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CHEMICAL ETCHING WITHOUT ACIDS: FROM EARLY ETCHING SOLUTIONS TO TODAY'S CORROSIVE SALTS

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The first attempts to use etching in printmaking were, according to André Blum, in the early XV th. Century: "Quelquefois même des irrégularités de taille d'une épaisseur d'encre en relief laisserait même supposer de l'eau-forte aurait été pratiquée dans les premières années du XV^e. siècle, comme l'indique un manuscrit de 1431 de Jehan le Bégue à la Bibliothèque Nationale (ms. Lat. 6741), c'est à dire près de cent ans avant de Urs Graf, Dürer, Mazzouli de Parme, dit le Parmesan et Lucas de Leyde, considérés jusqu'alors comme les ancêtres de cette technique"¹.

One of the first persons to use etching was Urs Graf (Soleure 1485-Bâle 1527). His first known prints are from 1513. Two years later, Albert Dürer used acids to etch iron.

Apart from these first sporadic uses, the Italian painter Givolano Francesco Maria Mazzouli, well known as Parmigiano (Parma 1503 - Casalmaggiore 1540), is one of the pioneers of etching. From 1530 he strongly promoted the use of acid in printmaking. Antonio da Trento, one of his disciples, exported the new technique to France. There he was associated with the Fontainebleau painters and from there it spread all over Europe, from the second half XVI th century.

Benvenuto Cellini (1500-1571) sculptor and jeweller, was a contemporary of Parmigiano. In addition to working in Florence and Rome he also worked in

¹ Blum, A. *Les origines du papier*. (Paris: La Tournelle, 1935), p. 164

Author's note: At the beginning of the XV th. Century some irregularities in the marks are noticed as if they had been etched. So, we deduced that etching has first been used in the first years of the XV th. Century as it is indicated on the 1431 manuscript of Jehan Bégue located in the National Library (ms Lat.6741). It is nearly one hundred years before Urs Graf, Dürer, Mazzouli of Parme (called Parmegiano) and Lucas of Leyden were considered as the ancestors of this technique.

Fontainebleau. Two etch formulas appear in his jewelry treatise², for cutting and decorating metals and for making printing plates. About the formula for printing, the author wrote: “El aguafuerte de grabar se hace del siguiente modo: coge media onza de pez, una onza de vitriolo, media onza de alumbre de roca, media de cardenillo y seis limones; mezcla todas esas cosas, previamente bien pulverizadas, con el jugo de los limones, y haz que hierva esta mezcla durante un poco de tiempo, sin resecarse demasiado, en una vasija vidriada. Si no tienes limones utiliza vinagre fuerte que dará el mismo resultado”.

These old names correspond to the following substances:

- *vitriolo*= the author does not say if it is sulphuric acid or hydrated copper sulphate.
- *alumbre de roca* = aluminium and potassium sulphate
- *cardenillo* = copper acetate
- *salitre* = potassium nitrate

“En cuanto al aguafuerte de cortar, se hace del siguiente modo: Coge ocho libras de alumbre de roca quemado, otro tanto de excelente salitre y cuatro libras de vitriolo romano y ponlo todo en una redoma: junto con estas cosas pondrás también, un poco de aguafuerte que ya haya sido utilizada”³.

His jewelers etching solution was never used as an mordant but as a metal solvent. It dissolved metals such mercury, copper, tin, silver, etc. Delormois suggests, in 1771, substituting this mordant by “Espiritu de Nitra”, that is to say nitric acid⁴.

During the XVII th. Century etching became an art language as a result of the work of a number of artists, including Van Dyck, Jaques Callot, Hercules Seghers, Rembrandt and Ribera. We have inherited from Rembrandt the use of Dutch Mordant. It is a compound of hydrochloric acid, potassium chlorate and

² Cellini, Benvenuto. *Tratados de orfebrería, escultura y arquitectura*. (Reissue, Madrid: Akal,1989), p.146-147

Author's note: The mordent for etching it is made in the following way: take half an ounce of resin, one ounce of vitriol, half an ounce of rock alum, half of verdigris and six lemons; mix all those things, having previously well pulverized them, with the juice of the lemons, and boil this mixture for a little while, without letting them dry too much, in one glass pot. If you do not have lemons you can use strong vinegar and that will give the same result.

³ Author's note: As far as the etching to cut, it works in the following way: take eight pounds of rock alum, the same amount of excellent saltpetre and four Roman vitriol pounds and mix everything in one pot: together with these ingredients also put a little etching solution that had already been used.

