Etching Aluminum, Zinc, and Steel from Friedhard Kiekeben (http://www.nontoxicprint.com/etchzincsteelaluminum.htm)

Note of caution: all safer etching methods involve more or less hazardous chemicals and by-products, they are not ‘nontoxic’. Safe handling, informed training, and various protective measures are essential requirements in metal etching.

Both aluminum and mild steel are ubiquitous and cheap metals used in construction and industry, and both offer an interesting expressive repertoire when etched. The Saline Sulfate Etch works very well for straight tray etching of any of the silvery metals, and additional measures such as heating or aeration are not required. Zinc plates, especially, etch with great speed and ease. Often a deep etch is completed within a matter of minutes. A copper sulfate based etching solution was first suggested by two printmaking experts, NIK SEMENOFF (Salt Etch, Leonardo, 1998) and CEDRIC GREEN (The Bordeaux Etch), in response to health and environmental concerns.

The invaluable groundwork and feedback of Green and Semenoff helped me eliminate early issues with the Edinburgh Etch, and paved the way towards the formulation of a comprehensive metal salt etching system which can now serve as a complete replacement for the acid etching approach. In developing the Saline Sulfate Etch I was aiming to present the most effective and practical solution for artists and educators who want to etch zinc and the other silver-grey metals easily and safely. I believe that the new Saline Sulfate etching method provides an ideal substitute for the much more toxic nitric acid etch for these metals. Feedback from scientists and artists alike confirms this and the resulting prints speak for themselves.

A saturated copper sulfate solution makes a good mordant for zinc, but due to lack of a catalyst, etching is somewhat slow and the solution becomes exhausted quickly. Similar to my thinking behind the Edinburgh Etch, I looked into ways in which the electrolytic eroding potential of copper sulfate could be harnessed more fully. I reasoned that, as with ferric, the chemical ‘hydrolysis bond’ formed between the metal salt and water might account for a loss of reactivity. Tests showed that a solution made up from equal parts of copper sulfate and sodium chloride (i.e. cooking salt) activates the etch by diminishing the bond with water. The Saline Sulfate Etch for etching zinc is about three times more active than a straight copper sulfate solution without salt; it also produces a very crisp etch. During biting a coppery sediment of metal hydroxides and oxides floats to the surface, thus keeping the bitten work from clogging up. Etching can also be aided by occasionally brushing the plate surface with a soft brush; delicate marks, such as a spray aquatint or soft ground should, however, be etched without brushing. The solution works more effectively if floating solids are regularly skimmed off with a brush or strainer and removed from the bath, this keeps the solution from turning alkaline and extends its usable life.

The solution is made up from equal amounts of copper sulfate and cooking salt which readily dissolve in warm water. It is recommended to use anhydrous copper sulfate which is supplied at a reasonable price in larger quantities by chemical wholesalers. Do not use agricultural supplies as these may contain additives. As with most etching chemicals, specifically ask for technical grade or industrial grade copper sulfate. Laboratory grade chemicals are much more expensive and are less suitable for etching.

**MATERIALS**

Products and equipment needed to make up the Saline Sulfate Etch:

- anhydrous copper sulfate
- cooking salt
- supply of hot water
- heavy-duty gloves
- safety goggles
- dust mask
- wooden stick or stiff plastic brush for mixing
- bucket
- etching tray

**METHOD**
**make up the Saline Sulfate Etch as follows:**

1. Put on gloves, dust mask, and safety goggles when handling the crystals to avoid touching or inhaling dust particles.
2. Carefully place equal amounts of copper sulfate (e.g. 100g*) and cooking salt (e.g. 100g*) into a bucket or straight into a small etching tray. It is useful but not essential to premix the dry powders before diluting with water.
3. Add 500ml* of hot water and stir all the ingredients together with a wooden stick or a stiff brush. The solution turns into a green sludge.
4. Add another 500ml to 1liter* of warm water whilst stirring continuously. Most of the crystals should dissolve within 5 to 10 minutes of mixing, producing a dark green liquid.

