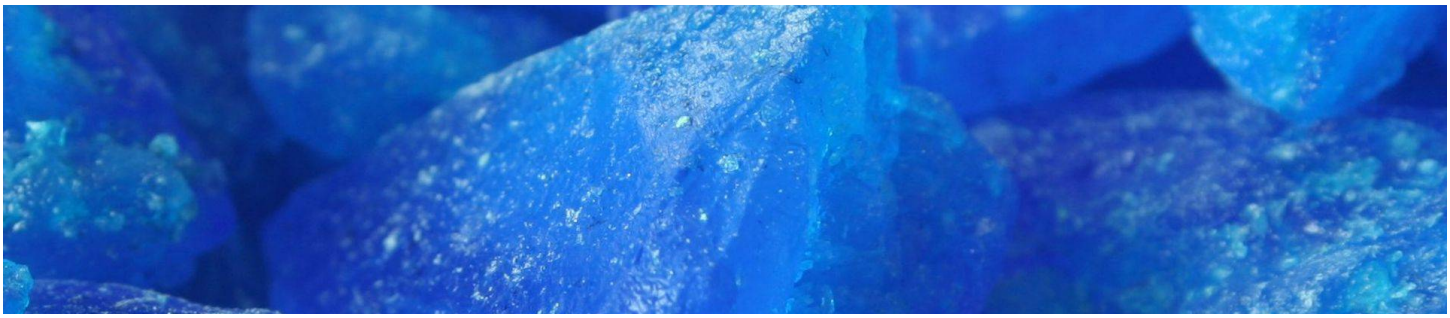
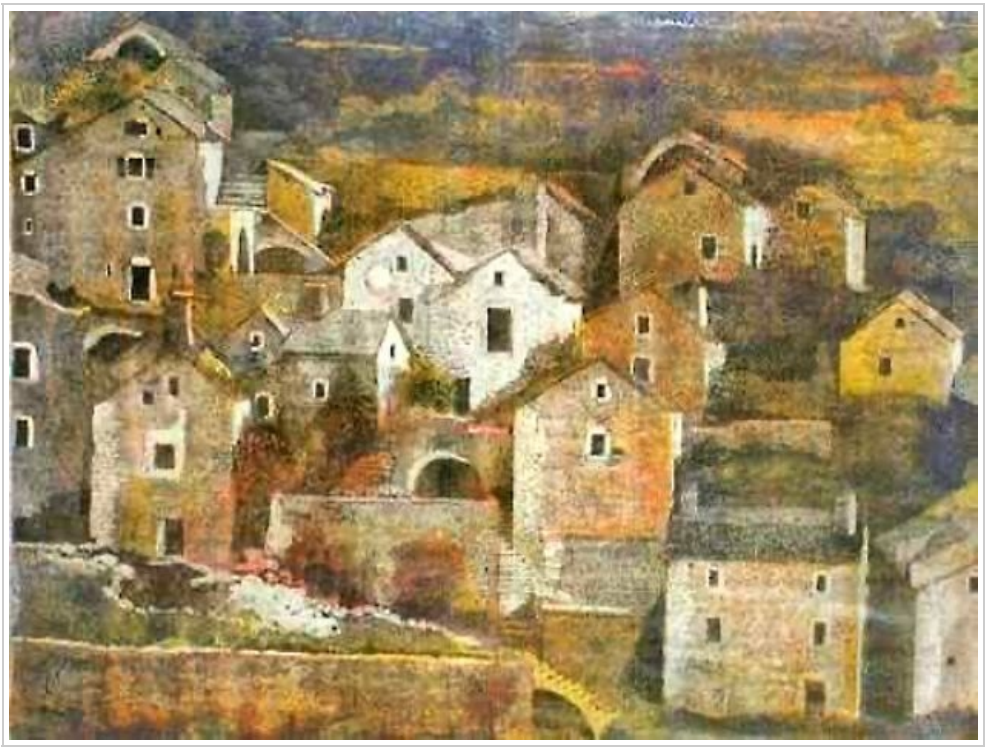
nontoxicprint



a copper sulfate crystal
(Wikipedia)

The Bordeaux Etch

by Cedric Green



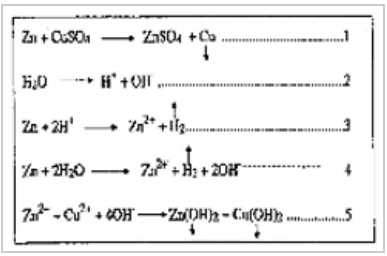
THE BORDEAUX ETCH -

AN ELECTROCHEMICAL

METHOD

- a color etching by Cedric Green made by using step-etching a plate in copper sulfate solution

(first published 1995, with recent additions)



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.