⁴ Delormois, Mr. *Arte de hacer las Indianas de Inglaterra...* (Madrid: Imp. Real de la Gazeta, 1771), p.55-56

salt. Nowadays, this mixture is not recommended at all due to its high level of toxicity.⁵

Abraham Bosse, a Callot disciple, published in 1645 one of the first treatises on etching entitled *Traité des manières de graver en taille douce et sur l'airin par le moyen des Eaux Fortes et des vernis dur et mol (1645)*⁶. In this treatise Bosse described the technique he had learned from his master Callot who had been taught to etch in Italy. It talks about the Luthiers varnish that Callot used - whose base is not wax but linseed oil which is harder than 'black varnish' and resistant to the "échoppe", a tool with which Bosse got as good results as with a burin. It is unknown if the etching solution proposed by Bosse was developed by himself or was learned from Callot – who hadn't written any handbook as far as we know - or if the compound was originated in Italy. In the following table the ingredients and amounts necessary for Bosse's formula are detailed.

Compound	Quantity
<i>Vinaigre</i>	<i>trois pintes*</i>
<i>Sel armoniac**</i>	<i>six onces***</i>
<i>Sel commun</i>	<i>six onces</i>
<i>Verdet****</i>	<i>quatre onces</i>

* 1 *pinta* = 0'568 l. (UK), 0'425 l. (USA)

** *Sel armoniac* = sel ammoniac= ammoniac chloride

*** *once* = 28'7 grams

**** *Verdet*= copper acetate

Manuel de Rueda, in 1761, wrote one of the first treatises in Spanish. He refers to several of Bosse's formulas: *Instrucción para gravar en cobre y perfeccionarse en el gravado al buril, al agua fuerte y al humo*⁷. The formula is as follows in the table below. The preparation process consists in mixing up all the ingredients in a clay pot – not in a metal pot which could alter the etch - which is then boiled over a fire. The amount of time required is difficult to quantify - in the text this is specified as the period needed to bring it to the boil three times.

⁵ Rossol, M. *The artist's complete Health and Safety guide*. (Canada: Allworth Press, 2001), p.212. ; VVAA. *Making Art safely*. (USA: John Wiley & Sons, Inc., 1996) p.219.

⁶ Bosse, A. *Traité des manières de graver en taille douce sur l'airin. Par le moyen des eaux fortes et des vernis durs et mols*. (Paris: 1645), p. 11

⁷ Rueda, Manuel de. *Instrucción para gravar en cobre y perfeccionarse en el gravado à buril, al agua fuerte, y al humo con el nuevo methodo de gravar las planchas para estampar en colores, à imitación de la Pintura*. (Madrid: Joachin Ibarra, 1761), p. 68-71

Table 2. Composition of Manuel de Rueda's etching fluid	
Compound	Quantity
<i>Vinagre</i>	<i>tres quartillos*</i>
<i>Sal amoniaco</i>	<i>tres onzas</i>
<i>Sal común</i>	<i>tres onzas</i>
<i>Cardenillo o verdete</i>	<i>dos onzas</i>

* 1 *quartillo* = 0'5 liter

** *Sal amoniaco* = sal ammoniac = ammoniac chloride

*** *onza* = 28'7 grams

**** *Verdete* = copper acetate

Comparing both compounds, and thinking about both formulas the amount of vinegar is almost the same, but we can see that the proportion of salts and verdigris is exactly double in Bosses's compared with that in Rueda's

We have made and tested both Bosse's and Rueda's formulae and the results are pretty similar although the intensity of the compounds is very different: Bosse's one bites more rapidly and Rueda's one is slower but produces very clear results.

How can we explain such a big difference of concentration over this period of just slightly more than a century? In my opinion the explanation of this difference is the way of applying the acid to the plate. Abraham Bosse⁸ explains carefully the way he does the etching: he doesn't dip the plate in an etching tray – as we do nowadays - but he sets the plate nearly vertically over a basin, supported on trestles and the etching is poured over it from above from a clay pot or something similar. So the solution goes down over the plate into the basin underneath, and then the printmaker collects it and pours it again over the plate. It is a slow process. The printmaker checks the depth of the bite as it goes, and stops out with a mixture of grease and oils, the lighter areas of the composition and then keeps pouring the etching solution in the same way until the desired results are obtained.

Antonio Palomino de Castro y Velasco, in *El Museo Pictórico y Escala Óptica*⁹, simplified the mechanism of the French author and proposed a wooden 'cradle' for holding the plate in an inclined position over the basin.

