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WET PROCESSES

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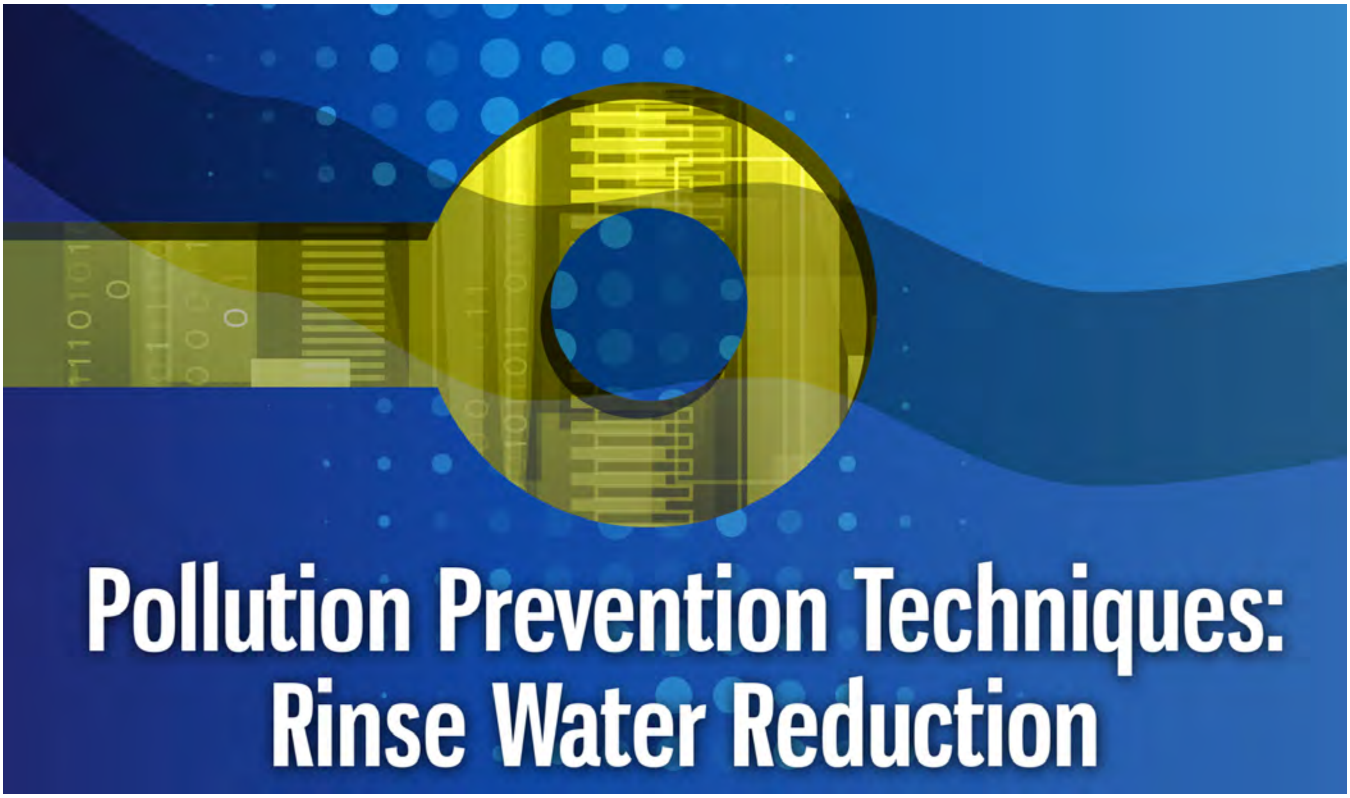

Pollution Prevention Techniques: Rinse Water Reduction

Article by Peter Moleux with contributions from Happy Holden

The first step in any pollution prevention strategy is to minimize chemical wastes and their rinse waters. There are five general categories of common techniques for pollution prevention in a PCB fabrication facility:

1. New processes to replace sources of pollution
2. Extend the bath's life
3. Rinse water reduction
4. Dragout reduction
5. Ventilation reduction

While this list is not all-inclusive, it provides an overview of the types of technologies used around the world that are important to consider. In this article, we will examine rinse water reduction.

