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Technical Information

Process Guidelines for Alkaline Etching

Introduction

Alkaline etchants were introduced in the mid-1970's as an alternative to other etchants for etching panels using pattern plated tin-lead as the etch resist. They quickly became the etchant of choice for etching such panels because of the capability of being regenerated for steady state operation, unlike persulfate based etchants or chromic-sulfuric acid etchants. From an environmental standpoint alone they are preferable to chromic-sulfuric etchant. Approximately half the etch systems sold by Chemcut have been alkaline etch systems.

The rest of this section is broken down into the advantages and disadvantages of using alkaline etchants, the chemical reactions and processing parameters of alkaline etchants and equipment parameters and considerations.

Advantages of using Alkaline Etch

- Compatible with most common metallic resists, i.e. tin/lead, tin, nickel.
- Relatively high etch rate – typically between 2 and 2.5 mils/min.
- Less undercut or sideways etch.
- Fewer environmental problems since supplier will take back spent etchant for copper and ammonia recovery.

Disadvantages of using Alkaline Etch

- Chemistry and etcher form a complex system that can be difficult to control for optimum performance.
- Low viscosity promotes chemistry migration.
- Crystallizes easily causing equipment problems
- Pungent ammonia odor difficult to control
- Difficult to use with fully aqueous dry film.

- Copper in rinse water is complexed with ammonia, which could pass through some waste treatment systems.

Chemical Reactions

Alkaline etch is basically cupric chloride with the copper complexed with ammonia to keep it in solution at a higher pH. In the correct pH range the etchant will still attack copper but is much less aggressive towards tin, solder and nickel.

The etching reaction:

- $2Cu^{0} + 2Cu^{+2}(NH_3)_4Cl_2 \rightarrow 4Cu^{+1}(NH_3)_2Cl$

The regeneration reaction:

- $4Cu^{+1}(NH_3)_2Cl + 4NH_3 + 4NH_4Cl + O_2 \rightarrow 4Cu^{+2}(NH_3)_4Cl_2 + 2H_2O$

- The ammonia (NH_3) and ammonium chloride (NH_4Cl) are provided by the replenisher solution. The oxygen comes from the air brought into the etch chamber by the ventilation system.

Chemical Processing Parameters for Alkaline Etch

There are four chemical factors that contribute to etch rate and undercut. They are:

- pH
- Copper content
- Chloride concentration
- Temperature

All of these factors must be analyzed and controlled in order to find the best compromise between the fastest etch rate and the least amount of undercut. The effects of each are discussed in the following paragraphs.

pH

The pH of the etchant is a measure of the relative amount of free ammonia (NH_3) that is available to the etching process. Most alkaline etch baths are designed to work in a pH range of 8.0 to 8.5 but there exist specific low pH alkaline etch formulations designed for fine line etching with pH as low as 7.8. The etch rate of the bath increases as the pH changes within these limits but the pH of the bath also has an important effect on the undercut. Under ideal etch conditions, the diamine monovalent copper complex $[Cu(NH_3)_2^+]$ formed during the etching reaction forms a film on the sidewall. This film acts as a natural banking agent protecting the sidewall from lateral etch. At the upper end of the pH range, however, the film is rapidly dissolved away in the presence of free ammonia and dissolved air. Typically the undercut is 30% to 40% more at a pH of 8.5 than it is at a pH of 8.1. For this reason Chemcut recommends that the etch bath be run as close to the lower pH limit as possible for best undercut results.

Operating below the recommended range will cause the etchant to attack the tin in tin-lead resists. Even worse, running under the recommended pH minimizes the effectiveness of the buffering system and the etchant could enter a condition known as “sludge out” where the copper-ammonia complex precipitates out of solution. Once out of solution the copper-ammonia complex will not redissolve and the etcher must be emptied and recharged with fresh etchant.

pH is usually controlled by a balance between the ventilation system, etchant temperature and replenishment system.

Copper Content

As the copper content of the etchant increases the amount of undercut decreases. On the high end of the copper content range there is more of the relatively insoluble diamine monovalent copper complex $[Cu(NH_3)_2^+]$ present to act as a banking agent. The recommended copper range for most alkaline etch baths is between 140 gm/liter Cu and 165 gm/liter Cu.