⁸ Bosse, A. (1645) p.30 and followings

François Courboin in *L'estampe Française*, named Bosse's etching method "eau forte à couler" because "il fallait la faire couler sans relâche sur le cuivre maintenu dans un plan incliné: ce dispositif es nécessaire pour entraîner les sels qui se forment à la surface du cuivre et qui arrêteraient l'action du mordant"¹⁰.

Manuel de Rueda explained how to dip the plate in a tray with a corrosive bath¹¹: "se coge una caja de conveniente magnitud, cuyas tablas (bien delgadas) tengan en los costados tres, ò quatro pulgadas de altura, ajustandoles bien, y pintando la caja à el oleo por dentro, u fuera, para contener el agua fuerte sin embeberla"¹². The tray is rocked from side to side to avoid salt deposits blocking the uncovered areas. Bosse didn't have this problem because the mordant runs down over the inclined plate. However, it had to be a stronger formula because its action over the plate was intermittent. If the plate is immersed in the tray the contact is constant and the mordant acts quickly.

Rueda recommended for bigger plates that the etcher should make a small wax wall for containing the mordant¹³ or, if he prefers, makes a paper wall using a thick folder paper. The paper should have been previously waterproofed with a mix of Venice turpentine, oil and wax. This way of working with wax was not really new, as Benvenuto Cellini had already described it in *Trattati dell'oreficeria*¹⁴ in the Italian Renaissance.

⁹ Palomino de Castro y Velasco, Antonio. *El Museo Pictórico y Escala Óptica*. (Madrid: Juan García Infaçon, 1724) Volume II 5th. ed. 1988

Author's note: It was necessary to keep it running on the copper from the top of the plate. The plate has to be in a near vertical position. It is necessary for avoiding the formation of salts on the surface of copper that would stop the mordant.

¹⁰ Courboin, François. *L'estampe Française*. (Paris), p.34

¹¹ The method followed by Le Clerc is explained in the Spanish handbook when he produces the new edition of *Traité des manières de graver en Taille Douce*. Ch. N. Cochin collects Le Clerc's process in the second new edition of the Bosse treatise and it is certain that Rueda transcribes it from this edition.

Author's note: A box of an appropriate magnitude is taken, whose tables (very thin) have to fit and have to be about three or four inches of height in the sides. The box has to be painted inside and outside with oil in order to contain the mordent without absorbing it.

¹² Rueda, Manuel de. (1761) p. 71

¹³ Rueda, Manuel de. (1761) p.145-151

¹⁴ Cellini, Benvenuto.(1989), p.147

Bosse had already described how to make a tray for containing the plate with wax in the paragraph where he speaks about using the soft varnish, or the black varnish that we currently use. The etching fluid is also different when he describes “eau forte de départ” or metal polishing solution, which is made of sulphuric acid or hydrated copper sulphate, potassium nitrate and sometimes aluminum and potassium sulphate, chemically combined. Cellini calls this etching fluid “agua fuerte de cortar” in his jewellery treatise.

Bosse recommends the first etching method because it is useful for both the hard ground and the soft (currently black one). Charles Nicolas Cochin, in his 1745 edition of his handbook, confirms Bosse’s opinions on using the “couler” etching method, but he for the first time invokes health reasons, rather than efficiency for using it: “... Elle est bien plus excellente que celle des Affineurs: elle n’est point si sujette à faire éclater le vernis ni a plusieurs accidents, par exemple d’être perjudiciale à la vûe et à la santé, comme celles de départ...”¹⁵

The “couler” Bosse etching method is, without doubt, less toxic than the immersion one. Vinegar and salt are among its main components. They are domestic and daily products with no toxicity effects. Copper acetate is soluble, affordable and it releases acetic acid when hydrolyzed; so it does not have the noxious effects of the strong mineral acids. It is generally used as an agricultural fungicide. If the ammonium chloride is exposed to high temperatures it becomes ammonia gas and hydrochloric acid gas¹⁶. This risk can be avoided if the vinegar is replaced by 1:3 proportion diluted of acetic acid¹⁷. In this way the salts can be dissolved cold and boiling the ingredients can be avoided¹⁸.

We have experimented with both versions. We can confirm that once the mordant has been mixed it doesn’t give off gases. However, there is a strong smell in both of them that makes advisable to put a lid on the tray while biting the plate.

¹⁵ Bosse, A. *De la manière de graver à l’eau forte et au burin. Et de la gravûre en manière noire. Revûe, corrigée & augmentée du double par Ch. N. Cochin.* (Paris: Ch.A.Jombert, 1745) p.93

Author’s note: It is much more excellent than the one of the refiners: it doesn’t break the varnish at all and also avoids other possible accidents. It is not, for instance, dangerous for the view and health, like those of “depart”.

