

Peroxide Acid Method



The ratio I start with is 2 HCl:1 Peroxide. I use the 3% peroxide. The higher concentration stuff will work faster. I've found that if I keep the color a clear to dark emerald green it tends to react quicker.

Here's how my stock vessel looks right now:



Here's the strainer I made to keep the scrap (fingers usually) separated from the gold foil/flake:



I typically agitate the bath twice a day by pulling the strainer out, waiting a moment or two, then slowly letting it back down into the bath. This causes the gold foils to go into the solution thru the bottom of the strainer and separates them from the finger boards.



Heat helps of course. If I want to hurry it along I'll add a little peroxide every so often to keep the solution warm (it heats and bubbles when you add more peroxide). Once the copper chloride concentration gets right (see the copper chloride document on my website) the solution works really good with an occasional kick start of peroxide. If the solution darkens or precipitates copper chloride (greenish white crystals) then add some more muratic to dissolve the precipitates. The solution will slowly dissolve gold if you get it too reactive (excessive peroxide). I'm not in any real hurry, so I typically set up a three gallon bucket (lowes) and let the scrap soak for a few days. I agitate it occasionally to keep the gold foil that has loosened from blocking the remaining copper plate. You can reuse the stuff forever if you keep it filtered and primed with HCl and Peroxide occasionally.

Here's the dirty foil before the rinses:



Notice the copper chloride (greyish white) and a state of the state of

Here's the 'gold mash' produced after washing and rinsing:



And finally here's the foils from the batch:



I hope this helps... any questions

Steve



HCl is actually hydrogen chloride (HCl) gas dissolved in water. The vapours are pure HCl. They will rust any iron or steel they come in contact with. They will also corrode many other metals, such as aluminium. They are poisonous in a confined area.

The method is safe to use indoors in a non-populated room. The fumes are not produced after the initial reaction except when evaporation occurs. The active ingredient in this formula is Copper Chloride, not peroxide or hydrochloric acid. The two ingredients initiate the production of copper chloride which in turn performs the dissolution of the base metals. You should read the document on my web site about copper chloride. Copper chloride is not volatile at room temperature and is safe if you wear gloves and don't drink it. You can not dispose of copper chloride down the drain!!!

I would recommend that you mix up a small batch of the mix and get familiar with the process before bailing out. Take a 4 cup Pyrex measuring cup and add an ounce of the fingers into the measuring cup. Add in 1 cup of peroxide and 2 cups of HCl. Let it sit in your bathroom near a window or somewhere else out of the way of pets, children, and traffic. Twice to three times a day swirl the mix and watch the gold foils begin to peel away from the finger boards. In four or five days all the foils should be loose enough to be washed off with a spray bottle of tap water.

You will be able to observe the reaction first hand on a small scale and then make your determination from there.

Steve

I must admit that, before studying the PDF yesterday, I though that this was a O2/HCl proposition. I now realize it's an O2/HCL/CuCl/CuCl2 proposition. You still need free HCl and O2 for the system - to convert the CuCl to CuCl2. Otherwise, when the CuCl concentration reaches only 20 gm/litre, the reaction will nearly stop. According to a link on the pdf, to dissolve a pound of copper, it takes 1.87 gallons of 3% H2O2 and .32 gallons of HCl. In the quantities you're using, the HCl starts at about 8 Molar. According to the pdf, the fumes are still pretty strong until this is reduced to about 4 Molar, whereas 2.5 to 3.0 Molar is said to be best. But, according to the pdf, this takes from 3 to 10 days to stabilize. What happens in the meantime? Also, in the pdf, it is stated that, at 1 Molar, there are still fumes, even though they are far less. **goldsilverpro**

No Urea is needed. Urea is used to neutralize nitric acid in AR. Just add SMB dissolved in water. Let it sit overnight and don't expect much gold to be in the AP solution if any. You can test the solution with stannous chloride, but it's sometimes hard to tell if there is gold present. If you plan on reusing the AP don't bother getting the gold out at all. I drop the gold from the AP when I'm ready to mix up a fresh batch. **lazersteve**

AP using high percentage peroxide- BE CAREFUL!

by The Refiner49er on Wed Feb 20, 2008 2:04 am

After running several batches using HCL/H2O2, I wanted to post the following observations.

