GREEN PRINTS

A HANDBOOK ON SOME NEW METHODS FOR NON-TOXIC INTAGLIO ETCHING AND METAL PLATE PRINTMAKING

Cedric Green FRSA



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All prints and photographs illustrated are by the author.

Above: "Athena" deep galv-etched zinc plate 25 x 16 cm. Proofed intaglio and relief from single plate.

Published by Ecotech Design 26 Botanical Road, Sheffield S11 8RP Printed in France

"Brantôme - Abbey" a 4 colour print from 4 galv-etched and fractinted plates - 33 x

ACKNOWLEDGMENTS

This booklet is intended primarily for printmakers with some experience of producing prints from metal plates - copper, zinc steel or aluminium. It assumes a reader with a basic knowledge of the traditional processes of etching, and like me, with a feeling of dissatisfaction with the toxicity and general unpleasantness of many of the processes involved, in particular the use of acid mordants, strong solvents and resin aquatint.

It was written to amplify articles I wrote for Printmaking Today published in Spring 1998, 1999 and 2002 (1). I am grateful to the editors, Rosemary Simmons and Anne Desmet, for encouraging me to write about my personal experience and search for safer integrated methods for producing etchings, and the revival of 19th century electrolytic methods. The discipline of having to put it into writing stimulated a certain rigour in recording what I was doing, and led to finding new and interesting expressive possibilities. The response I received to the first article put me in touch with many printmakers who shared my concerns.

At the same time I was persuaded by Geffrey Green to make the results of my researches freely and widely available by putting them on the Internet, and I am very grateful for his work in creating the original website (whose address is given below). I want to thank Tim Healey for the time he spent answering my questions about the chemistry of Bordeaux etch, and his advice on the dangers of etching zinc plates in ferric chloride.

Ad Stijnman kindly supplied me with background information and samples of vegetable cleaning agent (VCA). Thanks too for encouragement and comments from Nik Semenoff, who first published an article on electroetching in 1991 (18) and researched a new mordant for aluminium and zinc similar to Bordeaux Etch, which was published at the same time as my first article (16). Keith Howard has tried the techniques with his students and I am grateful for his appreciative and helpful comments. I acknowledge with thanks the information supplied by Prior and Co. in Sheffield about their equipment for industrial electrolytic etched marking. Lastly I'd like to thank those printmakers who freely supplied me with information on their methods.

In the course of many workshops at home and abroad, I have been stimulated by questions from the participants, to try new methods and to refine and improve the ones covered in this book. I have found that an interest in electrolytic etching methods extends a long way beyond printmakers, and I have been contacted by craftsmen and women in many different fields like emamelling (champlevé), jewellery, etc. I am very grateful also to Fabien Maison, Jean-Claude Pronier et Jean-Marc Couffin for their translation of the web pages and the booklet into French which is available free as a download.

Cedric Green, October 2013

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Above: "Dialogues" - collage of prints from plates produced by the passive Galv-On process 40 x 40 cms.



"Paysage prédateur" - colour relief print from 7 deep etched zinc plates - 55 cm x 28 cm







BACKGROUND

After years of working with traditional methods for making and proofing intaglio plates, and suffering all kinds of ill effects - sore eyes, eczema, asthma, sore throat, depression - I began to worry about the long term effects of the chemicals and processes on my health. Finally I was provoked by reading Tim Challis' "Print Safe" (2) to try replacing every toxic, unpleasant chemical or process, to make the whole physical process of making prints less of a tedious chore and more of an enjoyable creative process to match the pleasure of seeing the results coming off the press.

In particular, I'd been seriously inhibited about using the techniques that produced the results I liked best - deep etch with large areas of open bite, embossing, combinations of intaglio and relief - because of the prodigious quantities of acid used, and hours spent over zinc plates in ferric chloride brushing away noxious bubbles and removing the iron crust produced .

In short, over a period of years starting in 1992, thanks to articles in Printmaking Today (12, 13, 14, 15, 17), research into the history of electrolytic methods in the 19th century, contacts with other printmakers, advice from chemists and learning about some of the older methods using by commercial printing works, I gradually reformed all my practices and found safe substitutes for the methods that were clearly the most objectionable.

An important personal objective was to use inexpensive generic materials that are locally made or easily obtainable, and to avoid expensive, patented, registered or commercialised processes and products, and to look into the basis of some of these to find the generic or public domain process or chemical upon which they are based. In this area I made some interesting discoveries in the field of 19th century electrolytic etching methods that had been recently 'rediscovered', and patented, claiming that they were a new application. (see Appendix A - Electro-Etching 1855).

The alternative methods are not simply straight replacements that are cleaner and safer, but some of them can produce results and effects not possible with the original traditional methods, and the creative exploration of these is what makes them exciting to use. Also there is a kind of interdependence between them, for instance, electrolytic galv-etching processes make possible new grounding materials that cannot be used with acids, and which themselves allow galv-etch to produce effects not possible with traditional grounds. The galv-on method gives effects and textures that are a rich addition to the range available to printmakers. Bordeaux etch for zinc and steel plates can also produce the same effects as galv-on used as a "passive" electrolytic process. Plating and creating new plates by galvanoplasty extend the range of possibilities still further.

The results to date of this empirical and theoretical research are summarised in the table on the next page, and then are described in detail later.

Details of prints from plates produced by the techniques that will be described

COMPARATIVE TABLE

TRADITIONAL METHOD	ILL EFFECTS & DANGERS (3)	SUBSTITUTE METHOD.
Etching copper plates: nitric acid, hydrochloric acid, Dutch mordant, ferric chloride. Etching zinc plates: nitric, ferric chloride.	Nitrogen dioxide poisoning, damage to eyes, lungs, nasal membranes, skin damage.	Electrolytic processes: galvanography (galv-etch and galv- on for etching). 'Bordeaux etch' electro-chemical solution for zinc aluminium and steel plates.
Hard, soft ground: Smoked turpentine based wax and asphaltum grounds; turpentine based wax and grease	Irritation of mucous membranes, Nausea, headaches, toxic or carcinogenic fumes when heated, depression of central nervous system.	Insulating ink ground: relief printing ink applied by soft roller - after drying as hard ground - before drying as soft ground.
Aquatint: powdered pine rosin; powdered asphaltum	Rosin dust allergy, toxic rosin fumes, carcinogenic asphaltum fumes. Headaches, skin and eye irritation.	Fractint , Salt aquatint- grounding with relief printing ink, produced in press. (no aquatint box needed) Sugar lift tint with ink ground
Stopping out: methanol (methylated spirit) based varnish.	Methanol – Headaches skin and eye irritation	Ethanol (ethyl alcohol) based varnish: shellac flakes dissolved in rubbing or industrial ethyl alcohol. Acrylic varnish
Cleaning of varnish or ground: methanol, turpentine, naphtha (white spirit, turpentine substitute).	Methanol – Headaches skin and eye irritation Irritation of mucous membranes, depression of central nervous system, skin damage; suspected kidney damage.	Ethanol: ethyl alcohol for cleaning varnish, ink ground or fractint. Vegetable Cleaning Agent (VCA) or cooking oil for ink . Ecological 'white spirit subsitute' (ester of vegetable oil) . Vinegar for hardened ink ground
Cleaning inked plates or tools: turpentine, naphtha (white spirit).	turpentine and naphtha - Irritation of mucous membranes, depression of central nervous system, skin damage; suspected kidney damage.	VCA or vegetable cleaning agent or cooking oil - followed by mild household detergent. Ethanol for dried ink. Acetone for hardened ink.

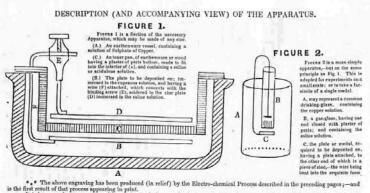
ETCHING WITHOUT ACID

A brief history of electrolytic methods

This chapter is a condensed version of "Electricity, Light and the Printed Image" Published by the University of Barcelona Press 2004

Galvanism, or chemically produced electricity, was accidentally discovered by Luigi Galvani in 1789 who was doing experiments on frog's legs and found that muscles twitched when touched by two different metals in contact, a phenomenon he attributed to a fluid in organic tissue. Soon after that Alexandre Volta showed that it was due to a direct electric current, and built a 'galvanic battery' formed by alternating zinc and copper plates separated by fabric soaked in an acidic solution (5). In 1834 Michael Faraday postulated his Laws of Electrolysis and established the scientific basis of the ranking of different metals according to their 'electrode potential' (6). Smee and Daniell invented improved versions of galvanic cells, using a copper plate suspended in copper sulphate and a zinc plate in salt or sulphuric acid with a permeable plaster of paris partition between them. Thomas Spencer found that copper was deposited on the cathode or 'negative metal' and the zinc pole was etched. He and John Wilson were granted a patent in 1840 for "Engraving Metals by Voltaic Electricity" (see Appendix B for text of patent). These discoveries were immediately utilized to make printing plates, reproduce seals and plate small objects by the process that became known as 'Electrotyping'.

Illustration by Thomas Spencer of his apparatus for creating the printing plate from which this illustration was printed in 1841 (20).



is the first result of that process appearing in given of what may be dune by it.—The lines were eight with the preceding pages;—and the first result of that process appearing in givine of what may be dune by it.—The lines were originally cut in a sheet of soft lead, bastily, and without reference to ornamental beauty of execution. The wint of a tool properly adapted to cut the lead, accurately, in the required manner, has made the lines less required information than they would not be the purched into the lead, with types. The lead, thus prepared, was then put into the apparatus it illustrates, and a plate to copper deposited, the lines less required manner and a plate of compared proper deposited, the lines

It was soon found that applying a direct current from a galvanic cell to a *separate* 'cell' containing a couple of parallel metal plates in a metallic salt solution (the electrolyte) dissolved metal from the anode (+ve) and deposited metal on the cathode (-ve). This is explained by the fact that an electrolyte, consisting of positive and negative 'ions' will conduct a direct electrical current, which carries the ions to the plate of the opposite polarity. In a copper sulphate solution the positive copper ions collect on the negative copper plate, and negative sulphate ions react with the bare metal of the copper anode - etch it in fact - and create new copper sulphate. Thus the electrolyte stays at the same concentration, creating the illusion that copper particles are transferred from one plate to the other - a common fallacy.

The process of electrotyping become very widely used for creating printing plates, plating metal objects, decorating silverware and marking cutlery. In **1852** Charles V Walker documented and described all the processes that were currently known in his book *Electrotype Manipulation*, which went through 29 editions by 1859 and was also published in the USA (7). Part II included detailed descriptions of a patented process called *'Electro-Etching'*, and

another called 'Electro-tint' (see Appendix A for excerpts). The word 'Galvanography' was synonymous with 'Electrotyping', basically meaning a plate made by depositing metal over a mould, a process which is called 'galvanoplasty'', but other processes of etching or plating, which used the same electrolytic principles and equipment were included in the original meaning. The term 'Galvanography' was used to distinguish the graphic use of the Electrotyping process from the industrial use or the production of text type plates. The French name for the Electrotype process is 'galvanotypie' and a plate made by the process was called a 'galvano'.

The indisputable 'inventor' of photography, Joseph Nicéphore Niépce, like many extraordinary men of that period, was interested in a wide range of subjects, and he began his photographic researches in 1816 from a background in lithography. He compensated for his lack of talent as a draughtsman. by using a camera obscura and was obsessed with the idea of being able to fix the images he obtained in it. Niépce had his first success in 1822 with bitumen of Judea mixed with oil of lavender, exposed for several hours under an engraving which was oiled to make it transparent. The areas not exposed to light could be washed away with turpentine and oil of lavender, and the dark areas etched in acid. In 1826 he produced a pewter printing plate of the Cardinal d'Amboise - the first successful attempt at photomechanical reproduction.

After the invention of photography, there was international competition to find ways of making permanent ink prints of photographs, and many of the methods used electrolytic processes in one way or another. The earliest attempts, by Alfred Donne in 1839, and Joseph Berres in 1840 started with a daguerreotype, which was a photograph on a silvered copper plate, which was plated and then etched (8).

From then on, there was international competition to find ways of making permanent ink prints of photographs, and many of the methods used electrolytic processes in one way or another. At that time there was an acknowledged need for an easier way of producing high quality reproductions of works of art, original works or popular views to illustrate books, which up to then required the making of steel engravings, each of which could take up to a year to produce.

Printed photographs were perceived as the solution and the competition was later stimulated by a prize of 2000 francs offered by the Duc de Luynes in 1856 for the best method of photomechanical printing. One of the most talented early experimenters, was the painter and photographer Charles Negre who took up the methods originated by Niepce and his cousin, and elaborated them by introducing an electrolytic step, plating the partly developed steel plate with gold to protect the half tones, then aquatinting it and etching it in nitric acid. He received a French patent in 1856 and was a finalist in the Duc de Luynes competition (8).

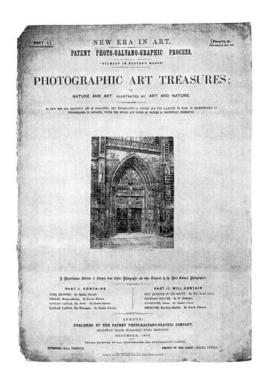
Hippolyte Louis Fizeau developed probably the most successful method, patenting it in 1843 [13]. He boiled the daguerreotype in potassium hydroxide to strengthen the resist dots, lightly etched it in nitric acid and then wiped it with heavy linseed oil, as if for printing in intaglio. Then he electroplated it with gold, which was deposited only on the highlights not protected by oil. He removed the oil and etched it again to deepen the dark areas, and finally electroplated the whole plate with copper to strengthen it so that many prints could be pulled [4]. The plates required some hand retouching, and the results were impressive despite difficulties in achieving good half-tones, but the method was too complicated and expensive to



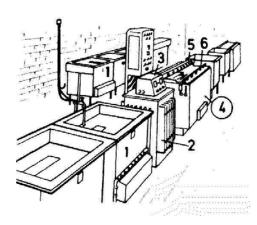
The first real photograph taken from his window in 1826, by Niépce. A prepared pewter plate in his camera obscura was exposed for 8 hours, washed and etched. Daguerre, in partnership with Niépce's cousin, discovered a method of fixing an image onto a silvered copper plate in 1835.



Print from a photographic printing plate produced from a daguerreotype by Hippolyte Fizeau in 1843



Photograph reproduced on the title page of "Photographic Art Treasures" published by the photo-galvanographic company of Paul Pretsch. The earliest printed photographic reproductions in England



Commercial electrotyping and printing block making plant. 1 - cleaning tank. 2 - rectifier. 3 - control unit. 4 - electroplating tank. 5 - anode rod. 6 - plate rod (cathode).

catch on.

But the Austrian, Paul Pretsch took a different approach and patented a process called 'photo-galvanography'', in which he began with a photographically exposed dichromated-gelatine mould which was made to reticulate, from which he produced a copper intaglio plate by galvanoplasty. He formed a company in London to produce the first commercially printed photographs called "Photographic Art Treasures" in 1856 (9).

Alphonse Poitevin, aware of the pioneering work of Pretsch on the reticulation of gelatine, filed a number of patents in 1855 for a very similar process, substituting a plaster of Paris mould for the gutta percha. But he turned his attention to the behaviour of dichromated albumen exposed to light on a lithographic stone, and it is with this method that he won the prize for photomechanical printing offered by the Duc de Luynes in 1867.

Electrolytic processes were much used in France for intaglio plate-making in the nineteenth century. Early Ordnance Survey Map plates were produced by a special application of galvanography originally used by Spencer.

In 1962 S W Hayter described the electrolytic process of depositing metal into lines drawn through a ground on a metal plate that he had developed and used at Atelier17 in Paris before the war (22). In industry electrolytic processes were used very widely, mainly for plating and protecting metal. Sheffield in England was a centre of electrolytic development, producing a fine silver plating method called 'Sheffield plate' Anodising was an electrolytic process for protecting aluminium. In 1943 a US company called Lectroetch adapted the Electro-Etching process to marking metals of all kinds, and is still supplying equipment and materials for the purpose. Many other companies have started to provide the same service, and electro-etching became well enough known for artists who were interested to learn about it.

In Canada Nik Semenoff and Christine Christos carried out research into electro-etching in 1989, and published a paper in *Leonardo*, an art journal in 1991, detailing the method for artists, the equipment required, its advantages regarding safety. (18). In Sweden Ole Larsen developed electrolytic processes, and one that he called "Polytype" was in essence the same as the "Electro-Tint" process described by Charles V. Walker in his 1855 book (12). In the USA Marion and Omri Behr learned about the electro-etching process originally patented in 1840 by Thomas Spencer, and they received a US patent in 1992 for their improved equipment, and registered the names 'ElectroEtch', and 'MicroTint' (13). The basic process itself has been shown to be in the public domain, as all the references to it, and its use by artists since 1840 have shown

For historical reasons, I prefer the original etymology, and the prefix *galv*-. So I use the name *'galv-etch'* for applications in which the plate is etched, and for consistency, other names using the prefix *'galv-'*, like galv-on, *galv-tone*, *galv-plate*, or *galv-type*, which will be used throughout this booklet. The names therefore can be used freely, as can the 1850's name 'electro-etching'.

WHAT IS GALV-ETCH?