¹⁶ VVAA. *Making Art safely.* (USA: John Wiley & Sons, Inc., 1996) p.191

¹⁷ Pure acetic acid or in a 50% concentration is very corrosive for fabrics and could cause skin burns. In non-corrosive concentrations it is not toxic. Its salts and esters are called acetates.

¹⁸ Perrot, A.M. *Nouveau manuel complet du graveur ou traité de l’art de la gravure en tout genre.* (Paris: Encyclopédie Roret, 1830). Facsimil Inter-Livres, 1988.

The “à couler” Bosse etching method featured as the most important one in printmaking handbooks until the middle of the XIX th. Century, when it was replaced by the nitric acid compounds and hydrochloric acid that we know nowadays. Excluding the Dutch mordant, we can see that in the old printmaking workshops less toxic mordants were used than in the present ones.

The first Spanish treatise that mentions commercial nitric acid for etching is *Instrucción para el pueblo. Cien tratados sobre los conocimientos más indispensables* by Basilio Sebastián Castellano de Losada, date in 1851¹⁹. This handbook is the result of a work of diffusion and translation of many different texts, mostly of them written in French.

During the first part of the XIX th. Century both old etching solutions and new acids were curiously coexisting together. In 1830 A.M.Perrot in the Printmaking volume of the *Encyclopédie Roret* describes, for instance, a German formula as follows: “On fait fondre dans l’acide nitrique tout le cuivre que le liquide peut dissoudre, et, d’un côté, on prépare une solution saturée de sel ammoniac dans un bon vinaigre. On mélange alors 3 parties en volume de la solution cuivrique avec 1 partie, aussi en volume, de solution ammoniacale”²⁰. Also oddly the following one: “Para las planchas de acero: Yodo en escamas (50gr), yoduro potásico (125 gr.), agua (1l.), sulfato de cobre (125 gr.), sal amoniaco (184 gr.), vinagre destilado (3l.), nitrato de plata (1.8 gr.), alcohol (200 gr.), ácido nítrico (100 gr.), agua destilada (1500 gr.), alcohol (100 gr.) y ácido nítrico (100 gr.)”²¹.

In some XIX th. Century handbooks, the old Bosse formulas are quoted as a curiosity²² and those based on acids that we use now are recommended. Although Melis-Marini²³ advises in 1916 of the health hazards of using acids

¹⁹ Castellanos de Losada, Basilio Sebastián. *Instrucción para el pueblo. Cien tratados sobre los conocimientos más indispensables*. (Madrid: Establecimiento Tipográfico de Mellado, 1851) Tomo II, tratados 51 al 100

²⁰ Perrot, A.M. (1830), p.37

Author’s note: Dissolve in nitric acid all the copper that could be diluted (dissolved?) in the liquid, and, and separately a saturated solution of sulphate of ammonia is prepared in a good vinegar. Then mix 3-volume parts of cupric solution with 1 part, also in volume, of ammoniac solution.

²¹ Camps Armet, C. *Diccionario Industrial (Artes y oficios de Europa y América)* (Barcelona: A. Elías y comp. 1887), p.827

Author’s note: For steel plates: Iodine in grudges (50 gr.), potassium iodide (125 gr.), water (1l.), copper sulphate (125 gr.), salt ammonia (184 gr.), distilled vinegar (3l.), nitrate of silver (1,8 gr.), alcohol (200 gr.), nitric acid (100 gr.), distilled water (1500 gr.), alcohol (100 gr.) and nitric acid (100 gr.)

²² Adéline, J. *Vocabulario de términos de Arte*. (Madrid: La ilustración española americana, 1888); Melis Marini, Felice. *El aguafuerte y demás procedimientos de grabado sobre metal* (Milano: 1916) (Barcelona: E. Meseguer 1954) 2a.ed. 1973 p.21

²³ Melis Marini, F. (1916) p.41- 42

because of 'poisonous gases' (they give off nitric) and he designs as a preventive measure, a gadget for biting the plate avoiding any human contact. In the XIX th. Century awareness of health hazards and worries about the dangers of etching with acids were not perceived.

At the end of the XX th. Century health and environmental awareness first appears in printmaking publications and consequently alternative mordents to the acids are being proposed.

Some of them were already known like the use of ferric chloride. Others are new but based on old compounds like salts and sulphates. It can be seen that the investigation on new materials and procedures means a return, a renaissance, to the first printmaking compounds.