Using HCL and 3% peroxide at a ratio of 2:1 didn't seem to be very effective unless it was warmed, still quite slow at attacking the heavier or more resistant substrates. It works well on fingers and thinner Au coatings, but if you are processing outside and the temperature is less than 50 F, the reaction is impaired considerably.

I have just finished two runs of AP using 27.5% hydrogen peroxide- a pool shock product that Lou recommended. I used a ratio of 1000 ml HCL to 55 ml H2O2 (1/9th the volume of a 3% peroxide). The reaction was immediate and vigorous, the solution heated up moderately with observable vapour rising off the container. It stripped the parts in a relatively short period of time.

I am in complete agreement with Lou, GSP, Irons and others in regards to minimizing the H2O in this solution. **But use caution**, and add the peroxide a little at a time, it is definitely hot stuff!

I am impressed with the effectiveness of a more concentrated solution.

by Lou on Wed Feb 20, 2008 2:00 pm

Yes, be very careful with concentrated hydrogen peroxide. It becomes very dangerous at concentrations of 27% and above. 35% will bleach your skin and clothes instantly, 50% will give horrible boils and burns, and the 90% material will often explode upon touching organic material (it's also like maple syrup in consistency). That stuff is used as rocket fuel all by itself!

Also, let me mention that halides decompose peroxide (amongst other things, like fine metal powders, sunlight, and heat).

So if you do anything with peroxide, keep it away from bromide and iodide, it will rapidly decompose the peroxide, often explosively (I once had a steam explosion making bromine with peroxide solution).

Lou

35% H2O2 with AP

by lazersteve on Wed Apr 16, 2008 7:37 pm

I have several gallons of 35% H2O2, but I still use the weaker 3% stuff in my AP. The main reason is for the extra water. The water allows the Copper II Chloride to become mobile in the solution and keeps the rejuvenation cycle going. The other main problem with the concentrated stuff is that you end up dissolving your gold along with the base metals due to the excessive amount of chlorine produced.

If you think about the etching reaction you will realize that the active ingredient is the copper II chloride, not the peroxide or the muratic acid. With this in mind the water is necessary to allow the exchange of the copper metal ions in liquid form. If the solution becomes saturated due to lack of solvent (water), the copper won't convert to from the deactivated (and insoluble form) of copper I chloride back to the soluble desirable form (copper II chloride). If you find a lot of off white to grey colored sludge in your batches you are producing copper I chloride. It becomes discoloured by the saturated etching solution which appear very dark brown in color and very thick.

Here's the overview of the chemistry:

pcbfab.com wrote: Hydrogen Peroxide as a Replenisher

The Hydrogen Peroxide H202 system of replenishing has been unpopular in the PCB industry, for no outstanding reason, but not in the closely related Photo-Chemical Milling industry. Perhaps the real reason why it is not popular, is that a reliable control system, for both components required to replenish the system, Hydrogen Peroxide, and Hydrochloric Acid, has only recently become available. Previously, it was probable that those people who took on the challenge of devising their own control system would likely have chosen the least expensive, and easiest system to control replenishment system, which is the Chlorine system. The overall etch/replenishment reaction for Hydrogen Peroxide is:

H202 + Cu* + 2HCl -- CuCl2 + 2H20



The use of Hydrogen Peroxide also produces a purer Cupric Chloride, without Sodium Chloride (NaCl) impurities, but the Hydrochloric Acid level must be carefully monitored, as it is consumed in the regeneration part of the reaction. This replenishment method also suffers from the fact that over-replenishing with the Hydrogen Peroxide can generate free Chlorine gas.

The fact that the replenisher ingredients are supplied in water solutions, as well as the fact that the replenishment reaction produces water, limits the maximum Cupric Chloride content of the etch, but it is still possible to get to as high as 40* Be', depending on the concentration of the Peroxide and HCl replenishers.

••

Just like the Cupric Chloride etchant, the Copper that is already in solution in the etchant, dissolves the copper metal on the board.

Key things to remember to sort this explanation out:

1. The metal is dissolved by being "Oxidized", which means that it loses electrons, which changes it from the orange metal to a water-soluble blue compound.