Rinse Water Reduction

Most of the waste generated in the manufacturing of PCBs is from cleaning, plating, stripping, and etching. This section describes some of the techniques available for reducing the volume of rinse water used.

While we stress the need to reduce individual rinse water flow rates when a conventional wastewater precipitation system is anticipated, there may be at least one possible exception. If in excess of 95% of all chemicals are recovered, the chemicals do not enter the rinse water collection system, and a central membrane filtration or deionization system is used to produce a zero-effluent system; then, the need to reduce rinse water flow is reduced. However, one must also consider the capital and operating costs for the central system.

One author wrote the following concerning rinse flow rates in the case of a zero-effluent system [1].

"It should also be noted that in a well-engineered zero liquid discharge environment, water conservation is unnecessary. Instead, the focus is total dissolved solids (TDS) budgeting throughout the plant, along with an analysis of specific critical contaminants. Water supply is only limited by the size of the pumps. For instance, to maximize absorption in the fume

scrubber, 10 gallons/minute of DI water can be fed continuously into and out of the scrubber system reservoir… With a closed-loop system, there is no sacrificing of rinse quality to save water. Lift stations integrated with conductivity sensors can automatically identify an out-of-control waste stream as it happens, allowing for quick corrections by maintenance. Also, fresh rinse-water conductivity is always DI quality."

Particulate Filtration on Deburr and Panel-scrubbing Operations

Deburrers are used to remove stubs of copper formed after the drilling of holes in double-sided and multilayer panels before they enter the copper deposition process. Scrubbers are used to remove oxides from printed circuit laminates, clean the surface prior to a surface coating to provide better adhesion and remove residuals after etching or stripping. In deburring and board scrubbing, particulate materials are added to the water and are removed by various methods based on size and the weight of the copper particle such that the wash water becomes suitable for up to 100% recycling. The types of filtration available for this operation are cloth, sand, centrifugation, and gravity settling with filtration.

Etcher and Conveyorized Equipment Design Modifications

Etching machines can be the single largest source of copper waste in the discharge from a PCB facility. The amount of copper discharged, and the rinse flow rate from that machine, is a function of the machine design.

An older etching machine will contain a single-stage etchant replenishing module positioned between the etching chamber and its continuously flowing single or multiple stage water rinse chamber. Fresh etchant is fed to the replenishing module to wash the panels, and that etchant (now containing copper washed from the freshly etched panels) then flows (in a direction opposite to the direction of the panel movement) into the etching chamber. The continuous water rinse can contain from 100 to 500 milligrams per liter (mg/l or ppm) of copper, depending on the configuration of the rinse module. Companies that use this type of equipment, with a single-station rinse module, normally have floor space restrictions in their production area. The etcher design affects the rate of etchant solution dragout as does the volume of panels being processed and the quality of the etchant solution control.

By way of comparison, adding a second stage replenisher station will reduce the range of copper dragout in the following rinse from 50 mg/l to 300 mg/l. We have observed more than one etching machine–using a four-stage replenisher module and a combination of water recirculating with a single-stage rinse module–produce a rinse effluent containing from less than 1.0 mg/l up to 2.0 mg/l of copper. That is the option that we recommend to clients when etchant recycle, and copper recovery are not practical or economical.

Use of recirculating rinse modules will decrease the required flow rate of rinse water (by about 50%) without requiring significantly more floor space, compared to single-station spray rinse chambers (without recirculating rinses). In this application, fresh water is used for the final top and bottom nozzles in a rinse module. This water is collected in a sump located below the rinsing compartment. A pump recirculates this water through the first set of top and bottom nozzles (instead of using fresh water). As more fresh water enters the sump, the excess water overflows through a pipe fitting to drain. While recirculation modules are available for purchase, they can also be custom-built by each PCB factory.