In earlier editions I assumed too much basic knowledge of the scientific basis of electrolytic processes, which has led to very many questions, and a few printmakers making some mistakes that would have been avoidable had they understood the principles behind the galv-etch processes more clearly. Skip this section if you know all about electricity and electrolysis

For many centuries the traditional process used for etching a plate for printing was to use acid, either nitric, hydrochloric, and more recently ferric chloride, which is weaker but still relatively dangerous to use. Galv-etch is an electrolytic process, the principles of which have been known since the early 19th century, and the original process was described as 'engraving by voltaic electricity' and patented in 1840. Later it was described in 1855 and called 'electro-etching' (see a brief history of electrolytic methods). It is similar to the process that takes place when a wet battery like a car battery is charged, and a reversal of the process that takes place when a battery is discharged. A battery produces a direct current, unlike the mains electrical supply, which is an alternating current. In order to charge a battery, a direct current must be used, and similarly, an electrolytic etching process requires a direct current, which is why the mains supply cannot be used until it has been 'rectified' and reduced in voltage from 230 or 110 volts to very much less, usually not above 6 volts. The equipment to do this is known as a transformer and rectifier and the most common household examples are the little power supplies that one can get for battery driven transistor radios and other electronic equipment. But these are not usually sufficiently powerful for electrolytic etching purposes, but another commonly used, off-the-shelf, transformer and rectifier that can be used is a car battery charger. The most convenient to use is a laboratory power supply, which is a little more expensive, but allows the voltage or amperage to be held constant or regulated.

the electrolytic process

If two metal plates, say of copper, are placed parallel, but not touching each other, in a conducting solution of the same metal, say of copper sulphate, and they are connected to the terminals of a battery or of a source of direct current, then the current flows from one plate to the other through the solution. A complex process takes place in which the separate positive and negative 'ions' that make up the solution are separated and are attracted to the plate of the opposite polarity. Copper sulphate consists of copper ions and sulphate ions. Normally they are in equilibrium and they stick together like the positive and negative ends of two bar magnets. The current is actually able to flow because of the ions that give the solution the ability to conduct electricity. The positive copper ions are attracted to the negative copper plate (called the cathode) and the negative sulphate ions are attracted to the positive copper plate (called the anode). The copper ions stick to the cathode (if it is clean enough) and the sulphate ions are attracted to the bare areas of copper of the anode where they react with the copper of the surface, 'oxidising' it and therefore corroding it in the same way that an acid would. In fact at the point of contact, the process is exactly the same as being etched by an acid. It is as if an acid is being generated very temporarily right at the point of contact! While copper ions are becoming solid copper on the cathode, an equivalent amount of copper is being removed from the anode, and the copper sulphate is being kept in its original concentration, the copper removed from the anode, combining with the sulphate ions to form new copper sulphate at the same rate that it is losing copper ions at the cathode. So etching of the anode happens as copper ions pass into solution. The copper that passes to the cathode can form a skin of copper that



Crystal of pure copper sulphate



Small laboratory power supply.

is bonded to it, 'plating' it if the metal is clean. If the cathode is another conducting film like graphite the skin of copper can be removed, and if the cathode is a shaped mould then the skin of copper is a negative of the mould shape (see *cold casting in copper*). This is the process of 'galvanoplasty' or galv-plating.

There is a common fallacy that copper particles flow from one plate to another, but this is a misleading simplification.

electrical units and Ohms law

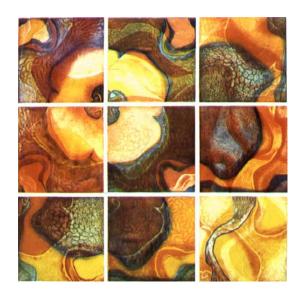
It is important to understand something about the units in which electricity is measured. If all this is familiar then skip this section. The 'strength' of electricity is called the **potential difference** and is measured in Volts, and it is usually called the voltage. You can think of it like the pressure of water in a pipe due to the height of the water in a tank above a tap. The tap may be shut but the pressure is there all the same. The 'rate' at which the electricity is passing is the current and is measured in Amperes, and as the name 'current' implies, you can think of it as the rate of flow of water in a pipe only when the tap is opened. The 'power' of the electricity that flows is the potential difference (volts) multiplied by the current (amps), and is measured in Watts. The power or 'strength' of water flowing out of the tap depends on the pressure in the pipe and the rate it is allowed to flow by the tap. The quantity of electricity is the power multiplied by the time and is measured in Watt hours. Using the water analogy, when the tap is opened, a bucket can be filled at a certain rate, say a litre per minute, and the quantity is the total volume of water that has flowed into it after a given time.

When a current flows in an electrical circuit it meets a resistance measured in Ohms that reduces its rate of flow. In that it is like the tap, which increases its resistance as it is gradually shut, slowing down the rate of flow of the water. As an electrical resistance decreases, the potential difference, the voltage decreases and the current, the amperage, increases, and if the resistance increases, the voltage increases and the amperage decreases. The ratio between volts, amps and ohms is very simply expressed by Ohms Law. **Ohms = Volts divided by Amps (R = V / A).** The inverse of resistance is the conductance \mathbf{G} , which is important in helping to calculate the time required to etch a plate. \mathbf{G} is calculated by dividing the Amperage by the Voltage.

The current flowing between copper plates in an electrolyte is related to the voltage of the power source and the resistance provided by the electrolyte. If the plates are very close together the electricity has little resistance to overcome to flow between the plates, and for a given voltage the amperage will be high. On the other hand, if the distance between the plates is greater or if the electrolyte is diluted and therefore offers a greater resistance (because the concentration of ions is lower in the solution), then the amperage will be lower. So a voltage of 4 volts meeting a resistance of 2 ohms will cause a current of 2 amps to flow. But 2 volts meeting a resistance of 0.5 ohms will demand a current of 4 amps ($\bf A = V / R$). I hope that this simple explanation of principles and units will make the subsequent discussion of current, voltage, resistance simpler to understand and demystify the subject a little.

advantages of galv-etch over acids

- 1 The greatest advantage is that with the same equipment, plates can be either bitten down or built up to give a much richer variety of results, and that qualities of tone and texture can be produced that are not possible with other methods of etching and tinting. In addition, new plates can be created by 'electrotyping' from wax or other moulds or from relief created on silvered copper plates -- the original meaning of the word galvanography.
- 2 Working with copper plates the chemical copper sulphate is absolutely safe to use, but gloves should be worn to protect the skin from drying and discolouring. With zinc plates the electrolyte zinc sulphate is much safer than acids, but must be used with care, avoiding contact with skin or eyes, and storing it safely out of reach of children.
- 3 For steel plates galv-etch is the safest method, although Bordeaux Etch) can be used as a mordant (see section on Bordeaux Etch later). The electrolytes for steel ferrous sulphate or ammonium ferrous sulphate are classified as safe chemicals, but I find it prudent to wear gloves where there is any danger of skin contact.
- **4** The solutions are not weakened by use, in fact, the same solutions can be used for years and eventually pose no serious disposal problems (see section on *safety precautions* and *Bordeaux Etch* for method of disposal).
- 5 No gases or fumes are generated nor is there any precipitate or deposit formed in the bite, although a fine sludge from impurities can build up in the bottom of a tank, which needs occasionally to be filtered out.
- **6** The length of time taken for a given depth of bite on the same size and type of plate, under the same conditions of voltage and current, is always the same, and the biting can be controlled by time-switch, leaving one free to get on with other things.
- 7 Another advantage is that the backs of plates do not need protecting the strength of the electrolytic action is proportional to the distance between the electrodes, so that only the edges and perhaps a narrow strip around the edge at the back need be varnished. The Galv-on semi-dry method leaves the backs of plates completely untouched.
- **8** The long-term cost is much lower as no very special expensive equipment is needed, especially with the galv-on semi-dry method, and the amount of electricity used is negligible about as much as a light bulb. There is no danger from electric shock, because both voltage and current are low (0.5 to 8 volts at 0.5 to 10 amps). The electrolyte solution will last indefinitely, if it is not used for different metals.
- **9** The electrolytic action is not like the corrosive action produced by an acid, and so the range of varnishes, resists and grounds that are effective is much greater, because they must be simply electrically insulating and not acid resistant. Some heat-sensitive grounds require a low current and cool electrolyte, because galvetch generates a little heat at the point where the etch acts.
- **10** The electrolytic action between the plate (anode) and the cathode is directional at right angles to the face, and so the edge of a resist is not significantly eroded or undercut.
- **11** The **galv-on** semi-dry method of etching simplifies the equipment required and allows one to work on only a portion of a large plate at a time, and can produce a great variety of textures, tones and images quickly with relative ease.

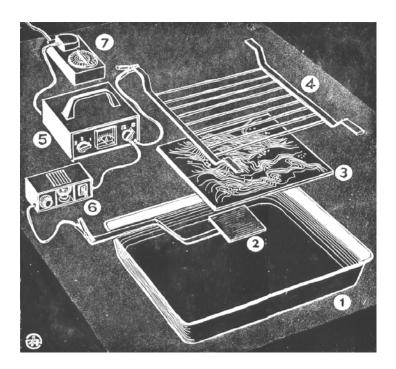


"Fleurs imaginaires, variations 1 - 9"-- a collage of printed squares, from 3 galv-etched plates, combined in different orientations and colours. The plates were stopped with ethanol + shellac and an open bite was applied in several layers.

EQUIPMENT AND MATERIALS

This guide assumes that someone using galv-etch for the first time will be making medium size prints - from plates up to about 50 cms on the longest side, and will be wanting to etch grounded needled, or tinted plates (see fractint later) or etch areas of open bite. Larger plates can obviously be made but to start off you may not want to invest a lot of money, and can make use of existing equipment like acid etching trays or photographic developing trays. In particular the galv-on semi-dry process (described later) can be done with the simplest equipment of all. Some readers may not be printmakers at all and will want to etch other objects like badges, name plates, dials, knife blades etc. I hope these pages will be helpful to them too, and I would only warn that if very small areas are to be etched, the current and voltage required must be low or the resists required must be very robust. Nearly all the equipment needed can be bought from DIY stores, electrical and electronic suppliers, motor spares suppliers or hardware shops.

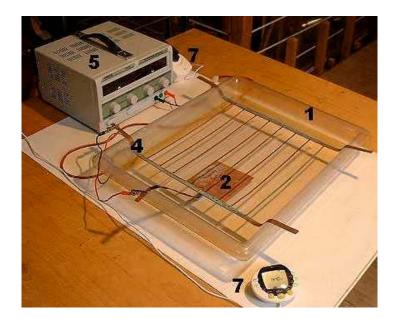
Expanded diagram of standard allpurpose equipment for galv-etch - Key below. (relief print from galv-etched and fractinted zinc plate)



- [1] Deep plastic tray with appropriate electrolyte.
- [2] "Backplate contact" flat metal plate with metal strap soldered to back, varnished except face for contact with back of plate.
- [3] Plate prepared for galv-etching, with area on back unvarnished to allow electrical contact on backplate contact.
- [4] Grid to form cathode; heavy metal strips silver-soldered or mechanically fixed to frame, bent to allow grid to touch surface of electrolyte.
- [5] Power supply direct current, switched voltages, ammeter, overload cutout, and short circuit protection.
- [6] Control box to use with any power supply without voltage switchable below 6 volts and without voltage output meter. Details of control box on page 24.
- [7] Mains switched socket with time switch.

Power supplies

The most important piece of equipment is a direct current power supply unit with switched voltage outputs and voltage and amperage displays. The most satisfactory and versatile type is a DC regulated laboratory power supply. In Europe, Velleman Instruments (website address: www.velleman.be) are distributors of a range of power supplies of this type. There are models which can be switched from 0 volts upward and with maximum outputs of 5, 10 and 20 amps costing from about 75 - 300 Euros. To begin without spending a lot of money, you can use a 6 volt car and motorcycle battery charger, with built-in ammeter, and fused short circuit and overload protection. With a battery charger it is necessary to have a control box as shown and described below, which can be made up by an electrician. The use of 6 volt batteries in motor cycles is becoming rare, but heavy duty 6/12/24 volt chargers can still be found capable of up to 20 amps. but voltages higher than 6 volts should never be used. For etching very small areas at low voltage, you can use a direct current mains adapter which can be switched down to 1.5 volts. Similarly, for small plates I have successfully used a small array of photovoltaic solar cells producing between 4 and 0.5 volts in bright sun. The control box for the last two options only needs a sensitive voltage and amperage display. There are other sources of direct current that can be used, like rechargeable batteries, but never use more than 6 volts, and then only with a control box to adjust and display the voltage by introducing a fixed and/or variable resistance. An accurate display of amperage is very useful also, which is used for calibrating the system to calculate the time required to etch (see times and tests).



Typical tray based galv-etch equipment

[1] plastic tray

[2] copper backplate contact or plate to be etched with copper strip taped to back

[4] copper grid

[5] laboratory 10 amp power supply with regulated variable voltage and amperage, digital displays, overload and short circuit protection

[7] Electronic mains supply timeswitch and control with display.



Three Laboratory power supplies from Velleman.

(The Velleman website lists European retailers of this equipment) In each country there are different local manufacturers of power supplies. The least expensive usually have analogue displays of voltage and amperage

A purpose made control box is not necessary with these power supplies.

Left – switched 0- 15 volts and 0- 3 amps (approx 75 €)



Left - switched 0 - 18 volts and 5 amps (approx. 125 Euros).



Left - switched 0 - 30 volts and up to 10 amps, with digital displays (approx. 220 Euros) A larger model is available with output up to 20 amps.



Power supply for galv-etching small needled plates up to 300 sq. cms. - small DC mains adapter with a switched output of 1.5 volts and about 2 amps output at 1.5 volts. Shown next to control box, which can simply have voltage and amperage meters showing up to 3 volts and 3 amps.



12 amp 6/12 volt battery charger unit with switches and ammeter, and left - a purpose made control unit with halogen lamp, variable resistance, ammeter and voltmeter (details on page 23) to use with any direct current power supply other



Robust battery charger for 6/12/24 volts capable of up to 20 amps. For large plates with open bite or for galvanoplasty, or galv-on, this option used with the control box may be required when large amperages are demanded. But never use 24 volts or 12 volts.



Solar photovoltaic collector power supply, for small etched areas. For this and the mains adapter shown above the control box need not have a halogen lamp voltage reducer and the displays should be more sensitive and display only up to 3 volts and 3 amps.

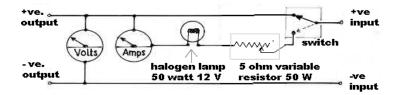


Purpose made control box to use with 6/12 volt battery charger or battery - model with voltmeter and ammeter. Note ventilating metal grille over halogen lamp



Back of control box. In the centre at the back is the knob for the 50 watt 5 ohm variable resistor and on the right the switch for output either through resistors and ammeter or direct to crocodile clips.

Below - Circuit diagram of control box. Note that the voltmeter should be able to register the maximum output of the power supply when switched direct, and the ammeter in series only measures the current when the resistor and lamp are switched in The wiring should be heavy duty enough for the maximum



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chemicals and materials

For working with copper plates you will need copper sulphate (Cu SO₄); for zinc plates: zinc sulphate (ZnSO₄), and for steel plates: ferrous sulphate (FeSO₄) or ammonium ferrous sulphate (NH₄Fe(SO₄)₂). The chemicals can be obtained from suppliers of industrial chemicals. Pure copper sulphate crystals may be obtainable from gardening shops where it may be sold to make up Bordeaux mixture, used to spray plants against mildew. But do not use ready-made Bordeaux mixture that contains other ingredients. The amount of chemical will depend on the size of tray or tank you want to fill.

In general, the electrolyte solutions, all the cathode plates, plate contacts, grids, etc. should be of the same metal as the plates with which you are working, so in the section below I will use the word 'metal' to avoid repetition and confusion. So for example if you are working with copper plates, you will use copper sulphate, and the cathode plate or grid will be of copper, and any other metal like solder, bolts or pop rivets must be varnished. Similarly, if you are using zinc, substitute the word 'zinc' for 'metal'. Never mix metals or galv-etch one metal in the sulphate of another (see the section on ''chemistry of Bordeaux etch' for an explanation).

Do not be tempted to use Salt solution (or brine) as an electrolyte as has been suggested on various websites, as the results of the electrolytic action with brine are to generate chlorine gas, hydrogen gas, to turn the electrolyte into caustic soda or sodium chlorate, and with different metals as the plate or cathode, to be left with a toxic brew of different chemicals (see links for further information)

To begin you can use standard flat trays or vertical tanks used for traditional etching, provided they are deep enough. Later on when you become more ambitious and if you plan to do large areas of plating, or galvanoplasty, you may need a deeper vertical tank in which to hang plates. Photographic developing trays are quite suitable, and the type of tray used does not need to be acid resistant, but must not be metal even if enamelled or plastic coated.

For the galv-on semi-dry process (described later) you will need thick blotting paper and sheets of good quality felt 10 mm thick, 5 mm thick, and flat metal sheets and strips and self adhesive tape.

You will also need an assortment of strong electrical crocodile clips, heavy duty insulated wire and strips of copper, zinc or iron, depending on what metal you are using. For etching in flat trays you will need metal grids which are simple to make up out of wire and metal strips (illustrated later) or you can adapt off-the-shelf stainless steel grids by plating them with the appropriate metal. For etching in a vertical tank you can make up a metal cradle to hold the plate to be etched if you are using plates with backs already protected (described later).

preparation of the electrolyte

Add the sulphate to distilled or de-mineralised water until you have a saturated solution - when no more will dissolve. Approximately 250 grammes of copper sulphate or 500 grammes of zinc sulphate will dissolve in 1 litre of water, or 210 grammes of ammonium ferrous sulphate in 1 litre. The stronger the solution, the faster will be the rate of etch, but also the electrical resistance will be lower, so if you are galv-etching a large plate and find that your power supply is being overloaded, then you can dilute the electrolyte further to increase its resistance. If you then add 3 litres of water to the concentrated solution you will have a 1:4 solution. In the case of a 1:4 copper sulphate solution that means adding 62.5 grammes of copper sulphate to every litre of water.



Small photographic plastic trays in a shower tray used as a sink.

plate contacts

The simplest way of making a contact for a plate to be etched, is to tape one or two thin flat metal strips to the back of the plate to be etched. Cut a piece of self-adhesive plastic sheet the size of the plate and put the flat strip against the back of the plate and then stick the plastic sheet over it. This way the back of the plate can be protected against being lightly etched. The flat strip can be bent up to sit clear of the electrolyte and the crocodile clip fixed to it. The strip also helps you lift the plate out of the solution and carry it around

backplate contacts

Another method you can use for making a contact with a plate to be galv-etched in a flat deep tray is to solder or tape a flat metal strip to a small flat plate of the same metal to lie on the bottom of the tray, which makes a contact with a bare area in the middle of the back of the plate. I will call this a *backplate contact* from now on. The back of the backplate contact and its strap should be varnished or covered with plastic.

The back of the plate you are galv-etching need not be varnished, as the electrolytic etching action is strongest on the face directly opposite the cathode. Only the edges and perhaps a strip around the edges need to be protected. If you use plates with backs ready protected, in a flat tray, then you will have to use a cradle making contact with the bare edges of the plate as described later.

cathode grid

The method that I recommend for a flat deep tray is to use a *grid* for the cathode (-ve), made from wires or strips of metal soldered or mechanically fixed to a frame. The frame of the grid should be bent so that the wires of the grid are just immersed in the surface of the electrolyte. The spacing of the wires should be slightly less than the distance from the grid to the plate. A stainless steel off-the-shelf grid can be used for galv-etching, as it will be soon plated with the metal. But it must be completely degreased and the current turned on the moment it is immersed in the electrolyte or else it will begin to be etched by copper sulphate (see Bordeaux Etch).

