Electrolytic Etching.

A safer method of etching for the small jewellery workshop.

By Dauvit Alexander

Abstract

This paper outlines the process of *electrolytic* etching, a method of etching which uses an electric current - NOT acids or caustic chemicals - to etch metal. It can be used on precious and non-precious metals.

The electrolytic process produces no noxious fumes; the electrolyte (the solution in which the process occurs) uses chemicals broadly classified as "safe" and the solutions are reuseable, thus the process is more environmentally friendly and less hazardous than other methods of etching. Copper, steel, brass, silver, and carat gold can all be etched by this method.

At the end of the paper, a guide is given to a novel method of creating resists using a laser-printer.

NOTE

While every effort has been made to ensure the accuracy of information detailed in the following article, use of this information shall be soley at the user's own risk. The author assumes no responsibility or liability for the accuracy, fitness, proper design, safety or safe use of any information, technique, tool, design, material etc. contained in this article. The reader waives any and all liability, damages, causes of action, claims, etc. against the author resulting from any personal injury, wrongful death, or property damage resulting from the use or application of any design, technique, process or other information contained in the article.

This process should not be attempted by anyone who is not completely familiar with the risks of using electricity or by anyone who is unfamiliar with the handling chemical solution.

Throughout this article, it is assumed that the reader has a familiarity with the basics of "traditional" acid or chemical etching.
A glossary is provided in *Appendix 1*.

Introduction

Electrolytic etching is a surprisingly old process, dating from the middle of the 19th Century (1840), when a patent was filed for "Engraving Metals by Voltaic Electricity"[1]. The process described in this patent is largely the same as the process detailed below.

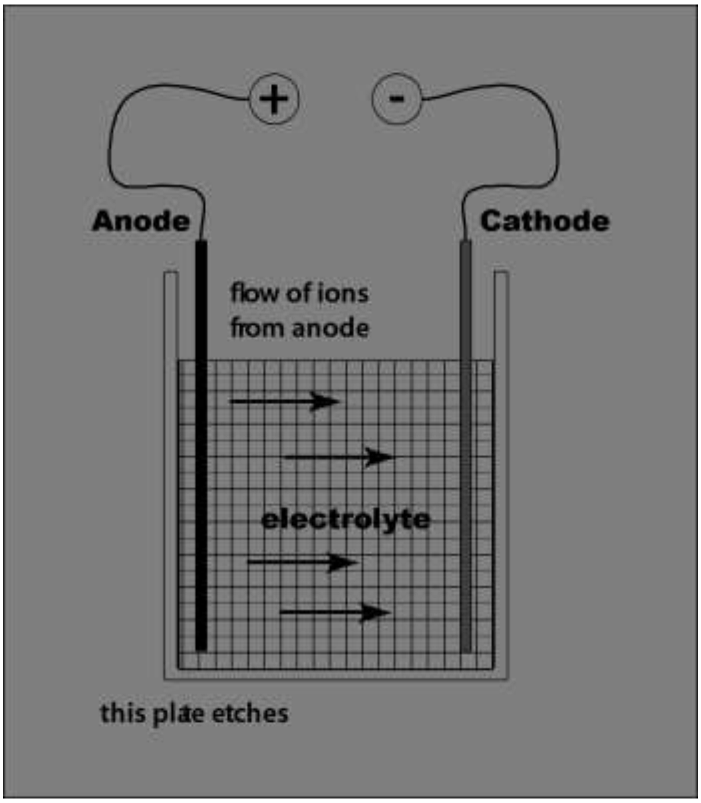
Quite why this process is not better known to jewellers and metalsmiths is unclear - the process is still widely used by metallurgists - as it offers many advantages over the more “traditional” forms of etching with acids:

- The chemicals used are safe, provided basic handling and storage procedures are followed.
- The voltages used are safe (0.8 – 8v and 0.5 – 5amps)
- The process requires no special equipment or apparatus.
- The solutions are not weakened by use and may be used time and time again, posing little or no disposal problems when they are no longer needed.
- The only “fumes” generated are oxygen and hydrogen, which are non-toxic but flammable. However, these gases are produced in such small quantities as to present no hazard.
- No deposit is formed on the plate being etched.
- Any deposit formed in the electrolyte is deposited metal and may be removed by simple filtration.
- The process is reliably repeatable. The length of time taken to cut a plate to a given depth is always the same for plates of the same size in the same solution at the same voltage.
- The etch occurs in a “line of sight” manner, making masking of the back and edges of the plate less critical.
- Due to the “line of sight” etching, undercutting is minimised.
- The cost of this process is far lower than that of acid etching.
- As caustic solutions are not used, the range of useable resists is much increased.
- In addition to jewellery metals, steel can be neatly and safely etched for roll-printing and other tool purposes.