**SAMPLE QUANTITIES**

<table>
<thead>
<tr>
<th>small project</th>
<th>large project</th>
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<tbody>
<tr>
<td>100g copper sulfate +</td>
<td>1kg copper sulfate +</td>
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<tr>
<td>100g sodium chloride added to</td>
<td>1kg sodium chloride added to</td>
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<tr>
<td>500ml hot water</td>
<td>5 liters hot water added to</td>
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<td>500ml to 1 liter warm water</td>
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*The above ratios/quantities should suffice for a small etching project, using a small tray. For bigger projects simply increase the quantities accordingly.

In a busy studio it is advisable to make up a substantial quantity of Saline Sulfate Etch in a large tray or tank. This may contain even several gallons of solution. The increase in electric charge makes a large volume of metal salt solution longer-lived than a small one. The kind of high-sided plastic trays with lids sold for under bed storage make ideal metal salt etching trays. Acid unit manufacturers and other plastics prefabrication companies can manufacture professional trays from welded polypropylene to specification. A deep tray is best fitted with a slatted plastic or wooden grid to elevate plates above the crystalline deposit that builds up in the bath, and to help when removing plates from the bath.

The Saline Sulfate Etch can be used as a universal etching solution for all three metals: zinc, mild steel, and aluminum.

**TIP: Using and Purchasing Copper Sulfate**

**Safe to Use: Use it Safely!**

Remember, Copper Sulfate is still a chemical and toxic to humans if ingested, so make sure you follow safety instructions and read MSDS sheets prior to use. Always wear gloves, goggles and a mask when handling any etching chemicals. Do not touch, inhale or ingest.

**Safe to Ship**

For the metalsmith who wants to use the Saline Sulfate Etch, getting hold of small (rather than industrial) quantities of Copper Sulfate is easy. I recently ordered a 5lb bag of Copper Sulfate Crystals over the internet. Because it is a low hazard material, the delivery came by ordinary mail services - simple, safe and economical too. No need for the specialist carriers required when shipping traditional printmaking mordants. You can also use locally available “Root Kill” from Home Depot.

For Copper Sulfate Supplies: Wammock Farm Services Inc.  www.wammocks.com
Etching Aluminum
Unusually, neither of the basic components of the Saline Sulfate Etch, i.e. copper sulfate and salt, have any corrosive effect on the metal by themselves. Etching becomes possible when both substances act on the metal in combination. While all other metals easily erode as long as they are grease free, the surface of aluminum plates is best treated with fine wire wool to make the surface more susceptible to the etching process. This should be done before any resists are applied to the plate.

As with zinc, the Saline Sulfate Etch for aluminum produces of a loose coppery sediment which floats to the surface and needs to be removed regularly. Unlike with zinc, a continuous rising of small hydrogen bubbles (not considered a hazard) also indicates that etching is in progress.

Etching Steel
Steel plates need to be purchased as cold rolled mild steel; tempered or hot rolled varieties of steel plate are not suitable for etching. Plates usually have a coating of grease which needs to be removed before any creative work with resists can commence.

When etching steel, use the same recipe for the Saline Sulfate Etch as given above.

Once a plate has been etched to the required depth and rinsed it is crucial to blot off any remaining dampness with paper towels and then speed dry plates otherwise the steel surface will quickly rust.

The Magic of Electro-Chemical Etching
Metal Salt etching is a new methodology which is fundamentally different from the aggressive chemistry of traditional acid etching with its hazardous gas emissions and by-products. The new method is akin to creating a liquid battery. The etching battery consists of two types of metal that act as the charged poles of the battery - anode and cathode - and an electrolyte medium (here the salt solution) that transmits electric charge and allows metal ions to migrate. The process lacks none of the mystique of acid etching. The alchemical magic of seeing a solid metal vanish in a liquid is in many ways an even more tactile and engaging activity and produces startlingly good results.