If a PCB factory must evaluate the purchase of a new etching machine, we recommend that a photoelectric cell be included on the load module to sense when panels are being processed. This can be used to activate and deactivate the rinses on that machine. Water used for rinsing will begin to flow only when a panel enters a rinse chamber, and a timer will determine (based on the speed of the conveyor belt carrying the panels) when the last panel will exit that rinse chamber.

The rinse water inlet connection to any rinse chamber should be fitted with a flow restrictor connection that will limit the rate of rinse water used for that application. It is critical that the flow restrictor, if available, not be bypassed under any condition.

A process schematic of a typical etching machine and our recommendation for a new machine are included in Figure 1. The configuration used to reduce the flow and copper dragout in the recommended machine will require a longer machine than the typical etching machine. We recommend that a four-stage replenisher module be used to wash the panels with fresh etchant to remove about 99.9% of the copper before the panels enter the following rinse chamber.

In Figure 1, we recommend the use of another four-stage module to be used as a rinse chamber following the four-stage replenisher module. This is a little unusual. In some cases, this rinse will be sent to an industrial waste pretreatment system containing a high concentration of ammonia. Ammonia in the incoming rinse may cause an occasional problem with that system. Our objective is to reduce the volume of this rinse water to a "drumable or truckable" volume so that this waste could be batch treated. The use of a four-stage module should meet that objective.

As an alternative to the four-stage rinse module following the four-stage replenisher module, we recommend the use of a recirculating rinse module in series with a single-stage rinse module, as shown at the end of the proposed etching machine line in Figure 1. This combination is used to minimize the flow from any conveyorized rinse system (where the rinse from the single station becomes the source of water for the recirculating module). This is an example of a counterflow rinse design.

Conveyorized equipment can also be used for, at least, inner layer and outer layer photoresist stripping, inner layer and outer layer