At the moment, this process is largely undeveloped and unexplored by jewellers and metalsmiths. It is hoped that this article will encourage experimentation with the process.

Electrochemistry

In order to understand electrolytic etching, a basic understanding of the chemistry of the process is required. Consider first, **Diagram 1**:



If two metal plates are placed parallel but not touching each other in a conducting solution and they are connected to the terminals of a **direct** current, then the current flows from one plate to the other through the solution by means of positive and negatively charged ions. In simple terms, the positive ions flow to the cathode (-ve, negative) and the negative ions to the anode (+ve, positive).
The only part of the process of concern to the jeweller is the reaction at the cathode, where the metal "dissolves" into the electrolyte, removing metal from the surface. This metal can be seen in deposits at the anode: in effect, the process is the absolute inverse of plating, with which many jewellers are familiar. While it is not strictly accurate, it is useful to think of particles of the cathode "jumping off" under the influence of electrical energy and passing through the solution to the anode *in a straight line*[2].

If resist is used to mask off part of the plate, the only the sections of metal to etch will be those in contact with the electrolyte and in direct "line of sight" approach to the anode.

In most cases, the electrolyte used will be a solution based on the metal being etched eg: Copper sulphate ($CuSO_4$) solution for a copper plate, Iron sulphate ($FeSO_4$) for an iron (steel) plate. This, however, is not a hard-and-fast rule as it is often not economically practical to use gold solutions for the etching of gold and substitutes can be used instead, giving equally good results at a fraction of the cost.

Etching

1) Equipment.

The equipment required is likely to be found in most homes or workshops:

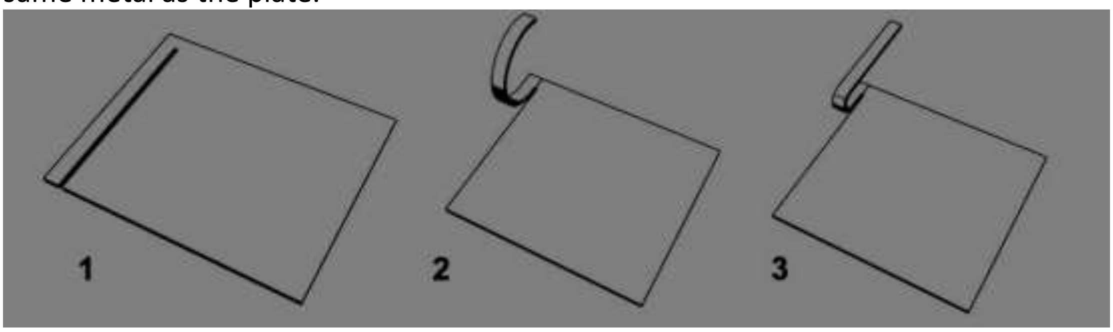
- Etching tank – this must be large enough to hold the plate being etched, but not so large that it takes excessive amounts of electrolyte to fill it. Plastic containers are ideal as they do not conduct electricity. Milk cartons, plastic cups and plastic food-saver type containers may be used. For flat plates, square and rectangular containers are most useful.
- Power supply – there are many options available which produce the required Direct Current of not more than about 10v, 5A. A 9v battery can be pressed into service, but it is better to have a constant mains-operated power supply which plugs into the domestic power main. Examples of these include Bench power supplies, lab-packs, car battery chargers and old computer power supplies, all of which can be used with care.

(NB: NEVER connect mains electricity to any liquid directly.)

- Clips – crocodile clips, bulldog clips.
- Wires – plastic-coated electrical wire.
- Mixing containers – plastic containers and spoons for mixing electrolytes.
- Cathode – depends on the material being etched. See **Table 1**
- Supports – to hold the metal in place in the tank. Non-conducting or conducting as appropriate. A conducting "bus-bar" (the illustration of the tank below shows a "bus-bar" in use: it is effectively an extension of the anode wire) can be used to allow multiple plates to be etched simultaneously.

