" point shape in situ.

20X eyepiece with grid as below:

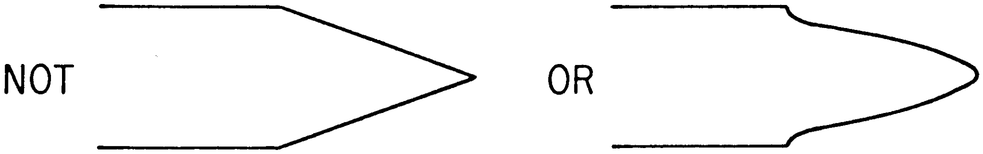


Whisker point is considered to be portion below:



The general taper should be smooth and clean from excessive dirt particles, blackness and lack of uniformity.

Taper should be "convex", not straight or concave.



Dimensions should be about 5-7 small grid lines "bluntness" or "sharpness" about 1 grid line at very tip.

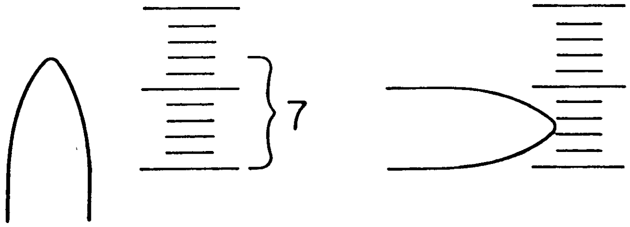
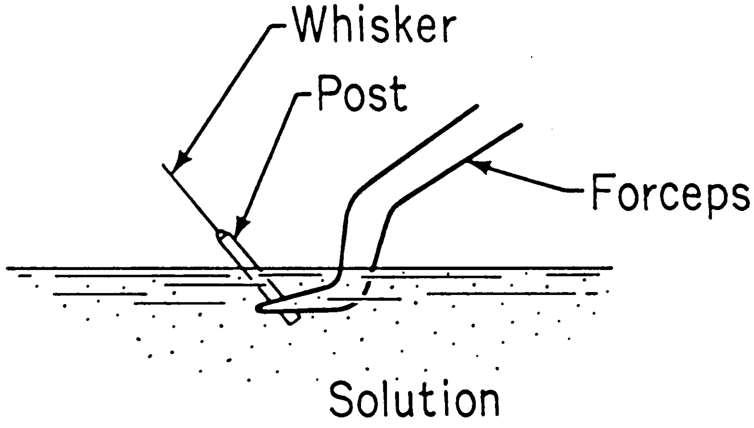


Fig. 7. Proper point shape.



Immerse as shown below to avoid excessive buildup on whisker point.

Fig. 8. Gold plating whisker

Dry with nitrogen gas by blowing along whisker post as below:

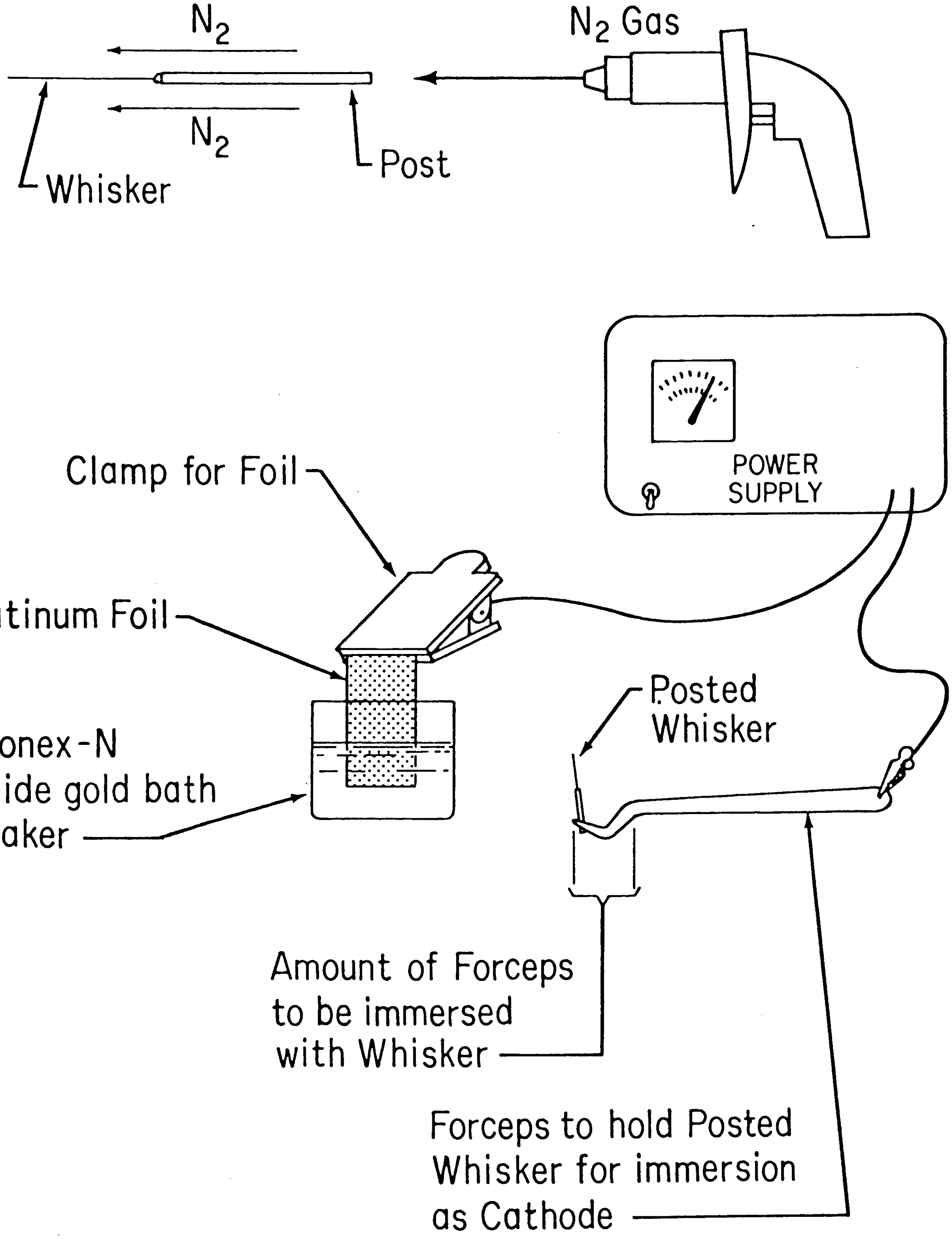


Fig. 9. Plating pointed whisker

15. Water rinse and blow dry with nitrogen gas gun, in direction that tends to straighten the whisker, not bend it.

16. Take SEM picture to determine final suitability.

VII. Observations and Miscellaneous Information

1. Hardness of plate: Some tests ought to be run to test degree of hydrogen embrittlement of gold plate. It may be that the knoop hardness of BDT 200 gold can be reduced, where it is currently somewhat less than satisfactory.

2. Electroforming: It may be beneficial to switch from the zincate process to directly copper-plating phosphoric acid anodized aluminum.

3. Anodes: Anodes should be carefully considered for each bath. For instance, chloride ion passivates platinized titanium over a period of time. Sulfate copper baths react in a much better way if phosphorized copper is used rather than normal copper. It should be noted that excess chloride ion in cubath #1 baths deactivates the anodes.

4. Pulse-plating: This has been tried in cubath #1 for electroforming. It caused more harm than good.

5. Gold recovery: Gold should be recovered from BDT-200 bath by careful addition of H_2SO_4 to pH 1.0 filtration and heating filtrate to 2100°F to melt.

6. Copper flash removal: A 10% HNO_3 solution in glacial acetic acid appears to work quite well.

7. Aluminum mandrel removal: 50% HCl seems to work the best overall. The aluminum should be "eaten out" at room temperature until the last traces of aluminum slow things down too much. Then mild heating on a hotplate will speed up dissolution of the remainder of the aluminum. Hot HCl dissolves a

slight amount of copper, however, as is evidenced by the appearance of a yellow color. The amount of Cu dissolved will seldom be significant, however.

8. Copper removal from aluminum: This sometimes must be done to avoid wasting a mandrel that was improperly copper flashed. Swirling in concentrated nitric acid until all copper is removed does the job. Then rinsing and starting over from the first step allows the mandrel to be reused.

9. Gold-stripper: A suitable gold stripping composition consists of 30 g. sodium metanitrobenzenesulfonate plus 120 g. sodium cyanide in 1 liter of solution. It dissolves gold and copper off aluminum at room temperature.

10. Copper strike remover alternative: As a possible alternative, where nitric and/or acetic acids are deemed inadvisable to use, a combination of 19.8 grams ammonium persulfate (or peroxydisulfate) plus 88.5 mls. conc. ammonium hydroxide in 1 liter solution may be used to remove copper flashes from inside electroformed mandrels.