If you use the equipment for plating or galvanoplasty (creating a new negative plate against a mould), or for depositing a dark tone onto an area, you will be removing a significant amount of metal from the grid (anode in that case), then you will need a plate suspended to touch the electrolyte. You can use the standard grid with a plate the right size fixed below it with plastic self adhesive tape.

flat tray for galv-etching line or tint

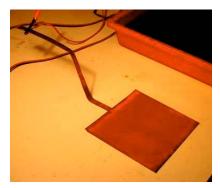
To start with, if you are galv-etching plates that have been grounded and needled, or fractinted, you can use a conventional flat etching tray. The tray needs to be quite deep, at least 6 cms. If you have not got a tray deep enough, you can use the kind of plastic food storage trays sold in supermarkets, because the galv-etch solutions are not corrosive, and don't need the special materials required for acids. Don't use metal trays though, even if enameled, in case of electrical short circuits.



Above - self adhesive plastic tape laid over back of plate to fix copper contact strips.

Below - strip bent up to project out of





Copper backplate contact with copper strip bent up to project out of electrolyte - strip protected by strong varnish.





In order to calculate the time required to galv-etch you will need to "calibrate" the setup you are using - a process which is more fully described in the section on 'times and tests'. For this you need a test plate with exactly 100 square centimeters of exposed metal.

vertical tank

The alternative to a deep tray is a tank in which plates can be hung vertically from a bar or over the edge of the tank.. Vertical tanks are increasingly used for etching and most of them can be adapted for galv-etch if they have sufficient depth to hang the plate and the cathode opposite and parallel with about 5 cm between them. Vertical tanks can be made for galv-etching from large polypropylene or other plastic 'jerry cans' or water storage containers with built -in taps as shown below. It is a good idea to have a tank with a tap a few centimeters above the bottom, in order occasionally to empty it without stirring up the deposit that eventually accumulates on the bottom. Using a vertical tank with sufficient depth is a much better way of doing galvanoplasty or plating, but can be used for all purposes if it will take your largest plate.

Vertical tank with tap, 35 x 35 x 15 cm holding 18 litres, with cradle and anode copper sheet for plating. Tank made from a heavy duty plastic storage can with the top cut off and edges bent in. The large volume of electrolyte is not exhausted by galv-etching or plating, and does not pose a disposal problem.



Detail of deep etched zinc plate etched in vertical tank

supporting a plate in a vertical tank

If you wish to use a larger tank with the plate vertical, one way to suspend a plate and to provide a contact and protect the back is to cut a sheet of self-adhesive plastic sheet to the size of the plate and fix two thin strips of metal against the back of the plate. The strips can be bent over to hang over the edge of a vertical sided tank or to hang from a metal bar across the tank. Contact from the power supply can be made to the metal strips or to the end of the metal bar. If you are using plates with backs ready protected the plate can be held on a metal cradle hooked over the edge of the tank, made from a broad strip of the correct metal with the edge turned up on which to rest the plate with a bare area to make contact with an unvarnished area on the edge or back of the plate.. All the metal bars, straps, clips, rivets etc. must be well varnished against being etched, just leaving the points of electrical contact with the plate bare

For the vertical tank make a cathode plate of the correct metal by soldering or taping thin metal straps to each end, to hang over the edge of the etching bath. Alternatively a square plate with a long single strap can be used, which can be lowered into the tank to control the resistance. The cathode strip or square should be able to hang opposite the centre of the plate and be parallel to it. If it is not, the galv-etch may not be even in depth. To stop them being etched and prolong their life, seal all the metal crocodile clips, backs of plates, bars, straps etc. with ethanol varnish, or a strong stop-out varnish, leaving bare only those areas to be in direct contact with the plate. A grid cathode can be used in a vertical tank as well, unless you are using it for plating or galvanoplasty.

PROCEDURE IN GALV-ETCH

using a standard tray and grid system

Fill the tray with electrolyte to the height of the bottom of the grid and then remove the grid. Lower the plate to be etched into the electrolyte by its strip contacts. If you are using a backplate contact, put it into the tray with the strip bent up at the right position for the edge of the plate, then lower the plate into the solution onto the centre of the backplate contact. Place the grid onto the tray, with its wires just immersed in the electrolyte. At this stage make sure that the battery charger is switched off, either at the mains, or by a switch or timeswitch on its output.

Attach the positive **(red)** terminal of the battery charger to the plate contact strip or the backplate contact, and the negative **(black)** terminal to the grid or cathode. Check that you don't have any short circuits - leads, straps or crocodile clips touching. Then switch on for a moment, and watch the ammeter and voltameter to check that the current and voltage are OK and note the readings. If the needle goes off the scale, or the digital display shows above 10 amps or 5 volts, switch off quickly, lower the voltage setting and try again.

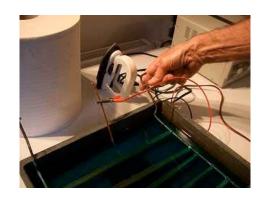
At this stage you may be calibrating your system with a test calibration plate, in which case follow the procedure detailed in the section on *times and tests*. If you are etching a prepared plate, calculate the time you need from the voltmeter readings (see section on *times and tests*). Then set the time switch, if you have one, leave it to etch for the required time. It is a good a idea to keep a record of what you have done on every plate.

If the ammeter reading is very high because the exposed area of your plate is large, then the voltage should be lowered by switching it a lower setting, or the resistance increased by switching in the control box described earlier, or by the other means described later (galv-etching very large plates).

An uneven bite can be caused by the cathode grid or plate not being parallel to the plate and opposite its centre. There is a slight tendency for edges to bite more deeply than the centre, which can be counteracted by having the cathode grid slightly smaller than the plate if you notice a problem. Narrow open bite areas tend to bite more deeply than broad ones, something that can only be avoided by biting in short steps and stopping them out sooner. Similarly, isolated lines bite slightly more deeply than closely spaced hatching.

open bite or galvanoplasty in a flat tray

A flat tray can be used for plating or open bite provided that you have some means of controlling the surge of current caused by the very low resistance of a plate with large areas of bare metal in the electrolyte. The control box shown in the diagram earlier can be inexpensively made up from off-the-shelf components. Note that adding a resistance like this in series, has the effect of reducing the voltage over the anode and cathode (see section on **times and tests**). For plating, a grid (which becomes the anode) is not ideal as it is etched away and a solid plate can be attached to the underside of the grid.



Connecting crocodile clips to grid and plate connecting strip



etching a plate in a vertical tank

A large tank requires a larger volume of electrolyte, but its greater width allows you to see the progress of the etch more easily and you can have more control over the distance between the plate and the cathode grid or plate. The cathode should be about the same area as the plate, and it should be hung directly opposite its centre. The tendency for lines or areas near the edges of a plate to be etched more deeply than the centre can be counteracted by making the cathode plate slightly smaller and therefore closer to the centre of the plate to be etched.

When plating or deep etching large areas of open bite with a strong current (amperage) there is often some loose deposit produced, and the advantage of a vertical tank is that it does not drop back onto the plate, but sinks to the bottom of the tank. This can then be emptied and filtered and the clean solution returned to the refilled tank. If you don't have a tank with a tap, use a plastic tube as a siphon, and start the siphon going by holding it all under the electrolyte surface (with gloved hands) until it is filled with liquid. Then close both ends and take one end out and put it into the receptacle to store the electrolyte. **Don't start the siphon by sucking the liquid up it** For storage I use plastic camping water storage jerry-cans, with taps.

deep etch and open bite

Large exposed areas of a plate will increase the current required from the power supply and lower the voltage (if it is not electronically regulated), so to keep the current within the limits of the power supply's ammeter, the resistance can be controlled by lowering the voltage output of the power supply with the controls that you have. This will increase the time taken to etch, but will decrease the intensity of the etch per unit area.

There is not usually any need to protect the whole of the backs of plates because very little electrolytic action will take place "round the corner" as it were. The ions in the solution are most strongly attracted to the nearest surfaces, which are the facing sides of the anode and cathode plates. This also makes it easier to make an electrical contact with the back of the plate, avoiding the need for crocodile clips and possible marks on the surface. The best way to make an electrical connection with plates that are supplied with the backs ready protected, is at the edges. Cut a strip of metal the width of the plate plus an extra to project well out of the electrolyte and bend it to grip both edges of the plate. Tape it to the back to stop it slipping.



«Paysage nu » Relief print from 3 zinc plates galv-etched with salt tint, 33x56 cm.

GALV-ON SEMI DRY METHOD

For certain purposes - for etching a small portion of a large plate; for applying a particular texture over an area without using fractint (see later) or aquatint or other alternatives - I have adapted a method that does not require immersion of the plate in the electrolyte, and therefore does not need a tray, grid, or vertical tank with cradles etc. The method is best suited as an alternative to open bite, but it can be used to etch needled lines or tint, and is proving to be rich in new possibilities. I have called the new method "galv-on" as it expresses the way that it is done flat on a surface by forming a sandwich of felt and other absorbent materials soaked in electrolyte on top of the plate to be etched, backed by a cathode plate.

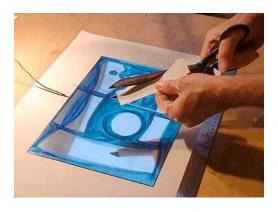
For zinc, aluminium, or steel plates, I have developed a similar method which does not require a power supply, because it uses Bordeaux etch (copper sulphate), *without salt solution*. If the sandwich is of zinc + copper sulphate + copper plate, it becomes a primitive battery and generates its own current, and I have called this method **Passive Galv-On** (described in greater detail in Bordeaux Etch later).

The area of the metal plate to be etched is prepared - masked with varnish or a stencil - then the plate laid face up on several sheets of blotting paper or newsprint on a flat level surface, with a thin strip of metal under the edge to attach to the positive terminal of the power supply. A thick pad of good quality well-washed felt is soaked in the electrolyte, allowed to drip dry for half a minute, and then placed over the whole area to be etched. A flat plate of the same metal as the plate is placed over the felt area, connected to the negative terminal.

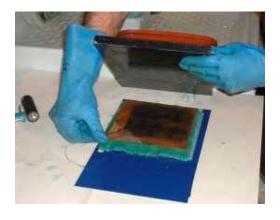
Then place a block of wood or board on the cathode plate and weight it with something heavy until some of the electrolyte squeezes out of the edges of the felt. The amperage should not exceed about 10 amps, so if you are using a battery charger, it may be necessary to have an additional resistance as previously described switched in (page 23). Turn on the current for slightly longer than you would need to etch in a tray or tank, but the precise time required will have to be calculated by experiment as described in the next section.

The current will pass through the electrolyte held in the felt and will etch a texture over the area that will depend on the quality and condition of the surface of the felt. The texture is usually more or less uneven but never uninteresting. To make the texture more even, several layers of thick blotting paper soaked in electrolyte can be placed between the surface of the plate and the felt, and trapped bubbles of air squeezed out with a roller. To reduce the unevenness still further, the felt/blotting paper can be moved a couple of times in between a series of short etches. Other porous materials can be placed next to the plate under the felt to produce different textures, like soft non-sized papers, fabrics etc. A paper with a strong printed image or with a design in a water resistant varnish, soaked in electrolyte, laid face down on the plate and backed with blotting paper will leave a ghostly negative image etched into the plate. I have experimented with etching through negative screened laserprinted photographs, soaked in electrolyte, and then placed face down on the plate cleaned with acetone, with interesting results. But this cannot be considered yet as a method for precise photomechanical reproduction, but the ghostly images etched will appeal to some printmakers.

One way in which the galv-on method can be used is to create a 'collage' of various cut and torn papers, thin felt, fabrics and materials over a masked area, backed up with the thick soaked felt.



Preparing a plate - pieces of blotting paper and felt laid over exposed areas of plate.



The sandwich of plate, dry blotting paper, tissue papers, felt etc. backed by the thick layer of soaked felt and then, the copper cathode plate and board being laid down to receive the



Weight on Galv-On sandwich - 5 litre can of



Detail of a print from a plate produced by the galv-on semi-dry method - layer against surface of plate: dry crumpled tissue paper, backed with layers of thick blotting paper and



"Eclipse 7" – galv-on, 3 zinc plates 35 cm x 25 cm, proofed in 5 colours, 2 colours intaglio and 3 colours overprinted in relief from the same plate

The different porosities and textures will offer different resistances to the current and will etch to different depths to reproduce the collage in different tones and textures. If the *elements* of the collage are not wetted first in electrolyte, then they will buckle as the electrolyte soaks down into them with unpredictable but always very interesting effects. A mask or stencil made with a slightly porous material like thick cartridge paper, previously soaked in water (so that it does not buckle) will show as a lighter tone with a soft edge. If air bubbles are created by the wetting and buckling, they will not be etched at all.

needled lines or tint with galv-on

To etch lines needled in a ground, or a uniform aquatint or fractint use several sheets of good quality clean blotting paper well soaked in electrolyte under the felt layer. Divide the time required into 3 or 4 equal intervals and in between each, examine the progress and lift up and rotate or move the blotting paper and felt to even out the variations in strength of etch. Areas not etched at all are due to air bubbles that can be eliminated by using a small hard rubber roller on the back of each blotting paper layer. New felt must be very well washed in strong detergent to remove the natural oiliness in the wool. After a while the top of the felt will collect metal that has not stuck to the cathode, which has to be washed out. Pieces of blotting paper can be reused if they are clean, but when they become too discoloured, discard them.

TIMES AND TESTS

To appreciate the text of this section it is useful to understand the meaning of the electrical units used which are explained earlier (what is galv-etch: electrical units). The time required to etch to a given depth can be simply calculated if you have a means of measuring the amperage and voltage that the power supply is delivering when the plate is in place and the system is switched on. These are dependant on the resistance provided by the area of bared metal on the plate, the strength of the electrolyte, the distance between plate and grid and to a small extent, the temperature. But all these factors can be taken into account by 'calibrating' your setup by making a special plate about the size of the grid or cathode plate, with an area of bare metal measuring 100 square centimeters (15.5 square inches). Protect the back with a self adhesive plastic sheet (holding the contact strip), place the plate in the electrolyte and switch on. Leave the current on for a minute to let the amperage and voltage settle down and note the readings on voltmeter and ammeter. If you have a regulated power supply, set the voltage at 1.0 and take an ammeter reading, then set it at 1.5 volts and note the amperage and so on up to about 3.0 volts. You can then calculate the resistance R of the system by dividing the voltage by the amperage. You may get slightly differing results for R at different voltages, but if they do not differ greatly, take the average and note it down for future reference.

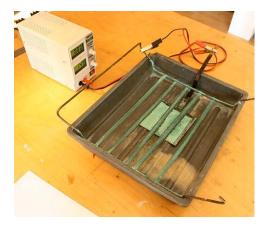
calculating the time to etch

Then when you have a plate with lines drawn in a hard ground, prepared for etching, in the same tray or tank, with the same electrolyte and distance, you can calculate how long to give it to bite the lines very lightly or to bite them quite strongly. The table below gives a series of numbers **F** for copper, zinc and steel (iron) plates, which you multiply by the resistance **R** you obtained by calibration and then divide by the voltage that you are using (if you have a regulated power supply on which you can set the voltage). If your power supply is unregulated - a battery charger or rechargeable battery pack, then you must put the plate in and turn on for long enough to read the voltage (see discussion later in this section).

 $T = F \times R/V$; where T = time in minutes; R = resistance obtained by calibration with 100 sq.cms., and V = volts; F is obtained from the table right:

Simply, the time taken to etch a plate depends on the voltage - the higher the voltage, the less time it will take and vice-versa. Each printmaker has his own preferences about the depth of bite required, so the values for **F** are a guide based on my own ideas of the meaning of 'lightly etched' etc. It is harder to give a method for calculating the time required for deep etch or open bite, as these are more subjective and depend on an individual's expressive intentions. Note that this method of calculation does not depend on the size of the plate but is valid for any plate size within limits (within the limits of a given tray/grid/electrolyte calibration test).

If you are wanting to etch a plate with open bite or any kinds of treatment that do not fall into the category of needled lines (like fractint, salt tint or sugar lift tint described later), make a test plate of the size you will most often use, with a typical range of the kinds of marks you use. Calculate the time for a light etch as above, halve it and then galv-etch it. Take it out, dry it and stop out a strip, and put it back for the same number of minutes, and so on in about 8 - 10 steps, noting exactly what you were doing. Then clean it and proof it, and keep it as a guide to the times to achieve the results you want. For very deep etch the times for each step should be doubled or tripled.



A setup of tray, grid, electrolyte at a particular concentration and depth between grid and plate can be calibrated once, and need not be done again.

Values of F for 1 ohm	Needled lines (lightly etched - 0.2 mm)	Needled lines(heavil y etched - 0.5 mm)
copper	20	60 - 80
zinc	30	90 - 110
iron	40	100 - 120

Table to estimate time T.

plate size

Note that very small test plates can give a very misleading idea of how larger plates will behave, because the current intensity could be so great that grounds will be lifted and the bite will be irregular and results discouraging. So trials on small plates must be at lower voltage and current than you need use for larger plates.

Larger plates in a tray with large exposed area of open bite may overload a small power supply, and if that happens, there are a number of different options:

- 1. If you do not have a power supply in which you can regulate the voltage from 0 - 5 volts, you can insert a resistance like a 12 volt halogen lamp and/or a ceramic resistance in series, that is, between one lead from the power supply and either the anode or the cathode. The voltage over the anode and cathode will drop and the time taken for the galv-etch will increase accordingly. A more sophisticated means of control is the type of box illustrated with a variable resistance, halogen lamp, fixed resistance and twoway switch, voltage and amperage meters. (see equipment).
- 2. You can dilute the electrolyte this will increase the resistance and lower the voltage and amperage, and the etch will take longer, and be of a lower intensity. If you change the electrolyte concentration, then you will have to recalibrate it.
- 3. You can use a different power supply like a rechargeable battery or a laboratory power supply with switchable output voltage. If you use a battery it is essential to have a control box with voltage and amperage displays.

the effect of voltage and amperage

As can be seen from the tables below, the voltage output at the electrodes is not the same as the voltage set on an unregulated power supply like a battery charger, a battery or produced by a solar photovoltaic array, but is reduced when the resistance of the plate is low, and is reduced still further by the addition of a resistance in series. In fact it is not *voltage* that is important, but *amperage* that determines the quality of bite. The ratio of voltage to amperage is constant for a given resistance and reducing the voltage reduces the amperage proportionally. If the time calculated to deep etch a plate at low voltage is considered too long it can be increased, and the amperage intensity per unit area will increase proportionally, but the type of resist will need to be more robust.

