

Electrolytic Etching Copper and Silver Using Copper Nitrate, a replacement for Table Salt (NaCl) by Ben Dory



Introduction and Acknowledgements

Personal and environmental safety is often at the forefront of decision making when setting up new systems in the studio. Etching can now join this conversation, as safer and more efficient systems are becoming increasingly common. Inquiries by printmakers over the past decades have led to the rediscovery of a system of etching that uses electrolysis - where an electric current is the catalyst for chemical reactions. The comprehensive guides, both in print and online, are an invaluable resource for e-etching¹. Yet, metalsmiths often have different end goals. Rather than etching a line or area deep enough to hold ink, we often want a deeper etch with a surface that is a finish in itself.

The caustic nature of nitric, hydrochloric and sulfuric acids as well as the mess and limitations of ferric chloride can be replaced with self-sustaining systems that can be operated with minimal safety equipment. An acute vision for the potential of e-etching has developed within the metals field, providing both an incomplete summary of the process and a limited view of the spectrum of health and studio benefits that come with e-etching. The term 'salt-etching' or 'salt water etching' is often synonymous with 'electrolytic etching' (e-etching). This has led to the use of sodium chloride as the salt, which can be problematic and counterproductive to good intentions of personal and environmental health when compared to one prominent alternative. With this, article, copper nitrate will be presented as a replacement for sodium chloride. This writing is meant to be a reference and springboard for metalsmiths, not an exhaustive text. My aim is to present more standardized systems for electrolytic baths through chemistry, vocabulary and examples from which metalsmiths can explore and share their results and experiences. The information that follows can be implemented into home and academic studios - heightening personal safety, efficiency and consistency.

My thanks to the enormous amount of work completed by member of the printmaking community on e-etching, the influential *Relief Electro-Etching for Champlévé Enameling* by R.L Jackson and the previous SnagTech article on e-etching. I would also like to thank all the individuals who have helped me along the way.

¹ Nik Semenoff, Cedric Green, Alfonso Cuijera and Friedhard Kiekeben's additions to www.nontoxicprint.com: Cedric Green's Green Prints and

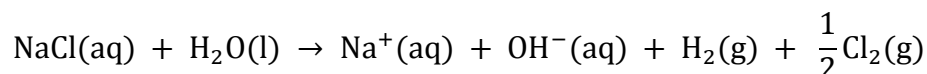
Benefits of Copper Nitrate

- Efficient - Only one bath needs to be made - solutions can be taken from a larger bath as needed and returned when etching is complete.
- The bath is self-perpetuating. The by-product is more copper nitrate. Newly available copper ions bond with the nitrate to start the reaction anew.
- The amperage raises to a steady level, as opposed to copper sulfate baths where it drops
- Consistent - The results are repeatable with the same bath over time.
- There is no off-gassing.
- The only upkeep is to maintain the water level if it evaporates.
- Disposal is only necessary when the bath is of no more use. The solution may be stored when not required.

Sodium Chloride - Table Salt

For all the reasons that sodium chloride is used for e-etching such as safety, ease, accessibility and effectiveness, upon closer examination, those same reasons argue against the use of table salt as an electrolyte. A number of chemical reactions make this common mineral less attractive for etching:

- The bath is short lived since the oxidizing agent, chloride, is quickly spent.
- The current is inconsistent as the bath chemistry changes.
- At concentrated levels, chlorine ions (-) are converted to gas and released at the anode.
- The chemistry²:



Aqueous sodium chloride dissolved in water forms sodium cations (+) and hydroxide anions (-) while releasing hydrogen gas and chlorine gas.

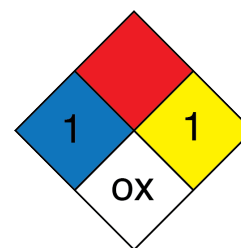
- The sodium bonds with newly formed hydroxides to create sodium hydroxide (NaOH), or caustic lye at the cathode. This compromises the effectiveness of the bath chemistry and raises the pH. Resists are more likely to break down in an increasingly base solution.
- If the NaOH is not contained on the cathode side of the bath, it will bond with the chlorine gas to form sodium hypochlorite, a precursor to household bleach³.
- Sodium chloride etching solutions quickly become a complex blend of chemicals.
- Copper ions release from the anode into the bath without the ability to plate on the cathode.
- A great amount of time is spent in making and properly disposing solutions for such a short lived etching bath, which weakens until it is spent.

