CHAPTER 15 To make vermilion
Para fazeres vermelhom

Figure 1 *Main steps in the making of vermilion.*

"To make vermilion, take five pounds of quicksilver, that is mercury, and place it in a bottle or large glazed bowl, and take a pound of very fine virgin sulphur. And pour the powdered sulphur over the quicksilver little by little until it is well incorporated, always stirring it with a dog's foot that has its hair and wool, until the fire turns to ashes. And once the fire has thus died down, place it in two new pots that are made like bottles, broad below and narrow above. And seal them, leaving only a small hole through which the vapor will escape. And place the pots on the fire on their holders and cover them well with clay, and place a bowl over the holes. And when you see the smoke coming out red and not malodorous, place a thin spit in it.

And if anything sticks to the spit, remove the pots from the fire and let it cool. And once it is cool break the pots and you will find the vermilion made. With these measures you ill made as much vermilion as you wish: for a terça of mercury take five pounds of sulphur, and for five pounds of mercury take one pound of sulphur. And regulate the first in such as way that it does not [10v.] burn, and keep the fire moderate, neither quick nor slow. On this note, if by chance the vermilion burns, break the pots and grind it and incorporate it and mix it with another measure of mercury and sulphur, and place them in other pots and proceed as described. And pay attention to the vapours that escape, thus you will never ruin anything." [1]

Reproduction

The *olhas* (clay container) were designed, handmade using white or red clays, and fired as necessary to obtain a ceramic pot. In this reproduction, we used a white crucible made of two parts: a base where metacinnabar is heated and a cover.

The proportion present in the treatise was followed: 1.047 g of mercury and 0.1674 g of sulphur were weighed and ground in an agate mortar with a pestle.

To improve the incorporation of both compounds, sulphur was slowly added and mixed with mercury, until all were bound and a silver-black-greyish compound was formed. What is observed may be described as in the treatise "until the fire turns to ashes" [1]. This step takes time and patience.

Black mercury sulphide, was then transferred into the base of the clay crucible, which was covered and sealed with fresh clay.

Experiments placing the pot directly into the fire were carried out. When needed, small amounts of water were dropped over the necessary areas to avoid flames or lowering the temperature. For maintaining the embers, combustion air was introduced with the aid of a wooden air blower.

In a successful experiment, after two and a half hours, the pot was taken from the fire and cooled to room temperature. Afterwards, the *olha* was opened and vermillion was found inside its base.

Rationalisation / Chemical reactions

In the first step, mercury and sulphur are ground to produce metacinnabar, a silver-black compound with a cubic crystal structure, which is the kinetic product of this reaction [2-5], being thermodynamically stable only for high temperatures, above about 370º C. The thermodynamic stable form at room temperature is the hexagonal mercury sulphide (vermilion).

For more details please see [2-11]. In a second step, metacinnabar is heated at 350-370º C, and will rearrange into the hexagonal form that corresponds to the red product, vermilion.

It is important to stress that, for our experimental conditions, the production of red mercury sulphide – vermilion – is a solid-state reaction and not a sublimation process [13, 14]. When sublimation occurs, for temperatures higher than 580º C, a black product, not yet characterized, is formed. This product can be a mixture of meta and hipercinnabar [4].

Key aspects

Reaction stoichiometry: one mole of sulphur reacts with one mole of mercury.

Mixing mercury with sulphur to produce black mercury sulphide may be achieved by a thorough grinding, heating or using amalgam. In our reproductions we tested both thorough grinding and amalgam formed by heating sulphur: both worked in the same way, although in the text grinding is described and with very specific details.

Temperature at which black metacinnabar is converted into red vermilion is "the crucial" parameter. To transform the black mercury sulphide form (α'-HgS) into the red form (α-HgS), it is necessary to avoid temperatures above about 400-450º C. On the other hand, the higher the temperature the more efficient will be the solid state reaction that enables the conversion of the cubic black form into the red one. To test the influence of temperature control over reaction yield, sand baths were used and temperature was measured over time in the sand. For our experimental conditions, starting with about 0.5 g of black metacinnabar, we found that introducing the pot in the sand bath heat at 285º C for 2h30 and afterwards rising the temperature (heating rate of 15º C / min) until circa 350º C for 2h30 produced the best results.