The tables below are examples and a guide to voltage and amperage at various switch settings, using an unregulated power supply like a battery charger. The first table is for a small needled plate, and the second, a plate with a large area of open bite. These represent the extremes in normal practice.

1 - Table of **voltages** and amperages for a needled copper plate 275 sq. cm. in 1:4 copper sulphate, with 6 cm between plate and grid.

Switch se	ettings	+ 5 ohm resistance	+12 VOİt bulb	current direct to
6 volts	low	1.1 x 0.7 (amps)	2.4 x 1.6	4.2 x 2.4
o voits	high	1.3 x 0.9	2.9 x 1.8	5.5 x 3.1

2 - Table of **voltages** and amperages for a large copper plate with 625 sq. cm. (100 sq. inches.) of exposed metal in 1:4 copper sulphate, with 6 cm between plate and grid.

Switch settings + 5 ohm resistance +12 volt halogen current direct

6 volts	low	0.5 , 0.7	1.3 , 1.8	3.8 , 4.2
	high	0.6, 0.9	1.6 , 2.2	4.5 , 5.5

The use of a very low amperage and voltage is advisable only if one is using a fragile resist on a very small plate. After a little experience the voltage required to produce an acceptable amperage for a given plate size and treatment can be found and noted. For practical purposes most useful electrolytic action from a printmaker's point of view takes place in the range of about 5 amps down to 0.5 amp, and a creative printmaker must use the level that is appropriate to her/his work:

low (0.5 - 2 amps) for special purposes: turpentine-based soft ground and other greasy fragile resists;

medium (2 - 5 amps) for most purposes: galv-tone, etching lines in hard ground, aquatint, ink ground or fractint;

high (5 - 10 amps) for deeply bitten sculptural or textural effects or to create relief, viscosity or embossing printing plates using very strong resists, or for galvanoplasty or plating.

It is always a good idea to start with a very short bite and take out the plate, rinse it and examine it carefully with a magnifying glass for pinholes or scratches which should show clear and bright in a dark ground. The galv-etch process is unforgiving about carelessly grounded or ill-treated plates. Stop any faults and then continue with the process. If a ground shows signs of breaking down, then lower the amperage by turning down the voltage, or increasing the resistance of the system.

A time-switch is a very useful accessory - There are a large variety of simple off-the-shelf mains electronic time-switches which can be quickly set to cut the power supply to the battery charger after the set time.

galv-etching very large plates

If the size of plate overloads the power supply, the safest solution is to lower the voltage by switching to a lower setting or if you are using an unregulated supply like a battery charger, include a 12 volt, 50 watt halogen lamp in series in the circuit, or make up the control box described on page 24, and accept that the time taken will be much longer.

If the nature of your image allows you to work on smaller areas of a large plate at a time, then the **galv-on** semi-dry method will provide a simple solution without needing a heavy duty power supply.

If you are working with very large areas of open bite for relief or viscosity printing, and where you do not want the galv-etch to take a very long time by reducing the voltage and amperage considerably as previously described, you may have to have a very heavy duty power supply with a capacity of 20 ampères or more, with a very strong resist over unetched areas.

If your plate is very large overall, it is more practical to use a deep horizontal tray with a grid cathode. But the grid cathode frame must be made of metal heavy enough to prevent it from sagging in the middle, and joints should be mechanical rather than soldered - that is, passed through holes in the frame and bent to hold. The electrolyte may have to be further diluted to increase the resistance and keep the load on the supply within limits.

If you intend to etch very large plates read the section on **safety precautions** first.

Etching times with mixed metals and electrolytes

If all the metals in the solution, in the plate (anode) and in the grid (cathode) are the same, then the chemical electrolyte will remain the same, and can be used time after time, and the time calculated for etching will remain the same.

But if for example copper is etched in another metal solution, say in sodium chloride (salt), or in any non-copper salt (like zinc sulphate) then there are quite different reactions, some of which may be dangerous (see dangers of etching in brine or salt solution below). As the solution changes, the time required will change, and become unpredictable. Worse still the solution may become a toxic brew of different metal salts, and the cathode may become plated with a different metal.

So do not experiment with etching in anything but the solutions recommended, and above all, do not galv'etch in salt solution.



An electronic timer unit to control the mains electricity supply to the power supply unit (battery charger or other) with digital display and setting buttons on an extension lead.

Example of open bite producing graded galv-tone on a copper plate - at each stage the polarity was reversed to darken the tone



"Brantôme reflections" Proof from galv-toned zinc plate, printed intaglio 33 x 33 cms

special effects

One of the features of the way galv-etch works is that it is sensitive to the surface it is biting - edges are bitten more quickly than flat planes, and irregularities like lines, texture, are enhanced, rather than etched out. So an area of open bite will be slightly deeper at the edges up against the stopout varnish or ground. Any lines in an area of open bite are retained, although broadened progressively. Any texture, even the grain of the metal, and any oxidized area, is enhanced to give a fine grained matte surface which prints as a very fine tone. I call it galv-tone, because it is like a deep even plate tone. So the tones in any print can be subtly darkened, simply by stopping out and giving a very short galv-etch. A plate open bitten in stages after progressive stopping out will show a gradation of tones, the edges of which will be clearly defined by a line - the change of level. The tone at any level can be darkened by reversing the terminals for a time, which will deposit metal back onto the developing texture and around the edges of any ground or varnish. This amplifies the crystalline effect of the bite and softens the hard lines around the areas of tone. The longer the time given to the reverse 'galv-plating' stage, the darker the tone, which will resemble the effect of 'carborundum'.

A deep galv-plated area can be burnished or scraped and treated like a mezzo-tint. But it cannot produce the very deep blacks that are the attraction of real mezzotint. See later section on galvanoplasty for more on mezzotint.

Zinc plates give a greater range of galv-tone than copper or steel. A series of overlapping areas of very shallow open bite will progressively darken the overlaps more noticeably than successively deeper layers. On copper, the galv-tone seems to be slightly darker if a very low voltage and current is used. The tone can be made even darker by allowing the electrolyte to dry and crystallize on the open bite area and leaving it to oxidize for a while before continuing with the open bite. After the first galv-tone, you can draw over the matte finish with wax crayon or lithographic pencil, which will resist further action and show up as lighter lines or shading.

The quickest and easiest way of producing a deep tone is to use the **galv-on** semi-dry method, or salt tint . The texture in the tonal area will depend on the absorbent material soaked in electrolyte that is in direct contact with the plate.

Don't try to galv-etch zinc, steel or aluminium plates or electrodes in copper sulphate, because zinc tends to precipitate copper ions from the solution and weaken it (see *the chemistry of Bordeaux Etch*).

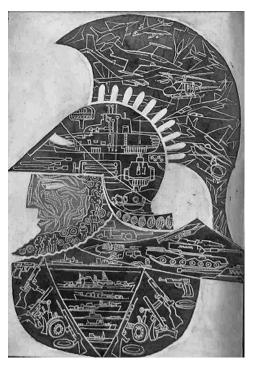
galvanoplasty or galv-plating

If instead of biting into a needled grounded plate, you reverse the terminals and make your plate the cathode, metal will be deposited into the lines, and built up in relief. If the projection is very fine, no more than one would get with a drypoint burr, then the plate will print rather like a drypoint, only last longer because the projecting metal is less fragile than a burr. But more interesting to me than just reproducing the effect of a traditional method, is the completely original effect of applying an open bite over a plate with strong relief lines either produced as described above, or by drawing lines onto a bare plate through carbon paper. The results are unique to this process, and give a print with very subtle tones and grain, in which the raised lines act like a burr in the tonal areas, and if they are lightly burnished, print as white lines, an effect quite unobtainable in traditional intaglio printing.

The voltage and current need to be low, and the lines very clean, so it is essential to thoroughly degrease the plate. A way to clean lines is to galv-etch the lines first very slightly, before reversing the terminals, which establishes an electrically 'clean' line in which to deposit metal. But if the line is deep, then the burr' will be doubled, building up on both edges of every line, a phenomenon that can be exploited for expressive effect. It is also possible to prepare a complete copper plate for mezzotint by first etching it all over lightly, and then depositing copper back over the whole plate. So, after the etching phase, without taking the plate out of the solution, just reverse the terminals and galv-plate it until the surface is rough enough to print black. It is best done in a vertical tank with a concentrated solution, at a low voltage for a long time, with a solid copper plate as the other electrode.

Another way of using relief is in the way galvanoplasty was originally used, by creating a new plate by depositing copper over three-dimensional modelled relief made with wax, glue, card, tissue paper, or any other means from which you couldn't normally print. The relief is then brushed with a liquid silicone wax and coated with graphite which provides an electrically conducting layer, and connected to the cathode (-ve) and 'plated' with copper. Then the new plate, which is the negative of the original relief, is backed with a filler of epoxy resin (often sold as 'liquid metal') to stop it being flattened in the press, and then is parted from it. It can be printed in relief, intaglio or a combination, using different viscosity inks (see section on proofing). If you want to reproduce the relief of the original plate rather as a positive, then you will have to make a mould of your original with wax, plaster of paris or similar moulding material, which can be coated with graphite before depositing the metal. Before making the mould, the original should be dusted with French chalk or any substitute (not containing asbestos) to aid separation. Then dust the graphite powder onto it with a brush. If it does not stick, try breathing on the mould to make it slightly humid and then the graphite should stick to most materials. If that does not work on some materials try a very thin coating of liquid silicone furniture wax before brushing on the graphite.

The copper 'electrotype' produced is capable of reproducing the finest detail and even brush strokes of varnish or of silicone wax will show when proofed as an intaglio. If a silver-plated sheet of copper is painted with layers of thick varnish which dries to a slightly rough textured surface, prepared as described above, then a negative electrotype of it will reproduce it quite closely, the proof showing darker tones where the varnish is thickest. This is the technique described in the nineteenth century as 'Electro-tint' (7)



« Ares » print in Atlantis series with relief lines and galv-tone open bite



Proof of small deeply sculpted plate produced by galvanoplasty - proofed intaglio and overprinted in relief.

Equipment and tools for casting small copper objects – 10 amp power supply, small tank with bar to hang moulds, wax, modelling tools, graphite powder, copper and brass wire, small wax moulds ready for modelling



Tools for modelling wax mould – various linocutting, wood cutting and scraping knives.; square mould with copper ring setin beeswax



cold casting copper

The following illustrations and description shows the process, step by step, of making small objects like pendants, medallions or badges that will be of interest to jewellers, enamellers and other metal workers. I suggest that printmakers thinking of using the process to make larger printing plates should start on a small scale like this before taking the plunge.

The first step is to make a blank beeswax slab which can be sculpted into a negative of the object to be cast. The depth should be enough for the relief required. Melt beeswax and pour it into a shallow non metal tray which can be formed out of card or thick paper. While the wax is still soft, press a ring of copper wire into it to form the electrical contact and edges of the object. The wire ring should have a projecting piece long enough to suspend it into the electrolyte. Later the wire ring can be cut off if required, or incorporated into the object.

Next, when the wax has hardened, sculpt the design using whatever tools will suit the forms and textures you want. An alternative is, while the wax is still soft, you can press metal or other hard objects into the wax to make a mould that will reproduce the original object.

Then dust the surface of the wax mould with graphite powder and brush it into all the hollows and crevices with a soft brush. Make sure the copper ring has not sunk below the level of the wax scrape any wax off all round so that the graphite is everywhere in contact with the ring.

Hang the mould in a tank of concentrated copper sulphate electrolyte, by turning over the projecting end of the wire to hang over the edge. A number of moulds can be plated at the same time by hanging them all on a thick metal bar across the tank. Make an anode by taping 2 thick copper strips to the back of a clean copper plate. Bend the strips to hang the anode over the edge of the tank facing the moulds. Varnish the part of the strips in the electrolyte, to prevent them being etched away.

Connect the negative (black) crocodile clip from the power supply to the wire of the mould, or to the bar suspending a number of moulds. Connect the positive (red) wire of the power supply to the anode plate. Turn on the power supply, and select a low amperage, by regulating the voltage. If the amperage is too high, the temperature at the point of plating may be too high and the wax may melt and distort. If you have used the galv-etch process with a traditional soft ground, you will know how low the amperage and voltage must be. I recommend starting with less than 1 volt and 2 amps in a trial. The time required to build up sufficient thickness may be as much as 12 hours at a low voltage.

Left - wax mould ready to deposit copper by galvanoplasty, to create a pendant.

Right – finished pendant

Here wax is poured into a shallow paper tray, onto which a copper wire ring is pressed, then the design is carved with linocutting tools, brushed with silicone wax, and coated with powdered graphite.



Alternatively the mould can be made of some other modelling material that hardens sufficiently to resist melting, like plaster of paris or modelling clay that can be hardened in an oven. In that case the amperage and voltage can be as high as the power supply can provide, for a shorter time to build up the thickness. The only limitation is that the design can have no undercutting that makes it difficult to remove the mould.

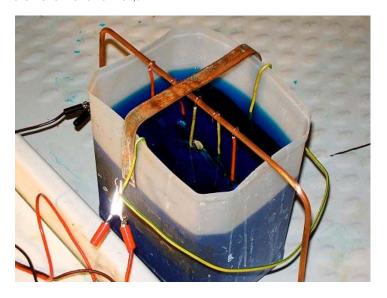
Enamellers can use this method as an alternative to 'champlevé' or 'cloisonné' by engraving shallow lines in a thin sheet of wax poured on a copper plate. The result is a cast flat sheet of copper with raised lines, in between which the enamel can be fired.

After sufficient depth has been deposited, the mould should be easy to remove, and possibly be reusable for another cast. The contact wire will have a knobbly fringe of copper that can be cut off or filed off, or even left as a part of the object.

The back of the cast may be very rough , depending on the thickness of the copper. It can be left as a feature, and protected by an transparent enamel or varnish. An alternative is to back the object with epoxy resin with a copper powder filler. Another option, which I used, is to back it with a hard wax with a smooth surface, graphite it, and plate it with a very thin layer of copper (protecting the front with a varnish).



Group of moulds ready for plating



Plating tank with a number of moulds hanging from copper bar – note positive (red) clip to anope plate and negative(black) clip to bar



A group of copper pendants

Precautions in using galv-etch

A special warning is added here about using salt solution (brine) as an electrolyte because a number of books and recent websites have suggested using salt or adding salt to electrolytes. Using brine as an electrolyte generates chlorine gas, hydrogen gas, and produces caustic soda. Different toxic chemicals are produced when etching metals like zinc, aluminium, and steel. Free copper deposit produced by etching zinc plates in saline sulphate etch forms a 'shortcircuited zinc copper couple' which generates a current and produces chlorine, hydrogen and caustic soda. Free chlorine and hydrogen gas in a confined space like a covered etching tray can form an explosive mixture. If the chlorine gas is not channelled and collected, but mixes freely with the caustic soda, then sodium chlorate is produced. Sodium chlorate is a very toxic chemical banned since 2008 in the European Union where it was used as a powerful weed killer. (see the links page for the websites giving further information about the processes of electrolysis brine)

The area where you do galv-etch should be free of solvent fumes of any kind (as the whole working space should be). Make sure all your electrical connections from power supply to the mains are correctly made and that the whole system is protected by a mains switch which is easily accessible. If you are using a time switch on the mains input, it should be switched on the input.

On the low voltage direct current output from the power supply (battery charger) you will usually find a pair of large crocodile clips, the positive on a red wire, negative on a black wire. While the system is not in use clip these both to an insulating strip of plastic or card so that they cannot touch accidentally.

When you are preparing to start a galv-etch, put the plate on its back plate contact or cradle, and place the grid or plate/strip cathode into the electrolyte and make all the connections before switching on. Do not make or unclip any connection while the current is flowing or you may create a spark - if you have to stop the etch quickly, turn off at the mains switch or switch from the battery.

Take great care using a flat tray with a grid cathode, and do not try to control the current by lowering the grid into the electrolyte. If you are using a vertical tank and lowering the cathode into the electrolyte to control the resistance, start off with it just touching the surface and clipped to the side, switch on and then unclip it, lowering it slowly while watching the ammeter, and reclip it when the right level is reached. To avoid an uneven depth of etch, check that the immersed part of the cathode is opposite the centre of the plate.

If the power supply is overloaded, switch off quickly and first check that you don't have a short circuit somewhere - a plate bar strap touching a grid support for instance. If not, use a diluted electrolyte, a different power supply like a rechargeable battery or solar cell array, or include a resistance like a 12 volt lamp in series in the circuit, or a control box as shown in **Equipment.** Note that adding a resistance reduces the voltage and produces a more gentle galv-etch that takes much longer.

If you use a lead acid rechargeable battery (6 volt motor cycle battery) you must have very heavy duty connecting wires - I recommend car jump leads to be on the safe side. Wire a mains switch into the positive (red) lead. Galvanoplasty or galv-plating puts a much heavier load on the power supply, partly because the cathode - this time the plate on which you will be depositing metal (-ve) - will probably have a large conducting surface, and if so, the anode (+ve) must be a plate and not a grid.

If the rate of etch seems too fast or vigorous, include a resistance like a 12 volt halogen lamp **in series** in the circuit, or make up and use the control box (shown in **Equipment**) with a 12 volt 50 watt lamp, and a 50 watt, 5 ohm variable resistance, a 2-way switch, and voltmeter and ammeter, which can be used to regulate the amperage and voltage output from the battery or other unregulated power supply. Note that when this control box is used it reduces the voltage and the amperage, and in consequence a longer time is required for the galvetch, which may be necessary if you are using traditional soft ground or producing textures by pressing oily materials onto a bare plate.

At any time that your hands might be in contact with the electrolyte, wear thin waterproof gloves because the sulphate solutions are slightly acidic, and in particular with zinc sulphate, take care to avoid any contact with skin or eyes, and keep all the solutions out of the reach of children Store it in a safe place, well labelled to avoid anyone having an accident or drinking it, as it is a clear liquid. No special precautions are required for copper sulphate, except perhaps wearing gloves to protect the skin from drying out and staining blue.

Before lifting a grid cathode or the etched plate out of the galv-etch tray, make sure the current is off - cut by the timeswitch or off at the mains. If using a battery charger or mains rectified power supply, when you have finished work, switch off the mains supply to the unit. If you are using a battery, remove the leads from the terminals of the battery.