² Boundless. "Electrolysis of Molten Sodium Chloride." Boundless Chemistry. Boundless, 17 Nov. 2014. Retrieved from <https://www.boundless.com/chemistry/textbooks/boundless-chemistry-textbook/electrochemistry-18/electrolysis-132/electrolysis-of-molten->

Copper Nitrate, a Salt

A definition of salt must be clarified. Generally speaking, table salt in its many forms comes to mind, which is primarily composed of sodium chloride (NaCl). Chemically speaking, salt is formed from the neutralization between an acid and a base, creating a positively charged anion and a negatively charged cation that balance or neutralize each other. Copper nitrate is the result of combining copper and nitric acid (bear in mind that this creates a much safer product; ex. table salt (NaCl) is the combination of sodium hydroxide and hydrochloric acid). The neutralization creates bonded copper cations, Cu^{+2} , and nitrate anions, $(\text{NO}_3^-)_2$. It is the polarity of these ions that allow electrolysis to occur. Other common salts found in the metals studio include sodium bicarbonate (baking soda), sodium bisulfate (pickle) and calcium nitrate (investment).

Be aware that copper nitrate is an oxidizer and should be stored separately from flammable chemicals. NFPA, the National Fire Protection Agency, who provide the useful fire diamond (standard 704) to the right, shows that copper nitrate is a mild irritant (blue), can be unstable at high temperatures (red) and is an oxidizer. They also release standard 430, storage of liquid and chemical oxidizers. On a scale from 1-4, copper nitrate is a level 1 oxidizer, which "does not moderately increase the burning rate of combustible materials with which it comes into contact."⁴



Compare this with hydrogen peroxide, one of our everyday household goods, which is a level 2 oxidizer, where the flammability of combustible items increases. The 3% solution we use at home is dilute enough to render this dangerous trait harmless, and the solution of copper nitrate presented here is comparably safe.

Purchasing Copper Nitrate

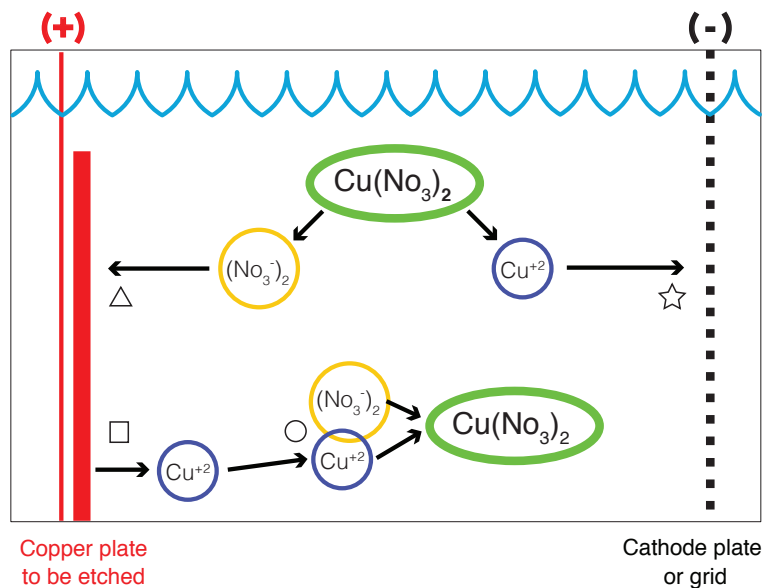
When looking to purchase copper nitrate for your studio, a number of options are available online. The Science Company has been a reliable source for a number of chemicals over the years. Cupric nitrate is sold from 100g to 2.5kg. Cheaper options are available on Ebay, but I defer to the credentials of the Science Company. The specific chemical that they sell is cupric nitrate trihydrate.