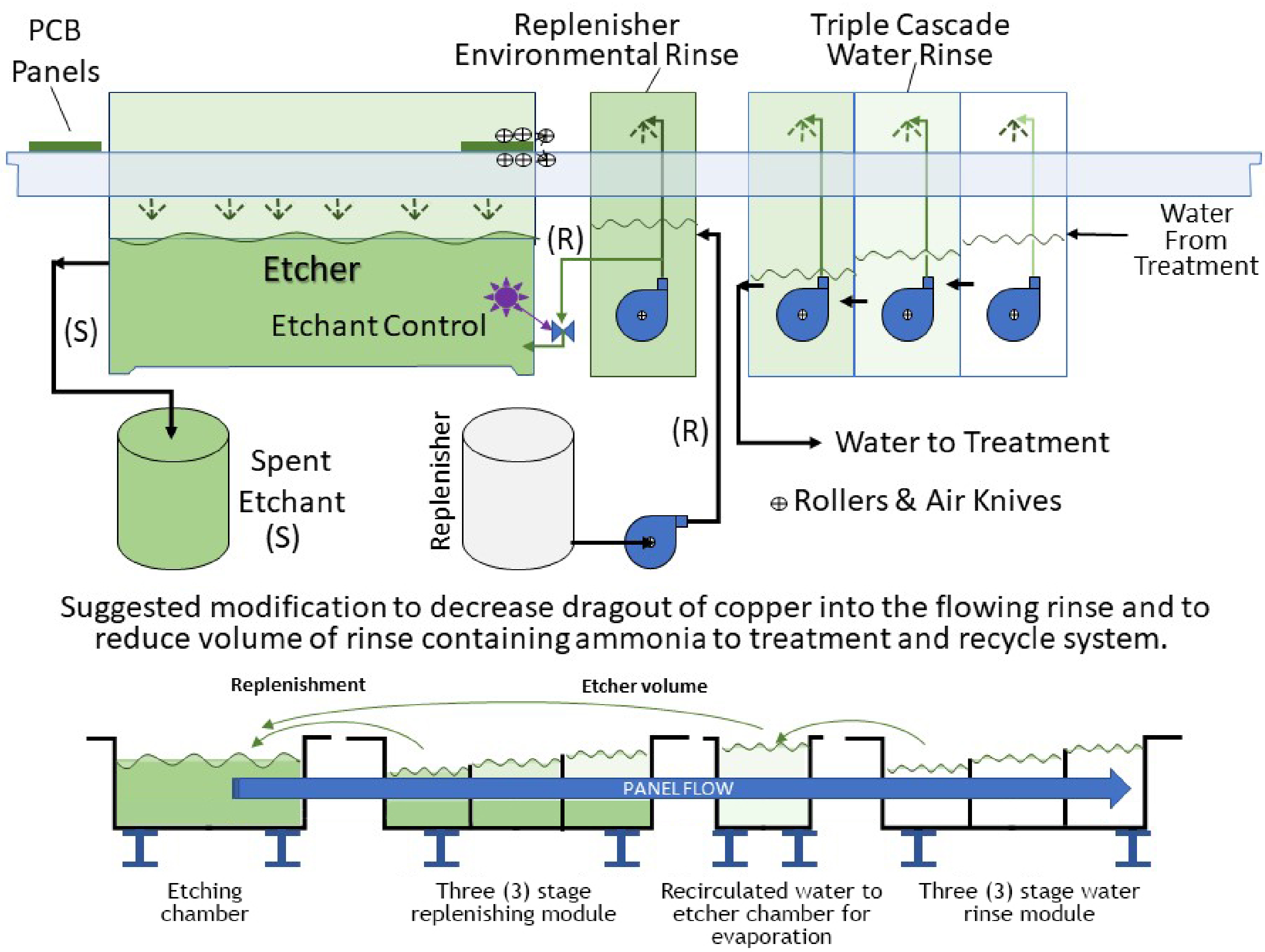

Figure 1: Modifications to inner/outer panel etching equipment.

photoresist developing, deburring, and panel scrubbing. Similar techniques to reduce water flow can be applied to these operations.

Both the volume of wastewater and its copper content may be minimized by selecting a properly designed new or modifying existing conveyorized machine. The numerous options presented in this section must be evaluated on a case-by-case (and site-by-site) basis. Please be aware that some of our recommendations for waste minimization require additional floor space in the production area, that may not be currently available.

Before a final decision is made to purchase or to modify a machine, it is advisable for each PCB factory to weigh the alternative equipment and operating costs. However, if the available production floor space is already stretched too thin, this comparison and its effort may be a waste of time.

Before a final decision is made to purchase or to modify a machine, it is advisable for each PCB factory to weigh the alternative equipment and operating costs.

Use of recirculating rinse modules in the etcher and other conveyorized equipment will decrease the required flow rate of rinse water for that process step by about 50% without requiring significantly more floor space, compared to single-station spray rinse chambers (without recirculating rinses). In this application, fresh water is used for the final top and bottom nozzles in a rinse module. This water is collected in a sump located below the rinsing compartment. A pump recirculates this water through the first set of top and bottom nozzles (instead of using fresh water). As more fresh water enters the sump, the excess water overflows through a pipe fitting to drain (Figure 1).

Conveyorized equipment can also be used for, at least, inner layer and outer layer photoresist stripping and inner layer and outer layer photoresist developing, deburring, and panel scrubbing. Similar techniques to reduce water flow can be applied to these operations.

Immersion-type Counterflow Rinses

Counterflow rinsing, employing several single-stage rinse tanks in series, is one of the most powerful waste reduction and water management techniques for inner layer processing and in the electroless copper process. These operations use a cage-type carrier that holds many inner layer panels in a side by side configuration for processing. Immersion rinsing of panels is also required following the cleaner bath in the pattern plating operation and in other operations.

While multiple tanks can be connected in series, we prefer using one properly designed counterflow rinse tank to minimize floor space requirements. However, this opportunity to reduce the rinse flow rate does require more floor space than a single-station rinse tank.