The copper content is controlled by adding replenisher solution based on etchant specific gravity.

Chloride Concentration

The chloride concentration indicates the amount of ammonium chloride (NH_4Cl) present in the system. As the chloride concentration increases, more copper metal can be held in solution, allowing a decrease in the amount of undercut. The chloride component also acts as a buffering agent in the etchant, permitting a narrow pH window.

The ratio of chloride concentration to copper concentration is important in the etch bath. The etch solution will become more corrosive as the amount of chloride above the stoichiometric balance (2 moles of ammonium chloride per mole of copper) increases. In this condition the etch solution will readily dissolve away the protective film on the sidewalls formed by the diamine copper complex. Chemcut recommends that the molar concentration of the ammonium chloride be kept between 1.9 and 2 times the molar concentration of the copper for best undercut results. For example, if it is desired to run the etch bath at a copper concentration of 160 gpl then the chloride concentration should be:

$$\text{Moles of copper in solution} = \frac{\text{160 gpl Cu}}{\text{63.546 gm / mole Cu}} = \text{2.52 moles}$$

$$\text{Moles of } NH_4Cl = \text{2.52 moles Cu x 1.9 moles } NH_4Cl \text{ / mole Cu} = 4.79$$

$$NH_4Cl \text{ concentration} = \text{4.79 moles x 53.453 gm/mole } NH_4Cl = \text{256 gpl}$$

There currently exists no easy way to automatically control the chloride content of the etch bath. Under normal operating conditions with good pH and specific gravity control the chloride content of the bath will be fairly stable with the ammonium chloride brought in by the replenisher solution replacing any loses. Chemcut recommends that the chloride concentration in the etch solution be checked at least twice a shift.

Temperature

Etch rate will increase with increasing bath temperature but so will the undercut. The best compromise between etch rate and minimum undercut exists when alkaline etch baths are run at temperatures between 110^{o}F and 120^{o}F although the maximum operating temperature can be up to 130^{o}F. Lower etchant temperatures drive off less ammonia, making control of the pH much easier with the ventilation and replenishment systems.

Summary of Best Operating Chemical Parameters for Alkaline Etchant

- pH - 8.1 to 8.2
  - (7.9 to 8.0 for low pH formulations)
- Copper concentration - 160 to 165 gpl
- Chloride concentration - 240 to 270 gpl NH_4Cl
- Temperature - 110^{o}F to 130^{o}F

Equipment Parameters

This section provides information for sizing equipment to meet production goals, control considerations for maintaining the pH and copper concentration of the etchant and other equipment parameters that may affect the etching process.

Equipment Sizing

Chemcut etchers are modular so they can be put together in any combination or number needed to meet production goals. The exact number of etch chambers required is of course dependent on the panel size and throughput requirements, the thickness of the copper to be etched and the etch rate of the alkaline etchant being used.

The first thing that needs to be done is to determine the required conveyor speed to meet production goals. This is calculated by multiplying the throughput in number of panels per minute by the length of the panel plus the space between panels:

Conveyor speed needed = Panels/min. x (Length of panel + Space between panels)

In order to calculate the etch conveyor length needed to achieve this throughput the total etch time is needed. The copper thickness divided by the etch rate will give the time needed to etch through the copper to the substrate, known as the breakthrough time. The overetch factor is the extra etch time needed to remove the foot and straighten the sidewalls as much as possible. In most cases the extra etch time needed for foot removal and sidewall straightening is assumed to be 20% of the breakthrough time and an overetch factor of 1.2 is used for estimating total etch time:

$$\text{Total Etch Time} = \frac{\text{Copper Thickness}}{\text{Etch Rate}} \times \text{Overetch Factor}$$

Note: When etching high density circuits (lines and spaces < 5 mils) the total etch time should be increased by another 20% to account for diffusion layer effects. In this case use an overetch factor of 1.4

The total length of effective etch chamber length is determined by multiplying the required conveyor speed by the total etch time:

Effective length of etch chamber = required conveyor speed x total etch time.