⁴ <http://webcache.googleusercontent.com/search?a=cache:knvIvMesnMAI:d.vim9.com/ka/groups/8655011/870361457/name/nfpa%2B430%2B->

Electrolysis

Electrolysis occurs when a forced (external) current [in our case from a rectifier or a plug-in power adaptor (for LED lights, phones, etc.)] acts as the catalyst for a reduction-oxidation reaction. Oxidation occurs when a material loses electrons. Conversely, reduction occurs when a material gains electrons. We can think of etching as synonymous with oxidation. Where we selectively oxidize the surface, our designs will appear lower than the protected surfaces.

With copper nitrate we can create an ideal etching environment. The Cu and NO₃ ions are forced apart by the positive and negative electrodes, which are connected to the power source. Positively charged copper ions plate on the cathode, gaining electrons. Nitrate ions oxidize the copper anode, losing electrons. The new copper ions released from the anode bond with nitrate ions to create new copper nitrate, recommencing and perpetuating the process.



The process begins with Copper Nitrate $\text{Cu}(\text{NO}_3)_2$ in solution with H_2O

When a current runs through each lead:

The charge at each electrode separates the $\text{Cu}(\text{NO}_3)_2$ into oppositely charged ions



☆ Cu^{+2} is attracted to the negatively charged cathode grid, plating the surface

△ $(\text{NO}_3)_2^-$ is attracted to the positively charged exposed areas of the copper plate

□ $(\text{NO}_3)_2^-$ oxidizes the exposed copper, releasing Cu^{+2} from the plate and into the solution

○ Cu^{+2} bonds with the free $(\text{NO}_3)_2^-$ creating new $\text{Cu}(\text{NO}_3)_2$

The process repeats as long as a current is present.

Materials

Accessibility is one of e-etching's greatest strengths. While there are many options for more expensive equipment, the same results can be achieved with easily available and affordable items. In every set up you will need:

- DC power source - This can be a plating rectifier (3A will be plenty for the vast majority of projects). A DC wall plug with wires stripped at the end is cheap and useful if you are etching small pieces (the amperage rating is not high enough for larger ones).
 - Copper nitrate trihydrate - this only needs to be purchased once (500g ~ \$30)
 - Positive and Negative leads with alligator clips
 - Plastic or glass container to fit your plate horizontally.
- or-
- Plastic or glass container in which you can vertically submerge your plates
 - Cathode - copper, silver or stainless steel sheet or mesh; half to the same size as the surface area to be etched. Match copper to copper/silver to silver. Stainless works for both
 - Anode - copper or silver to etch
 - Bus bars from which to hang the anode and cathode (optional)
 - Plastic clamps to hold the anode and cathode vertically from the bus bars or against the container wall (optional)
 - Distilled water
 - Etching resists - vinyl, BioLac, Lascaux acrylic resist, tape, spray paint, paint pen, waxes, oil based crayons, etc.
 - Steel wool or steel scraps in water for converting copper ions
 - Washing soda/soda ash or baking soda for neutralizing
 - At least an N95 particulate mask
 - Nitrile gloves

Mixing solutions

Wear gloves, eye protection, and a mask when working with the copper nitrate crystals. This is precautionary; the crystals are not a fine dust and do not release caustic fumes. Since 1ml of water almost exactly equals 1g, mixing solutions by weight can be quite simple. I have found that a 25% solution of copper nitrate in water provides great etching results. To mix this, begin by zeroing a metric scale with your chosen container on top. Add water until the mass matches the volume that you want and set to the side. In a separate container measure out the copper nitrate to a mass that is 1/4 of the water mass. Add copper nitrate to the water. Stir until the crystals have dissolved.

1000g H₂O + 250g Cu(NO₃)₂ = 25% solution copper nitrate in water

Set-up Notes

Use the smallest size container that is available. This will create less resistance in the bath, raising the amperage to etch more efficiently. I try to keep the distance between the anode and cathode to 2" - 4". In academic environments, setting students up with their own bath in quart containers rather than having 1 large bath is helpful for the same reasons. The copper nitrate solution can be added back to one main container and used over and over again.

Ensuring that the anode and cathode are parallel to each other will make for a consistent etch. This can be done with either a vertical or horizontal etching bath.

My preference is to use a vertical bath in a beaker with the anode and cathode clamped parallel to each other to the side. When using mesh as the cathode, I will clamp the metal to acrylic supports so as to not bend the material. In vertical baths where the anode and cathode hang from a bus bar, keeping the two sides parallel can be difficult unless the plates are heavy enough to stay vertical. It is helpful to use heavy square stock (any material) as a bus bar from which you can clamp a rigid hanging wire.