2) Prepare the plate.

Consideration must be given to the manner in which the plate is to be connected to the power supply. A tag of metal may be cut and folded up, or a wire soldered on. A small amount of metal will always require to be left unetched for the purpose of attaching the metal to the power supply. This cannot be avoided, but the size of the tag can be minimised. If a wire is soldered on to attach the plate, it should be of the same metal as the plate.



The plate must be clean and free from oxides or grease. Preparation is the same as for traditional etching or as for enamelling, and pumice, fine emery or nylon scourers are all suitable for cleaning and keying – or finely roughening - the surface. This keying allows the metal to accept the resist applied to it and reduces the chance of it flaking or peeling off during etching. The plate should be abraded under running water until the water does not "pool" on the surface: soap can be used provided all residues are removed. A final wipe with alcohol (methylated spirits) may be given. After scouring and cleaning, the plate should be handled only by the edges to prevent contamination with skin oils.

3) Resists
There are many useful resists. It has been found that the following are excellent for the electrolytic process:

- Parcel tape – strong and waterproof and can be cut to shape.
- Self-adhesive vinyl films (sign vinyl) – as above.
- Dry transfer lettering.
- Beeswax – applied to heated metal in a thickish, even layer and allowed to cool. Patterns can be scribed into it.
- Hard and Soft grounds – traditional etching resist, applied hot.
- Panama hat varnish.
- Shellac.
- Nail polish.
- Press 'n' Peel Blue[3].
- "Incorrect" photocopies *(Appendix 2)*.

Some other resists, such as resist pens and permanent markers are removed very easily by the process.

Although it is not strictly necessary, it is advisable to mask off the back and edges of the plate. Parcel tape is well-suited to this purpose.

4) Electrolyte and Anode
The electrolyte can be varied to suit the metal being etched. For example, silver may be etched in a silver nitrate solution, iron in ferric sulphate and copper in copper sulphate. This gives an exceptionally clean etch but very good results on copper, brass, iron, steel and aluminium can be obtained from the use of a saturated solution of table salt (NaCl).

It is important to note that table salt will not reliably etch silver or gold but a good result can be obtained by using sodium nitrate solution ($NaNO_3$).

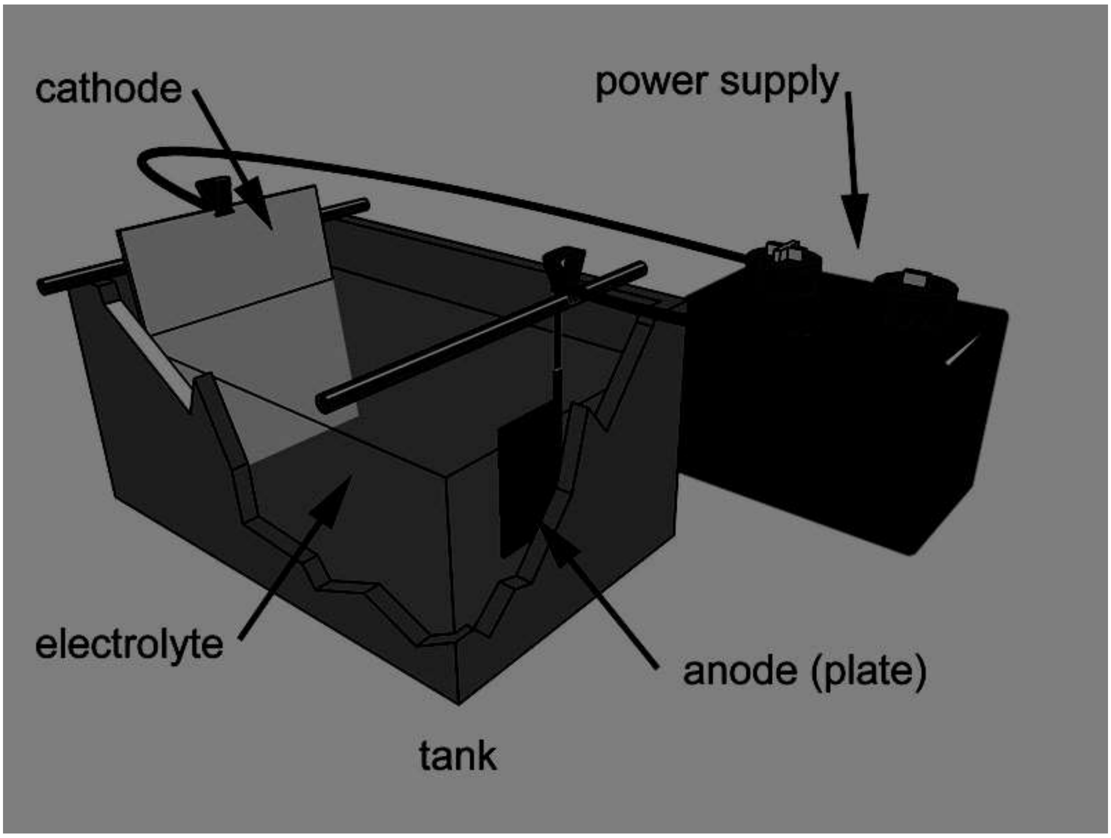
The anode can be either the same as the metal being etched or stainless steel. This holds for all metals being etched, excepting aluminium, which can only be etched using a stainless steel anode.