2. The electrons are initially removed from the Copper on the panel by the copper that is already in solution. This seemingly unlikely idea can only happen because copper can exist in 3 forms:

1. Orange Metal - copper with a "correct amount of electrons"

2. Cupric salts, Cu++ (blue) -- copper missing two electrons. This is the blue, water-soluble form we are all familiar with.

3. Cuprous salts, Cu+ (white) -- copper missing one electron, or half way between form 1. and form 2. This form is usually insoluble, unless it is chelated, and is not often seen in a board shop in large amounts.

The actual etch reaction is:

Reaction 1. Cu* reacts with Cu++ to give 2 Cu+

The cuprous salts are then (supposed to be) immediately oxidized (electrons removed) by the Oxygen in the air which is being pulled through the etcher. In the process, the spent Oxygen is converted to water. (See reaction 2.)

Reaction 2. 2 Cu+ + 0(air) + 2 H+ -- 2Cu++ + H20

I find the extra water is to an extent is helping, not harming. I think the optimal amount of water is just enough to hold the copper II chloride that you need to etch the proper amount of copper off of the scrap.

Steve



AP and HCl-Cl references

by lazersteve on Wed Jan 09, 2008 6:15 pm

GSP wrote: Steve, do you have more data on this - or, your original source for your statement? Seems iffy, to me, but there could have been some isolated usage, I guess. Have you yet thought of an economical, efficient, fast way to use either of them on a grand scale? You could very well be on that threshold.

Chris,

I was using AP and HCl-Cl long before I realized it was used in bigger refineries as I have mentioned.

Here's the reference for my statement:

Small Scale Refining of Jewelers Wastes by Roland Loewen pg.175-176 C1995 wrote: Hydrogen Peroxide and hydrochloric acid will dissolve gold. This is used in several refineries. One refiner reported that the recovery of PGMs was much improved when hydrogen peroxide rather than nitric acid was the oxidizer. The known affinity of platinum and palladium for nitrogen compounds make this a believable conclusion. Unless extended boiling of solutions to remove nitrogen compounds is done it is quite possible that some forms of nitrogen could combine and hold PGMs.

We have no experience with hydrogen peroxide oxidation. The use of the 50% grade is reported. We speculate that the metal is in hydrochloric acid solution and is treated by adding the H2O2. Because hydrogen peroxide is an unstable material considerable care in its use is needed. The stream of peroxide should not be introduced under the solution because of the chance of draw back to the supply tank. There the metals present will likely catalyze peroxide decomposition which can be explosive.

Hydrogen peroxide is a very reactive chemical. It also decomposes and a product of decomposition is a gas (oxygen). In low concentration and with a stabilizer this decomposition is slow. At high concentrations and/or in the presence of a catalyst (many metals are such catalyst) this decomposition goes at explosive rates. Damage can be severe.

A through education in the characteristics of hydrogen peroxide must proceed any work with this material. The manufacturers of hydrogen peroxide can usually give considerable information and advice.

The dissolution reaction is probably :

2Au + 3H2O2 + 6HCl = 2AuCl3 + 6H2O

I have also found this same formula in several texts.

What is odd to me about his mention of the use of peroxide is his lack of references cited on the source of the material. He has references throughout the book (just about every paragraph) on many subjects, but not this one. Just above this section he mentions HCl and Chlorine gas without reference also.

I experimentally stumbled across the use of AP for stropping base metals around three years ago. I've own this book for less than a year. I used AP to dissolve me first batch of monolithic capacitors around two years ago. The 3% stuff is super slow, but it works years well on Palladium. I really dislike evaporating nitric acid based PGM solutions. With AP the approximation of states are approximately across the states are accounted by the states around the states are accounted by the states around the states around the states around the states are accounted by the states around the

As for up scaling the reaction, yes. I have pencilled out a contraption to use AP in a continuous configuration which works with circulating pumps, filters, and electrolytic reactions. Theoretically you can electrolytically rejuvenate the AP as it's saturated and recover the copper moss, returning the rejuvenated solution to the reaction vessel. In essence you can dissolve pounds of copper based pins in a very short time and retrieve the gold foils when the copper is gone. The copper ends up in a separate bucket in mossy form.

I built a prototype and turned it on, but the spent AP I used was too saturated when I first started the device Huge amounts of chlorine gas were evolved in just a few seconds of operation. Ideally you would start with a fresh solution and turn on the electrolytic cell to maintain the proper CuCl2 concentration to affect rapid dissolution while plating out the dissolved copper.

