CHAPTER 11 Making verdigris (from copper)

Pera fazer azinhafre mui fino

Figure 1 *Main steps in the making of verdigris*

'In order to make very fine verdigris, take very thin leaves* of copper and moisten them in very hot and strong vinegar. And put them in a pot leaning on its side, and smear the mouth of the pot with honey and cover it with potsherds, and bury it under the manure of large animals, and let it stand there for thirty-one days. And after these days take the pot out and you will find verdigris, and scrape it with a spatula. And if you want to make more, repeat as directed, and you will have good verdigris.' [1].

**in Portuguese Strolovich transliterates as 'toma folhas de cobre muito delgadas e moles'.*

Reproduction

The surface of a leaf of copper foil was cleaned with sandpaper and immersed in strong, pre-heated at 60–70° C and filtered vinegar, pH ≈ 3, for 10 min.

It was then placed inside a pot of clay, sealed (with clay), and the board was coated with honey.

The sealed pot was carefully put inside a larger clay pot, covered with potsherds, and let stand for 31 days buried in horse manure or in sand.

After the 31 days, the pot was carefully opened, and the leaves were found covered with verdigris.

Rationalisation / Chemical reactions

When copper or copper alloys are exposed to acetic acid solutions (such as vinegar), in a closed vessel, the surface of the metal is corroded, due to the oxidation of copper [2]:

$$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$$

At the same time, in the interface between the metal surface and the acidic solution, the electrons provided by copper oxidation reduce atmospheric oxygen, producing water:

$$O_2(g) + 4H^+ + 4e^- \rightarrow 2H_2O(l)$$

Acetic acid, a weak acid, in solution establishes an acid-base equilibrium:

$$CH_3COOH\ (aq) \rightleftarrows CH_3COO^-\ (aq) + H^+(aq)$$

Therefore, the acetate ions bind to the copper cations, producing insoluble copper acetates.

$$Cu^0 + 2CH_3COOH + \tfrac{1}{2}O_2 \rightarrow Cu(CH_3COO)_2.H_2O$$

These copper acetates may differ in their acetate to hydroxide component ratio and degrees of hydration. These variations have impact on the colour, in the sense that they can produce different shades of blue and green [3-7].

In our experimental conditions, only the formation of the neutral copper acetate $Cu(CH_3COO)_2.H_2O$, was observed.

Key aspects

Reaction stoichiometry: The electrolytic corrosion of the copper leaves occurs in a proportion of one mole of copper per two moles of acetic acid, however we should consider more complex reactions, as discussed above.

Corrosion of copper leaves: For the redox reaction of copper it is important to leave the copper foil in contact with air to improve the production of verdigris, as opposed to submerging the copper in the acetic acid solution.

Missing / Obscure indications

Amount of vinegar: The recipe says to 'moisten' the thin leaves of copper foil in 'very hot and strong vinegar'. The moistening suggested in the treatise appears to be insufficient to oxidize the entire surface of the copper foil; it is possible that the information on a vinegar deposit, to be included in the vessel along with the copper, is missing.

Type of vinegar: In this recipe the vinegar is described as 'strong', but no other description is given. Strong could mean a high concentration of acetic acid and thus a strong smell and a lower pH. During our experiments, several types were tested, such as commercial white and red vinegars (pH = 2.5) and oak-matured homemade vinegars (pH = 3). The best results were achieved with a 50-year-old homemade vinegar [3,4].

Sealing method: The exposure to high acetic acid concentration in the gas phase is important for the reaction yield. Thus, the sealing of the pot should be very efficient (to concentrate acetic acid in the gas phase), which is not clear on the recipe.

Comments

Vinegar is only introduced for moistening the copper leaves. To improve the reaction yield, vinegar must be available on the bottom of the pot to corrode the copper foil, otherwise only the non-flat areas and the borders and cracks of the copper leaves will accumulate small amounts of vinegar and, therefore, the verdigris will be produced in small restricted areas.

There are other recipes from that period, such as the ones found in treatises like *Mappae Clavicula* or *De diversis artibus*, which suggest the continued exposure of the copper leaves to vinegar vapours. Our experiments suggest that a higher yield is obtained from the continued exposure to vinegar vapours than by moistening or immersion.