Metal to etch	**Electrolyte**	**Cathode**
Silver	Silver nitrate; sodium nitrate	Silver; stainless steel
Gold	Sodium nitrate	Gold; stainless steel
Copper	Table salt; copper sulphate	Copper; stainless steel
Brass	Table salt; copper sulphate	Copper; stainless steel
Aluminium	Table salt	Stainless steel

Table 1

5) Set up bath

The bath should now be set up. **NB:** <u>There is an error in the following diagram and should be used for guidance only</u>! The ANODE or the plate being etched is the POSITIVE terminal (+) and not as shown.



Ensure that the only parts of the setup in contact with the electrolyte solution are the anode and the cathode plate. Allowing clips or wires to contact the solution will contaminate the electrolyte, damage the clip/wire and lessen the effectiveness of the etch. It should also be ensured that the plates cannot touch or move together during the etch. Some sort of support may be used, but it must be remembered that the plates require a direct “line of sight” to etch properly, so introducing barriers into the tank is not an option.

6) Etch

The current is turned on at the required level. If everything is connected and operating, the plate should darken. There may be some bubbling at the cathode. If this bubbling is too vigorous, reduce the current. Remember that any bubbles formed will be of hydrogen – which is highly flammable. It is advisable to keep the tank well-ventilated to prevent the accumulation of the gas.

While a very clean etch will result from the most basic setup, the best and sharpest etch is achieved by agitating the tank during the etching process. HOWEVER, if any sort of fluid current occurs, this will create marks on the finished plate similar to drag marks familiar from over-polishing, thus electromagnetic stirrers are not really suitable, unless they pulse backwards and forwards.

In the electronics industry, bubbles of air are passed through the tank, which achieves mixing without any directional influence. This can be achieved with a simple aquarium aerator and only needs to be placed near or behind the plate to mix effectively. It is probably best if the aerator is not placed directly under the plate, as the rising bubbles could create directional marks. It should be checked that the aerator is made of a material which will withstand the chemicals in the electrolyte.

Gentle vibration of the tank can also be considered, though may be harder to achieve. Lab supply companies offer a range of mechanisms which can be used for this. One suggestion found online was to attach an aquarium pump to the *outside* of the tank and turn it on, the vibration of the running pump being enough to move the solution.

Tapping the sides of the etching tank manually every five to ten minutes has proved to be effective in moving residues and bubbles away from the etching surface.

It is essential to keep checking on the etching process and to remove the plate as soon as it has etched to the required depth. It does absolutely no harm at all to remove the plate and wash it, and the depth can be tested by feel – touching the edge of an etched section with a stainless steel needle is the classic artist's method – or by using a vernier or simply by looking at the edge under a lens. Cold running water should remove enough residue to allow this checking. If the plate is not etched deeply enough, simply re-connect the plate and continue.

It IS possible to etch right through a plate! Some experimentation has been done with etch-piercing, using resist on both sides of the metal and two cathodes, but the "pierced" edge tends to be ragged.