This result is the minimum effective length of etch chamber needed to meet the production goals and, once known, the number of etch chambers needed for the system is easy to determine.

The following is a list of the effective lengths of various etch chamber combinations.

Effective Conveyor Lengths for various Etch Chamber Combinations

- 547XLi PEM - 37 inches
- 547XLi DPEM - 74 inches
- Sigma OS06 chamber - 46 inches
- Sigma OS08 chamber - 59 inches

Example Calculation: A customer wants an alkaline etching system capable of running 200 panels per hour. His panels will be 1 oz. foil and panel size is 18 in. by 24 in. Normal spacing between panels is 2 inches and the customer is not sure what his etch rate will be because he has not used alkaline etch before and hasn't selected a vendor for the etchant yet.

Solution:

- Minimum conveyor speed needed to reach 200 panels per hour:

$$\frac{200 \text{ panels/hr}}{60 \text{ min/hr}} \times (18 \text{ in. panel length} + 2 \text{ in. space between panels}) = 66.7 \text{ in./min.}$$
$$= 5.56 \text{ ft/min.}$$

- Total etch time:

In the absence of etch rate data assume an etch rate of 2 mils / min. Most alkaline etchants can achieve at least this rate.

$$\frac{1.38 \text{ mils (thickness of 1 oz Cu)}}{2 \text{ mil/min. Etch rate}} \times 1.2 \text{ overetch factor} = 0.83 \text{ min.}$$

- Minimum conveyor length:

66.7 in/min. conveyor speed x 0.83 min. etch time = 55.4 inches

The customer will need an etch chamber with an effective length of 55.4 inches to get the production rate he requires under the above conditions. From the list on the previous page it can be seen that a single OS08 etch chamber will meet his needs.

Question: After going through these calculations the customer mentions that the panel design for his main product includes some high density areas with 4 mil lines and spaces. Will this make any difference in the calculations?

Answer: Yes it will. When etching circuits with less than 5 mil lines and spaces extra etch time must be allowed for. These high density areas take longer to etch because it takes longer for the fresh etchant to diffuse to the copper surface than in areas with more space between the lines. In this case we should have used an overetch factor of 1.4 instead of 1.2 to take into account the extra etch time needed for the 4 mil line and space circuitry. That would change the total etch time to 0.97 minutes which would in turn increase the minimum conveyor length to 64.7 inches. As can be seen from the list of conveyor lengths the etch system would have to have two OS06 etch chambers or one 547XL DPEM to guarantee the production rate the customer wants.

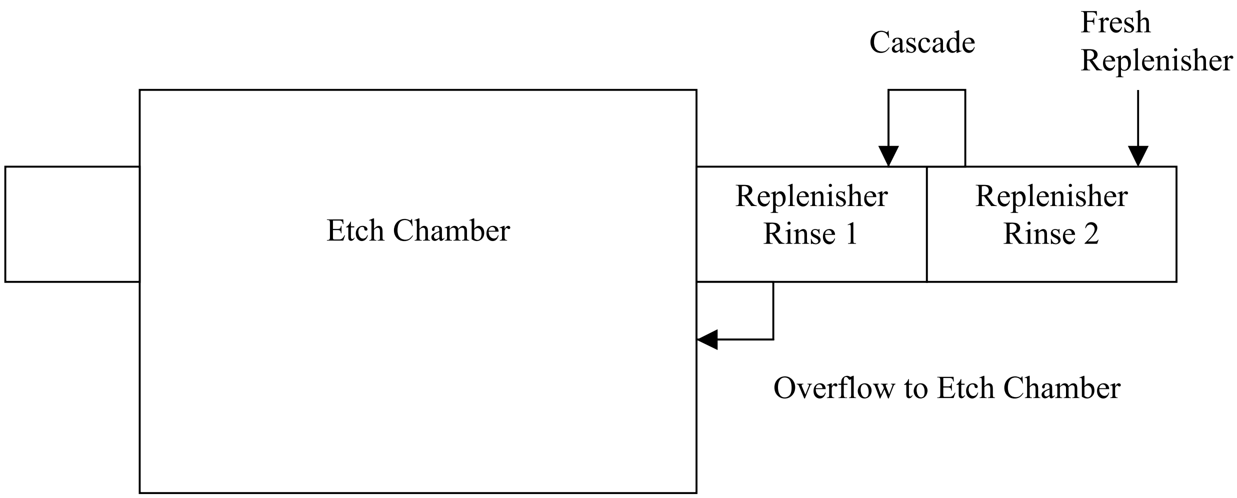
In the calculations above, the 2 mil / min. etch rate, the 1.2 overetch factor used to account for the 20% extra etch time needed to finish etching a line, and the 1.4 overetch factor to account for the extra time needed for dense circuitry, are all on the conservative side. There is enough safety factor in all of them that they can be used with confidence in all situations without having to worry that the etch system as delivered will be too slow to meet production goals.