Steve

Here are some chemistry lessons:

Any solution containing chlorine ions is capable of dissolving gold.

Oxygen from the air can get absorbed into HCl and oxidize gold. The gold ions then form complexes with the chlorine ions to give auric chloride.

The truth is a very tiny amount of gold will dissolve in HCl until all available oxidizers are used up. This amount may not be detectable.

Acid peroxide is just a weak form of aqua regia. Aqua regia works by having the nitrate ion oxidize gold as ions and allowing chloride ions to form complexes. This is why you don't need nitric acid to make a gold dissolving solution: just use sodium nitrate (which is an oxidizer) for poor man's AR. Those brown fumes come from the nitrate ions being reduced by the gold as the nitrate ion gives up oxygen to become NO.

Acid peroxide is the same idea. Instead of nitrate as an oxidizer, you're using hydrogen peroxide, which is also a powerful oxidizer. The hydrogen peroxide oxidizes the gold and the chloride ions form soluble complexes. Also happening is the dissolution of oxygen into the acid, which helps dissolve gold.

Nitric acid will actually dissolve a tiny undetectable amount of gold into ions, but since gold will not form soluble compounds with the nitrate ion, the gold does not continue to dissolve.

The reason why nitric acid will dissolve base metals such as copper very fast while hydrochloric acid will not dissolve it fast is because HCl is a non-oxidizing acid.

HCl cannot oxidize copper metal into an ion so the copper stays intact. It will react with oxides of copper forming water with the oxygen and hydrogen ion leaving a copper ion to form a compound with the chloride ion. If there is oxygen in the air that can dissolve into the acid, then that dissolved oxygen can oxidize the copper which then forms compounds with the acid. In effect, the acid makes the copper corrode from the air faster because the chlorine is stripping away the protective oxide layer.

Nitric acid is different because it can oxidize copper. The nitrate ion plays a dual role. Free nitrate ions give up oxygen to oxidize copper. The oxidation of copper simultaneously reduces the nitrate ion into nitrogen monoxide gas. Free hydrogen ions combine with oxygen to form water and free nitrate ions combine with the copper ion to form copper nitrate.

The reason why AP is preferred over AR is because it doesn't give off horrible fumes. Gold is least likely to dissolve in both AR and AP, but each metal does not dissolve precisely sequentially. There is some overlap. Galvanic action can help make the process more sequential, but not everything is electrically connected so it doesn't happen effectively.



You can in theory dissolve base metals only with aqua regia by controlling the amount of nitrate ions you put into the acid. The reason why AR dissolves everything is because we make it such that it will dissolve everything, but if we limit the amount of nitric acid or NaNO3, then we mimic the effect that acid peroxide does.

AP will dissolve everything like AR does if and only if you put in wayyyyyyy too much peroxide without diluting it too far. It will take a long time but it will happen.

When an AP batch is done, the reason why gold flakes remain is because the oxidizer is all used up, and gold chloride displaces base metals and gets deposited as a black powdery film. <u>badastro</u>

AP Questions

by lazersteve on Sat Feb 21, 2009 6:33 pm

Astraveller wrote: 1. I have been using two strengths of acid (HCl) -20% and 32% - the 20% seems to work best - (BTW - both work). Palladium, I know your post answered this question but can I ask it again? Does 20% work better than 32% for the AP process?

A little extra water won't hurt the AP process, it may even help to keep the gold foils from dissolving if too much or too strong of a peroxide solution is used. *Astraveller wrote:*2. Am I right in assuming that 32% will work better in the Clorox process?

I would use the 32% for sure. The 20% will work, but will retain more chlorine gas due to the extra water. This dissolved chlorine will help the gold foils dissolve, but any extra after the foils are gone will need to

be removed with heating. *Astraveller wrote:* 3. When I am filtering, I filter the AP and foils first – keep the AP and return it to the dish – I clean the fingers in fresh water and discard the stripped ones. Then I clean the un-stripped ones with a created on the stripped ones.

with a spay bottle and put the fresh water and foils through the same, or different, filter. On this second pass I have noticed that I sometimes get Gold foils with a grey sludge on top instead of clean gold. What is this grey/green sludge?

