Immersion Silver Processing Guide

FOR PRINTED CIRCUIT BOARD MANUFACTUERS

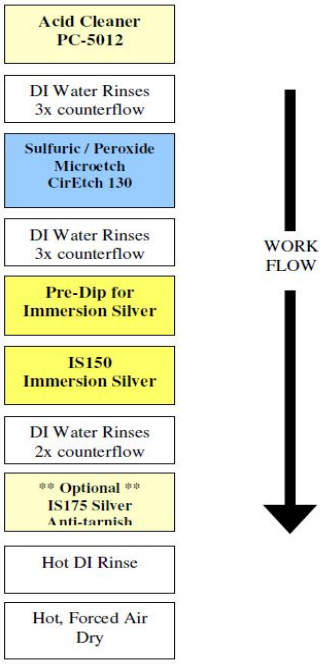
PROCUT OVERVIEW

Florida CirTech's Immersion Silver process plates a silver coating on copper. This silver coating is used as a lead-free solderable finish on printed circuit boards. Immersion Silver is a co-planar, dense finish that contains only silver. It is compatible with all assembly fluxes and solder pastes.

Our Immersion Silver process consists of an acid cleaner, a peroxide-sulfuric microetch, an acidic pre-dip, the IS150 immersion silver bath, and an optional anti- tarnish bath called IS175. In the unlikely event that silver tarnish forms, we can provide a silver tarnish remover called STR199 that can be used to remove silver tarnish.

Florida CirTech's Immersion Silver finish has a shelf life greater than 1 year, and is solderable through multiple assembly operations. Immersion silver does not migrate into copper, like immersion tin. As a result, the shelf life of immersion silver is much longer than immersion tin finishes.

IMMERSION SILVER PROCESS FLOW



NOTES:

- DI water must be high purity, and be free of halides (e.g. chlorides).
- If halides are drug into the IS150 bath, then silver will precipitate out, and the silver deposit quality will decrease.

EQUIPMENT SPECIFICATIONS

MATERIALS (Listed in order of preference.)

TANKS: Polypropylene, Polyethylene, or CPVC. Do not use PVC
RACKS & BASKETS: Plastic coated stainless steel; use polypro or Halar (black or green). Do not use PVC.
HEATERS: Quartz, Enamel, Teflon, or PTFE
PUMPS: Non-metallic centrifugal or magnetic-drive
FILTERS AND HOUSINGS: Polypropylene, Polyethylene. Do not use PVC

EQUIPMENT REQUIREMENTS FOR THE ENTIRE LINE

1. Ventilation recommended for each chemical tank.
2. Work-bar agitation recommended for the line to aid in chemical action and rinsing.
3. Do not use air agitation in any step of this process.

EQUIPMENT REQUIREMENTS BY CHEMICAL BATH

PC-5012 Acid Cleaner

- Heated to 110 - 130 F.
- Circulation pump recommended, but not required.

CirEtch 130

- Heatedto75-85F.
- Ventilation is required for thisbath.

Immersion Silver Pre-Dip

- A heater is recommended, but not required.
- Circulation pump with filtration required.
- Circulation rate of 3 - 5 turnovers per hour.
- Filter ratings of 20 micron.
- Ventilation is required for this bath.

IS150 Immersion Silver

- Heated to 110 - 130 F.
- Circulation pump with filtration required.
- Circulation rate of 3 - 5 turnovers per hour.
- Filter ratings of 20 micron.
- Ventilation is required for thisbath.

IS175 Silver Anti-tarnish

- Heated to 90 - 110 F.
- Circulation pump recommended, but not required.

Water Rinses

- All rinses must be De-ionized water and cannot contain halides (e.g. chlorides).
- Rinse volume turnover of 2 -4 times per hour.
- The final DI water rinse is heated to 110 – 130 F, mainly to speed drying.

OPTIONAL

Horizontal conveyorized equipment can be used, with immersion, flood bar agitation.

CHEMICAL BATH MAKEUP, CONTROL, AND OPERATION

General Comments

Bath makeup must be done with reagent grade nitric acid, and DI water. Contamination of the pre-dip or silver baths with impurities like halogens (chlorides) can lead to precipitates and poor bath performance. For example, chlorides added to the silver bath will result in precipitation of the silver as silver chloride, which is a white, insoluble powder. Tap water commonly has chlorides added to it, so the use of DI water for bath make-ups and rinses is critical.

The pre-dip and silver baths should be analyzed and additions made on a regular basis. The pre-dip bath contains nitric acid and organic compounds. The silver bath contains nitric acid, silver, and organic compounds.