The Bordeaux Etch, proposed by Cedric Green²⁴, for instance, is a concentrated solution of copper sulphate and it bites zinc plates without giving off poisonous gases. A similar compound for biting aluminum and zinc is Nik Semenoff's one, based on the copper sulphate, salt and sodium bisulphate²⁵. As we can see these compounds and others recently proposed are not too far from Abraham Bosse's ones.

We have experimented with Abraham Bosse's formula on different metals and we can affirm that it corrodes copper, zinc, aluminum and iron. The different metals require the appropriate concentration and length of the biting. With the mordant proposed by Manuel de Rueda on a copper plate very clear and deep marks were obtained with no widening of the marks.

In this paradigm of non-toxic printmaking, the etching solution par excellence is ferric chloride. Although safety measurements are needed (gloves and mask) during preparation and manipulation, most of the researchers affirm that it is much less toxic than nitric or hydrochloride acid²⁶ so it is a good substitute. Friedhard Kiekeben has carefully studied the different ferric chloride compounds and they have been adapted to different metals (zinc, copper, aluminum, steel...) and they have been applied either in tray or in a vertical tank: they are known as a Edinburgh Etch²⁷.

²⁴ Green, Cedric. *Green Prints* (Sheffield: Ecotech Design, 2002)

²⁵ Semenoff, Nik.; Bader, L.W. "Intaglio Etching of aluminium and zinc using an improved mordant", *Leonardo*, v. 31, 1998.

²⁶ Hoskins, Stephen. "The chemistry of ferric chloride" a: *Printmaking Today*, vol.4, núm.2 1995

²⁷ Kiekeben, Friedhard. "The Edinburgh Etch: A breakthrough in non-toxic mordant", *Printmaking Today*, vol. 6, n. 3, 1997

The vertical tank, proposed by the Canadian Keith Howard²⁸ is, as its name indicates, a tank to bite plates vertically, which can be used with ferric chloride. The advantages of this procedure are many: the salts are not deposited in the furrows; the surface of mordant in contact with the air is considerably reduced compared with the tray system; a circulation system, similar to that used in aquariums, causes turbulence in the mordant, so that it is agitated and reactivated and the plate is evenly bitten; a number of plates can be bitten at a time, with the advantage that it takes less space and the placing of the plates is easier; due to the darkness of the perchloride a view of the plates is not possible.

This proposal, the vertical tank of Keith Howard, is an evolution of Bosse's "à couler" etching method that has been described previously.

Other current topic is the waste elimination once the mordant has been exhausted. The investigators propose different solutions, from neutralization and re-use in other procedures to, when there is not another solution, a negotiation with the local service of toxic product collection. Environment respect and human health care constitute two of the main objectives in the art of printmaking.

Parallel to the substitution of the components in mordents is an evolution in other technical aspects of printmaking. The first uses of etching were for drawing on the plate, to facilitate the later work with the burin. The old dominance of the burin etching – there are some exceptional cases aside, like Rembrandt or Callot - dissipates as the practice of burin engraving almost disappears. In the XIX th. Century, and fully in the XX th., the etching is the protagonist: it is an easy and quick process that does not demand the skill of the practice of burin. The consolidation of indirect techniques (mordents take over the incision process) and the flood of new processes based on them, explains the increase of new formulae for mordants. Commercial chemicals provide much more elaborated products, gradually avoiding the necessity to mix diverse products to obtain compounds. The effectiveness of these products and their ease of use have given us to the formulae that we used in our workshops, mostly based on nitric and chloride acids. But we may have been unaware of the possible consequences of use and abuse of these products. They give off gases, there was little ventilation of the workshops and little personal protection (such as masks and gloves, etc.). These are factors that expose us to the possible health problems that can result. Likewise, there has been little care when it comes to the moment for disposing of the mordents, which are very toxic and highly dangerous for the environment.

Lastly, it has been demonstrated that we can print with environmental friendly products. This tendency, as we have already shown, means a revival of materials and procedures from the past. Not just mordents – based on salts and sulphates – but products and methods like methods for cleaning the inked

²⁸ Howard, Keith. *Non-Toxic intaglio printmaking*. (Canadá:1998), p. 30-32

plate with oil and water, de-greasing it with salt and vinegar²⁹, or talc mixed with water, among others.

We have initiated a hopeful century, in which an environmental conscience is developing in printmaking and, what is most important; the expressive resources are preserved and increased in this artistic language. We do not forget that in any artistic manifestation, technique is at the service of expression and creativity. Our obligation as researchers/professors and artists is to provide much more sustainable practices for the future of Art and to disseminate this knowledge and these methods, since the respect for the environment depends on the wide use of these techniques.

²⁹ Cochet, Gustavo. *El grabado*. (Buenos Aires: Poseidón, 1947), p.189