In counter-current rinsing, after exiting the process bath, the boards move through several rinse contact stages, while water flows from stage to stage in the opposite direction. Over time, the first rinse reaches a steady-state concentration of process dragout contaminants that is lower than the process solution. The second rinse (away from the process bath) stabilizes at even a lower concentration. This enables less water to be used to produce the same cleanliness compared to a single-station rinse tank. The higher the number of rinse stations connected in series, the lower the rinse rate needed for adequate removal of the process solution from the panel.

A multistage counterflow rinse system allows greater contact time between the panels and the rinse water, greater diffusion of the process chemicals into the rinse water, and more rinse water to encounter each panel. The disadvantage of multistage rinsing is that more steps are required as well as additional equipment and workspace. Generally speaking, it is impractical to use more than a four-stage rinse tank. Conventionally, a two-stage rinse which has been properly designed should be sufficient to minimize flow. Typically, a two-station counterflow rinse requires 2–3 U. S. gallons per minute (gpm) of rinse water compared to 5–10 gpm for a well-used single-station rinse. A three-station rinse requires only 1–3 gpm. A four-station rinse may be used when a rinse must be collected and batch treated in a small volume. For initial planning purposes, a dilution ratio of 1,000 to 1.0 is used to determine proper rinsing.

Every rinse tank water inlet pipeline should contain a flexible orifice-type flow restrictor limiting the flow rate of water while the rinse tank is in use. For constantly used rinses, continuous low flow is desirable (for example, where selective ion exchange systems will be used to remove copper). Under other conditions, water use should be intermittent. For these applications, a solenoid valve, timer, and activation system (a tank- or wall-mounted push button or a foot peddle, which is less desirable) should be provided.

Turn off the rinse water when the rinse is not required. This can be accomplished on conveyorized equipment by installing photoelectric cells and/or timers on the immersion rinses to activate and deactivate the water inlet lines only when required. Just being able to activate a rinse and deactivate a rinse when the machine is activated is not enough.

Alternating Side Spray Rinses

Side pulsating spray rinses for the acid copper and etch resist plating lines are an alternative to flood rinsing to conserve water. We recommend evaluating the use of single-stage pulsating spray rinses in place of immersion rinses in acid copper plating lines. The reduction in water consumption using a pulsating spray rinse is about 85–90% of that consumed using an immersion-type rinse.

In practice, the fan-type water spray pattern would first be applied to one side of the panel, and then the source of water would alternate to spray the other side of the panel. This will require two (normally closed) solenoid valves for each rinse station where the spray system is used. The system would be activated by a wall- or tank-mounted push button. When the spray rinse is activated, its instantaneous flow rate may be as high as 95 lpm (25 gpm). However, the rinse would only be activated when a panel requires rinsing, and the panel is located within a specific rinse tank. For example, assuming a one-minute immersion time for each load of (or "work rack" carrying) panels and 30 loads during a 40-hour week, the weekly average rinse flow rate could be as low as 1.1 lpm (0.31 gpm) compared to 18.9 lpm (5 gpm). That is a reduction of 94% for just that flow rate.

Another advantage of spray rinsing is that it will eliminate the need to dump the entire contents of an immersion-type rinse tank, for cleaning purposes, on a periodic basis.

Flexible Orifice-type Flow Restrictor Fittings (If Available)

The use of flexible orifice-type flow restrictors with timers may be more efficient than conductivity controllers for immersion-type rinse tanks. We recommend the use of a flexible orifice-type flow restrictor located on the water inlet to every immersion-type rinse tank. We are not in favor of using conductivity sensors unless they can be calibrated at least once per week. Conductivity controllers are useful when one desires to reduce water consumption.

One reason to use a conductivity controller is when one must collect and then batch treat a rinse if that rinse cannot effectively be treated in the continuous wastewater treatment system. The purpose of an efficient conductivity controller is to reduce the volume of waste, the floor space required, and the cost required to treat a specific waste.

With conductivity sensors, the rate of rinse water flow into a rinse tank is a function of the water inlet pipe size (diameter) and the water pressure in the pipeline. The larger the pipe and the higher the pressure, the higher the rinse water flow rate. A conductivity controller is used to open or close a valve based on measuring the cleanliness of the water in the rinse tank (assuming the conductivity probe is located properly). Solenoid valves are electrically actuated valves that are commonly used with conductivity controllers. A solenoid valve is either fully open or fully closed; its purpose is not to control the rate of water flow.