If you are using a horizontal bath when the plate is too large for a beaker, you can either float the plate to be etched on insulation board, similar to ferric etching, or have the anode resting on the bottom of the bath. I prefer the prior, as it is easier to set up, and you do not have to worry about etching through the anode hanging wire.

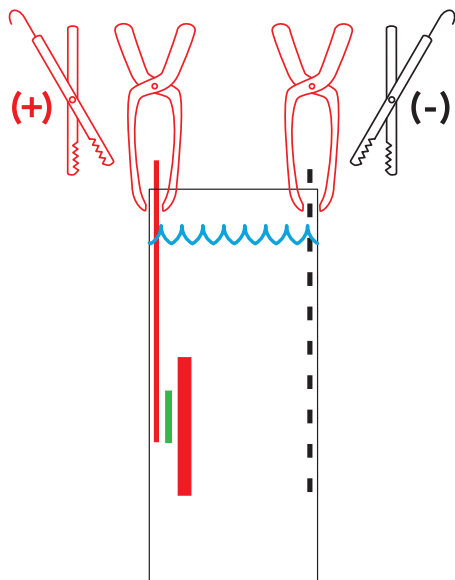
Instead of connecting the anode wire directly to the etching plate, use a small sacrificial plate (~.5" x .5") on the back of the anode to prevent etching into that surface. Then attach the hanging wire. Solution inevitably works its way next to the anode hanging wire at the point of contact.

Use heat shrink tubing or tape to seal and protect exposed areas of the anode hanging wire from etching.

Attach your positive line (red) to the anode via the hanging wire and do the same with the negative (black). Alligator clips make for a handy connection device. If you are using a rectifier, make sure the connections are secure and turn on the machine. Set the voltage to 3 volts.

When voltage is set to 4 or higher, you will start seeing small bubbles form at the anode and cathode. This is oxygen escaping as gas at the anode and the same for hydrogen gas on the opposite side as water molecules split. You want to keep these together.

At lower voltages, the etch will take longer, but the quality of the etch will be improved. Corners will stay sharper and surface of the etched areas will be more refined.



 **Plate to be Etched**

 **Cathode Plate/Grid**

(+) **Positive Lead**

(-) **Negative Lead**

 **Bus bar**

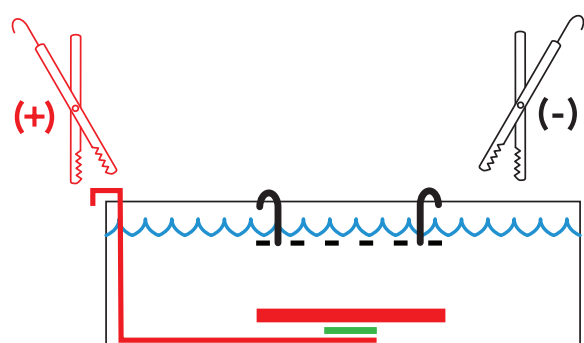
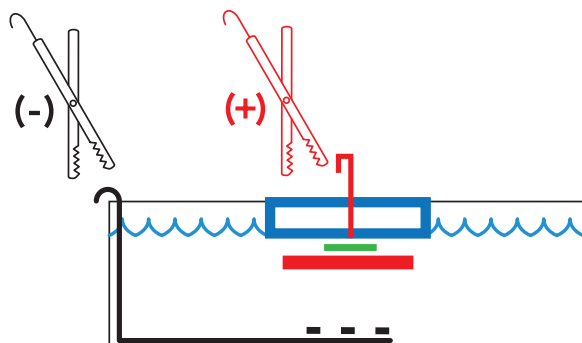
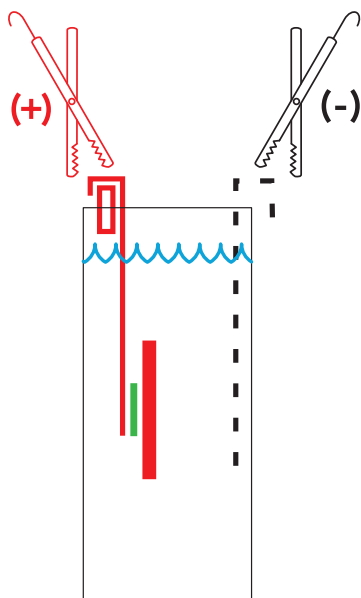
 **Sacrificial Plate**