BORDEAUX ETCH

etching safely with copper sulphate

There is a safe way of etching zinc plates and also steel and aluminium plates that is electrochemical rather than electrolytic, and will satisfy those who want a single solution which is inexpensive and easily obtainable. That is to use a pure **concentrated** solution of *copper sulphate*.

For etching mild steel plates I have found that adding an equal quantity of sodium chloride (common salt) solution is more effective than pure copper sulphate, which has a tendency to 'plate' the steel and stop the etch. This mixture of salt and copper sulphate will also etch aluminium with the addition of sodium bisulphate - a weak acid - as has been shown by Nik Semenoff (16). I prefer to keep the mixture as simple as possible and avoid the addition of salt or any acid.

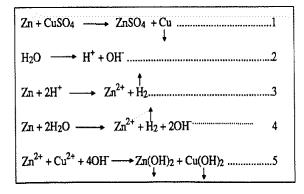
I have called this **Bordeaux Etch**, because a copper sulphate solution is better known to vine growers, farmers and gardeners as Bordeaux mixture (Bouillie Bordelaise), very widely used as a spray against mildew. The solution is very much safer to handle than ferric chloride, although gloves should be worn to avoid skin contact because it is very slightly acidic and will stain fingers blue. Add the copper sulphate to distilled water until you have a saturated solution - when no more will dissolve. Approximately 250 grams of copper sulphate will dissolve in 1 litre of water. When a zinc plate is etched in the concentrated solution an insoluble deposit of copper is produced which is very easy to remove by brushing with a feather or a large soft brush in a flat tray. The other advantage is that the initially blue solution remains quite transparent, and turns paler as it is exhausted, and the progress of the etch can be very easily seen in a tray by the formation of the deposit. For etching steel, add an equal volume of sodium chloride made up of 250 gms. of salt added to 1 litre of distilled water



'Hauterives - Gorges de Tarn' - Zinc plate etched in Bordeaux Etch, then Fractinted and etched again in 4 steps . Proofed in 3 colours from same plate by method described later.

the chemistry of Bordeaux etch

The chemical process involved is basically very simple. Zinc has a much higher electrode potential (Zn^{2+} = -0.76) than copper (Cu^{2+} = +0.34), and as a result it displaces copper ions from the copper sulphate solution ($CuSO_4$), and the zinc ions combine with the sulphate (SO_4) ions to form zinc sulphate ($ZnSO_4$). If the copper deposit remains in contact with the zinc there could be a side reaction - the metals in contact in a slightly acidic copper sulphate solution form a short-circuited galvanic cell called a zinc-copper couple - producing a very small quantity of hydrogen and thus



making the solution less acidic (more alkaline). As the alkalinity builds up so that the pH goes above 7 there will be a reaction with the zinc and copper ions to give an additional precipitate of zinc and copper hydroxide. This side reaction can be exploited to create a texture over areas of open bite. But normally it is a good idea to brush away the deposit as it is formed which results in a more even bite and prolongs the life of the solution. There is usually a fine layer of black hydroxide adhering to the etched open areas which can be washed off, or comes off with the first proofs. Then the etched areas have a fine crystalline texture, similar to galv-tone, which helps to hold ink.

Dangers of using salt solution

Some sites and books have recently suggested adding salt to copper sulphate to create 'Saline sulphate etch', which you may think can be used in the Galv-On process on zinc, or by mistake used to etch copper electrolytically. But there are dangers in using salt or sodium chloride in solution, either added to copper sulphate or by itself. Using brine as an electrolyte generates chlorine gas, hydrogen gas, and produces caustic soda. Different toxic chemicals are produced when etching metals like zinc, aluminium, and steel. Free copper deposit produced by etching zinc plates in saline sulphate etch, forms a 'short-circuited zinc copper couple' which may generate enough current to produce chlorine, hydrogen and caustic soda. Free chlorine and hydrogen gas in a confined space like a covered etching tray can form an explosive mixture. If the chlorine gas is not channelled and collected, but mixes freely with the caustic soda, then sodium chlorate is produced. Sodium chlorate is a very toxic chemical banned since 2008 in the European Union where it was used as a powerful weed killer. (see the links page for the websites giving further information about the processes of electrolysis of

the dangers of ferric chloride with zinc

Zinc plates are now very widely used by printmakers who are not concerned with trying to make huge editions, or who deep-etch plates for viscosity printing or embossing effects. Zinc is very much less expensive than copper and can be bought from building materials suppliers in large sheets, and are easy to polish. Students learning printmaking use zinc plates a great deal, and they can be bought ready polished and backed with a resistant coating.

Many printmakers believe that using ferric chloride (FeCl₃) is a completely safe alternative to using acid. This is only partly true for copper plates, where the products of the chemical process are a deposit of cupric chloride and a solution of ferrous chloride. But ferric chloride is a strongly acidic chemical, very unpleasant to use and gloves, vapour mask and good ventilation are required (14).

But etching *zinc* plates in ferric chloride is a different matter altogether, and the process gives off bubbles of hydrogen gas which is explosive in air, produces a deposit of iron, which forms a crust over the etched surfaces, and the spent solution contains zinc chloride which is more corrosive than ferric chloride. The bubbles of hydrogen require removal with a feather to prevent an uneven bite and the iron crust is abrasive and the process of removing it

damages the edges of the needled ground or a sensitive aquatint. When a deep bite is required over large areas of exposed metal, the chemical reaction heats the solution and gives off an extremely corrosive vapour of hydrochloric acid, carried up by the hydrogen.

As any experienced printmaker knows, having to brush away bubbles and the deposit means bending over the etching tray, exposed to the vapours or gas given off, and wearing goggles, and vapour mask is uncomfortable and inhibiting. Vertical tanks are unusable in these conditions. As the solution becomes weaker ferric hydroxide is deposited and darkens it, and zinc displaces ferric ions in the solution forming the iron crust which becomes harder and harder to remove and the solution then is a mixture of unused ferric chloride and zinc chloride, which is more corrosive than the original and is very difficult to render safe for disposal. The chemical reactions are described in detail in the equations below.

A development that alleviates the unpleasantness of ferric chloride is Edinburgh Etch developed by Friedhard Kiekeben, which involves adding citric acid which speeds up the bite, and dissolves the sediment (15). But it is still an acid and many the objections of its use with zinc still apply, and my personal preference is to avoid the use of all acids.

disposal of used Bordeaux etch

As the spent Bordeaux etch solution becomes too weak to use, it is a mixture of unused copper sulphate and zinc sulphate. As previously mentioned, zinc sulphate is slightly less safe to handle than copper sulphate, so avoid direct contact with the skin and eyes, and keep out of the reach of children.

Disposal can be done in two ways depending on whether you have added salt to the solution. If you have not, it will be possible to filter and save the spent solution to use as the electrolyte for galv-etching zinc plates. There will always be a little copper sulphate in the solution and the bare plate will be blackened instantly on putting it into the solution, which does not happen with pure zinc sulphate. If you have too large a quantity of spent Bordeaux etch solution, then it must not be put down the drain because of the zinc sulphate and the residual copper sulphate left in it.

To make it safe for disposal, you can add sodium carbonate (washing soda) or sodium hydroxide to it to neutralize it, until the pH value goes up to between 7.0 and 8.0, testing it with indicator paper. Copper and zinc hydroxide will be deposited as a sludge. Allow the sludge to settle, pour off the liquid, further dilute it and then it can be poured down the drain. Collect the sludge in plastic bags and dispose of it as required by your local authority. When neutralizing it, be careful not to allow it to become too alkaline because the hydroxides will be redissolved. If you do not have much solution to get rid of, it can be placed to evaporate in a flat tray. Collect the crystals, bag them and dispose of them safely.

If you are galv-etching copper plates as well as using Bordeaux etch, then keep the dilute copper sulphate used for that completely separate from the concentrated Bordeaux etch solution, in well marked containers. It is not dangerous to use the wrong one, but a diluted galv-etch copper sulphate will not etch zinc satisfactorily, and a partly spent Bordeaux etch solution, used electrolytically, will deposit zinc on your cathode.

"Forgeron" 22 x 33 cm. Created using the passive galv-on process - layers of cut-out pieces of paper and cloth

PASSIVE GALV-ON

Galv-etching without electricity

One of the slightly irritating things about Bordeaux etch and its variants, is the precipitate produced that must be brushed away and can clog the lines and that requires regular filtering of the solution. Galv-etch or powered electrolytic processes have the advantage that no precipitate is produced, but it seems that a few etchers are inhibited or intimidated by the idea of having to buy electrical equipment. But there is a way of using Bordeaux etch "electrolytically which dispenses with the need for an external source of power like a battery charger, or other power source - a "passive" electrolytic process which generates its own electricity.

An obvious way of eliminating the precipitate in Bordeaux etch is electrolytic, by having a small direct current passing through the solution to carry away the copper ions and deposit them on a copper plate. The earliest batteries invented in the early 19th century consisted of a zinc plate and a copper plate in an acidic copper sulphate solution and the early experiments in electrotyping – depositing copper on the cathode – were done in the battery itself. Thomas Spencer and John Wilson who were granted a patent in 1840 for "Engraving Metals by means of Voltaic Electricity", mention the possibility of two dissimilar metals in a suitable solution not needing to be connected to an external 'voltaic' battery .

So, to create your self-etching "battery" lay a copper plate in the bottom of the etching tray with a copper strip taped to the back and sticking out of the Bordeaux etch solution, then tape a copper strip to a bared area on the back of the zinc plate to be etched and connect it to the other copper strip, and lay the plate face down supported a centimetre away from the copper plate and leave it to etch. When you have given it about the same time as you would in a **concentrated** Bordeaux Etch solution take it out, and there will be little or no precipitate and the plate will be etched perfectly, showing all the characteristics of a plate etched electrolytically. If you put a multimeter across the terminals it will show a voltage of about half a volt – not a lot, but a sufficient flow of electricity to carry the copper ions away. In addition to the zinc plate being etched, the copper is 'plated', if it was very clean, or will have the precipitate collected on it.

the passive galv-on procedure

But there is another much more interesting reason to use this 'passive' galv-etching process, and that is that it can be used in the Galv-On semi-dry process that I have already described. The Galv-On process is best used electrolytically, because any precipitate that is produced has a tendency to be drawn away from the lines or surface being etched, and it does not stay to clog the etched areas. But one of the problems of using a 'powered' electrolytic process is that the thin sandwich between the plates offers such a low electrical resistance that for large etched areas, a powerful and expensive direct current source is needed, or else the amperage has to be reduced so much that the time taken is far too long, with the practical consequence that it is a method suited only to small plates. But if you do not have a powerful supply, and wish to etch large zinc plate areas, the 'passive' procedure is the solution.

The initial procedure is as already described for Galv-On. The zinc plate is prepared, and the layers forming the design are backed with felt soaked soaked in strong Bordeaux etch (copper sulphate). The sandwich is finished with a flat copper plate connected by a copper strip to the zinc plate. The small distance between the plates is a positive advantage and a current is generated, carrying away all the

precipitate. All the effects possible with the 'powered' galv-on process are possible and there is no limit to the size of plate that can be etched. The time taken does not increase with larger plates, as it does with the 'powered' process, as the current automatically increases with the size of the plates.

The electricity generated results from the difference in what is called the 'electrode potential' between zinc and copper, and closing the circuit between the plates allows a current to flow, 'pushed' by the flow of positively charged copper ions up towards the copper or negative cathode, displaced from the solution by the zinc. The felt can be squeezed out, the Bordeaux etch filtered and used again. The disadvantage is that it becomes exhausted as its copper is gradually replaced by zinc, and it must be disposed of safely (see above).

For those willing to tangle with a powered electrolytic process the advantage is that the electrolyte can be used for years, and one is not limited to etching zinc, steel or aluminium.

For existing users of Bordeaux etch or its variants like 'saline sulphate etch', I expect it will be good news to be able to eliminate annoying precipitates and to be able to use the galv-on semi-dry method, without having to invest in electrical equipment, special etching tanks, and grapple with the mysteries of voltage, amperage and calculations of the time required based on plate area. For many courses and studios that have to provide facilities for numbers of students at a time, the passive galv-etch and galv-on processes should be a welcome development.

Plate with black printing ink ground



Below – needled fine lines show very clearly on a black ink ground on a zinc sheet. Traditional hard ground must be smoked to have the same contrast.

GROUNDING WITHOUT WAX

Relief printing ink ground

The reasons for not using a ground of melted wax and asphaltum are not just health, but because the substitute - linseed-oil based relief printing ink - is so versatile that it can replace hard ground, soft ground and aquatint, **if you are galv-etching the plate**. Ink ground can produce effects impossible with the traditional grounding methods, but cannot be used with traditional mordants. The reason is that an oily ink ground in acid (even weak ferric chloride or vinegar) is lifted off or broken down, lines are widened, and there is often foul-biting, whereas with galv-etch, the oily ink film electrically 'insulates' the plate and the biting proceeds only in uninsulated areas. The way galv-etch works without clogging fine lines or texture with bubbles, precipitate or a crust, means a completely clean bite, without any need for attention to it, except to check periodically for pinholes or depth of bite. Acrylic ink grounds do not seem to work well with electrolytic processes.

Ink hard ground

I use linseed oil based black ink thinned a little if necessary, with raw linseed oil, and a few drops of cobalt dryers to speed up hardening, rolled onto the cleaned plate with a soft rubber or treothene roller. The exact viscosity of the ink must be judged from experience, but I have found that the viscosity and thickness on a plate that prints well in relief is right for a ground. I sometimes use white ink for fractint or salt tint on copper plates, or other colours to be able to see a design already etched or transferred through carbon paper.

When it is completely dry to the touch it can be needled with all the usual tools, and generally treated as you would a traditional ground. It is more resistant to accidental scratches and can be drawn on with spirit-based felt pens. Designs can be transferred by drawing through carbon paper. White transfer paper is obtainable for a black ground

Ink ground can be cleaned before it has hardened with vegetable oil, or VCA (see vegetable cleaning agent later) but as soon as it has dried enough to needle, it can be cleaned off with ethanol (95% industrial ethyl alcohol), followed by cream non-abrasive bath cleaner. An alternative to using Cobalt driers is to dry the plate in the sun, which seems to produce a better ground in the end.

If there is no sun, dry the plate on an electric warming plate. If the plate is too hot, and the plate is left on it for too long it, can become baked enamel, and might be hard to needle. To take off the ink ground then immerse it in a tray of vinegar for half an hour, and the ground will float off,

Another advantage of ink ground is that you can work on the plate out-of-doors, and full sunlight will not melt the ground and reseal the lines, which happens so easily with traditional wax grounds.

soft ground

A insulating ink ground behaves in some ways like a traditional soft ground before it has hardened, and if you draw through a thin textured paper over the inked plate, the etched plate will produce a result similar to a soft ground etching, except that the evenness of the ink ground, and the nature of the galv-etch bite will produce a much more sensitive impression, and a greater variety of responses to types of paper, hardness and shape of pencil etc.. Cobalt dryers should definitely not be used in the case of a soft ink ground, so you may have to wait longer for it to harden in the sun, or on a warm electric plate.

There are a great variety of effects that are possible with soft ink ground put through the press against different materials and objects. If the grounded plate is press against things like lace, plants, thin flat objects and left to dry, and then galv-etched, effects similar to traditional soft ground can be produced.

One of these effects is **Fractint**, described in the next section, where the grounded plate is pressed against a smooth plastic or other non-absorbent sheet.

Like traditional soft ground, ink soft ground also requires a low voltage and amperage with galv-etch, and so if you are using a 6/12 volt battery charger as your power supply, use the control box shown in equipment to switch to the lowest voltage possible.





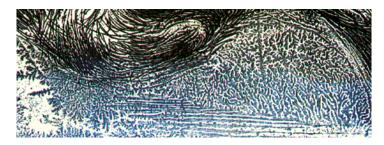
Magnified detail of proofed ink soft ground

Right « Hauterives » proof from plate needled lightly, etched, and then inked with white ink and put through the press against smooth absorbent paper, dried, selectively stopped and galvetched in stages

TINTING WITHOUT ROSIN

fractint, salt tint, and sugar lift tint

Magnified photograph of intaglio proof of fractint on copper plate - note the vertical line produced by fine scratch on plate

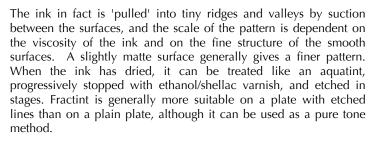


The first alternative to rosin or asphalt aquatint I call 'fractint' because of the textures produced which can resemble some computer generated fractal patterns. It relates closely to insulating ink ground in that it uses linseed oil-based relief printing ink which functions as an insulating layer.



Plate to be fractinted face down on plastic sheet on platen of etching press with card strips to lift the roller to prevent the plate from being pushed along the sheet of plastic.

After applying a thin even coat of ink to the plate with a roller, before it is dry, place it face-down against a flat smooth non-absorbent surface like a polished metal plate or a rigid plastic sheet, and then put it through the press taking care not to let it slip against the surface. This can be done by laying strips of card slightly thicker than the plate on either side, projecting towards the roller to lift it to the level of the plate edge. Then the plate is pulled carefully off the surface, and the ink will be found to have formed a fine complex branching organic pattern which fills the spaces between any previous lines or lowered areas.



Fractint is very sensitive to specks of dirt, hairs, and bits of skin in the ink and produces patterns around any 'impurities' on the plate or plastic sheet. Often these are interesting and can be incorporated, but to avoid them, the ink must be very smooth, without lumps, and the plate, plastic sheet, inking slab, and rollers should be wiped clean before starting. But these accidental effects can be enhanced by allowing a very fine grained powder to settle on the inked plate much finer than the rosin in an aquatint box.



Detail of print from plate fractinted all over and stopped and etched in stages.

salt tint

The second method using ink ground, is an adaptation of salt tint, which has been used before with traditional grounds, but which, when used with an ink ground, has the advantage over fractint of very closely resembling resin aquatint. But this use of it also has the advantage of not requiring an expensive aquatint box or needing to be heated to melt it onto the plate (the fumes from heated resin are as damaging as turpentine fumes).