Equipment Related Process Control Issues:

Chemcut provides etch systems with controls for etchant temperature, conveyor speed, spray pressure, replenisher addition and ventilation. Optional controls are available for specific gravity, anhydrous ammonia sparging for tighter pH control, and air sparging. Temperature, conveyor speed and spray pressure controls are self explanatory. Ventilation for pH control and specific gravity control are extremely important to operation and are discussed in detail below.

Specific Gravity (Replenisher) Control:

Below is a block diagram of a typical alkaline etch system:



As copper is etched from the panel surface into the etch solution the specific gravity of the etch solution begins to rise. This rise is sensed by the specific gravity controller and, upon reaching a selected set point, a pump is turned on and a solenoid valve opens to allow fresh replenisher solution to flow into the second replenisher rinse. This chamber cascades into the first replenisher rinse which in turn overflows to the etch chamber. The pump is on a timer and is turned off at the end of the add cycle. The specific gravity is checked again and the controller will turn on the pump for another cycle if the specific gravity is still above the set point. This process continues until the specific gravity has returned to the set point. A high level sensor will pump out the excess etchant.

The arrangement shown in the figure above has a two stage, cascaded replenisher rinse following the etcher. This design is recommended because the replenisher solution must do three things:

- Provide a source of ammonia [NH_3] and ammonium chloride [NH_4Cl] for the regeneration reaction and replace losses for pH control and solution buffering.
- Rinse off water insoluble ammonium compounds from the panel surface.
- Control copper drag out on the panel surface.

The last two items are the primary reason for cascading replenisher rinses after the etcher. Ammonium salts must be rinsed off the panel surface before the panel enters a water rinse. Most of these salts are not very soluble in water and will remain on the panel surface after water rinsing if not removed before. This cascade design also allows most of the copper containing solutions dragged out of the etch chamber on the panel surface to be concentrated in the first replenisher rinse and subsequently returned to the etch chamber.

Specific Gravity Controllers

Specific gravity control is the primary control for alkaline etch systems. The replenisher solution brought into the etcher to reduce the copper concentration and lower the specific gravity also brings in the ammonia and ammonium chloride for regeneration and pH control. A quality specific gravity controller and good vent control is all that is needed for chemistry control in most cases.

Chemcut includes pumps and solenoids for transferring replenisher solution from storage to the replenisher rinses in the alkaline package. Most vendors of alkaline etchant supply a specific gravity sensor and controller for at low charge. For most work these controllers are more than adequate. However, for fine line circuits with tight tolerances on line width it is necessary to control the copper concentration of the etchant solution to within ±2 grams per liter. The optional specific gravity controller offered by Chemcut for the alkaline etch package is capable of this tight a control. Chemcut's controllers are much more sensitive (± 0.001 specific gravity units) than the typical controllers offered with alkaline etchant packages.

Regardless of whose specific gravity controller is used, each alkaline etch system must have one. Make sure it is clear to both you and your vendors who is supplying it.

Sizing Pumps for Replenisher Solution Supply

In most cases, Chemcut supplies the pump and tubing to get the replenisher solution from storage to the replenisher rinse. It is important to know the projected replenisher flow rate so the pump and plumbing can be sized correctly. The amount of replenisher solution needed per hour is dependent on the amount of copper etched and the copper content of the etch bath. For every gram of copper etched, one gram of copper must be removed from the etchant to maintain a steady state specific gravity.

Example: How much replenisher solution will be needed per hour in the example used for sizing the etch chamber?