7) Clean metal
After the metal has reached the required depth of etch, remove it from the bath and wash it thoroughly. Gentle scrubbing with a nylon scourer under running water will remove any metal/chemical residues. The chemicals used are largely inert and do not require neutralising. The plate can be rubbed with bicarbonate of soda to neutralise the slight acid of the solution, but this has not been found to be necessary.

It then only remains to remove the resist by whatever method is suitable for the particular resist used.

The metal can now be used exactly as metal etched by traditional methods.

8) Recycle cathodes and electrolyte
The cathode is likely to be covered in a layer of powdered metal from the etched anode. It might even have a layer of oxide on it. This depends on the metal being etched and, to an extent, on the electrolyte used. In most cases, the metal or oxide will rub off very easily. Metal can be recycled and melted down or sent for processing. The oxides of iron and copper present no hazard and can be wiped off

and thrown away.

Electrolyte is best filtered and stored for the next etch. The only contaminants in the electrolyte should be metal powder or an oxide of the metal being etched. See notes above for dealing with the filtrate from the electrolyte.

In Conclusion

It is to be hoped that this article has fired the imagination of jewellers and metalsmiths. There is much experimentation to be done and there are many tantalising comments on the Web about other areas which might be explored, such as the etching of titanium or aluminium by this process.

Other areas which might be of interest to experimenters include:

- Etching mokume-gane;
- Using multiple resists to etch different levels;
- Etching for inlay or enamel (perhaps even etching around enamel);
- Etching metals not discussed above (pewter, titanium, aluminium, etc.);
- Etching shaped and formed surfaces using shaped cathodes.

Appendices

Appendix 1

Glossary

- Anode – the positive terminal in an electrolytic reaction (the "+" on the battery, sometimes written +ve).
- Bath – The container and liquid in which the etch occurs.
- Bite – The depth to which the metal is etched (eg: "Deep bite" or "Shallow bite"). This can also relate to the quality of the etch, such as "Foul bite" = a ragged etch.
- Cathode – the negative terminal in an electrolytic reaction (the "-" on the battery, sometimes written -ve).
- Electrolyte – the solution in which the etching takes place.
- Etch – The removal of metal by etching.
- "Line of Sight" – in terms of etching, imagine looking out from the plate. If you can see the anode, it is in your "line of sight". If you are round a corner or on a curve, you might not be able to see the anode, so etching will not occur.
- Mordant – the name for the "traditional" (acid or caustic) etching fluid.
- Plate – the metal being etched.
- Resist – the material used to block off the metal plate and prevent etching. Selective removal of the resist allows the creation of patterns on metal.
- Undercutting – the removal of metal from the edge of an etched area which leads to softening of edges and "fuzziness".

Appendix 2

Resists from 'incorrect' photocopies.

This is a very "quick and dirty" process for transferring images from a computer to metal, using a laser printer or laser photocopier (referred to from here as "laser printer": the process is the same for both). As with the electrolytic etching process above, it is an area which requires further exploration.

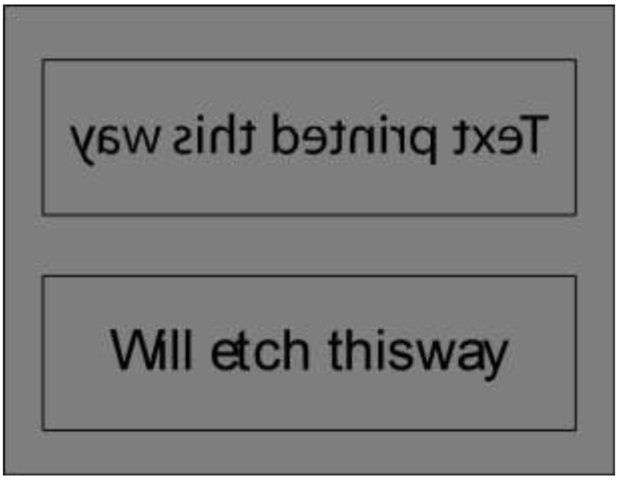
This process relies on the fact that laser printer toner is a heat-fusing plastic and that if it is not applied to the correct paper, it doesn't bond to that paper.

1) Image

The image used should be high-contrast black and white and should be at the maximum resolution for the printer you are going to use. While 150 dpi printers give perfectly good results, better results are achieved at higher resolutions.

The image should be the same size as the piece you wish to etch. It is important to realise that screen-size and print size are not always the same thing.