The combined foils from the filters and the bottom of the bucket should remain in the reaction bucket until they are thoroughly washed free of the gray sludge (copper I chloride). The CuCl is washed out using HCl followed by water after all the gray sludge is gone. Once the gray sludge is removed and the foil wash water is 100% clear then transfer the foils to the filter or better yet, directly to the Clorox reaction beaker.

Basically after filtering the AP solution wash the foils that were caught in the filter back into the mash of foils in the bottom of the bucket. Then wash all the foils together with HCl then water.

*Astraveller wrote:*4. Can I put these (the foils with a bit of sludge) through the Clorox process as they are? Or should I put them through the AP again?

No. See above.

Astraveller wrote: 5. Can I put the 'clean' filter papers into the Clorox solution as they are or scrape out the gold and keep the filter papers for a separate process?

The filters should be washed down into the reaction backer with the main foil mash and washed with HCl and water. After this the clean foils are transferred firecry to the clorox reaction beaker. The filters go in your filter burn box. Steve



Here are the pics of our first real AP processing and the four tubs system. And btw, thanks to all the Steves et. al.













Bubbling Air during AP use

by lazersteve on Sat Feb 02, 2008 5:49 pm

Skyline,

Bubbling air thru the AP solution as it etches speeds things up a bit, but it tends to spit and splatter everywhere, so cover the bucket with a loose fitting lid.

The solution merely grows in volume as it consumes more base metals. The copper chloride formed is the dissolving agent and is recycled when oxidized. Saturation can occur when the solution has absorbed more copper than the volume of liquid will hold. Adding a bit of HCl, water, or peroxide will activate it again. Which one to add and how much is determined by several factors.

The details of what to add when are in a Copper Chloride document on my website, <u>http://www.goldrecovery.us</u> which anyone interested in the AP reaction should study throughly. It seems all to often people are asking questions here when the answers have previously been accumulated and provided here and/or on my website, but they refuse to read the documents provided.

Study your reactions and documentation thoroughly before you begin to use them and it will serve you far better than any outside assistance. Who knows maybe you can even figure out a something that will make the reaction work better.

Steve

ACID ETCHING USING CUPRIC CHLORIDE

•Acid cupric chloride is used widely in the PCB industry as an effective etching solution for removing

unwanted copper from copper printed circuit boards.

•The etching reaction can be expressed ionically as: -

CuO + Cu2 + => Cu+ + Cu+

•Etching one atom of copper (CuO) with one cupric ion (Cu2+) produces two cuprous ions (Cu+). These

cuprous ions are inactive in etching terms and, as their concentration in the solution increases, the etch

rate falls.

•To maintain the desired etch rate it is therefore necessary to either regenerate the etchant or replace

spent etchant with fresh. Regeneration is the action of oxidising the cuprous ions to convert them back to

cupric.

•Two methods of regeneration of the etchant are currently employed, namely chemical and electrolytic.

CUPRIC REGENERATION & COPPER RECOVERY SYSTEM

CHEMICAL REGENERATION

•The technique involves the use of chemical oxidation using chlorine gas or hydrogen peroxide to convert

the cuprous ions to active cupric ions. Surplus cupric chloride is produced, which increases the level of

dissolved copper in the etching until it reaches a level where etching is inhibited. Therefore, excess



solution must be removed and acid and water introduced to maintain the correct copper concentration.

This can be done on a feed and bleed basis, with excess solution stored ready for disposal. •The oxidation reaction can be expressed as:-

Two Cuprous ions produced during etching + Hydrogen peroxide => two Cupric lons Cu+ + Cu+ + H2 O2 => Cu2+ + Cu2+

•One Cupric Ion in the solution is required to maintain copper concentration for etching, the other is

removed by adding HCl and water to maintain the correct copper concentration.

•The result is a large volume of excess etchant which has to be disposed of.

CUPRIC REGENERATION & COPPER RECOVERY SYSTEM

ELECTROLYTIC REGENERATION

•Electrolysis is the action of producing chemical changes by passing an electric current through an

electrolyte.

•Reactions taking place at the anode, or +ve electrode, are oxidations, (removal of electrons) and those

occurring at the cathode, or -ve electrode, are reductions, (addition of electrons).

•Electrolytic regeneration of cupric chloride is achieved by taking advantage of these two simultaneous

reactions.

•The cupric chloride in this case is the electrolyte.