Missing / Obscure indications

Pot design: There is no precise information about the shape of the *olha*. Strolovitch in his translation refers to it as a vessel "like bottles, broad below and narrow above", [1]. In Spain the term "olla" is currently used to refer to a cooking pot with a lid, traditionally an earthen pot that may be found in many shapes. In this recipe *olha* could stress the fact that the pot was covered.

Heating temperature and time: the only information given is "place the pots on the fire" and "keep the fire moderate, neither quick nor slow", [1]. Usually, embers' temperature fall between 620 – 670º C. We do not know if the pots should be placed directly on the fire neither for how long (a couple of hours? all day?). Where was this fire made? In a special apparatus or just on the ground? How was it maintained and controlled? We infer, from the lack of information, that the experiment time was to be expected more in the 1-2h range than in the 3h-6h.

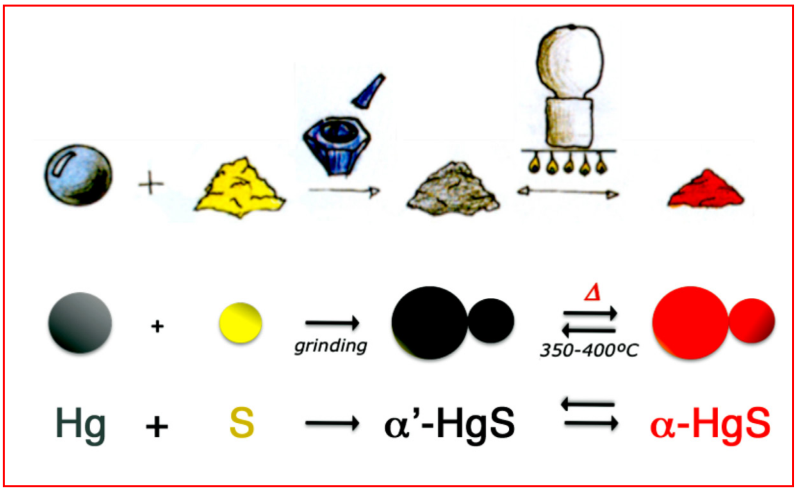

Figure 2 Reaction scheme for vermilion synthesis.

Figure 3 Examples of vermilion on Portuguese medieval illuminations. From left to right: Santa Cruz 20, f.137v: the red is pure vermilion paints and the dark red is a mixture of vermilion with lac dye; Alcobaça 419, f.91v: pure vermilion paint; De Avibus (Lorvão 5), f.25: the vermilion is admixed with the extender calcium carbonate; and Lorvão Apocalypse, f.210: vermilion with red lead.

Heating time and red smoke: The information present in the treatise says "and when you see the red smoke coming out red and not malodorous, place a spit in it. If anything sticks to the spit, remove the pots from the fire and let them cool" [1]. However, no red smoke was observed in any of the many experiments conducted. The only smoke observed was black, probably the result of metacinnabar sublimation.

Comments

heating temperature: The reference of "red smoke" as a signal for the complete transformation of metacinnabar into cinnabar, prompt us to considerer that a sublimation process could be present. In fact this smoke colour was never observed. The only "smoke" we observed was black, and an indication of the formation of a black product due to overheating.

heating time: Although there is no specific information about the heating time, it is clear that this reaction takes hours and not days.

pot design: The olha's base thickness is essential on allowing a controlled heating rate and on maintaining a constant temperature inside the olha, undoubtedly the two determinant parameters of this recipe.

the dog's foot: "always stirring it with a dog's foot that has its hair and wool until the fire turns to ashes" is possibly one of the most precise instruction found in a medieval treatise. Those who have tried to mix sulphur with mercury know how "fugitivas" the small drops of mercury may turn to be. The use of a fluffy surface could help in capturing Hg, facilitating the grinding and reaction of big amounts of Hg and S, as those described in the text. Also, the description "until the fire turns to ashes" conveying a beautiful image it depicts accurately what is observed; indeed, during the grinding, the yellow sulphur and the bright mercury are transformed into a greyish colour that may be described as "ash colour".