The dissolved copper ions (from copper sulfate) create a powerful electric potential which literally pulls away the surface atoms of the silver-grey metal plates it comes into contact with. The more copper ions there are contained in the solution the greater the etching potential of the bath; therefore this process works best when used in a larger tray or tank which has a greater electric charge and can etch more metal for longer. The etching process produces various solid by-products; the metal oxides and hydroxides of the etched plate on the one hand, and a fine deposit of pure atomic copper on the other.

While a Saline Sulfate bath is active and usable it retains a green colour, although after a while the original translucent green is replaced by what looks like a much more unattractive soup of green sludge. But worry not: the sludgy looking bath etches just as well as a translucent one. Stir up and mix this sludge with a stick or a brush before each etching session. This re-dissolves the copper compounds that are crucial to building up electric charge for further etching.

Once the etching capacity of the bath does slow down, there are two options: Refreshing the solution or Recycling, Neutralization and Disposal.

Refreshing a Saline Sulfate Solution
In previous publications I advocated recycling the Saline Sulfate solution once spent, but recently I have found a way to significantly extend its usable life. Simply make up a further batch of a copper sulfate or sodium chloride mixture in a bucket and add just enough hot water to dissolve. Add this refreshing mixture to the etching tank; stir, and the bath will be reactivated. This procedure can be repeated three or four times, and the usable life of the bath can thus be extended from several weeks to up to half a year. As time goes on more solids will build up in this long-lasting bath and can eventually affect the cleanness of the etch. Etching plates on a slatted grid that elevates them above the salt deposits can remedy this unwanted effect.

I have also observed an effect, first described by Nik Semenoff, when a seemingly spent copper sulfate based etching solution self-regenerates; this is indicated by the return of the green coloring to a solution that has been left unattended for several weeks (regular stirring and the addition of hot water aids this process). The solution has regained dissolved copper ions and an electric charge, and can be used for etching once again.
Recycling, Neutralization and Disposal  The process comes full circle. The very action that makes the Saline Sulfate Etch work so wonderfully as an etching bath - the depletion of copper ions - also facilitates its recycling. Concentrated copper ions are regarded as an aquatic pollutant and must not be allowed to get into waste water. As more and more copper ions react with the metal plate during etching these are converted into their inert cousins: solid copper atoms. If a sufficient quantity of metal is etched, eventually all copper ions are removed. A fully depleted bath is recognizable by two features: (i) the solution no longer corrodes metal and (ii) the solution is no longer green, it is clear.

Spent solution easily separates into a clear liquid and solid particles.

METHOD

Prepare a spent etching bath for recycling as follows:

1. Add hot water to the bath to re-dissolve any solid sulfate particles and stir.
2. Add a pile of metal off-cuts - zinc, steel or aluminum - to the tray
3. Leave to act overnight.
4. On the following day, drain off the liquid into a bucket and add sodium carbonate (about two or three cups per bucket).
5. Once fizzing stops the liquid can be discarded.
6. The remaining solids can now be left to dry out. Keep in labeled, sealed containers and then treat as dry waste.

Environmental Safety

Although copper sulfate is a comparatively safe chemical for etching, it is considered a marine pollutant, and if present in rivers or lakes it can kill fish. It is crucial that solutions containing this salt are never poured down a drain without following the above instructions. Only a spent solution that is lacking the green coloration (which indicates the presence of copper ions) and that has been neutralized with sodium carbonate is safe to be discarded.

The Small Business section of your local Environmental Protection Agency offers free advice on the safe disposal of exhausted metal salts and liquid ferric-based etching solutions. Solid zinc, aluminum, steel and copper residues may be safe for local disposal once any copper sulfate content has been fully removed. Professional printmaking studios should utilize a commercial chemical disposal firm to pick up spent etching by-products. Visit your local EPA page for details of local firms. Visit www.epa.gov.