•Cuprous ions are converted to cupric ions at the anode by oxidation, whilst at the cathode, cupric ions

are converted to metallic copper by reduction. It is possible to continuously regenerate etchant while

removing excess dissolved copper, in metallic form.

•Copper represents the only significant waste product from the process and uses no chemical additives to

achieve the conversion. The only other losses in the system are due to drag out or evaporation. •The process is achieved by the use of a divided cell containing an anode in one compartment and a

cathode in the other, separated by a cationic membrane. An electrical current is passed through the

membrane. (see Diagram 1)

•The oxidation reaction at the Anode can be expressed as:-

Cu+ + Cu+ - two electrons => Cu2+ + Cu2+ Similar to that of chemical oxidation. Two Cupric lons are

now present.

•The Electrolytic process has the second step, where the excess Cupric Ion is removed by a reduction

reaction at the Cathode. This can be expressed as:-

Cu2+ + two electrons => CuO

•Copper metal is plated onto the Cathode within the cell

CUPRIC REGENERATION & COPPER RECOVERY SYSTEM

PROCESS DESCRIPTION

•Etchant is pumped from the etching machine into the anode compartment of an electrolytic cell at approx 150

ltr/min per 2kg cell. The cell is divided into an anode and cathode compartment by means of a membrane.

•The ORP (oxidation/reduction potential) of the etchant is monitored. When the ORP falls below a pre-set level

(approximately 524mV) power is applied to the cell and regeneration takes place.



•In the anode compartment, electrolytic oxidation occurs and cuprous ions are converted back to cupric ions.

Solution returns to the etching machine.

•Simultaneously, a proportion of the etching solution is bled into the cathode compartment, where electrolytic

reduction occurs and copper is removed from the solution in metallic form.

•Copper depleted catholyte solution is returned to the etchant solution to maintain both anolyte and catholyte

volumes constant. The rate at which etchant is introduced is regulated by the rate at which copper is plated out,

thereby maintaining a constant copper concentration in the catholyte (plating) solution.

•The copper is plated in dendrytic form and is removed from the cathode by an oscillating scraper mechanism

and falls to the bottom of the cathode compartment. The collected copper is periodically removed manually.

GENERAL SPECIFICATION

Systems are sized according to the maximum rate that copper is removed from the printed circuits. They typically

vary from 6kg an hour to 24kg an hour. Each electrolytic cell is capable of removing 2kg an hour and requires

approximately 2000 amps at 7 volts electrical power to achieve this.

Anolyte (Etching) Solution Copper concentration 130 – 140 g/ltr. Hydrochloric acid concentration 2.0 - 3.5 N ORP

(oxidation/reduction potential) to suit etch rate, normally 524 – 560 mV.

Catholyte (Plating) Solution Copper concentration 25 - 45 grams/litre. Hydrochloric acid concentration 4 - 6 N

CUPRIC REGENERATION & COPPER RECOVERY SYSTEM

PROCESS SUMMARY

•Etchant comprises CUPRIC ions (Cu2+)

•During the etching process one CUPRIC ion (Cu2+) becomes two CUPROUS ions (Cu+ + Cu+) •During the electrolytic oxidation process at the Anode the two CUPROUS ions (Cu+ + Cu+) are converted to two CUPRIC ions (Cu2+ + Cu2+). The Copper removed from the PCB is now in the form

of a surplus CUPRIC ion (Cu2+) in the Etch solution (Anolyte). This is the same result as is achieved by

using the Peroxide oxidation process.

• Rather than removing this surplus Copper as waste solution, the ions are removed by being plated

out as copper metal.

•The surplus CUPRIC ion (Cu2+) is transferred to the Catholyte (plating solution) by a dosing pump,

sufficient to feed the plating process at approximately 2Kg per cell per hour. The copper concentration in the Catholyte required to achieve the correct plating rate can be controlled by an optional density controller.

•During the reduction process at the Cathode, the surplus CUPRIC ion (Cu2+) is converted to copper

metal, plated in a dendritic form onto the carbon graphite Cathode plate.

•An oscillating "scraper" mechanism passes both sides of the Cathode plate, removing the copper dendrites, which fall to the bottom of the cell.







ALL FREE ----- ALL THE TIME

GOLD REFINING FORUM.COM © 2009

