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Alkaline Etch Control for Low Use Systems

We have been getting a lot of inquiries from customers having problems controlling their alkaline etch baths under low copper loading situations. This most commonly occurs when the etcher is used mostly for low volume, high value panels where there may be only a few lots a day run with a long time between lots. The problem encountered is that the pH of the etch solution drops continuously. The only way to get the pH back in spec is to add more replenisher solution to the bath to bring the pH up but then the specific gravity drops because not enough copper is being etched to keep the specific gravity up to where it needs to be. Adding more copper by etching dummy panels or scrap panels to get the specific gravity back into spec drops the pH again, requiring more replenisher additions, which drops the specific gravity again, etc. It isn't long before the whole system is out of control and frustrations mount.

The good news is that there are ways to keep the system under better control. The bad news is that it will require a little more work and extra effort. Before we get into that, however, let's look at how alkaline etch systems are supposed to work.

Short History of Alkaline Etch

Alkaline etch came into use in the early 1970's to etch copper circuits without attacking the metallic etch resists or coatings, such as tin, nickel, and solder, used for various reasons in circuit manufacture. Prior to the development of alkaline etch most metallic coated boards were run using a chromic acid/ sulfuric acid etchant or ammonium persulfate. Both were batch etchants and chromic/sulfuric acid was preferred because of its high metal loading (up to 11 oz./gallon) and leaving a nice bright surface on the metals after etching. Alkaline etch is basically cupric chloride complexed with ammonia (NH_3) molecules. This diamine complex allows copper to stay in solution at pHs in the 8 to 9 range (hence alkaline etch) and continue to attack copper without also attacking the tin, nickel, and solder. In addition, the Cu^{+1}diamine complex reaction product, which doesn't etch, could be re-oxidized to the Cu^{+2}diamine complex in the presence of excess ammonium chloride (NH_4Cl) for a continuous etch process. The alternatives quickly fell by the wayside, Chromic/Sulfuric for environmental reasons and Ammonium Persulfate due to its low metal loading, and today alkaline etch is the only viable alternative available to etch copper without undue attack on the other metals present.

How the Alkaline Etch System Works

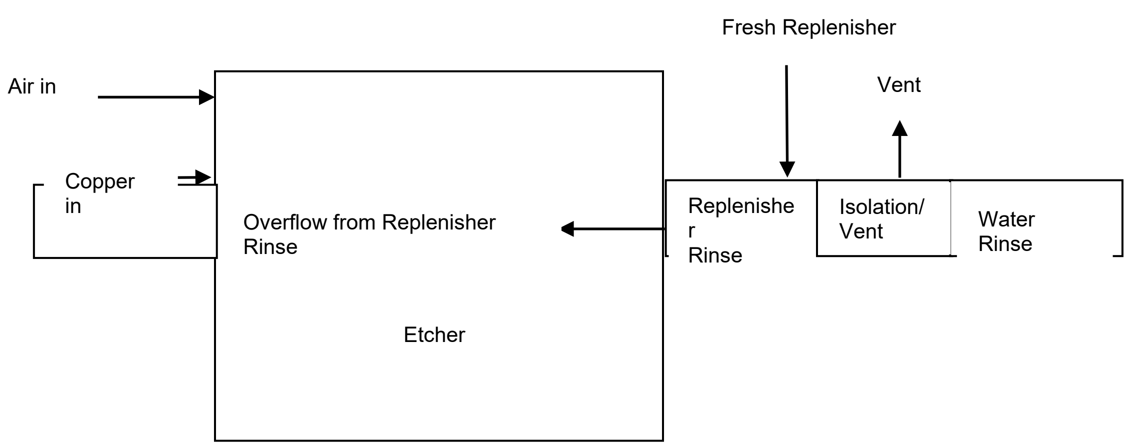
For the etchant to work at peak efficiency three chemistry parameters must be monitored and controlled. These are: 1- specific gravity, 2- pH, and 3- chloride concentration.

The specific gravity controls the copper content of the bath which affects etch rate and etch factor (amount of sideways etch) within the recommended operating range for the copper (usually between 150 to 170 grams/liter or 20 to 23 oz/gal). The etch rate decreases as specific gravity goes up but the sideways etch decreases with increasing specific gravity.

The pH is a measure of the relative amount of free ammonia (NH_3) available to the etching process within the recommended operating range of the etchant, usually between a pH of 8.0 and 8.5. Etch rate increases as pH goes up as does the sideways etch. Operating below pH 8.0 will cause the etchant to begin to attack tin and minimizes the effectiveness of the buffering system, causing the copper-ammonia complex to precipitate out of solution, a condition known in the industry as 'Sludge Out'. Once this happens the copper-ammonia complex will not redissolve, and the etcher must be emptied and recharged with fresh etchant.