Bath Replacement

The pre-dip and immersion silver baths need to be replaced based on usage. During use, the immersion silver bath dissolves copper. When the immersion silver bath reaches 5.0 g/L of copper, both the pre-dip and the silver bath should be replaced. Furthermore, when 5 metal turnovers are reached in the silver bath, both the pre-dip and silver baths should be replaced.

Tank Preparation

All process tanks should be prepared by leaching with appropriate chemicals, followed by several rinses with DI water. The leaching processes are shown below. In each case, the tank should be filled with the appropriate chemical, and then recirculation pumps turned on (if present). The dwell time for each step is at least 1 hour. If the step states 2x, then that particular item should be repeated twice, for at least 1 hour each time.

Process Step	**Leaching Step 1**	**Leaching Step 2**	**Leaching Step 3**
Acid cleaner	2x Tap water	2x DI water	---
Rinses	2x Tap water	2x DI water	---
Microetch	5% by wt. sulfuric acid	2x Tap water	2x Di water
Rinses	2x Tap water	2x Di water	---
IS150 Pre- dip	5% by wt. nitric acid	2x Tap water	2x DI water
IS150 Silver bath	5% by wt. nitric acid	2x Tap water	2x DI water
IS175 Anti-tarnish	2x Tap water	2x DI water	---
Rinses	2x Tap water	2x DI water	---

DI Water Test

It is critical that the DI water used in this process is free of halides. A simple test can determine if halides are present in the water.

Halide Test Procedure for DI Water

1. Add about 50 – 75 mL of DI water to a clean, dry beaker.
2. Add about 5 mL of 50% by vol. nitric acid, reagent grade.
3. Drop in 0.1 M silver nitrate solution, slowly while mixing.
4. If turbidity, or a precipitate forms, then halides are present in the water.
5. If the mixture stays clear, then the water is free of halides.

If halides are present in the water, then it cannot be used in this process. Contact your local water purification company for recommendations on how to remove halides. Typically this is done by using either DI (deionized) or RO (reverse osmosis) purified water.

DI water rinses should be run at flow rates of 2 - 4 volume turnovers per hour to ensure adequate rinsing.

Bath Makeup

The makeup quantities are shown below for both the Pre-dip and Silver baths. Follow the order given in the table for additions, and mix well after each step.

Bath Makeup Step	**Pre-dip**	**Silver Bath**
Step 1	Add about 75% by volume of DI water*	Add about 75% by volume of DI water*
Step 2	Add 1% by volume of nitric acid, reagent grade, 68-70%	Add 2% by volume of nitric acid, reagent grade, 68-70%
Step 3	Add 2.5% by volume of IS150B	Add 5% by volume of IS150B
Step 4	Bring tank to level with Di water	Add 5% by volume of IS150A
Step 5	---	Bring tank to level with DI water

*** It is critical that the water be free of halides. See the test above.**

All analysis procedures are detailed in section V. below. A summary of the control ranges for each bath are shown in the table below.

Component	**Pre-dip**	**Silver Bath**
Acid normality	0.2-0.4 N	0.4-0.6 N
IS150B concentration	2.0-2.5% by vol	4.0-5.0% by vol
Silver metal	---	1.0-2.0 g/L
Copper metal	---	Below 5.0 G/L (5000 ppm)

Chemical Bath Analysis Summary

We highly recommend doing routine chemical analysis of all process solutions. When first using this process, analysis should be done more frequently, e.g. daily. After an analysis and addition pattern has been established, then analysis can be done less often, as determined by the volume of work processed. A quick summary of the analysis required is shown in the table below.

Chemical bath	Controls	Additives Needed
PC-5012	Concentration analysis by titration	PC-5012
CirEtch130	Hydrogen Peroxide analysis by titration Sulfuric Acid analysis by titration Copper concentration by titration	Cir130A Sulfuric Acid Cirl130W, Cirl130M (make-up only)
Pre-Dip for Immersion Silver	Silver metal content by AAS Acid Normality by titration IS150B analysis by titration Copper analysis by AAS	IS150A Nitric acid, reagent grade, 68% IS150B
IS175 Anti-tarnish	Bath replacement based on loading area	IS175

*Analytical procedures and control ranges can be found in the Technical Bulletins for each product.

Reagent Information

The following reagents are required for the IS150B titration. They can be purchased from Sigma-Aldrich at 1-800-558-9160. The catalog number information is shown below.

Hexamethylenetetramine solution [CAS# 100-97-0]
Makeup: 20% by weight dissolved in DI water
Sigma-Aldrich Catalog #: H11300-500G

Chromeazurol S indicator [CAS# 1667-99-8]
Makeup: 0.1% by weight dissolved in DI water
Sigma-Aldrich Catalog #: 199532-25G

Copper (II) nitrate hydrate [CAS# 19004-19-4] - 0.01 M
Makeup: Dissolve 2.32 grams into 1 liter of 2% by vol. nitric acid
Sigma-Aldrich Catalog #: 467855-50G

TYPCIAL BATH OPERATION FOR IMMERSION SILVER

PC-5012 Acid Cleaner

Copper cleaning action and drag out reduces the concentration of PC-5012. Weekly analysis and addition of PC-5012 concentrate is recommended.