 **Insulation Board**

 **Electrolyte Surface**

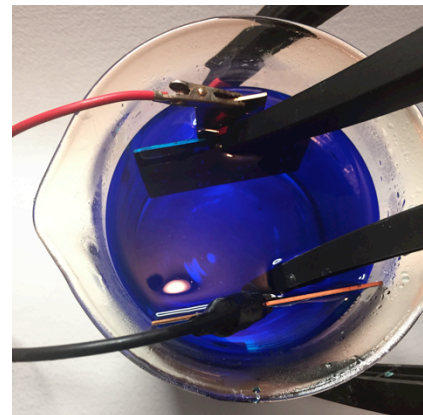
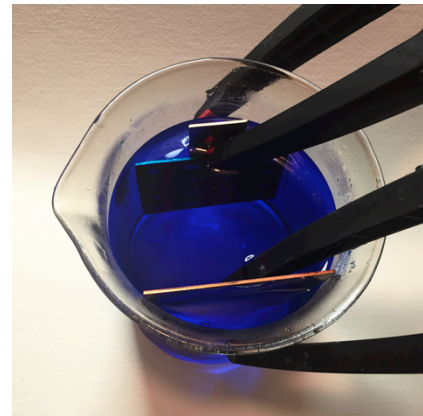
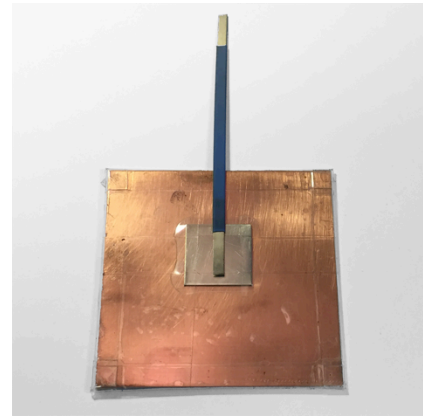
 **Cathode Hanging Wire(s)**

 **Anode Hanging Wire**



Process

- 1 - Clean your anode and cathode plate. Make sure the surfaces are free from oxides and fingerprints.
- 2 - Wearing gloves, apply your resist. The tests here are all done with vinyl cut stencils (see appendix for transfer method).
- 3 - After vinyl or resist is applied and has dried, tape off other exposed areas on the front.
- 4 - Flip the plate over and tape on the sacrificial anode.
- 5 - Connect the anode hanging wire
- 6 - Submerge the anode in your etching bath
- 7 - Clamp or hang the cathode across and parallel to the anode
- 8 - Connect your leads - positive (+) to the anode and negative to the (-) cathode
- 9 - Turn the rectifier on or plug in your power source at 3 volts - the amperage will rise and stabilize.
- 10 - Once you have etched to your desired depth, turn the power off and place the anode in a bath of steel wool and water - the rustier the better. Wait a few minutes.
- 11 - Neutralize in washing soda or baking soda
- 12 - Rinse, clean and finish



Results

At 3 volts in a 1000ml bath with a 25% solution of copper nitrate in distilled water:

Thinner lines to about 2mm will etch to ~.5 mm in 40 minutes. For the enamellists working with 18 gauge, this is perfect for champlévé. For imagery and contrast using patinas, the etch time can be greatly shortened. Remember that larger, open areas will etch more slowly.

Difference in Line Quality Between an E-Etched Line and an Acid Etched Line.

These two processes create inverse results. Where acid will most often etch the middle of exposed areas more deeply and then undercut the edges, e-etching oxidizes the edges of exposed areas more deeply while maintaining vertical or slightly beveled edges. It is important to be aware that because of this 'edge effect' the middle of open areas can remain noticeable higher than the edges. Using mesh as a cathode rather than a plate will help to counteract this. Undercutting does not occur in e-etching due to the nature of electron flow. They move out from the anode in a manner similar to magnetic fields where the middle flow runs perpendicular from the electrodes and increasingly curve as they move to the edges.