Solution: The system was designed for 200 panels per hour, 18 in. x 24 in. panel size, 1 oz. copper foil, and an etchant copper concentration of 160 gpl.

The amount of replenisher needed is dependent on the amount of copper etched from the panel surface. From a pump and plumbing size standpoint the worst case conditions will be the highest flow rate needed. To allow some safety factor for unanticipated problems it is best to assume 100% of the copper is removed from the panel.

Total Area etched = 200 panels/hr x 18 in. x 24 in. x 2 sides = 172800 in^2/hr = 1200 ft^2/hr

Weight of Cu etched / hr = 1200 ft^2/hr x 1 oz. Cu / ft^2 = 1200 oz./hr = 34019 gm/hr
= 34.019 kg Cu / hr

If 34kg of copper are etched from the panel surface in one hour then to maintain a constant specific gravity, etchant containing 34kg copper must be removed from the etch chamber and replaced with replenisher solution.

$$\text{Amount of Etchant to be removed} = \frac{34019 \text{ gm Cu/hr}}{160 \text{ gm/liter}} = 213.2 \text{ liters/hr} = 56.3 \text{ gal/hr}$$

Therefore the pump and plumbing must be capable of delivering 56.3 gal / hr or about 1 gal / min.

If a single etch chamber is used then the entire overflow from replenisher rinse 1 goes into the etch chamber. If a two chamber etch system is used then the flow should be split so an equal amount of replenisher solution goes into each chamber.

Chemcut recommends two stage replenisher rinse modules for single chamber etch systems. For multiple chamber etch systems a three or four stage replenisher rinse should be specified to ensure adequate rinsing of copper from the surface of the panel and allow for enough response time for process control. Experience has shown that using a 4 stage replenisher rinse for after a single etch module looses too much ammonia up the vent between the time the replenisher solution enters the fourth chamber and finally gets to the etch chamber. Consequently, it becomes very difficult to maintain pH control. The only way to prevent ammonia starvation in this situation is to split the flow of replenisher solution so a percentage enters the etch chamber directly. Unfortunately, this reduces the flow through the cascade rinses and reduces its copper rinsing efficiency

Note: Replenisher rinse modules are available from Chemcut with 2,3, or 4 cascade stages, depending on the speed of the conveyor.

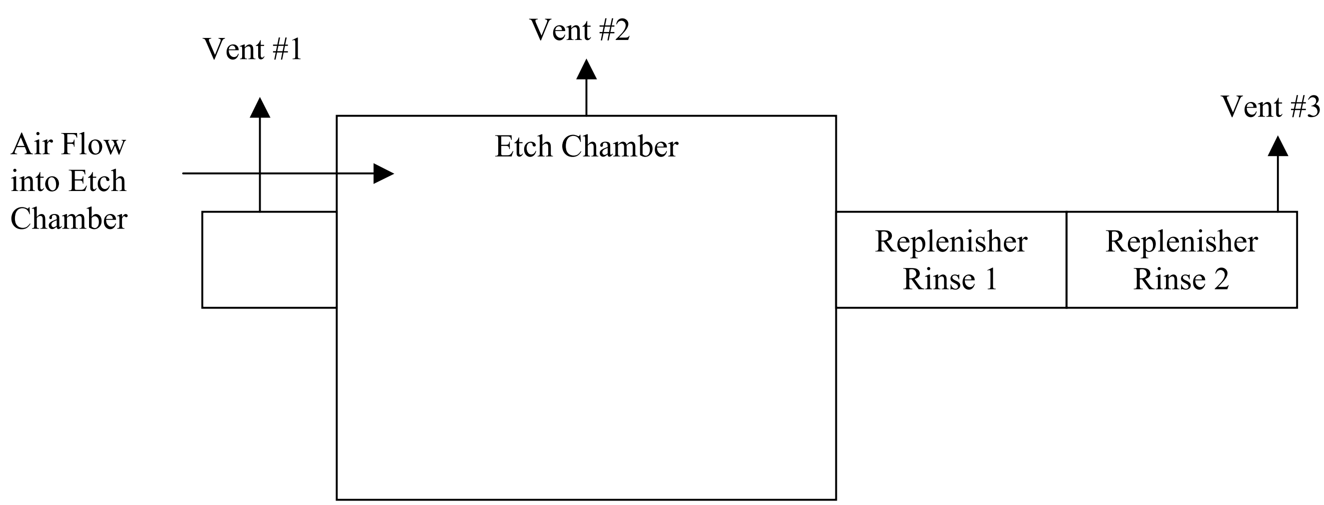
Ventilation Control:

Proper ventilation control is vital in maintaining the pH balance of the etchant during the etching process and the environment around the etch machine. It is also the least understood and most abused of the alkaline etch control parameters.

The vents on an alkaline etch system must do three things:

- Maintain a comfortable working environment around the machine, i.e. keep ammonia fumes in the air to a safe and tolerable level.
- Provide enough air flow into the etcher so there is enough oxygen available for the regeneration reaction to occur.
- Remove excess ammonia from the replenisher solution. Most replenisher solutions have excess ammonia in them to compensate for losses during shipping and storage. Control of pH is much easier if some of this excess can be removed in the replenisher rinse before getting to the etch chamber.

Below is a block diagram showing an alkaline etch system with the vents in the proper places:



- Vent #1 – Fume Control Vent: This vent is for control of fumes from the front opening. If Vent #3 is working properly this vent should not be needed and should be left closed. In any case the air flow should never be higher than 5% of the total flow of Vent #3.
- Vent #2 – pH Control Vent: This vent should have an automatic valve and should only open for pH control. As the pH rises above the set point the vent should open to exhaust excess ammonia. In some cases an etcher may be supplied with two pH control vents on the etch chamber, one on the rear deck lid and one on top of the etch chamber. The rear deck vent is opened first in a high pH situation and if the pH continues to rise then the second vent on the etch chamber is opened.
- Vent #3 – Main Vent: This is the vent that should do most of the work and should be mounted on the last replenisher rinse stage. The flow rate here needs to be high enough to put the system under negative pressure and pull in outside air through the front conveyor opening.

The most common problem in venting is too much flow through Vent #1. The tendency is to open this vent as much as possible to prevent ammonia fumes in the loading area where an operator is most likely to be. This interferes with air being pulled into the etcher through the front conveyor opening. Since this is the only source of oxygen for the regeneration reaction preventing this air flow could cause oxygen starvation in the etch chamber and a dramatic loss in etch rate. Also, having Vent #1 open too much will pull fumes from the etch chamber that will then condense and crystallize in the conveyor opening which may lead to mechanical failure of gears and drive motors. Crystal build-up can get to the point were it will scratch the panels as they enter the etch chamber. Enough flow through Vent #3 will pull air through the front conveyor entrance, minimizing the need to open Vent #1. The flow through Vent#1 should never be more than 5% of the Vent #3 flow.

The next most common vent problem is the wrong flow through Vent #3. As stated earlier, too little flow and not enough oxygen is drawn in to maintain the regeneration reaction. Too much flow and too much ammonia is drawn out of the replenisher solution causing pH control problems in the etchant.

The proper amount of flow through Vent #3 is not easily calculated but it must be enough to pull the amount of air needed for regeneration into the etch chamber. Calculating the required amount of air necessary for regeneration provides an approximation of the flow needed through Vent #3

Example: How much air must be pulled into the etch chamber in the previous example to regenerate the etchant?

Solution: From the regeneration reaction it can be seen that each 4 moles of copper etched requires 1 mole of oxygen (O_2) for regeneration. From the prior example we know that the amount of copper etched per hour is 34119 grams.

$$\text{Moles Cu etched} = \frac{34119 \text{ gm}}{63.54 \text{ gm / mole Cu}} = 537 \text{ moles Cu}$$

$$\text{Moles oxygen needed for regeneration} = \frac{537 \text{ moles Cu}}{4 \text{ moles Cu/mole oxygn}} = 134.2 \text{ moles oxygen}$$

$$134.2 \text{ moles } O_2 \times 32 \text{ gm } O_2 \text{ / mole} = 4294 \text{ gm } O_2 \text{ needed for regeneration}$$