The chloride concentration is the amount of ammonium chloride (NH_4Cl) present in the system. The ammonium chloride reacts with oxygen in the air to re-oxidize the Cu^{+1} diamine complex back to the Cu^{+2} diamine complex. The recommended concentration of the chlorides is 2 to 2.5 times the molar concentration of the copper. (The molar concentration of copper is the grams per liter of copper concentration divided by 63.5 [the atomic weight of copper]). The recommended chloride concentration is moles of copper x 2 to 2.5 x 53.5 [atomic weight of ammonium chloride]. For example, if you wanted your copper concentration to be 170 gpl (specific gravity around 26°Be or 1.22) then your Ammonium Chloride concentration should be between 290 and 360 gpl (170 gpl Cu divided by 63.5 times 2 or 2.5 times 53.5 equals gpl NH_4Cl). Chloride concentrations too much above the recommended ratio causes the etchant to become more aggressive and drastically increases sideways etch. Concentrations too much below this range will cause the copper to precipitate out of solution in the form of a light blue mud that will clog nozzles and filters. This is a recoverable situation, however, since the copper will redissolve when the chloride concentration is brought back to the proper level.

The major control mechanism for keeping the etch solution in balance is the maintenance of the specific gravity by the addition of fresh replenisher solution to the system. The replenisher solution is basically etch solution with no copper and an excess of ammonia and ammonium chloride. Please refer to the simple block diagram of an alkaline etch system below. Copper is etched in the main etch chamber with the etched copper dissolving into the etch bath. As more copper is etched the specific gravity of the etch bath goes up. When the specific gravity goes past the set point for the desired specific gravity a pump is triggered and fresh replenisher solution goes into the replenisher rinse and overflows into the etcher until the specific gravity is back to the set point. The excess ammonia and ammonium chloride in the replenisher solution maintain the pH and chloride levels replacing the losses of ammonia from the venting and ammonium chloride from the chemical reactions necessary to re-oxidize the Cu^{+1} complex to the Cu^{+2} complex, to maintain a steady etch rate. The replenisher rinse is necessary, not only as a reservoir for the replenisher solution, but to rinse off any water insoluble ammonia salts generated during the etching reaction and capture any etchant dragout on the panel surface and return it to the etcher where it belongs.



Block diagram of a typical alkaline etch system.

The vent shown on the isolation/vent module is also an important component of the system. It must draw enough volume, so the etcher is under slightly negative pressure in relation to the outside pressure, drawing air into the etcher for fume control and oxygen supply. The oxygen in the air is needed to complete the re-oxidation of the Cu^{+1} complex to maintain a constant etch rate. The volume drawn through this vent is a delicate balance, however. Too little draw means not enough oxygen for etchant regeneration and fume control, too much draw pulls excess ammonia from the etcher making it that much harder to control pH. An effective way to check the airflow into the etcher is to soak the end of a rag in some hydrochloric acid and bring it to the etcher entrance. In the presence of ammonia, the rag will smoke. Open the vent on the isolation/vent module until the smoke is just drawn into the entrance of the etcher. This should be enough draw to control fumes and provide enough air for the regeneration reaction without removing any excess ammonia. Any vents at the etcher entrance should be open just enough to remove any stray ammonia fumes from the loading area but not enough to interfere with air going into the entrance. It should also be noted that there must be an isolation area between any water rinse and the replenisher rinse. The water curtain from the spray in the water rinse is very efficient at attracting ammonia from the replenisher rinse so a lot of ammonia ends up in the water rinse instead of the etcher for pH control.

In essence then, a single control point, specific gravity, is used to keep specific gravity, pH, and chloride concentrations in balance and has proven to be very effective. Copper is etched into solution, the specific gravity goes up, replenisher solution is added to bring the specific gravity back down and replace any losses in pH and chlorides. Under the right conditions, the system will operate consistently all day, day after day.

Why Does the System Break Down With Low Copper Loading ?

The weak point of the system is that it assumes there is a steady supply of copper being etched with no long breaks in between etching sessions. The replenisher solutions are formulated based on this assumption, with the amount of extra ammonia and ammonium chloride in them just enough to keep the chemistry balanced under continuous operation. Problems begin to appear when production is limited and there is no longer a steady supply of copper being etched. Without a steady flow of replenisher solution to control the specific gravity the pH will drop since the system must be vented to control fumes around the etcher and ammonia will continue to be lost. To prevent the pH from becoming dangerously low the only alternative for most is to add extra replenisher solution. Unfortunately, the amount of extra replenisher solution needed to restore the pH is enough to radically drop the specific gravity and change the etch rate. Etching additional copper in the form of dummy panels or scrap to bring the specific gravity uses up chlorides which are not replaced because there is no fresh replenisher being added. This is because the specific gravity is well below the point to trigger the flow of new replenisher. In the meantime, the pH is still continuously dropping and the addition of more replenisher solution is required to bring the chlorides and pH back up which, of course, drops the specific gravity again and so on and so on in a never-ending loop.

How Can I Keep or Regain Control of My Low Usage Alkaline Etch?