The image should be in mirrored:

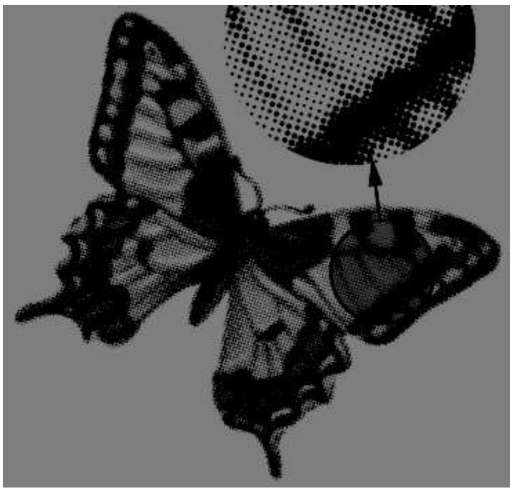


Remember that black areas on the copy will stand proud and “white” areas will be etched away. In the above diagram, the text would stand proud on an etched background, with a proud border.

To begin with, do not attempt to use too large or too small an image. Something of around 4cm x 4cm would be ideal, preferably with a good balance of black and white.

It is possible to use “halftone” images successfully but greyscalegrayscale images will not work well at all.

(Grayscale images being images – like a black and white photograph – which are made up in varying shades of grey. Halftone is a process by which greyscale is emulated using a filter which converts the greys into differing dot densities on the page. See the illustration below.)



Grayscale Halftone

Explain the difference between greyscale and halftone.

2) Printing

The “trick” of this process is to print the image on *glossy* ***INKJET*** paper.

It really is essential that the image is not printed on paper which is meant for laser printers: the toner will bond to this. The inkjet paper will not accept the toner properly and the glossy surface helps it to transfer onto the metal. Even reasonably cheap paper will work well.

It is worthwhile printing several copies of the image, especially to begin with. Once the process has been carried out a few times, it becomes easier and larger or smaller plates are possible.

The paper should be handled by the edges both before and after printing, and after printing care should be taken not to touch or abrade the image.

The image should be cut to size, leaving a small border and any tabs required to allow for positioning (see next step).

3) Transfer

The image is transferred to the metal using heat. The metal should be prepared by being polished and then thoroughly cleaned with soap and water to remove all traces of polish, OR by being lightly abraded. In both cases, the surface must be free of all traces of grease and must be dry. After preparation, handle only by the edges.

The metal plate is then placed on a hotplate. An electric clothes iron (no steam) turned upside-down and set to its highest setting is ideal. Kitchen hotplates or the plates of a vulcanising press could also be used. The hotplate should be set to around 230°C and should be allowed to come to that temperature and stabilise. It is very helpful to clip the metal to the hotplate using a “bulldog” clip or similar as this prevents it slipping during the next part of the process

When the metal has heated up, place the image *toner side down* on the metal and do NOT allow it to slip about. A solder pick or similar can be used to press the image gently onto the metal surface until it begins to stick.

Use a heated burnisher to rub the image down onto the metal. It will take a few minutes to do this. Rub evenly and gently, or the molten toner can spread out and smudge: important on highly detailed images. Sometimes, the image can be seen appearing through the paper, though this depends on the paper used.

Remember that the metal is at around 230°C: precautions must be taken to prevent burns. The burnisher should be held in a wooden handle and the same general caution exercised in the soldering area should be observed here.

At this stage, remove the metal from the hotplate with the image in place. Allow the metal to cool. Do not attempt to peel back the paper at this stage: it will remove the resist if you do.

When the metal is cold, place it in hand-hot water for 5 minutes and allow the paper to soften. Take it out and gently rub the paper off the metal. As it peels off, the toner is left, bonded to the metal. If any paper seems stubborn, re-soak and try again. A bristle or nylon brush can be used to remove the paper residue.

The toner will appear black or black with a white/grey film over it. So long as there is no paper left on the areas which are to be removed by the etching, the white or grey residue is not a problem.

The metal is now ready to etch. It should be handled only by the edges. If plates have to be stored, ensure that the resist does not scratch.

Errors in transfer or damage can be touched up with nail-polish or asphaltum.

The toner resist removes with acetone (nail-polish remover), fine emery paper or sandblasting.