First the plate is grounded with ink as for needling or as for fractint, but without cobalt dryers. The ink ground should be as even and thin as possible. Then the plate is laid face up onto a sheet of paper or card larger than the plate. While the ink is still wet, a layer of fine salt is sieved all over the plate, until it is even all over. It does not matter if it ends up quite thick. The salt may need to be ground in a pestle and mortar if comes out of the packet too coarse. You may have to make a special sieve (as illustrated) with a finer mesh than the average domestic sieve.

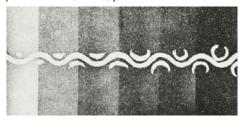
Lift the plate and card carefully and transfer it onto the bed of the etching press. Lay another sheet of thick paper over it all. Back the sandwich with a thick felt blanket, and roll it through the press. The salt lying on the ink ground will be pressed through to the bare plate, displacing the ink and forming a finely reticulated pattern which closely resembles a resin aquatint.

After the ink has completely dried, perhaps accelerated by putting it in the sun, or on a hot plate, shake off the excess salt, and lay it in a tray of warm water to dissolve the salt.

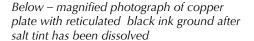
The plate can then be stopped out exactly as if it is a resin aquatint, and galv-etched or if it is a zinc, aluminium or steel plate, etched in Bordeaux etch.



Equipment needed for salt tint – ink grounded plate on card, sieve, pestle and mortar, salt



Print of copper test plate with salt tint, stopped and galv-etched, in 6 steps of 20 minutes each at 1volt







Lrft - Small print from salt tinted and galvetched copper plate

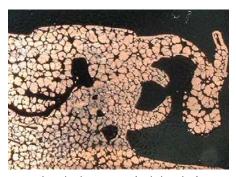
Above – small copper test plate after sugar lift tinting and stopping in 7 steps of about 15 minutes at 1 volt.

Below - intaglio proof of plate above





Sugar lift on copper showing reticulation of black ink, before etching.



Reticulated ink in magnified detail of sugar lift tint on copper plate above .

sugar lift tint

Traditionally, sugar lift has to be given a grain by aquatinting it so that it prints dark in intaglio. But the combination of ink ground with sugar lift can be used to advantage to produce a texture without the separate step of aquatint, and will provide a 'tooth' to hold the ink within the sugar lift area, in a one-step process. Sugar lift is used because it is a positive process - that is, if the plate is to be proofed in intaglio, what you see is what you get.

The way that this is done is as follows: Prepare a saturated solution of sugar dissolved in distilled or demineralised water, add a few drops of black Indian Ink to colour it, and a drop of washing up liquid or liquid soap to help it to stick to the plate.

Apply the sugar lift solution to a degreased plate with a brush, as evenly as possible, to those areas to print as a tone. Allow it to dry a little, hastening it if required with a hair dryer, until it is tacky. Then carefully blot the whole plate or the areas you want to print with a tone with a sheet of tissue paper. Smooth the tissue paper down over the areas of sugar lift until you can see the sugar lift through the tissue paper. With practice you can judge how to vary the final effect by varying how hard you press the tissue against the sugar lift, or the number of times you repeat the blotting process. Peel off the tissue paper and discard it. The tacky sugar lift areas should be matte instead of glossy.

Let the sugar lift dry further, If is has dried too much and does not feel slightly tacky, breathe on it to make the suger absorb the moisture of your breath, until it feels tacky again. Then apply the ink ground with a soft roller, pressing the ink hard into the sugar lift, to squeeze it through the pores created in the film of sugar, and to press the ink in around the edges of the areas of sugar solution. The oily ink will draw away from the slightly damp sugar lift areas as it dries and the texture created should be visible as a fine network of lines of ink. How fine the texture is depends on how tacky the sugar was when the ink was rolled over it. The drier is is, the finer the texture.

After the ink has completely dried, perhaps accelerated by putting it in the sun, or on a hot plate, lay the plate face up in a tray of water and the sugar will dissolve. It should all come off without having to use a brush over the surface. Let it dry completely without blotting it or wiping it, and it will be ready to etch. A variety of textures and of degrees of granularity can be produced with experience. The secret is not to remove too much of the sugar lift by being too impatient and blotting it too soon. The ink should be allowed to dry properly before putting it in water and etching it.

galv-etching fractint

Galv-etch and Bordeaux etch work particularly well with fractint, salt tint and sugarlift tint because of the tendency to bite vertically and not to eat away at the edges as much as acids do. The first stage must usually be longer to break through the very thin film of oil left in the valleys betweeen the dots of ink resist. With each successive stage, the valleys are deepened and become slightly wider. After cleaning the plate with ethanol, and proofing it, if the results in some parts of the image seem too light or too coarse, a second fractint will fill the spaces with an even finer pattern. Alternatively, areas can be darkened by galv-toning after stopping out. The effect of the open-bite over a previously galv-etched fractint is to darken it much more drastically than the effect on a bare plate.

Bordeaux etch works on fractinted zinc plates in a way very similar to galv-etch because it is an electrochemical reaction, not a corrosive action. But the copper deposit has a tendency to clog the finest lines and texture after an initial bite, which can be deliberately used to preserve fine lines.

special effects of fractint

The results have their own unique character, with many advantages over aquatint that can be exploited for expressive effect. One of the most interesting qualities of fractint is the way the pattern relates to lines already etched on the plate - they are integrated into the pattern in different ways depending on their depth and spacing. The pattern never crosses lines but 'grows' outwards from the line edges to fill the spaces between. The finest lines on the plate are respected in this way (unfortunately sometimes even scratches on the plate). Parallel lines are often doubled, that is, two parallel lines of ink are formed along the edges of the original lines and a new line is etched between them. Unprotected isolated lines are widened with a fine variable organic growth on either side. Fractint is not a technique for those who want mechanical evenly graded tones, for its results are often slightly unpredictable, and there is the opportunity for a creative response to the patterns formed around the lines already on the plate. Around the edges of the plate the fractint pattern changes, which can be used creatively and exploited for expressive effect. But to avoid this fringe effect, instead of using a rigid plastic plate to create the pattern, you can use a thinner and more flexible nonabsorbent smooth film like heavy polyethylene sheet, or tracing film. The way that the sheet is peeled off the plate has a very distinct effect on the nature of the pattern.

variations and refinements

Sometime I have used another polished plate in the press to produce the fractint pattern, then I have etched the second plate instead of the original, which mirrors the image, and produces a slightly more grainy tint. When the original plate is pressed against a smooth plastic sheet, enough ink is left on it to use to transfer to a second polished plate, which shows the original lines clearly, and after the ink is dry, can be stopped and galv-etched to provide another plate for colour. I often conceive, deep etch and print the additional colour plates in relief, inked up by roller, and printed in quick succession face down onto the redamped paper carrying the original intaglio impression.



"Casse noix" - etching and fractint using ink ground - zinc plate printed in intaglio and relief - 25 cms square

Below – detail of print above

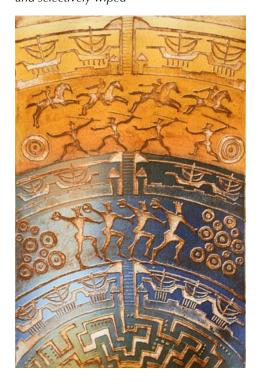




"Penne - Aveyron" - etching with fractint, 1 zinc plate 33 cms square, printed intaglio in 3 colours

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Detail of "Variations on a back" - 4 intaglio plates with fractinting, overprinted in relief in three colours from the same plates, inked with roller and selectively wiped



« Atlantis – fragment » deep etched zinc plate proofed intaglio in raw siena, and in relief in ultramarine and burnt umber 16x25 cm. This print shows the effect of slight offset in registration.

proofing galv-etched plates

Every printmaker has his own particular proofing tricks and methods, and in general plates produced by the methods described do not require any special methods. Etched lines and tint can be inked and wiped in the traditional way.

But I have found that galv-etched plates with significant areas of open bite, or produced by the galv-on process, require the use of particular techniques to get the best prints from them.

I mix my ink from medium plate oil and powder pigment as thickly as possible with the addition of a very small amount of lard or butter, and apply it on a slightly warmed hot plate (a domestic plate warmer with a thick flat copper plate on top) using either thick cards or a nylon spatula cut to form a precise edge to spread the ink thinly. As much surplus ink as possible is removed with cards or spatula, and then I hand-wipe the plate to leave the required tone in the galv-toned areas. I find that tarlatan leaves the plate too clean and lacking in the character produced by the techniques.

Over a long period I have evolved a method for printing in colour, that is slightly slower than using multiple plates, one for each colour. I use only one intaglio plate proofed initially in one colour, usually the darkest. Then, when the ink is dry, I redamp all the proofs, and, having cleaned the plate, I ink it selectively with a roller with coloured relief printing ink. I wipe the colour away from where I don't want it. I place the intaglio proof face up on the bed of the press, and lower the relief inked plate exactly over the image, and print it.

It is surprisingly easy to get the registration exactly right. If other colours are required. I quickly wipe the plate clean, roll it up with the next colour, wipe some areas clean, and repeat the process. All the time the paper stays face up on the press, and will not shrink. This method makes the printing much more of a creative process, and makes each print unique, a combination of intaglio base and relief monotype. The time saved by not having to make separate plates for each colour compensates for the slightly longer time in proofing.

This method is very effective for a single galv-etched plate with quite deep areas of open bite. If the registration of the relief layer over the intaglio layer is slightly offset by very little, then a white edge appears at the edges of the deep etched forms that heightens an effect of three dimensional relief.

CLEANING WITHOUT SOLVENTS

cleaning with cooking oil

For most of the uses for which one used to use naphtha (turpentine substitute, white spirit, etc.) - cleaning inked plates, tools, brushes, inking slabs, hands, or any surface covered with oil-based printing ink - the simplest substitute is a two part process - first use vegetable cooking oil, and then biodegradable domestic washing-up liquid. I use sunflower seed oil, or rape seed oil as it is inexpensive in France, but there are others that have the same effect and may be cheaper in other countries. Vegetable cleaning agent (VCA) can be used instead of the domestic detergent (see below).

The effect of the oil is to dissolve and thin the ink allowing it to be easily removed. To clean an inked plate, first pour a little pool of oil in the middle of the plate, and rub it all over with fingers, and if the plate has deeply bitten areas, use an old toothbrush, to get the oil well into the crevices. Leave it for ten minutes and then wipe off the dissolved ink. Repeat the process if necessary, before cleaning the oil off the plate with domestic detergent liquid, preferably biodegradable. The cloth or absorbent paper used to wipe the plate can be used to wipe palette knives, inking slabs and fingers. Rub clean oil into hands to remove ink residues, then wash with soap and water.

vegetable cleaning agent

There are sometimes occasions when very stiff ink, or slightly dried ink is difficult to completely remove, and that is when you can use Vegetable Cleaning Agent (VCA) to dissolve it.

Pour a very small amount in the middle of the plate and spread it with a plastic spatula and wear gloves (I find that VCA is not kind to the skin). Unlike cooking oil, VCA can be left on the plate for much longer to dissolve the ink, then used as a temporary protection against oxidation if the plate is going to be used again soon. But if plates are to be stored for a long time, clean them with biodegradable detergent, and brush them with a thin film of Vaseline oil, and wrap them in clingfilm.

VCA is now being promoted all over the European Community as a replacement for volatile cleaning solvents in the printing industry. It is now increasingly available in most European countries, and I can recommend it most strongly. It is becoming increasingly available in DIY stores as "Ecological white spirit sustritute" - look on the label for "Ester of vegetable Oil".

It can also be used for cleaning traditional hard and soft grounds and some quick drying oil based varnishes, which cannot be cleaned with vegetable cooking oil. Dried ink that has been used for a ground or to produce a fractint can also be cleaned with VCA. Normally if you have been using fractint and stopping out areas with an ethanol based shellac varnish, then you will have to remove that with ethanol (ethyl alcohol), and a lot of the ink ground will come off with the alcohol. But do not use "denatured alcohol" which usually has a high proportion of methyl alcohol.

Any ink ground residues that are left will probably come off after being left to dissolve in VCA. Failing that, soak the plate in a shallow tray of vinegar for a while , and the dried ink can be brushed off with an old toothbrush. If ink grounded plates have been left for months or dried on a plate at too high a temperature the ink may have become hard baked – like an enamel. A long



soak in vinegar will remove the ink. Needling an 'enamelled' plate may be difficult, and it may be better to remove the ink and start again. But if the enamelled ink is the result of baking it after a salt tint or sugar lift tint process, then you can continue to etch it, perhaps taking a little longer with the first step which has to break through the thin skin of residual oil on the plate.

Water-washable inks

Now, water-washable inks for intaglio and for relief printing are more widely available from printmaking suppliers. Their qualities have improved since they were first introduced. The intaglio inks from Charbonnel in France can be printed on damped paper without showing fuzzy lines. Earlier inks I tried dissolved into the paper.

Good water soluble inks will stay workable on the inking slab and pallet knives, and will not develop a skin, for much longer than oil based inks.



"Fruits imaginaires" deep etched open bite on 2 zinc plates, proofed intaglio and then over printed in colour from the same plates.

Right « Eclipse 1999» collage print in the 'Gutenberg' series – 9 plates made by the Galv-on process, proofed intaglio in raw siena and over printed in relief in 2 colours. The plates LE SOLEIL are overprinted with the plates LUNE

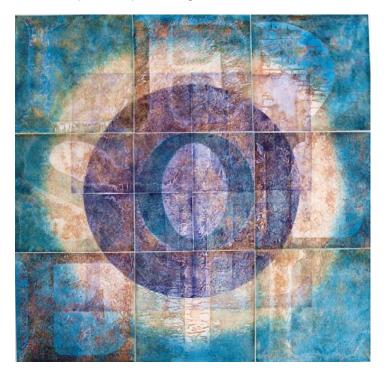
CONCLUSIONS

The alternative methods described above are in one sense traditional, in that they can be used to make conventional printing plates from copper, zinc, steel and aluminium using methods and materials that have been around for more than a century. In showing for how long electrolytic plate-making processes have been used, and how modern, inexpensive, everyday equipment and materials can easily eliminate what is clearly the most noxious etching process, I have tried to demystify and simplify galv-etch to make it as accessible as possible. In the course of my own printmaking practice using these techniques, and trying to modernise them, I have found new ways of grounding plates with relief printing ink, that are very well adapted to electrolytic and electrochemical processes.

I have found from the feedback that I get on the internet, that interest in electrolytic processes extends to many other crafts that use metals, and I have tried to extend my research and experience to describe ways of using galvanoplasty for instance.

The use of the linked methods of ink-ground and fractint, salt tint and sugar lift tint, have the same effect, of using economical, quick, and simple means and safe materials to remove the barriers and inhibitions to creativity that the traditional "cuisine" has imposed. I hope that the new possibilities that the combined techniques offer will stimulate, even perhaps galvanize, other artists into creative discoveries that go way beyond those I've described. Even if the additional possibilities offered by ink grounds are not taken up, galvetch can be used with traditional grounds and aquatint, or with a few other substitutes to produce a safer working environment.

Once the process of making and experimenting with plates has become simplified, made clean, safe, agreeable, and can be done in a normal studio environment without special ventilation, masks, goggles, or anxiety, then imagination is liberated at the point where it is most important in printmaking, in the creation of the matrix.



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(See also by the same author in Westminster Review, Vol 34, II, 1840 pp 434 - 460)

related internet web sites

Using brine as an electrolyte - the toxic effects of using a salt solution as an electrolyte in galv-etch or any type of electroetching.

A list below is of websites showing the processes of the electrolysis of Sodium Chloride, salt solution or brine, and others showing toxicity of the chlorine gas generated, of the caustic soda solution that is left, and the different toxic chemicals that are produced when etching metals like copper, zinc, aluminium, steel, brass. Some of these reactions can be found when adding salt to copper sulphate to create 'Saline sulphate etch', which may then be used electrolytically in the Galv-On process. Free copper deposit produced by etching zinc plates in saline sulphate etch forms a 'short circuited zinc copper couple' generating a current and producing chlorine and caustic soda. Free chlorine and hydrogen gas in a confined space like a covered etching tray can form an explosive mixture. If the chlorine gas is not channelled and collected, but mixes freely with the caustic soda, then sodium chlorate is produced. Sodium chlorate is a very toxic chemical banned since 2008 in the European Union where it was used as a powerful weed killer.

http://chemed.chem.wisc.edu/chempaths/GenChem-Textbook/Electrolysis-of-Brine-991.html

http://nj.gov/health/eoh/rtkweb/documents/fs/1706.pdf http://www.ncbi.nlm.nih.gov/pmc/articles/PMC2908650/ http://electrochem.cwru.edu/encycl/art-b01-brine.htm http://nj.gov/health/eoh/rtkweb/documents/fs/0057.pdf http://en.wikipedia.org/wiki/Sodium_chlorate

The following sites are those that deal specifically with safe and ecologically sound printmaking:

Printmaking Today

The quarterly international Journal created by Rosemary Simmons and edited by Anne Desmet, which covers all aspects of printmaking including non-toxic methods http://www.artnet.co.uk

Printmaker

A comprehensive listing of websites and pages dealing with printmaking and art, created by Chris of Printmaker, a studio offering printmaking editioning services and other resources to printmakers, especially those interested in screenprinting. Data and links to non-toxic printmaking sites and woodcut artists and techniques. http://www.printmaker.co.uk/links.html

Keith Howard's Non-Toxic Printmaking Page

A few extracts from "Non-Toxic Intaglio Printmaking", describing non-toxic photographic intaglio printmaking methods; Intaglio-Type method using ImagOn film; new grounding methods. Regularly updated with links and new material..

http://www.mtsu.edu/~art/printmaking/non_toxic.html

Edinburgh Printmakers Workshop

is an artists' studio and gallery dedicated to contemporary fine-art printmaking. Studio facilities are provided at reasonable cost for any artist who wishes to

work in etching, lithography, screenprinting or relief printing. They have developed and use non-toxic methods: Edinburgh Etch, Acrylic Resist Etching; Water-based screenprinting; Lithography using non-toxic chemicals. An extremely well designed and attractive site..

http://www.edinburgh-printmakers.co.uk

The Printmakers Council

Founded in 1965 to promote the art of printmaking and the work of contemporary printmakers. It continues to pursue this aim by organising a program of exhibitions in London, throughout the U.K. and world-wide. These exhibitions show both traditional skills and innovatory printmaking techniques.. http://www.printmaker.co.uk/pmc/index.html

Nik Semenoff - new lithographic techniques

Pages describing new techniques he has developed for waterless lithography; techniques using dry copier toner; electro-etching; a new mordant for aluminium plates. New Directions Art Gallery showing example prints. http://duke.usask.ca/~semenoff/Home.html