The best way to keep control is to find a way to control pH without adding large amounts of replenisher solution. The ultimate solution would be to bubble ammonia gas through the etchant using sparger tubes in the bottom of the etch sump. However, ammonia gas is as dangerous, if not more so, than chlorine gas. The process of getting permits from the local authorities and building the necessary safeguards for containment is more than most want to or can tackle. In addition, the permitting process may take months even if the local authorities are inclined to issue a permit at all.

A more practical option is to use an aqueous ammonia solution (30% or 26^{o} Be ammonium hydroxide) for pH adjustments. This is readily available in 15 gal carboys from most industrial chemical supply companies (industrial grade is fine. The solution doesn't have to be laboratory grade). There is a lot more ammonia here than in the replenisher rinse so you can use a lot less of it to bring the pH back in range. There will still be some specific gravity loss but far less than using replenisher solution for pH adjustment. Of course, a well-ventilated area for storage and transfer to the etcher is highly recommended.

Even with the use of concentrated aqueous ammonia solutions there will still be a drop in specific gravity when it is used to adjust the pH. At some point there will have to be excess copper etched, in addition to the copper etched in the production process, to bring the specific gravity back into spec. This, in turn, will use up some of the chlorides which must also be replaced to keep the copper to ammonium chloride molar ratio constant. Using the replenisher solution to bring the chloride content back up presents the same problem as using the replenisher solution to try and control pH. The amount of replenisher needed to raise the chloride level lowers the specific gravity of the etch solution significantly so more copper needs to be etched, then more replenisher needs to be added to bring the chlorides back up, and so on.

Maintaining the chloride levels without diluting the etchant can be accomplished by using ammonium chloride crystal to control the chlorides. There is no automatic way to determine chloride levels so the etchant will have to be titrated to determine the actual chloride level in respect to what you want the chloride level to be. The amount of ammonium chloride crystal needed to bring the bath into specifications can be weighed out into a bucket and brought out to the etcher. Some of the etchant can be added to the bucket and stirred to dissolve the crystal, then poured back into the etcher (just dumping the crystals into the sump will cause some of them to sink to the bottom of the etch tank and take a long time to dissolve). This procedure will allow the chloride levels to be controlled without diluting the etchant. Below is a sample calculation to determine the amount of ammonium chloride needed for a hypothetical operating etch bath.

Sample Calculation for Determining Chloride Addition

We have a small etcher with a 60 gal. (227 liters) sump. We wish to run the etchant at a specific gravity of 1.22 which is about 170 grams per liter copper. At this copper concentration, as calculated above on page 2, the chloride concentration should be between 290 and 360 grams per liter (2 to 2.5 times the molar concentration of the copper). We would like to run towards the lower limit of the recommended range to minimize the etch undercut so have decided our chloride concentration should be 300 grams per liter. Our titration shows the actual concentration is 290 grams per liter, right at the lower recommended limit so we need to add 10 grams per liter of ammonium chloride crystal to bring the chloride concentration back to 300 gpl. Therefore, 10 grams per liter of added NH_4Cl crystal times 227 liters equals 2,270 grams of NH_4Cl (2.27 kg or 5 lbs.) of ammonium chloride need to be weighed out and added to the etch bath.

Suggested Operating Procedure for Low Volume Copper Etching

If you have been having etchant control problems due to low volumes of copper etched, it is suggested that you start with a new bath before proceeding with a new operating procedure.

Before starting to etch:

1. Bring etchant bath up to operating temperature.
2. Check the vent after the replenisher rinse to be sure it is drawing just enough volume so there is negative pressure in the etcher and air is going into the entrance of the etch chamber.
3. Check pH and adjust with aqueous ammonia.
4. Check specific gravity and add copper via dummy panels or scrap if the specific gravity is below 1.2.
5. Titrate for copper and chloride concentrations. If the molar ratio (moles of chloride/moles of copper) is below 2 then add enough ammonium crystals to bring the chloride levels back to where you want them.
6. If everything is in balance, then etch your product.
7. If you haven't triggered the specific gravity control to add fresh replenisher at least once, run some dummy panels or scrap until you do.
8. When you are done shut off all the sprays (including water rinses) and close the vents. It should be noted that even in the off position the vent is not 100% sealed. The point here is to minimize the amount of air leaving the etcher, not to stop it completely.
9. Check the fluid level in the etcher. If it needs to be topped off use starter solution, not replenisher solution.
10. If you plan to run more product during the day return to step 2 before etching.
11. If you are done for the day turn off the heat.

If there are going to be days between etch sessions or over the weekend it is suggested that the etchant be removed from the etcher and stored in drums between sessions to prevent any further ammonia loss. As long as the etch solution is in the etcher there will always be loss of ammonia and a drop in pH no matter how well sealed the system is.

Conclusion

The above procedures will help in keeping control of the etchant and extending its life but as promised, it involves a fair amount of extra work and effort. Unfortunately, sooner or later depending on copper loading, there will come a time when the bath is no longer controllable. At this point it is better to start with a new etch bath and start again rather than trying to reclaim control. The savings in time will more than cover the cost of a new bath.