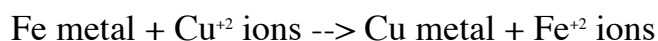
Disposing of a Copper Nitrate Bath

Although unnecessary until it is determined that your etching bath will be of no more use, proper disposal when the time comes is extremely important. Copper nitrate is toxic to plants and more so to invertebrates and marine life in many forms, especially in the concentrated solution used for an etching bath. This is due to how copper ions react in the aquatic system. Never pour your etching bath down and drain or dump outside! The most reliable way is contact your local hazardous waste disposal center. Again, keep using your bath and store it, sealed, until next time if you know you will be etching.



Rusty water with steel wool

Of more immediate concern is how to rinse your work after it is pulled from the bath. This is to be sure that you are not sending the copper nitrate solution down the sink. Converting the copper ions to solid copper is a simple process and is the first step in the safe, responsible disposal. Think about how iron or steel will immediately be plated with copper when added to an old pickle solution. The same chemical reaction will be used here to convert the free copper ions to solid copper. If there are any deposits of copper sulfate on the surface of your metal, you will observe the blue crystals change to a copper/rust color. You will end up with is extremely dilute iron nitrate and rusty water.



From there, dip the piece in baking soda or washing soda to neutralize any remaining acidic content. Rinse and clean.

Etching Silver

Sterling and fine silver etch in a similar fashion to copper. Using the same set ups and parameters, these metals tend to end up with a finer microcrystalline surface.

The etching shown here was created with a vertical clamp set-up @ 3v for 30 minutes with a solid sterling cathode. The anode and cathode were 3" apart. The deepest etch at the edges is .48mm while the shallower sections are .42mm

As you can see in the beaker to the right, silver solids are suspended in the liquid and gather on the bottom. After sitting overnight, the blue is back to the normal color of copper nitrate. There is another substance that remains mysterious for the time being. This bath has been used many times over and remains consistent from etch to etch.

There are also reports on the web that the silver can be reclaimed. If you pour the bath through a coffee filter, let it dry and burn the sediment and filter on a charcoal block, the silver collects into a small balls or an ingot. I haven't tried this yet and would like to know exactly what I'm incinerating before going through the process.

Speculative Chemistry

Even with the same set-up, I keep the my silver etching bath separate from the copper. This is because I suspect that the chemistry slowly changes from cuprous sulfate, where the copper has a +2 charge to cupric sulfate with a +1 charge. When the silver is oxidized and released from the anode with a +1 charge, it is more electron-hungry than the copper and will steal an electron to become a solid. You will see a grey sediment develop in the bath. This leaves the copper with a single charge that rebonds with the nitrate (NO_3), while any extra copper plates on the cathode. Cupric nitrate will continue to function as an electrolyte as the bath slowly diminishes. I think it will take a long time for the bath to be ineffective.



Appendix

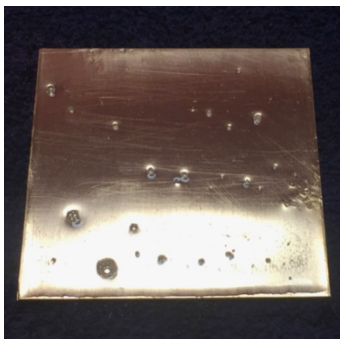
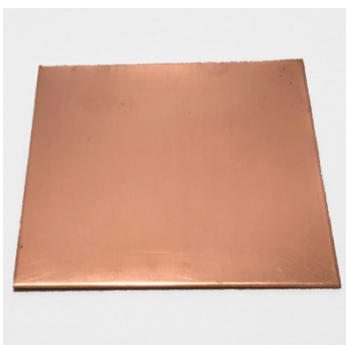
Vinyl Transfer

Although numerous acrylic and water-resistant materials are suitable to act as a resist in etching, my preference is to vinyl cut files that have been prepared in Illustrator or Rhino to maintain a consistent line quality.