CirEtch 130

Microetch rate is controlled by Cir130A concentration. We recommend an etch depth of 10-30 microinches. Sulfuric acid concentration controls the solubility of copper in solution. Cir130W can be added in small amounts to control misting. Bath analysis and additions of sulfuric acid and Cir130A should be performed daily.

Pre-Dip for Immersion Silver

As the pre-dip is used, the acid normality and IS150B concentrations drop. Additions of nitric acid and IS150B will keep the bath in specifications. Analysis should be performed weekly. Over time, the pre-dip can form a precipitate, which needs to be removed by filtration. The precipitate does not affect bath performance, and is normal. The pre-dip should be discarded and remade when the copper content of the Immersion Silver bath reaches the high limit, as detailed below.

IS150 Immersion Silver

As the Immersion Silver bath is used; silver, acid normality and IS150B content all drop, and copper content increases. Copper is dissolved as silver is plated. Additions of nitric acid, IS150A and IS150B will keep the bath in specifications. Analysis of the IS150 Immersion Silver bath and additions should be performed daily. When the copper level reaches 5000 ppm (5 g/L), then the Immersion Silver bath should be replaced. The pre-dip should also be replaced at the same time. Over time, the IS150 Immersion Silver bath can form a precipitate, which needs to be removed by filtration. The precipitate does not affect bath performance, and is normal.

IS175 Anti-tarnish

Anti-tarnish is consumed as the silver is coated with this protective chemical. There is no analysis for the active ingredient. This bath should be dumped and remade when approximately 600 square feet of circuit board area has been processed per gallon. The bath should also be remade if performance decreases.

CONTROLLING THE SILVER COATING

The immersion silver coating is comprised of pure silver over copper. We recommend maintaining the pure silver layer thickness between 5 and 30 microinches to ensure good solderability through multiple assembly cycles.

Silver thickness is best measured by XRF. We recommend the use of a collimator with a diameter that is at least 3x smaller in size than the feature that is being measured. Silver thicknesses on large pads can be much lower than on smaller pads. We recommend taking readings on various pad sizes, and using an average value for the measurement.

HANDLING AND STORAGE OF SILVER PLATED PRINTED CIRCUIT BOARDS

GENERAL HANDLING

• Immersion silver coated boards should be rinsed and dried thoroughly. They should be packaged in sulfur free plastic bags as soon as possible after coating.
• Wear gloves when handling silver plated PWBs. Fingerprints can cause tarnish and solderability issues.
• Store PWBs at room temperature in clean and dry areas. Contaminates and high temperatures will degrade the silver surface.
• Electrical testing after Immersion Silver processing is preferred.
• If PWBs are washed after routing, it should be done with clean DI water. Make sure that the PWBs are dried well after washing.

SILVER TARNISH

It is the nature of silver to tarnish, which appears as a yellow to yellow-brown color. Tarnish can be minimized or prevented by taking certain precautions. These precautions are detailed below.

• Follow the general handling guidelines above.
• Ensure that the rinses following the IS150 Immersion Silver bath are filled with clean DI water.
• Dry the PWBs promptly and completely after immersion silver plating, using a clean dryer.
• Store the PWBs in a clean and dry environment.
• Sulfur compounds will cause silver tarnish. Ensure that sulfur containing compounds do not come into contact with the PWBs.

STORAGE

It is good practice to store silver plated PWBs as soon as possible after plating. Store silver plated PWBs interleafed with paper, and inside plastic bags. The bags and paper must be sulfur free. Do not use rubber

bands. Contaminates in the rubber can cause markings and tarnish on the silver, even through plastic bags. Silver plated PWBs should be stored at room temperature and humidity.

REWORK OF THE SILVER FINISH

In the event that tarnish forms on the silver surface, tarnish can be removed by using our STR199 Silver Tarnish Remover. Contact your Florida CirTech representative for details. The process steps for STR199 are shown below.

Silver Tarnish Removal
1. Immerse the boards in STR199 solution.
(Read the STR199 technical bulletin for details)
2. Rinse several times using clean DI water
3. Dry completely.
4. Protect the silver coating using IS175 Silver Antitarnish.

It is possible to completely strip and re-plate the silver finish, if necessary. During silver stripping, cosmetic defects can form in the copper which are later translated into the re-plated silver deposit. It is very difficult to clean the copper sufficiently to remove these cosmetic defects. If silver stripping is necessary, then use the following process.