Horse manure: Animal manure was most likely used to maintain moisture and a certain temperature inside the pot, once its decomposition occurred [8]. This would promote the corrosion of the copper foil. Temperature could be a critical issue in cold climates.

Honey: This hygroscopic ingredient may improve the oxidation of the copper foil by increasing the contact area between the metal foil and the acetic acid.

Verdigris in Portuguese medieval illuminations

Green is an important colour in Portuguese medieval illuminations, particularly a certain deep green named *bottle green* ('verde garrafa' in Portuguese), which is based on synthetic copper proteinate [3,4], Fig. 2. According to some authors [10], copper proteinates may have been formed in the course of time, as a reaction between verdigris and a proteinaceous binder, meaning that this copper proteinate was not intentionally made. In our case studies, considering the consistency of the colour values and the absence of a heterogeneous surface, which could sign the presence of solid state reaction(s), we do not think this to be probable.

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Figure 2 *Examples of bottle-green in Portuguese medieval manuscripts, from left to right: Santa Cruz 20 Legendarium, f. 86; Santa Cruz 1 Bible, f. 37; Lorvão 15, f. 5v; Alcobaça Legendarium 421, f. 218.*

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Further reading

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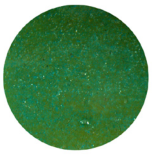
Main collaboration:
Juliana Buse and Catarina Miguel

Appendix

Verdigris characterisation: synthesised following 'The book on how to make colours', Chapter 11

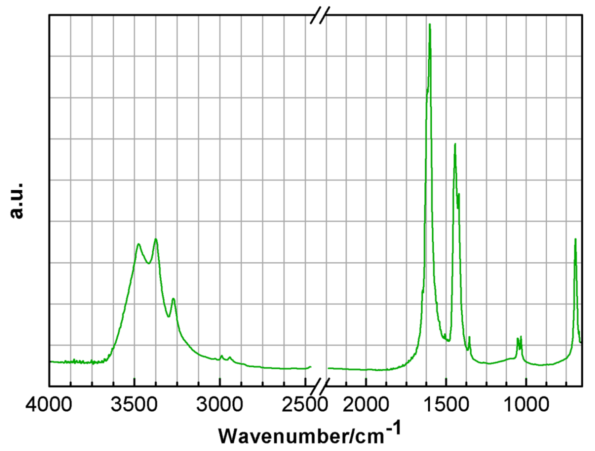


Colour

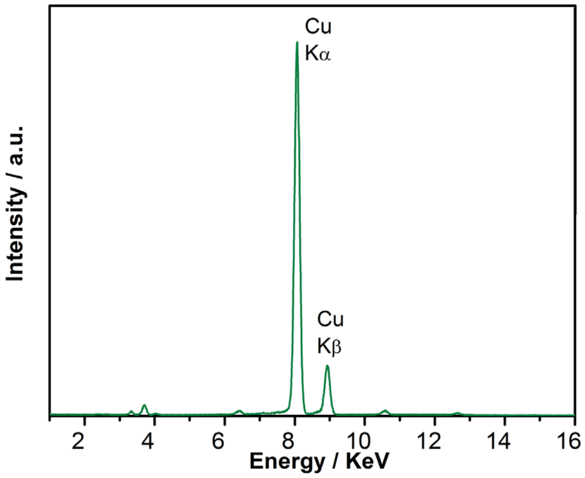
Table 1 Colour coordinates, Lab, for verdigris paint reconstructions using two different binders (arabic gum and parchment glue) applied over filter paper and parchment. Spectroscopic characterisation*

Support	Binder	L	a*	b*
Filter paper	Parchment glue	49.10	-64.86	-33.80
	Arabic gum	60.80	-65.28	-33.68
Parchment	Parchment glue	62.40	-20.86	2.06
	Arabic gum	60.80	-20.90	6.42

Spectroscopic characterisation



FTIR spectrum acquired with Nicolet Nexus spectrophotometer coupled to a Continuµm microscope with a MCT-A detector. Spectra were obtained in transmission mode with a resolution of 4 cm^{-1} and 128 scans.



EDXRF spectrum ArtTAX spectrometer acquired with an mobile arm with a molybdenum (Mo) anode, Xflash detector refrigerated by the Peltier effect. Experimental parameters: 40 kV of voltage, 300 µA of intensity, for 200 s, under Helium gas flux.