Flow restrictors, if available, are ordered based on the desired flow rate (we recommend a 2–3-gpm flow restrictor for a two-stage counterflow rinse tank) and the pipe size. If a minimum water pressure exists in the water inlet line (about 20 psi is considered minimum), the water flow into a rinse tank should not vary although the water pressure will most likely vary. Flow restrictors are not adjustable after they are installed. By providing pipe union fittings for both up and down of the flow restrictors, adjustments can be made. Flow restrictors with flexible diaphragms are rated for a specific flow rate in a specific pipe size. Typically, a 2–3-gpm flow restrictor is recommended for a two-stage counterflow rinse tank. If a minimum water pressure exists in the water inlet line (about 20 lbs/in^2 is considered minimum), the water flow into a rinse tank should not vary, although the water pressure will most likely vary. Flow restrictors are not adjustable after they are installed. By providing pipe union fittings both up and downstream from the flow restrictor fitting, the flow rate can be changed if necessary.

We recommend installing a flexible orifice-type flow restrictor or an automated control system to maintain and monitor the inlet water flow rate to every rinse tank. Existing conductivity sensors, if any, should be removed, unless they can be calibrated at least once per week. When rinse recycling or recovery equipment is to be specified, a designer must be aware of the maximum flow rate. The installation of a flow restrictor provides that assurance (if all rinse water passes through that restrictor).

Reuse of Rinse Water in the Electroless Copper Process

Chemical suppliers occasionally recommend the reuse of rinse water within an electroless copper line. This may require the use of pumps to transfer water from one rinse tank to another. As one alternative to reduce the volume of waste, we recommend that at least one of the possibilities noted in Figure 1 be tested at each facility in the short term to determine the effect. This opportunity should be discussed with the technical representatives of the chemistry supplier for that process line before the final decision is made to implement this task. The critical element is not to recycle rinse water upstream around the catalyst. It would be useful to have a detailed chemical analysis of the rinse water before having discussions with your chemical supplier.

Dragout Reduction by Using a Deionized Water Mist Spray as the Panels Are Withdrawn From a Heated Bath

This should be evaluated for, at least, the brown oxide bath and the etchback bath. Installing specially designed rollers and air knives to reduce the dragout from panels being etched and following the dragout still rinse station should be considered. Some plating rack designs allow the panels to be tilted to one side and the panel mounted at an angle (relative to the horizontal) to allow better solution drainage off the panel. This will decrease the dragout.

Eliminate the Need to Strip Racks on the Acid Copper and Tin-lead Line

By using plastic-coated racks, only the tips and contactors (that electrically and physically connect and support the panel to the carrying rack), having exposed conductive metal, must be stripped. We recommend evaluating the use of racks with disposable contactors. That would eliminate the need to strip the racks and could eliminate the use of nitric acid. These types of racks are commercially available and should be addressed in the short term.

Increase the Amount of Agitation in the Immersion Rinse Tanks

Agitation between the panels and the rinse water can be performed either by moving the panels in water or by creating turbulence in the rinse water. Since most PCB factories operate hand rack lines, operators could easily move workpieces manually by moving the rack.

However, the effectiveness of this depends on the cooperation of the operator.

Agitating the rinse tank by using oil-free low-pressure air (from a blower, not an air compressor) is the most efficient method for creating effective turbulence during rinsing operations. This type of agitation can be performed by pumping filtered air into the bottom of a rinse tank through a pipe distributor (air sparger). Air volumes typically recommended are 3–4 cubic foot per minute per square foot of rinse tank surface area. The delivered pressure should be about 1 psi for every 21 inches of liquid depth. Not every rinse tank should be agitated. There may be selected rinses that will produce excessive foam when agitated. Care should be used before agitating rinse tanks.

Not every rinse tank should be agitated. There may be selected rinses that will produce excessive foam when agitated.