Silver Stripping (Permanganate)
1. Immerse the boards in a working permanganate desmear type bath, until the silver is completely removed. An addition of about 5 – 10% by volume of ammonium hydroxide solution will speed stripping and brighten the copper surface.
2. Rinse several times.
3. Immerse in a working neutralizer bath.
4. Rinse several times.
5. Microetch about 40 – 60 microinches of copper. More may be required to clean the surface.
6. Rinse several times.
7. Run through an aluminum oxide jet scrub to buff the copper surfaces.
8. Run the boards through the complete immersion silver process to recoat with silver.

An alternate silver stripping procedure is shown below.

Silver Stripping (Alternate)
1. Run the tarnished silver boards through HASL to coat with solder.
2. Strip the solder using a standard tin/solder strip chemistry.
3. Clean the copper by microetching 40–60 microinches.
4. Run through an aluminum oxide jet scrub to buff the copper surfaces.
5. Run the boards through the complete immersion silver process to recoat with silver.

TROUBLE SHOOTING

Several defects can occur with immersion silver finishes. These defects will be discussed below.

TARNISH

The most common defect with immersion silver coatings is tarnish, or discoloration of the silver. This was discussed in the handling and storage section above. Some additional potential sources of silver tarnish are listed below.

• Contaminated rinses after the IS150 immersion silver bath, will cause tarnish. Rinsing with dirty water will cause tarnish. Clean DI water should be used for any rinse after immersion silver plating.
• Excessively long rinse times, especially in contaminated rinses, can attack silver and discolor it. Rinse times need to be long enough to remove the IS150 chemistry from the board, but not excessively long. Do not rinse for extended periods of time, e.g. longer than 5 minutes.
• Chemical fumes in the air can cause silver tarnish. Do not store silver coated boards in chemical process areas. Silver is especially susceptible to tarnish from sulfides. Do not store silver coated boards near waste treatment areas.
• Paper, plastics, and other materials can cause tarnish when in contact with the silver finish. Sulfur in the paper and plastic is known to cause silver tarnish. Ensure that sulfur free paper and plastics are used for board storage.
• If silver is plated too quickly or if the plating rate is too high, this can result in a porous deposit which can tarnish quickly. This type of tarnish is typically a brown color, which is indicative of oxidation of the copper underneath the silver. Proper maintenance and control of the immersion silver chemistry and process will prevent this type of tarnish.

MICROVOIDS

• Microvoids are small holes that form in a solder joint. These voids typically form near the surface of the pad, where the silver layer used to exist. Microvoids can compromise solder joint strength, making them more susceptible to fracturing
• The actual cause of microvoids is not well understood. There are several factors that can influence microvoid formation. Thicker silver deposits seem to be more susceptible to microvoids. Organic components that co-deposit in the silver coating have been identified as a possible cause.
• It is important to maintain the chemical baths within specifications, and run the process according to recommended guidelines. This will help to prevent the possibility of microvoid formation.

EXPOSED COPPER

• Exposed copper is seen as a red to orange/brown color showing through the silver deposit. This indicates that the silver deposit is porous and did not cover the copper completely.
• Contamination on the copper surface, from preceding processes can cause exposed copper. Thin solder mask residues can prevent silver plating, allowing copper to show through. Heavy copper oxides, if not completely removed, can inhibit silver plating. Other contamination on the copper surface can have the same effect. Proper solder mask development and final curing is necessary to prevent this problem. Proper pre-cleaning in the immersion silver process is a key to ensure complete coverage.
• If the pre-dip or immersion silver baths are allowed to go out of specifications, this can cause exposed copper. The pre-dip and immersion silver baths must be chemically maintained with regular frequency. Proper bath maintenance will help prevent exposed copper.
• Poor agitation in the immersion silver bath can cause exposed copper. Proper agitation in the immersion silver bath will make the silver coverage more uniform.
• A high plating rate in the silver bath can cause exposed copper. If bath components are accidentally overdosed, or if the bath temperature is too high, then the plating rate will be high. This may allow silver to plate quickly in some areas, while leaving exposed copper in other areas. Proper bath concentrations and temperature must be used to prevent this problem.
• Excessive rinsing, and rinsing with contaminated water can cause exposed copper. Extended rinse times (> 5 minutes), especially in “dirty” rinse water can actually cause copper color to show through the silver layer. Clean DI water rinses, and proper rinse times should be used to prevent this problem.

RELATED DOCUMENTS

Here is a list of related documents that are available from Florida CirTech.

Technical Bulletins:
PC5012

IS127
CirEtch 130
Immersion Silver IS150
Immersion Silver Process Flow

Other Materials:
Immersion Silver Presentation

CONTACTS

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Manufactures and sells all products for the Immersion Silver processes.