As a long time hazardous waste management professional, artists in the United States will have much better luck working with local governmental agencies than federal agencies like the EPA. A good way to find assistance with managing hazardous waste (like etchants) is by visiting www.earth911.com, typing the word "hazardous" in the search box, then entering one's zip code. If there's a local agency, it will probably be listed.

Next best? In a search engine, type the name of your city or state and the words hazardous waste and see which agencies (.gov) pops up.

Dave Waddell
dave.waddell@kingcounty.gov www.hazwastehelp.org/artchemicalhazards

Valuable Etching Residues

The left over copper residues from the etching process are a valuable resource. You may well be able to find a local recycling firm that actually pays for your etching residues - a substantial part of these is solid copper. Or, with the addition of sodium bisulfate to the etching residue you may actually be able to reclaim the solution a number of times. Nik Semenoff outlined this idea in the publication Leonardo in 1998:

extract from

Using a Safer Mordant Intaglio Etching on Aluminum and Zinc - Recycling the Spent Bath
“In the last couple of years, we have started to recycle the spent bath rather than throwing it away. It is placed in plastic
collectors and left to stand for a month or more. The other chemicals in the bath start to react on the copper sludge at the
bottom and soon the blue color returns. In the place of the dark metallic copper on the bottom, a whitish powder appears. If one
wanted faster exchange of the copper, I would suggest periodic stirring of the solution until the reaction is completed. The clear
blue solution is drawn off and put back into service. It is less corrosive in some ways and preferred by many students. Salt and
acid content seem to be sufficient and only copper sulfate is added as needed to keep the bath alive. This procedure has greatly
reduced the amount of copper sulfate we require in the etching studio. It has been found that the whitish sludge contains copper
compounds that can be reclaimed by adding sulfuric acid solution or a fair amount of the sodium bisulfate material. If your
solution is not recycling, try adding more sodium bisulfate to act on the copper particles.”

A Guide to the Safe Use of the Metal Salt Etching System

Prior to use, read the safety instructions given on all etching chemicals and in their MSDS sheets. Follow instructions carefully.

Do not touch, inhale or ingest etching chemicals. Always wear strong gloves, eye protection, a dust mask and long apron as
advised.

The Metal Salt Etching system is safe to use if the warm and the cold colored metals are etched in their respective warm and
cold colored solutions.

Use the rust/orange colored Edinburgh Etch (ferric based) for etching the reddish metals: copper or brass. See ETCH COPPER AND BRASS.

Use the blue/green colored Saline Sulfate Etch (copper sulfate based) for etching the silvery metals: mild steel, zinc, and
aluminum.

DO NOT use the Edinburgh Etch or a ferric bath to etch zinc or aluminum, as this may cause a hazardous chemical reaction.

It is recommended that print studios using metal salt etching systems display a notice such as the one below.

Also read and follow etching precautions given in The New Etching Chemistry page

NOTE: Although considerably safer, the new systems still utilize harmful corrosive chemicals and their reactive properties, and it
is very important to follow all safety instructions in their use. Medical science suggests that as an extra precaution women should
not engage in extensive etching practice of any kind (acid or salt based) during pregnancy to safeguard against the possibility of
reproductive damage.

Metal Salt Etching Safety Precautions. Strong long sleeved gloves, goggles, and protective clothing (e.g. plastic lab apron)
should be worn when handling metal salts and metal salt solutions. Use a dust mask when handling copper sulfate or etching
residues. In professional shops ideally there should be an emergency shower and eyewash fountain in the etching space, in an
artists personal studio make sure you have clean running water or an eye wash bottle nearby to use in case of splashes. Any
splashes in the eyes must be rinsed immediately with plenty of water. Immediately wash off any splashes on skin. Provide
supplies of sodium carbonate for neutralizing any accidental spills and run-offs in the etching space. Frequently clean the etching
spaces with warm water and mild detergent to prevent build up of salt residues. Keep all solutions and etching residues in closed
containers, and keep etching supplies in locked non-metal containers and cabinets.