Dragout Reduction

Bath dragout reduction can reduce recovery equipment and operating costs. Withdraw the panels slowly to allow ample drainage. The faster an item is removed from a process bath, the thicker the liquid film is on the panel, and the greater the dragout volume will be. The removal of racks containing panels is operator-dependent (unless automated hoists are used); therefore, the amount of dragout from each bath will be operator-dependent. The time allowed for drainage can be inadequate if the operator is rushed to remove the rack from the process bath and place it in the rinse tank. However, the installation of a rail above the process tank and the requirement that the operator place all racks on the rail for at least 10 seconds will reduce the dragout.

However, there are a few operations where concern about oxidization of the panel will not allow this method to be used to reduce the dragout.

Etcher Design

In the last section, we described the proper design for an etcher. In that case, a four-stage replenisher module reduced the dragout of etchant contaminated with copper more efficiently than a two-stage replenisher module. However, the four-stage (or even a three-stage) replenisher module requires more floor space than a two- or a single-stage module. If etchant recycling is contemplated, the etcher itself may be redesigned (eliminating the need for a replenisher module).

Increasing Dwell Time

Holding the panels over the process bath reduces the dragout. One can accomplish this either by slowly withdrawing the panels from a process bath or by installing a rigid supporting device to hang the rack with the panel over the process tank, for a period, before proceeding to the rinse tank.

Use of Automated Control and Wet Processing Systems

Computerized process control systems can be used for panel handling and process bath monitoring to prevent unexpected decomposition of a process bath, controlled rinse flow, and uniform panel withdrawal from each process bath. Since these systems require a significant capital expense for initial installation, only large PCB companies will incorporate this alternative into their manufacturing process.

Drip Pans

A drip pan (also called a drain board) is one of the simplest methods for dragout recovery. The drip pan will capture drips of process solution from racks and panels as these are transferred between tanks. Drip pans not only save chemicals and reduce rinse water requirements, but they also improve housekeeping by keeping the floor dry. We also stress the need for double containment of all plumbing to prevent leaks of corrosive chemicals onto the floor. Spillage from a process tank, pipe, chemical mixing area or etcher must be anticipated and methods provided to contain, collect, analyze, and process the liquids.

Automation

Computerized process control systems can be used for panel handling and process bath monitoring to prevent unexpected decomposition of a process bath, controlled rinse flow, and uniform panel withdrawal from each process bath. Since these systems require a significant capital expense for initial installation, typically, only large PCB companies will find this to be a cost-effective alternative.

DI and Soft Water for Rinsing

Natural contaminants found in water used for production purposes can contribute to the volume of waste produced. Silicates are a known contaminant in PCB chemistries. When using pretreated rinse water, the water requirements for each rinse are reduced.

Printed Circuits Handbook: Sixth Edition [2] states that many water supplies contain high levels of dissolved ionic minerals and possible colloidal materials that cause rejects in board production. Some of these impurities are calcium, silica, magnesium, iron, and chloride. Typical problems caused by these impurities are copper oxidation, residues in the plated through-holes (PTH), copper-to-copper peeling, staining, roughness, and ionic contamination. Equipment problems due to these impurities include, but are not limited to, water line and water spray nozzle clogging, corrosion, and other mechanical breakdowns. Process baths should be made using deionized water.

The presence of organics in water can adversely affect etching and another bath performance. Very good water may contain no more than 2.0 ppm of total organic carbon. The best plating practices suggest using good water quality for critical rinsing operations and high yields. While what is considered good water quality is not precisely defined, here are commonly used criteria:

• Total dissolved solids (TDS)	4-10 mg/l (or ppm)
• Conductivity	8-30 microsiemens/cm
• Carbonate hardness	3-15 ppm
• Chloride	2.0 ppm
• Turbidity	1.0 NTU

Somewhat lower quality is acceptable for less critical applications (deburring) while some other operations (for example, the developer rinse) require better water, such as water containing only 0.5–5 ppm of TDS (0.1–1 MEG). However, this depends on several factors.