Vermilion in Portuguese medieval illuminations

Vermilion red is an important colour in Portuguese Medieval manuscripts; it was used both to paint the rubricae and in the illuminations, displaying a very good conservation condition. Vermilion as a proteinaceous paint was applied as a pure pigment or mixed with red lead or/and calcium carbonate and white lead. The later compounds were added as extenders as they did not affect the final colour. In the Lorvão collection, we found pure vermilion in the lettering and mixtures of vermilion with variable percentages of red lead (from 5% up to 40% wt) or other additives in big size illuminations. To produce dark reds, it was mixed with lac dye, as found in Santa Cruz 20.

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Further reading

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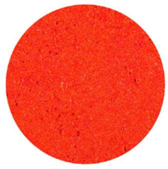
Appendix

Vermilion characterisation: synthesised following "The book on how to make colours", chapter 15

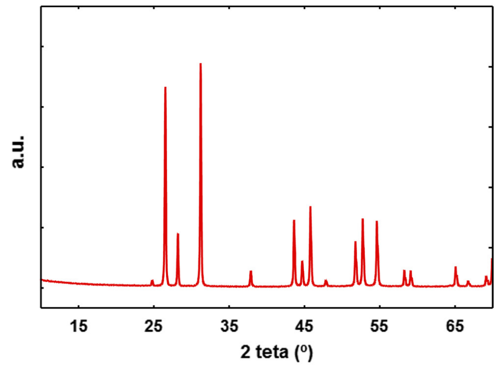


Colour

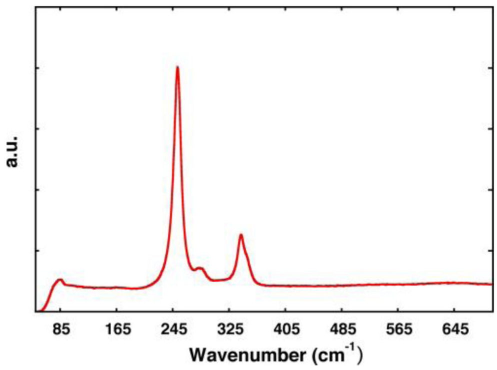
Table 1 Colour coordinates, Lab, for vermilion paint reconstructions using two different binders (arabic gum and parchment glue) applied over filter paper and parchment.*

Support	Binder	L	a*	b*
Filter paper	Parchment glue	49.72	36.97	19.96
	Arabic gum	49.64	38.30	22.68
Parchment	Parchment glue	46.64	36.18	26.30
	Arabic gum	46.56	37.24	27.77

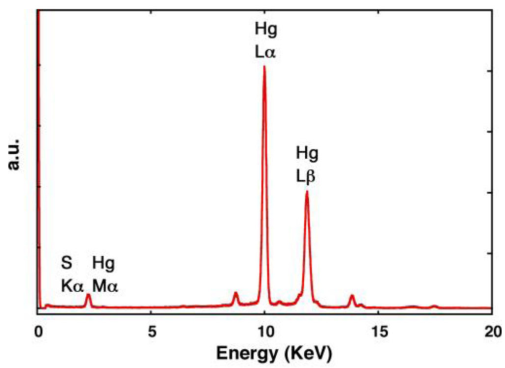
Spectroscopic characterisation



XRD diffractogram acquired with a Philips X'Pert diffractometer using monochromatised CuKα radiation in the 10◦ < 2θ < 70◦ range with a step width of 0.03º and a constant counting time of 1s per step.



Raman spectrum acquired with a Labram 300 Jobin Yvon spectrometerLaser excitation, 632.8nm; 100x objective ULWD; laser power 1.7mW (characteristic bands at 253, 285 and 343 cm-1)



EDXRF spectrum ArtTAX spectrometer of Intax GmbH, with a molybdenum (Mo) anode and Xflash detector. Experimental parameters: 40 kV of voltage, 300 μA of intensity, for 200 s, under Helium gas flux.