Appendix 3

Thanks and web resources

The author would like to thank the following people for their indirect assistance with this paper:

- Jake Von Slatt, information on electrolytic etching and toner resists: see http://www.steampunkworkshop.com/
- Gordon Stewart, information on toner resists.
- Dominic Snyder, information on “traditional” etching.
- The students on the NQ Jewellery Course at North Glasgow College for being guinea-pigs and working with this process as the research progressed: see http://www.north-gla.ac.uk/

Additional web resources:

- http://www.justified-sinner.com/ the author’s website, with photographs of some of these processes being carried out.
- http://en.wikipedia.org/wiki/Electrochemistry/ details about the theory behind the process of electrolytic etching.

About the author

Dauvit Alexander is a lecturer in Fine Jewellery at North Glasgow College, Glasgow, Scotland. His own work is generally based on found objects, often using corroded steel in conjunction with precious metals and gemstones to create small boxes which house these objects, pieces which he refers to as “Cabinets of Curiosities”.

His interest in electrolytic etching came about as the direct result of a health and safety ruling which banned the use of acids in the college workshops.

As a result of these experiments, he now uses electrolytic etching in his own work, especially in the creation of the metal “museum tags” which are a feature of his work.

COPYRIGHT

---

[1] British patent no. 8656, granted to Spencer and Wilson in 1840.

[2] In reality, a complex interplay of ions is taking place, involving dissolution and re-precipitation. The actual mechanism by which this works depends to a large extent on the composition and concentration of the electrolyte.

[3] A film product made for the production of etched circuit boards. It is very simple to use, clean and requires no drying time. PnP Blue is a resist bonded to a sheet of polyester. The design is transferred to the PnP with a copy machine or a laser printer. The PnP toner sheet is then transferred onto the metal with a household iron. The toner acts as the 'glue' attaching the resist design to the metal. The back and edges should be covered with some other resist. The limitations of this method are that only flat pieces of metal can be used, and it is time consuming for large runs.
A basic guide to use can be seen here: http://www.cibs.co.uk/etch/x7.html

Electrolytic Etching – An Update

Some of you may remember my talk at the ACJ Conference on my researches into the process of electrolytic etching metals using salt water and an electric current in place of acids, making the process simple, safe and environmentally responsible. Since that talk, I've been updating the process regularly and have made a couple of discoveries.

Before continuing, the process can be described briefly as follows: metal is prepared for etching in exactly the same way as for acid etching. The advantage of electrolytic etching is that softer resists can be used – indeed, “Sharpie” markers can be used as a resist. The metal plate is then attached to the positive terminal of a DC power supply and the plate is immersed in a strong solution of a conductive salt. Table salt is the usual solution, acidified with a touch of vinegar or lemon-juice. A stainless steel plate or plate of an identical metal – which remains untouched - about the same size as the plate to be etched is connected to the negative terminal and the unit is turned on. At a current of around 1A and 9 Volts, the etching will be substantial in about 20 minutes. The solution can be re-used and if it gets too messy, can be filtered and poured safely and legally down the sink, the filtrate being mostly metal and metal oxides which can be recycled.

The discoveries are as follows:

1) Mobile Phone Chargers

Almost everyone has old mobile phone chargers lying about in their home and they can be used as the power supply for the etching process, generating 0.6A at 6-9V, which may lead to a slightly slower etch. Cut the connector off the cable and the RED wire will be the postitive terminal which should be connected to the metal. The black wire is negative and should be connected to the other plate. If your wires are not coloured – as in some Samsung chargers – you can test the polarity with a multimeter. Note that old Apple chargers will not work as they contain proprietary circuitry;

2) Etching Silver efficiently and reliably

Silver can be etched with slightly acidic salt water but the process is much more reliable if a nitrate solution is used. At some concentrations, the salt forms a “crust” of silver chloride on the surface of the silver which stops it etching. Sodium or potassium nitrate work really well instead. It can be hard to find these chemicals but they are both sold as garden plant food and if all else fails, can be found in 100g packets on Ebay for a reasonable price. Silver nitrate can be used but is prohibitively expensive and degrades rapidly at room temperature and in the light.

I will be writing this material up more fully with illustrations in the near future. Keep an eye on the ACJ e-bulletin for links to the article which I will be making available to all members of the ACJ.

Dauvit Alexander
justified.sinner@gmail.com
http://www.justified-sinner.com/