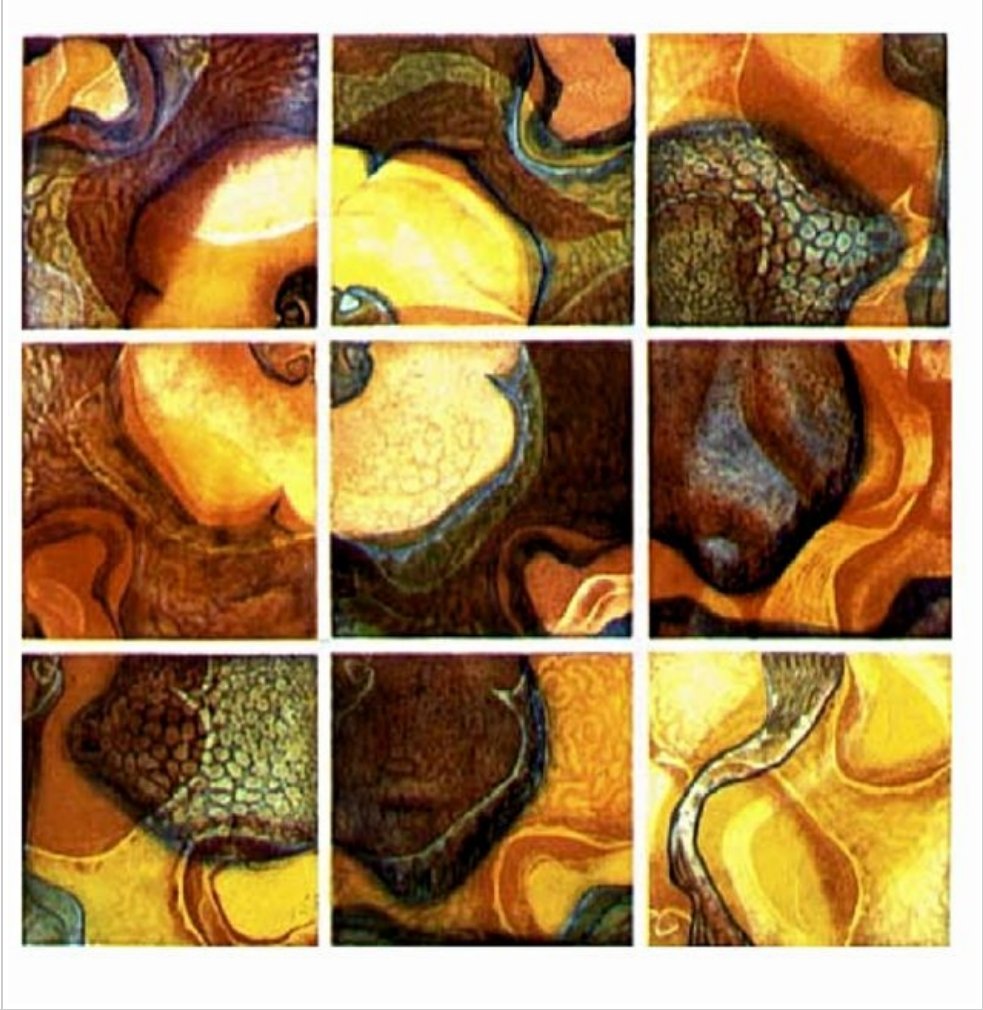
I have called this Bordeaux Etch, because a copper sulphate solution is better known to vine growers, farmers and gardeners as Bordeaux mixture (Bouillie Bordelaise), very widely used as a spray against mildew. The solution is very much safer to handle than ferric chloride, although gloves should be 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

the chemistry of Bordeaux etch

The chemical process involved is basically very simple. Zinc has a much higher electrode potential (Zn2+ = -0.76) than copper (Cu2+ = +0.34), and as a result it displaces copper ions from the copper sulphate solution (CuSO4), and the zinc ions combine with the sulphate (SO4) ions to form zinc sulphate (ZnSO4). 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
‘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.

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.



"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.

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 brine)

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 ($FeCl_3$) 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 re- dissolved. 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.

comparing traditional etching with Green Print techniques

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.