Printmaking Methods - A 'Print Australia' Listing

A comprehensive resource of information concerning methods of printmaking and general 'how-to' information, giving preference to sites promoting the use of non-toxic methodologies. A site filled with links to sites under different headings: http://www.acay.com.au/~severn/methods.htm

GreenArt - an Eco-Art directory

A selective list of websites and pages of artists and designers concerned with ecological, environmental and social issues in their work, under a number of headings: Printmaking (non-toxic, woodcuts), Architecture & Design (solar, energy conservation), Tapestry and Fibre-art, Sculpture & Painting (recycled materials and ecological themes), Travel, Organisations. http://www.greenart.info/guide

Printworks Magazine

A web magazine with content that regularly changes, often drawn from articles in Printmaking Today, originally created by Mark Millmore. Individual artists featured; articles on technical subjects, and techniques described. http://people.whitman.edu/~goodmal/print/works.htm

Printmaking Links

Middle Tennesee State University's site with a facility to search the site for information on all aspects of printmaking, including non-toxic techniques http:///www.mtsu.edu/~art/printmaking/print_links.html

Polymetaal

Manufacturer of printmaking equipment; Etching presses, litho presses, hot plates, relief presses, intaglio presses, acid trays etc. Also on this website you can find printmaking links as well as free exhibit space for printmaking artists. http://www.polymetaal.nl

The Printmakers' Experimentarium - was established in Copenhagen by Henrik Boegh in 1997. with the following aims: Testing and evaluating new printmaking techniques and materials based on acrylics and polymers; Imparting experience with such techniques and materials to the art schools and creative artists; Arranging workshops and demonstrations of Non-Toxic Printmaking; Advising schools and printmaking workshops on establishing and equipping a Non-Toxic Printmaking Studio..

http://www.artbag.dk/ge/uk/index.html

Printmaking Links - Middle Tennesee State University's site with a facility to search the site for information on all aspects of printmaking. A site very rich in information and links to other printmaking sites...

http://www.mtsu.edu/~art/printmaking/print_links.html

ElectroEtch

A commercial site with very little information about methods, promoting the expensive patented equipment sold by ElectroEtch Enterprises, developed and patented by Omri and Marion Behr.

http://www.electroetch.com

LectroEtch - an American company supplying materials and equipment for industrial marking by electrolytic etching since 1943 (no connection with the Behrs).

http://www.lectroetch.com

How a Wood Engraving is Made

A well illustrated and described process of the process of making a wood engraving, by Andy English. http://freespace.virgin.net/a.english/how.htm

Wood Engraving

Wood engraving is a refinement of the technique of woodcut, the carving of a design into a block of wood by cutting away all parts of the wood which are not part of the design. A site showing this and other techniques http://www.cbbag.ca/WoodEngraving.html

and a reminder of my website addresses:

http://www.greenart.info

APPENDIX A : ELECTRO-ETCHING (1855)

Extract from: WALKER, Charles V., Electrotype Manipulation: Part II. Containing The Theory, and Plain Instructions in the Arts of Electro-Plating, Electro-Gilding, and Electro-Etching; with an account of the Mode of Depositing Metallic Oxides, and of the Several Applications of Electrotype in the Arts. Nineteenth Edition, London, Published by George Knight and Sons, Manufacturers of Chemical Apparatus and Philosophical Instruments, Foster Lane, Cheapside. 1855.

Page 44. Para.149 "ELECTRO-ETCHING.- The results hither to treated on, have been (....) all obtained at the negative metal: but there is a class of results of no inconsiderable importance to be obtained at the other terminal. The plates of copper, in the decomposition cell, in connection with the copper of the battery, have been described as combining gradually with the oxygen released there, and being eventually consumed; so likewise the plates of silver or gold, which occupy the same relative position, are in a similar manner consumed. But as the varnish placed on moulds, effectively shields the parts protected by it, from the effects of electrolytic action, so also may the copper plates, or the plates of any metal connected with the positive end of the battery, be protected, and the destructive action localised at pleasure.

150. If, for instance, plates of copper be covered on any part of their surface with a stratum of varnish, that part will be excluded from the line of action, while all else is being consumed. Advantage has been taken of this, by coating plates with proper composition and then tracing through it any design, of which an etching is required. The plate in this condition is submitted to the action of the nascent oxygen, and the surface is readily and effectively etched. There is some superiority too possessed by this method, over the ordinary etching by the use of nitric acid; for the operation can be conducted with considerable regularity; it can be rendered a slow or a speedy process; and the result can be taken out from time to time, to be examined, and can be resubmitted in a moment, In fact, of so much importance has this mode of etching been deemed, that it is already one amongst the many applications of this principle for which a patent has been obtained.

151. Process of electro-etching.- Take a burnished copper plate, and solder to it a stout wire; heat the plate, and rub its surface with etching ground, wrapped in silk: be careful to obtain an even coating; then smoke the covered surface over the flame of a candle. Varnish the back of the plate as well as the wire with shellac. Trace the design through the etching ground with a fine point. This done, place it in a decomposition cell, and connect it with the copper of a Daniell's or other cell, placing opposite to it a plate of somewhat similar size; after the lapse of ten minutes, remove it, and "stop out" the fine parts with Brunswick black; return it to the decomposition cell for a second ten minutes; and again stop the half tints; again submit it to action for ten minutes, and the operation is complete. Remove the etching ground by means of heat, and a perfect engraving will be found on the plate. The exact duration of the several operations, as well as their number, must be regulated according to circumstances. Electro-etching is an interesting experiment for the lecture table. At the commencement of a lecture, I have submitted a plate to electric action, and before the hour has expired, have distributed proof impressions..."

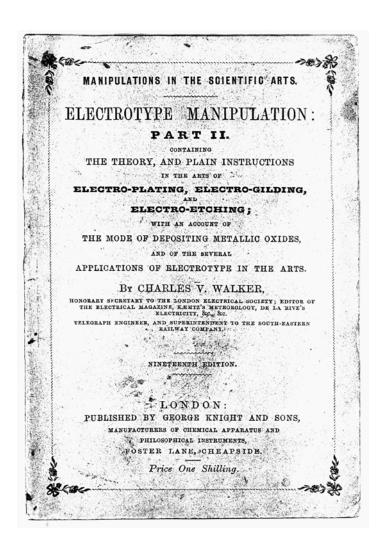
Comments on text: In introductory part of the text, Walker describes a 'decomposition cell' as a vessel in which the electrolytic action upon the plates takes place, connected to a Galvanic cell or a battery. A Daniell's cell is a source of Galvanic or Voltaic Electricity, and consists of a copper and a zinc plate in a vessel containing an acidic solution, and devices for maintaining the concentration and acidity of the solution. The etching time of a total of 30 minutes, indicated in para. 151, assuming he is talking about a small demonstration plate, would indicate a voltage of about 1 volt, the output of a single Daniell's cell. The 'copper' of the battery is the side which produces the 'positive' current. The words "rendered a slow or a speedy process" indicate

that the voltage could be low or high, regulated by a different number of cells in series. In another part of the text, a very low voltage is recommended for certain purposes, and the time required for electrotyping, of a week or more, also indicates the use of a low voltage and amperage.

Later in the text there is a section on "Electro-tint or Galvanography", (para 173) which is described as a "another form of deposite" produced by painting on 'white metal' with thick etching ground or varnish to create a textured relief, then the whole is ''plumbagoed', that is, covered with graphite, and then a tonal plate is created by the electrotyping or galvanoplastic process.

It was in this sense that Paul Pretsch called his process "photo-galvanography", patented in 1854. This is described in great detail in *Charles V Walker's "Electrotype Manipulation, Part I,* being the Theory, and Plain Instructions in the Art of Working in Metals, by Precipitating them from their Solutions, through the Agency of Galvanic or Voltaic Electricity" 29th Edition, George Knight and Sons,

London. 185



Title page of Charles V Walker's book

APPENDIX B - FIRST PATENT 1840



A.D. 1840 N° 8656.

Engraving Metals by means of Voltaic Electricity. SPENCER AND WILSON'S SPECIFICATION

TO ALL TO WHOM THESE PRESENTS SHALL COME, we,THOMAS SPENCER, of Liverpool, in the County of Lancaster, Carver and Gilder, and JOHN WILSON, of Liverpool aforesaid, Lecturer on Chemistry, send greeting.

WHEREAS Her present Majesty Queen Victoria, by Her Letters Patent 5 under the Great Seal of the United Kingdom of Great Britain and Ireland, bearing date at Westminster, the Seventh day of October now last past, did give, and grant unto us, the said Thomas Spencer and John Wilson, Her especial licence, full power, sole privilege and authority, that we, the said Thomas Spencer and John Wilson, our executors, administrators, and assigns, or such others as we, the said Thomas Spencer and John Wilson, our executors, administrators, or assigns, should at any time agree with, and no others, from time to time and at all times thereafter during the term of years therein expressed, should and lawfully might make use, exercise, and vend, within England, Wales, and the Town of Berwick-upon-Tweed, our Invention of "CERTAIN IMPROVEMENTS IN THE PROCESS OF ENGRAVING ON METALS BY MEANS OF VOLTAIC ELECTRICITY; " in which said Letters Patent there is contained a proviso, obliging us, the said Thomas Spencer and John Wilson, by an instrument in writing under our hands and seals, or under the hand and seal of one of us, particularly to describe and ascertain the nature of our said Invention, and in what manner the same is to be performed, and to cause the same to be inrolled in Her said Majesty's High Court of Chancery within six calendar months next and immediately after the date of the said Letters Patent, as in and by the same, reference being thereunto had, will more fully and at large appear.

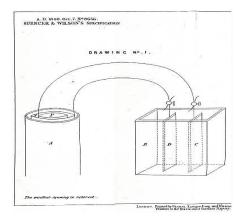
NOW KNOW YE, that in compliance with the said proviso, we, the said Thomas Spencer and John Wilson, do hereby declare that the nature of our said Invention, and the manner in which the same is to be performed, is particularly described and ascertained in and by the Drawings hereunto annexed, and as follows, that is to say :-

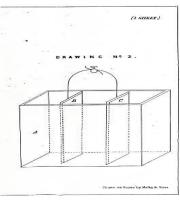
Metallic surfaces are generally engraved either by means of a graving tool, or etched by acids. We claim the application of voltaic electricity for the purpose of engraving metallic surfaces generally. When the metallic surface to be engraved is copper, it must receive a coating of varnish or other projecting substance. We prefer the composition usually termed etching-ground. The required drawing or design is then made with a pointed instrument, care being taken that the metallic surface be fully exposed where the lines or points are required. The surface thus prepared must now be put into communication with the copper or negative end of a voltaic arrangement, by means of a wire or a slip of metal, and then placed in a vessel containing a solution of sulphate of copper. Another copper plate or piece of copper wire must, in like manner, be made to communicate with the positive end of the voltaic apparatus, and must then be placed in the same vessel with the plate to be engraved. The circle being thus completed, the electric current will remove or bite out the metal from those parts of the plate which are not covered by the etching ground or varnish. When the surface to be engraved is in the form of a cylinder we place it within a hollow cylindrical piece of metal, which latter serves as the surface C in vessel B, No l in the Drawing. The distance of the two plates regulates the depth and width of the

lines or points; these are also influenced by the quantity and intensity of the electricity employed, and of the time allowed for action. The electric apparatus employed may consist either of a single pair of plates, or of a greater number. The size of the plates of the voltaic apparatus employed depends on the size of the plate or other surface to be engraved. In general we find that it is convenient to have the surface of the copper plate of the voltaic apparatus about the size of the plate to be engraved, and the plate C in vessel B, N° I, in the Drawing hereunto annexed must have a surface about equal to the surface exposed in 1he metallic surface D. In general we find that the plates or other surfaces C and D may be conveniently placed two or three inches apart; when placed at greater distances more time is required for the action. During the process the engraved plate may be withdrawn and examined to see whether the lines are of the required depth; if not sufficiently deep, the plate can again be 'placed in the apparatus and a greater depth be obtained. When some of the lines are required to be fainter than others, such parts of the design may be stopped out in the same manner as in the common process of etching. In the Drawing hereunto annexed, No I, A represents a vessel containing the plates of a voltaic arrangement, which may be excited by any of the methods at present in use. B, a separate vessel, containing the solution of sulphate of copper, or other salt, and the surfaces C and D; C being the conducting surface, which is placed opposite the metallic surface to be engraved, and which communicates with the zinc or positive end of the voltaic apparatus. A, D, contained in the same vessel, is the surface to be engraved, and which communicates with the negative end of the voltaic battery. In No I, P represents the zinc or positive plate, and N the copper or negative end. Another and simple form of the apparatus is represented in Drawing No 2; A, a vessel containing a solution of any neutral, or acidulous, or non-metallic salt, into which the metallic surface B to be engraved is immersed, and which must be connected by a conductor, such as a slip of metal with a surface electro negative in regard to the surface to be engraved. In general platinum may be employed for this purpose. A prepared metallic surface may be engraved even without the metallic contact with the voltaic battery, as described above, by placing it in a solution between the plates forming the poles or ends of the voltaic apparatus. When a surface of steel is to be engraved, we prepare it with the etching ground, and proceed in the same manner as when copper is engraved, but in the vessel B, No I, into which the steel is introduced, we place a solution of common salt, and substitute a plate or wire, of steel, or iron, or any conducting substance, in place of the copper plate employed in the former process. Instead of the solution of common salt, other solutions of alkaline, earthy, or metallic salts may be used. When we engrave a silver surface, we place a silver plate by preference, or wire, in the vessel B, along with a solution of sulphate of soda, or of sulphate of silver. When we engrave a surface of gold we employ a solution of hydrochloric acid, or a solution of a soluble chloride, and place along with it in the vessel B a plate or wire of gold. The other metallic surfaces may be engraved by processes in every respect similar to those described above. We do not claim the use of any particular form of voltaic or galvanic apparatus, nor of the particular solutions specified above. But we claim the use or application of voltaic electricity for the purpose of engraving metallic surfaces generally.

In witness whereof, we, the said Thomas Spencer and John Wilson, have hereunto set our hands and seals, this Sixth day of April, in the year of our Lord One thousand eight hundred and forty-one.

THOMAS SPENCER. (L.S.) JOHN WILSON. (L.S.)





APPENDIX C (GREEN PRINTS)

THE CHEMISTRY OF THE ELECTROLYSIS OF SALT SOLUTION USED FOR ETCHING DIFFERENT METALS

The use of Sodium Chloride (brine or salt solution) as an electrolyte in galv-etch or any type of electro etching is often advocated, and assumed to be safe, convenient and economical. But there are complex chemical reactions involved that are not as safe as the solutions recommended for etching Copper, Zinc and steel described in Green Prints and this website. They result from the separation of the Chlorine ions and the Sodium ions in the water solution, and their reactions with the metal ions of the anode plate or in solution. There are secondary reactions between the solutions produced which result in more or less toxic and unstable precipitations. For nearly all metals there are large volumes of insoluble precipitations produced, which can block lines and prevent even etching, and require frequent filtering of the electrolyte. There is always copious production of hydrogen which is explosive and to which many people are allergic. The process of electrolysis is not reversible, in other words, metal cannot be deposited on a plate or object by making it the cathode instead of the anode. The filtered solution cannot be used indefinitely as its chemistry and concentration can change over time, and must be disposed of safely.

For a printmaker, it is inadvisable to risk the contact with these solutions and gases, to have the problem of the unpredictability of the results of using a gradually changing electrolyte and to be faced with the necessity for disposal of spent solutions. It is extremely inconvenient to have large volumes of precipitate, and to have to a high level of ventilation over the etching tank to remove the gases. Remember that, for example, using a Zinc Sulphate electrolyte with Zinc plates, or Copper Sulphate with Copper plates, results in an unchanging solution that only requires occasional filtering, reversibility, no precipitate, and no gases. I have been using the same solutions since 1991, only filtering and topping them up very occasionally. Printmakers are not chemists and cannot be expected to take the extraordinary precautions that are required in a laboratory to isolate gases or dangerous chemicals or to know when the solutions they are using are changing and becoming unusable. The principle of precaution should be applied, and only tried and tested methods should be used.

SALINE SULPHATE ETCH

The use of a mixture of salt and Copper Sulphate called "Saline Sulphate etch" is promoted as a alternative to using "Bordeaux Etch" which is pure

Copper Sulphate for etching zinc, iron, and aluminium without needing to use electricity. Note that under certain circumstances Copper Chloride (CuCl $_2$) and Sodium Sulphate (NaSO $_4$) are produced when adding salt to Copper Sulphate. Copper Chloride is a very toxic chemical. Sodium Sulphate is known as "Glaubers Salt" once used as a laxative, and it is also a Eutectic salt, whose solid melting point of between 40°C and 50°C makes it useful for storage of heat. See below for precise details of the circumstances and the proportions of NaCl and CuSO $_4$ that can produce the reaction.

GENERAL DESCRIPTION OF PROCESSES

The descriptions below show in detail, the processes of the electrolysis of Sodium Chloride, 'salt solution or brine), and the reactions with the Chlorine gas that occur when different metals are etched. The secondary reactions between the metal Chlorides produced and the caustic soda that is always generated whatever metal is etched, are described and illustrated. The hazards and ill effects of the chemicals that are produced is listed. Some of these reactions can be found with Saline Sulphate Etch if it is used electrolytically in the passive Galv-On process or by mistake as an electrolyte for etching copper.

Electrolysis of Sodium Chloride solution produces Chlorine gas at the anode and hydrogen gas at the cathode, leaving a solution of Sodium Hydroxide (caustic soda). If the anode (+ve) is inert (for

Test setup for electro etching salt solution with different metals. Laboratory power supply, time switch, glass jar with salt solution, electrodes of each metal tested in turn. Fresh salt solution for each test



instance platinum or carbon) it will not react with the Chlorine ions, and the gas will be given off as bubbles and can be separated and collected. The positive Sodium ions will react with water rather than with the negative metal of the cathode (explained below) releasing hydrogen as gas. The water (H_2O) loses an ion of hydrogen leaving HO which combines with the Sodium to make Sodium Hydroxide (Caustic Soda).