Once the file is prepared and cut, the following step will help to transfer your image onto metal:

*remember - do not reverse your image - the vinyl should be the same as your final etch

- 1 - Clean your metal to be free of oils and fingerprints
- 2 - Using a scalpel or X-acto, weed your vinyl. Remove all the areas from the cut-out that you want to etch.
- 3 - Apply transfer tape to the top side of the vinyl. Trim off excess to be flush with the edge.
- 4 - Peel off the paper backside of the vinyl. The image will appear reversed.
- 5 - Spray transfer fluid onto the clean metal surface. This will allow you position the vinyl exactly where you want.
- 6 - Moving from the center outward, use a squeegee to remove excess liquid from under the transfer tape. Let the vinyl sit for 5 minutes.
- 7 - Working at a very low angle, peel off the transfer tape.
- 8 - Prepare the back of the plate, etch and finish



Voltage, Amperage, Resistance

Especially when preparing to etch and for troubleshooting, understanding Ohm's law will help tremendously. Ohm's law shows how voltage (V), current (I) and resistance (Ω) are always in proportion to one another

Voltage represents the electric potential between two points, or how motivated the electrons are to travel from point A to point B. These are measured in volts.

Current is the flow of electrons through any given point in a circuit per second. Current is measured in amps.

Resistance measures the forces that oppose the current from flowing. Resistance is measured in ohms.

Ohm's Law -

$$V = I \Omega$$

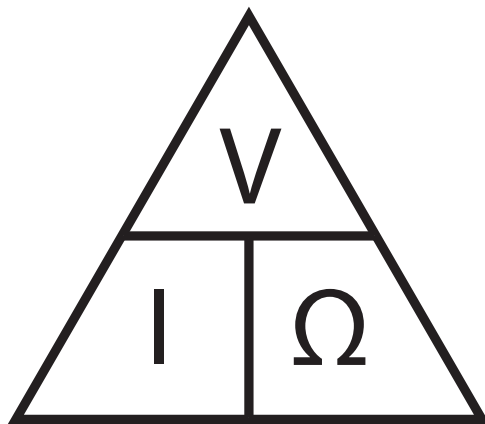
Voltage = Current • Resistance

$$I = \frac{V}{\Omega}$$

Current = Voltage / Resistance

$$\Omega = \frac{V}{I}$$

Resistance = Voltage / Current



Use the triangle as a memory tool. When solving for (I), you can see to divide volts (V) by resistance (Ω). Similarly, with I next to Ω , you know to multiply them to solve for V.

How does this apply to e-etching?

When the voltage is fixed and the amperage and resistance are variable, Ohm's Law can be used to make adjustments. If you are having difficulties pulling reasonable amperage, shortening the distance between the anode and cathode will lower the resistance because there is less distance for the current to travel. Conversely, if you are trying to etch a large plate, the resistance will be very low and your power source might not be able to handle the current. Increasing the distance between your anode and cathode will proportionately increase the resistance and lower the amperage.

With this data, you will be able to set up your bath to meet your specific needs. Using Ohm's Law, you will create consistent etches.

Resources:

Thank you to these sites and the individuals involved in their creation. Without their willingness to share their research, extending electrolytic etching into the arena of metalsmithing would be a tremendous challenge.

For more information on the history, chemistry, other uses for an electrolytic bath (plating) and safety please refer to:

<http://www.nontoxicprint.com> - A comprehensive site covering information on a number of printmaking techniques. In addition, chemical data information on the chemicals used in most forms of printmaking can be found. The following two artists are referenced within the site:

<http://www.greenart.info/galvetch/contfram.htm> - Cedric Green has written a great deal on the electrolytic process. He has made a PDF entitled *Green Prints*, which outlines the scope of electrolytic etching. Safety information and links to similar-minded sites are posted.

<http://www.crujera.com> - Alfonso Crujera's *Electro-Etching Handbook, a safe, non-toxic approach* is a concise and excellent guidebook to e-etching. The English edition is available at: http://www.amazon.com/Electro-etching-handbook-Alfonso-Crujera/dp/8493510092/ref=sr_1_1?ie=UTF8&qid=1389189386&sr=8-1&keywords=9788493510091

Relief Electro-Etching for Champlévé Enameling - R.L. Jackson reviews e-etching with copper sulfate and introduces the idea of etching with copper nitrate. Meticulous data charts are given to help with estimating etch times for a given surface area and depth.

<http://www.guildofenamellers.org/index.php/component/phocadownload/category/1-technical-documents?download=4:relief-electro-etching>