Air is 20% O_2 so 4294 gm O_2 x 5 = 21472 gm of air is needed to supply the necessary oxygen.
1 mole of air weighs approximately 30 gm and one mole of air occupies a volume of 22.4 liters

Air flow needed to supply enough oxygen for regeneration:

$$= \frac{21472 \text{ gm air}}{30 \text{ gm air / mole}} \times 22.4 \text{ liters / mole} = 16032 \text{ liters / hr} = 566 \text{ cubic ft / hr}$$

If the system were airtight then 566 ft^3 / hr would be all the flow needed at Vent #3. However, the system is not airtight and experience has shown us that the minimum amount of flow through Vent #3 should be approximately 5 times the amount of air needed for regeneration. To allow for heavy load periods it would be better to allow for 10 times the air needed for regeneration.

Therefore, the minimum estimate for the flow through vent #3 for this example would be 566 ft^3 / hr x 5 = 2830 ft^3 air / hr. or 47 ft^3 / min and a good approximation for the ventilator flow for this situation would be between 50 and 100 ft^3 air / min.

Optional Control Devices

Air Spargers: Highly loaded single etch modules and most multi-chamber etch systems will have trouble pulling enough air into the etch chamber for regeneration through ventilation alone. To be absolutely sure there is enough air for regeneration an optional air sparger can be added to the system. A sparger is a porous tube that runs along the bottom of the etch chamber under solution level that allows air to be bubbled through the etchant. The flow of compressed air to the sparger tube should be controlled at approximately 5 psi. Some care must be taken since too much air will lower the pH by accelerating the loss of ammonia from the system. It is possible to use an oxidation / reduction potential (ORP) probe to monitor or control the air flow. As the concentration of the cuprous diamine complex grows the ORP (displayed as millivolts) will decrease. As the regeneration process proceeds the concentration of the cuprous diamine complex will decrease as the cuprous ions are oxidized back to cupric ions and the ORP reading will increase. The ORP reading can be used to manually adjust the air flow to the sparger or used to automatically open and close a solenoid.

Anhydrous Ammonia Spargers : A sparger system to bubble ammonia gas through the etchant to keep the pH from getting too low is available from Chemcut as an option. It becomes part of the pH control system so that when the pH falls below set point a solenoid is opened, allowing ammonia gas to bubble into the etch solution and increase the pH. This approach should be used with caution, however, since ammonia gas is even more dangerous than chlorine gas should it get into atmosphere. Since most replenisher solutions contain more than enough ammonia to keep the pH of the etchant solution at the proper level during normal operation, a constant low pH condition may indicate problems that cause excessive ammonia losses. The most common cause of constant low pH is over-venting and reducing flow in the vents will almost always solve a low pH problem. Another common cause is a replenisher rinse that is too long for the etch system causing too much ammonia to be lost from the replenisher solution before it gets to the etch chamber. Usually this occurs when extra replenisher rinse chambers are used to reduce copper dragout. However, in systems where the etcher is not in constant use, such as in a prototype shop, an ammonia sparger may be the best solution to a low pH problem. In any case, the ammonia sparger tube should only be used as a last resort.

Other Etch System Considerations

Water rinses: After the replenisher rinse the panel must be rinsed with water before proceeding to the next process step. Because of water conservation considerations most alkaline etch systems include some type of cascade water rinse after the replenisher rinses. It is recommended that an open conveyor space be left between the water rinse and the replenisher rinse. The water spray draws ammonia from the replenisher rinse very quickly and the pH of the water can get as high as 12 in a cascade rinse with very low flow rates. If dry film is being used as the etch resist it will quickly be stripped from the panel surface in the water rinse. Under some conditions enough ammonia can be removed from the replenisher solution to cause pH control problems. If an open space between the water and replenisher rinses cannot be provided enough room should be left for a small vent to prevent ammonia from being pulled into the water rinse.

Spray Pressures: Spray pressure in the etcher can have a very dramatic effect on undercut. If the spray pressure is too high it will prevent the cuprous diamine complex from forming on the sidewalls of the circuits and there will be no protection from lateral etch. Chemcut recommends spray pressures between 20 psi and 30 psi.