If the anode is a metal plate to be etched then the -ve Chlorine ion combines with the etched +ve metal ion (charged by the current) to produce a Chloride, and most of the Chlorine is not released as a gas. For example, a Copper anode plate will be etched by loss of one Copper ion which bonds to two Chlorine ions, making Copper (II) Chloride (CuCl₂). Then the soluble Sodium Hydroxide will react with the soluble Copper Chloride to make insoluble Copper Hydroxide, and soluble Sodium Chloride (by exchange of ions). Being insoluble, the Copper Hydroxide will be seen first as a slight yeloow green cloudiness in the solution, and then in time will sink to the bottom as a solid powder precipitate. Similar

Test – etching copper electrodes in brine :175 gms.salt in 2.3 litres distilled water, 3 volts x 0.8 amps for 30 mins in 3 stages. Anode plate stopped with varnish brush strokes



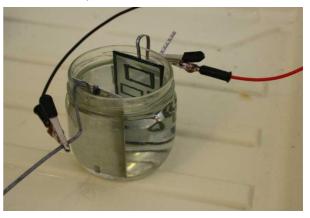
After etching has stopped the precipitate starts to fall to the bottom as it is formed by the reaction between cupric chloride and caustic soda



reactions are produced by Zinc, Iron, or Aluminium used as anodes, producing Zinc(II)Chloride, Iron(III)Chloride, or Aluminium(III)Chloride, and then reacting with the caustic soda, to leave Zinc Hydroxide (grey), Iron Hydroxide (black), or Aluminium Hydroxide (white).

In practice, depending on the current and area of metal surface, a foam can be produced on the surface, which is hydrogen in bubbles of the soluble metal Chloride and caustic soda (see illustration). Also while the current flows the formation of the precipitate seems to be slightly inhibited, so at that stage the electrolyte is a mixture of more or less toxic solutions. After the current is turned off, the precipitate forms more rapidly if the foam is stirred into the electrolyte and then the liquid clears slowly. Because of the precipitate a plate flat on the bottom of a tray with a grid cathode would etch very unevenly. Even with a vertical Zinc anode the Hydroxide forms a very hard layer on the etched surface which inhibits further etching after a while. Etching steel plates produces very varied results depending on the other metals that are alloyed with pure iron.

Etching zinc plate in brine – bubbles begin to form at cathode but no deposit is formed at first.



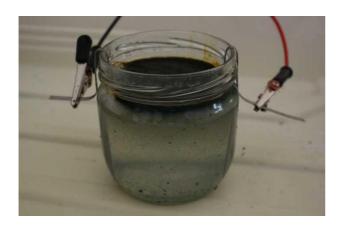
Etching zinc – bubbles streaming from cathode towards anode and water beginning to go grey.



Stainless steel should not be used as an anode, because it is very resistant to being etched, or in other words, it will not combine easily with the Chlorine, which is either given off as a gas, or reacts with the caustic soda to produce Sodium Chlorate, which is a weed killer now banned for use in the European Union.

After the etching has finished and the steel plate removed a dark brown crust remains on the surface and gradually the hydroxide precipitate forms and falls to the bottom





Etching steel (iron anode) in brine – black foam forms on the surface very rapidly. The bubbles are formed by hydrogen in caustic soda and ferric chloride.

Etching Aluminium anode in brine – the aluminium is slow to react with the chlorine which can be seen as bubbles being given off the anode plate and a thick foam forms very rapidly on the surface trapping bubbles of hydrogen and chlorine.



On removal of the electrodes gently the foam shows a crust of ferric chloride which has not yet reacted with the caustic soda



Slowly the precipitate forms as a heavy cloud that floats down to the bottom.



The following detailed descriptions of the chemistry and health hazards are derived from references in chemistry textbooks, internet sites (linked) and from direct observations of tests and from the basic equations..

Copper(II) Chloride

Electrolysis of Sodium Chloride with Copper electrodes

Electrolysis of aqueous Sodium Chloride with Copper electrodes produces (among other things) a bluegreen foam that can be collected and converted to the hydrate of Copper(II)Chloride (CuCl₂).

In theory, while the current flows the Copper anode is etched, releasing 2 Copper anions (+ve) which combine with one Chlorine cation (-ve) giving Copper(II)Chloride, which is soluble in water. But Copper Chloride reacts with the caustic soda to give a precipitate of Copper Hydroxide. This shows as a green insoluble deposit.

Addition of Copper Sulphate and Sodium Chloride (« Saline Sulphate etch »)

There are multiple ways of making Copper Chloride, one of them is by adding Sodium Chloride (table salt) to Copper Sulphate in the right proportions.

The chemical reaction here is a exchange of ions. $2NaCl(aq) + CuSO_4(aq)-->(Evaporation)--> CuCl_2(aq) + Na_2SO_4(aq)$

Theoretically it is possible to get 115 grams of Copper Chloride using 100 grams of Sodium Chloride and 213 grams of Copper Sulphate pentahydrate ($CuSO_4\ 5H_2O$). For a full explanation of this process see:

http://www.paulslab.com/experiments/making-copper-chloride.html

This reaction requires more examination, in particular when Saline sulphate etch is used for etching zinc, steel or aluminium, in particular the secondary reactions after the copper has been precipitated and the metal has combined with the sulphate ions. For instance does aluminium sulphate exchange ions with sodium chloride to produce aluminium chloride + sodium sulphate?

Health Hazard Information for Copper(II)

Chloride

Eye: Causes eye burns. Exposure to particulates or solution may cause conjunctivitis, ulceration, and corneal abnormalities. Contact with the eyes may cause corneal damage.

Skin: Causes skin burns. May cause skin sensitization, an allergic reaction, which becomes evident upon re-exposure to this material. May cause skin rash (in milder cases), and cold and clammy skin with cyanosis or pale color.

Ingestion: May cause severe and permanent damage to the digestive tract. Causes gastrointestinal irritation with nausea, vomiting and diarrhea. Causes gastrointestinal tract burns. May cause perforation of the digestive tract. May cause hemorrhaging of the digestive tract. The toxicological properties of this substance have not been fully investigated. May cause systemic effects.

Inhalation: May cause ulceration and perforation of the nasal septum if inhaled in excessive quantities. Causes chemical burns to the respiratory tract. Inhalation of fumes may cause metal fume fever, which is characterized by flu-like symptoms with metallic taste, fever, chills, cough, weakness, chest pain, muscle pain and increased white blood cell count. The toxicological properties of this substance have not been fully investigated. Aspiration may lead to pulmonary edema. May cause systemic effects. Can produce delayed pulmonary edema.

Chronic: Prolonged or repeated skin contact may cause dermatitis. Effects may be delayed. Individuals with Wilson's disease are unable to metabolize Copper. Thus, Copper accumulates in various tissues and may result in liver, kidney, and brain damage.

http://avogadro.chem.iastate.edu/MSDS/CuCl2-2H2O.htm

Zinc (II) Chloride

Electrolysis of Sodium Chloride with Zinc electrodes

Using Zinc electrodes in an electrolyte of Sodium Chloride a similar reaction to the above can occur producing aqueous Zinc Chloride (ZnCl₂) and aqueous Sodium Hydroxide (NaOH) and Hydrogen gas.

 $ZnCl_2$ (aq.) + NaOH (aq.) \rightarrow Zn(OH)₂ (ppt.) + NaCl (aq.)

The hydroxide is very quickly generated and forms a deposit adhering strongly to the anode creating a very uneven etch and stopping the etch completely in areas. After a while the chlorine cannot react with the zinc any longer and is given off as a gas with its attendant hazards (see chlorine hazards).

Health Hazard Information

Potential Acute Health Effects: Very hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion, of inhalation. Hazardous in case of skin contact (corrosive, permeator), of eye contact (corrosive). The amount of tissue damage depends on length of contact. Eye contact can result in corneal damage or blindness. Skin contact can produce inflammation and blistering. Inhalation of dust will produce irritation to gastro-intestinal or respiratory tract, characterized by burning, sneezing and coughing. Severe over-exposure can produce lung damage, choking, unconsciousness or death. Inflammation of the eye is characterized by redness, watering, and itching. Skin inflammation is characterized by itching, scaling, reddening, or, occasionally, blistering.

http://www.sciencelab.com/msds.php?msdsId=9927328

Ferric Chloride

This is well known as a mordant for copper in the electronics industry, and for a period was used as a mordant by printmakers and metal workers before its dangers were known, especially used as a mordant for zinc.

Electrolysis of Sodium Chloride with Iron electrodes

Using iron as the electrodes in the electrolysis of salt solution will produce negative chlorine ions, which combine with positive iron ions at the anode producing Iron(III)Chloride and etching the iron. At the cathode Sodium Hydroxide and hydrogen gas are produced.

When aqueous Ferric Chloride is allow to react with Sodium Hydroxide, reddish brown precipitates of ferric hydroxide are formed and the Sodium reacts with the chlorine to produce Sodium Chloride . The hydrogen and some of the chlorine form a foam with the chloride as a brown scum on the surface inhibiting the reaction with the caustic soda. $FeCl_3\left(aq.\right) + 3NaOH(aq.) --> Fe(OH)_3(ppt.) + 3NaCl\left(aq.\right)$

After the foam on the surface is stirred into the liquid the Ferric hydroxide settles to the bottom and after filtration dries as a black powder. Steel etching plates are alloys with other metals and the above reactions refer to pure iron. Steel alloys will differ depending on the reaction of the other metals in the alloy.

Using some kinds of stainless steel as the anode, which are very resistant to oxidation, inhibits the negative ions of chlorine combining with the positive ions of iron, and the formation of the iron(III)chloride, and so nearly all the chlorine is

given off as gas with its attendant hazards (see chlorine hazards).

Health Hazard Information

Iron(III) chloride is toxic, highly corrosive and acidic. The anhydrous material is a powerful dehydrating agent.

Although reports of poisoning in humans are rare, ingestion of ferric chloride can result in serious morbidity and mortality. Inappropriate labeling and storage lead to accidental swallowing or misdiagnosis. Early diagnosis is important, especially in seriously poisoned patients.

Very hazardous in case of ingestion. Hazardous in case of skin contact (irritant), of eye contact (irritant), of inhalation. Slightly

hazardous in case of skin contact (permeator). Corrosive to eyes and skin. The amount of tissue damage depends on length

of contact. Eye contact can result in corneal damage or blindness. Skin contact can produce inflammation and blistering.

Inhalation of dust will produce irritation to gastrointestinal or respiratory tract, characterized by burning, sneezing and

coughing. Severe over-exposure can produce lung damage, choking, unconsciousness or death. http://www.sciencelab.com/msds.php? msdsld=9924033

https://en.wikipedia.org/wiki/Iron(III)_chloride

Aluminium (III) Chloride

Using Aluminium electrodes in an electrolyte of Sodium Chloride a similar reaction to the above can occur producing Aluminium (III)Chloride (AlCl₃). But unlike copper and zinc, the aluminium is more resistant to oxidation, and chlorine is given off in greater quantities. Very slowly the aluminium chloride reacts with the caustic soda and a white scum of chloride bubbles form on the surface trapping hydrogen and chlorine gas. After the current is turned off, Aluminium Hydroxide slowly forms as a cloud in the solution rather than a deposit on the bottom. The Chloride remains as a scum on the top until it is stirred into the solution, releasing the gases.

Acute Health Effects

The following acute (short-term) health effects may occur immediately or shortly after exposure to Aluminum Chloride: Contact can severely irritate and burn the skin and eyes with possible eye damage. Inhaling Aluminum Chloride can irritate the nose and throat causing coughing and wheezing. Inhaling Aluminum Chloride can irritate the lungs causing coughing and/or shortness of breath. Higher exposures may cause a build-up of fluid in the lungs

(pulmonary edema), a medical emergency, with severe shortness of breath.

Chronic Health Effects

The following chronic (long-term) health effects can occur at some time after exposure to Aluminum Chloride and can last for months or years:

Cancer Hazard

According to the information presently available to the New Jersey Department of Health, Aluminum Chloride has not been tested for its ability to cause cancer in animals.

Reproductive Hazard

There is limited evidence that Aluminum Chloride may damage the developing fetus and affect male fertility in animals.

Other Effects

Repeated exposure to Aluminum Chloride may cause scarring of the lungs (fibrosis) and reduce lung function with symptoms of coughing and shortness of breath.

http://www.sciencelab.com/msds.php? msdsId=9922851

Synthesis of Sodium chlorate

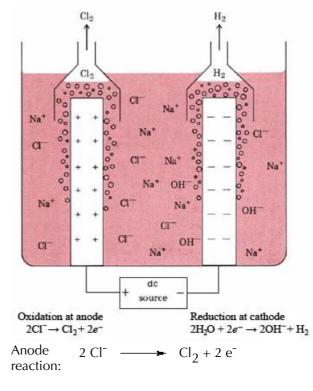
The <u>Chloralkali process</u> is an industrial process for the electrolytic production of Sodium chlorate. It can also be synthesized by passing <u>Chlorine</u> gas through a solution of <u>Sodium Hydroxide</u>. It is then purified by <u>crystallization</u>. If the Chlorine gas is not channelled and collected, but mixes freely with warm caustic soda, then Sodium chlorate is produced. Sodium chlorate is a very toxic chemical banned since 2008 in the European Union where it was used as a powerful weed killer.

Electrolysis of aqueous Sodium Chloride – technical description

Chlorine and Sodium Hydroxide (caustic soda) are presented together here, because industrially they are produced simultaneously by the same process, the electrolysis of brine (aqueous NaCl). These reactions assume electrodes of carbon. Other metals like platinum that resist oxidation may be used.

2 Na⁺(
$$aq$$
) + 2 Cl⁻(aq) + 2 H₂O(l) --->
Cl₂(g) + H₂(g) + 2 Na⁺(aq) + 2 OH⁻(aq)

During electrolysis, Chlorine is formed at the anode, and hydrogen and Hydroxide ions are formed at the cathode.



Cathode reaction: $2 H_2O + 2 e^- \longrightarrow H_2 + 2 OH^-$

Because the Cl₂ formed at the anode and the H₂ formed at the cathode can react explosively, they must be kept away from each other. Furthermore, the Hydroxide ions formed at the cathode can react with any Chlorine that remains dissolved in the brine. To keep the products formed at the two electrodes away from each other, a porous diaphragm is placed between the two electrodes in the electrolysis apparatus.

In the electrolysis of brine, water is reduced at the cathode. This occurs because water is more easily reduced than are Sodium ions. This is reflected in their standard reduction potentials, –2.71 volts for

Na⁺ versus –0.83 volt for water. At the anode, where oxidation occurs, the situation is not as clear. The standard oxidation potential of water is -1.23 volts, while that for Chloride ions is -1.36 volts. This means that water is more easily oxidized than Chloride ions. In spite of this, Chloride ions are oxidized at the anode, not water. The reaction that occurs is not what would be predicted by considering only the standard oxidation potentials because standard electrode potentials reflect equilibrium conditions, when no current is flowing. When current begins to flow, the distribution of ions around the electrodes changes, and the equilibrium electrode potentials no longer accurately apply. The potential of a cell depends on the magnitude of the current that is flowing through it. The difference between the equilibrium potential, at zero current, and the potential when current flows is called

overvoltage. The magnitude of the overvoltage depends on the composition of the electrode and electrolyte, as well as on the current. Generally, overvoltages are small, so predictions of electrode reactions based on standard electrode potentials are usually correct. However, in the electrolysis of aqueous Sodium Chloride, the overvoltage for the oxidation of water, which is a neutral molecule, is large enough to make it more difficult to oxidize than Chloride ions.

Health Hazard Information Chlorine

Chlorine gas is a pulmonary irritant with intermediate water solubility that causes acute damage in the upper and lower respiratory tract. Occupational exposures constitute the highest risk for serious toxicity from high-concentration Chlorine. Mixing of Chlorine bleach (Sodium hypochlorite) with ammonia or acidic cleaning agents is a common source of household exposure. As with all poisons, the dose determines the toxicity. Exposure to low concentrations of Chlorine for prolonged periods may have destructive effects, as might very short-term exposure to high concentrations.

Signs and symptoms

Symptoms may vary depending on the degree of exposure. Exposure possibilities include acute low levels, acute high levels, and chronic low levels. Low-level (3-5%, 1-15 ppm) acute exposure Most poisonings fall into this category and are caused by household exposure to low-concentration cleaning products. Manifestations are as follows:

- •Eye tearing, nose and throat irritation
- Sneezing
- •Excess salivation
- General excitement or restlessness

High-level (20%, >30 ppm) acute exposure In addition to the symptoms seen with low-level exposure, high-level exposure may result in the following:

- •Dyspnea: Upper airway swelling and obstruction may occur
- •Violent cough
- •Nausea and vomiting (with the smell of Chlorine in emesis)
- Lightheadedness
- •Headache
- Chest pain or retrosternal burning
- Muscle weakness
- Abdominal discomfort
- •Dermatitis (with liquid exposure): Corneal burns and ulcerations may occur from splash exposure to high-concentration Chlorine products
- Esophageal perforation

Sodium Hydroxide (Caustic Soda)

Like other <u>corrosive acids</u> and <u>alkalis</u>, drops of Sodium Hydroxide solutions can decompose <u>proteins</u> and <u>lipids</u> in <u>skin</u>, <u>eyes</u> or other <u>living tissues</u> via <u>amide hydrolysis</u> and <u>ester hydrolysis</u>, which consequently causes <u>chemical burns</u> and may induce permanent <u>blindness</u> if it contacts eyes. [3][4] Solid alkali may also express its corrosive nature if there is water, so <u>protective equipment</u> such as <u>rubber gloves</u>, <u>safety clothing</u> and <u>eye protection</u> should always be used when handling the material or its solutions.

Moreover, <u>dissolution</u> of Sodium Hydroxide is highly <u>exothermic</u>, and the resulting heat may cause heat burns or ignite flammables. It also produces heat when reacted with acids.

The standard first aid measures for alkali spills on the skin is, as for other corrosives, irrigation with large quantities of water. Washing is continued for at least ten to fifteen minutes.

Sodium Hydroxide is corrosive to several metals, like <u>Aluminium</u> which reacts with the alkali to produce flammable hydrogen gas on contact:

```
2 Al + 2 NaOH + 2 H2O \rightarrow 3 H2 + 2 NaAlO2
2 Al + 6 NaOH + x H2O \rightarrow 3 H2 + 2 Na3AlO3 + x
H2O
2 Al + 2 NaOH + 6 H2O \rightarrow 3 H2 + 2 NaAl(OH)4
```

Sodium Hydroxide is also mildly corrosive to glass, which can cause damage to glazing or freezing of ground glass joints. Careful storage is needed.

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