Old inks: plant-based inks

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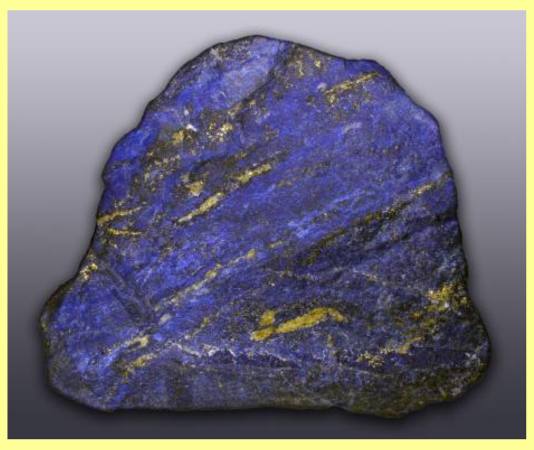
Thousands of years ago, natural pigments were discovered and they have been used ever since. Indeed, prehistoric people already used them to paint the walls of the caves in which they were living. A significant example of this is the Cosquer cave (-19,000 to -27,000 years) located near Marseilles (France).

Pigments and dyes can be classified into two broad categories: natural pigments and dyes and those called artificial. These categories are then subdivided into five families. The first one of these five families includes the mineral pigments. Among these we can find the clays (yellow ochre, red ochre, green clay, brown clay) and the stones like lapis lazuli (blue) and malachite (green). The second and third families gather the organic dyes and pigments. Those that have vegetal origins like indigo (blue), weld (yellow) and madder (red) compose the family 2 and those that have animal origins like cochineal (red) and kermes dyers (carmine) form the family 3. One family includes pigments and dyes stemming from chemical reactions such as verdigris or red lead (family 4) and the other one is made of the miscellaneous inks such as iron-gall type who are vegetal and mineral one (family 5).

All these pigments, although they have been used for centuries, have been replaced by synthetic dyes from the oil industry at the end of the 19[th] century. Indeed, they have the advantage of reproducibility of the properties unlike natural pigments. But the scarcity of oil causes a renewed interest in natural preparations. In such purpose, our laboratory in conjunction with the Abbey of Villers-la-Ville has decided to study natural derivatives for inks and focuses in particular on the extraction of pigments from plants.

Cosquer cave



Family 1
Lapis lazuli

Family 2
Weld

Family 3
Cochineal insect

Family 4
Verdigris

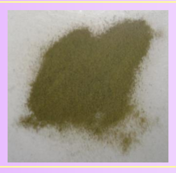
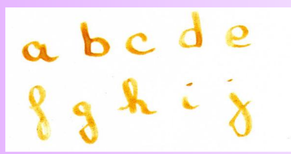
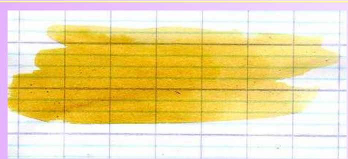
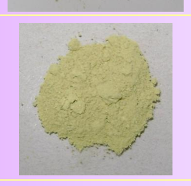
Family 5
Iron gall ink

Definitions

Decoction: *the liquid and the plant are boiled together.*
Infusion: *the plant is put to soak after the boiling of the liquid.*
Maceration: *the plant is immersed in a liquid at room temperature (for longer time).*

Alum stone: *the ordinary alum (also called Kalinite) is a salt with the chemical formula* $KAl(SO_4)_2 \cdot 12\ H_2O$ *(11* H_2O *for Kalinite).*
To mordant: *step of manufacturing an ink which allows the coloring substance present in a plant to bind to a metal salt and thus formed a solid complex, depending on the metal salt used the resulting color will be different.*

Results

Name of the plant	Extraction mode	Mordant	Yield	Color	Example	Remark
Madder (Rubia tinctorium L.)	physical with hot water	alum stone	14.1 %	red		
St John's wort (Hypericum perforatum L.)	alcoholic maceration	alum stone	40.6 %	pale green		
	aqueous decoction	alum stone	35.6 %	yellow-green		
	aqueous decoction	copper sulfate	-	brownish green		
German chamomile (Matricaria recutita L.)	aqueous decoction	alum stone	13.8 %	yellow		
Saw-wort (Serratula tinctoria L.)	aqueous decoction	alum stone	12.3 %	between green and yellow		
Meadowsweet (Filipendula ulmaria L.)	aqueous decoction	alum stone	29.5 %	yellow		
	aqueous decoction	copper sulfate	-	green		
	aqueous decoction	iron sulfate	-	grey-black		No precipitate but formation of a black ink.[1]
Turmeric (Curcuma longa L.)	aqueous decoction	alum stone	-	yellow-orange		
Pomegranate (Punica granatum L.)	aqueous decoction	alum stone	37.8 %	brown		Brown but yellow upon application.
	aqueous infusion	-	-	yellow		
Tansy (Tanacetum vulgare L.)	aqueous decoction	alum stone	85.3 %	yellow-green		
	aqueous decoction	iron sulfate	75.9 %	brown		
Burning nettle (Urtica urens L.)	aqueous decoction	alum stone	13.8 %	-	too light, due to the insolubility of pigments	
Common Grape Vine (Vitis vinifera)	aqueous decoction	alum stone	11.8 %	-	too light, due to the insolubility of pigments	

[1] Noémie Wymeersch; Isabelle Bouchat; Lauric Henry; Caroline Destrée; Anne Burette; Gilles Olive, Encres anciennes: l'encre ferro-gallique, Société Royale de Chimie, ed., Journée scientifique annuelle de la Société Royale de Chimie (SRC): l'analyse chimique, outil des experts. (October, 11[th] 2012, Louvain-la-Neuve (Belgium): 2012), P52.