One article [3] explained, "Aqueous dry film resists are susceptible to over development. If left too long in the developer, the exposed resist will be chemically attacked and will partially disintegrate…A short residence time in the development chamber helps minimize resist swelling."

Additional swelling that may cause adhesion failure must be avoided in the rinsing chamber. Distilled or deionized water used in the first developer rinse may rapidly penetrate the resist due to osmotic pressure. This may dilute the higher ionic strength developer solution trapped in the resist. To avoid this, the first rinse should have, according to this article [3], a relatively high ionic concentration by adding salts.

Water hardness in the first rinse of 140–350 mg/L of $CaCO_3$ is adequate for most work. If the rinse does not have sufficient hardness, use an acidic second rinse.

Another article [4] claimed that sufficient hardness must be available in the water used for the developer working solution makeup and the developer rinse for some resists. In those cases, magnesium sulfate has been added to the water when sidewall definition and resist toughness needs improvement. Other critical rinses are:

- The accelerator
- The catalyst
- The last rinse on the electroless copper line
- Before and following nickel
- The gold and palladium electroless/electroplating baths

The methods used to achieve these characteristics of water are beyond the scope of this series. Most resin and equipment suppliers recommend (or require) the use of softened water for this final (and sometimes every) washing stage. The requirement for soft water implies that the incoming unused process water must be processed to remove the hardness (calcium and magnesium ions) before it can be used for the final rinse in an exchange column. **PCB007**

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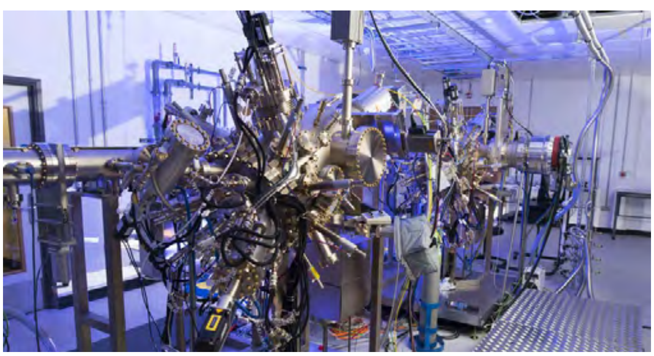
Cardiff Delivers Compound Semiconductor Breakthrough

Cardiff University researchers have developed a compound semiconductor (CS) technology that can drive future high-speed data communications. A team from the Institute for Compound Semiconductors (ICS) worked with collaborators to innovate an ultrafast and highly sensitive avalanche photodiode (APD) that creates less electronic noise than its silicon rivals.

A paper outlining the breakthrough in creating extremely low excess noise and high sensitivity APDs is published in *Nature Photonics*.

Cardiff researchers led by Sêr Cymru Professor Diana Huffaker, scientific director of ICS and Sêr Cymru Chair in Advanced Engineering and Materials, partnered with the University of Sheffield and the California NanoSystems Institute, University of California, Los Angeles (UCLA), to develop the technology.



"The innovation lies in the advanced materials development using molecular beam epitaxy (MBE) to 'grow' the compound semiconductor crystal in an atom-by-atom regime. This particular material is rather complex and challenging to synthesize as it combines four different atoms requiring a new MBE methodology," said Professor Huffaker. "The Sêr Cymru MBE facility, partly funded by HEFCW, is designed specifically to realize an entire family of challenging materials targeting future sensing solutions."

Dr. Shiyu Xie, Sêr Cymru Cofund Fellow, said, "The results we are reporting are significant as they operate in a very low-signal environment, at room temperature, and very importantly, are compatible with the current InP optoelectronic platform used by most commercial communication vendors.

The APDs have a wide range of applications. In LIDAR, or 3D laser mapping, they are used to produce high-resolution maps with applications in geomorphology, seismology, and in the control and navigation of some autonomous cars.

The findings can change the global field of research in APDs. The material developed can be a direct substitute in the current existing APDs, yielding a higher data transmission rate or enabling a much longer transmission distance.

(Source: Cardiff University)