À VOLTA DE UM VERMELHO

APRESENTAÇÃO DE EDIÇÃO D'*O LIVRO DE COMO SE FAZEM AS CORES*, SOB O OLHAR DA CIÊNCIA E TECNOLOGIA

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O processo de preparação da síntese de um vermelho medieval que a seguir se apresenta é o resultado de muitos anos de investigação em torno de um dos mais interessantes tratados técnicos medievais, *O livro de como se fazem as cores* [1]. Para este contribuíram, com inúmeras tentativas de reprodução da receita, os muitos alunos de História e Técnicas de Produção Artística do Mestrado em Conservação e Restauro da Universidade Nova de Lisboa, e mais recentemente, Catarina Miguel no âmbito do seu projecto de doutoramento, *Le vert et le rouge*.
A presente edição distancia-se em muitos aspectos de outras excelentes deste tratado, pois deseja actualizar práticas e materiais vindos de um passado longínquo. O que significa reproduzir, com sucesso, a receita descrita pelo praticante medieval. Se numa receita culinária, o sucesso é medido aferindo se o produto final é esteticamente apelativo e saboroso, no nosso caso, o sucesso é medido pela beleza (e durabilidade) da cor obtida. O desafio intelectual foi grande e podemos afirmar que este é um trabalho em aberto e novas descobertas na história e arqueologia do passado nacional permitirão maior rigor na reconstrução destes pigmentos e corantes medievais. Assim, optamos por uma edição on-line [2], de modo a permitir uma rápida partilha e discussão com outros investigadores e curiosos; o que, esperamos, levará a uma actualização eficiente.
Centramo-nos neste número especial no caso do vermelho [3], talvez a reprodução mais complexa de todo o tratado, para que o leitor participe na história do vermelho dos vermelhos, o mais utilizado na iluminura medieval, HgS.

1. A edição crítica pioneira foi a de Blondheim, a que neste momento se junta a mais recente tese de Devon Strolovich. A datação deste tratado tem intrigado estudiosos tendo sido reavaliada recentemente por um grupo de investigadores portugueses, em que se destaca a participação de Luís Afonso, Ivo Cruz e António João Cruz. Nas palavras de Luís Afonso, *O livro de como se fazem as cores das tintas*, translated into English as *The book on how to make the colours of the paints*, is a Portuguese technical text written during the Late Middle Ages dealing with the preparation of artists' materials. It is composed by forty-five chapters of different lengths, most of them concerning materials and techniques to be used in the illumination of manuscripts. (...) The text on colours is written in Portuguese language but using Hebraic script, making it an example of the practice of Iberian aljamia writing, that is the use of Arabic or Hebrew script to write a text in an Iberian romance language.

Para mais informação consultar a bibliografia abaixo elencada.

– Blondheim, S.1928. An old Portuguese work on manuscript illumination. Jewish Quarterly Review. 19: 97-135.
– Strolovitch, D. 2005. Old Portuguese in Hebrew Script: convention, contact, and convivência. PhD Dissertation. Cornell University. 116-184;
– Cruz, A.J. and Afonso, L.U. 2008. On the Date and Contents of a Portuguese Medieval Technical Book on Illumination: O livro de como se fazem as cores. The Medieval History Journal. 11: 1-28.
– Strolovitch, D.L. 2010. Old Portuguese in Hebrew script: beyond O livro de como se fazem as cores, in -Afonso, L.U. (ed.) The Materials of the Image. As Matérias da Imagem, Lisboa: Campo da Comunicação, 29-43.
– Afonso, L.U. 2010. New developments in the study of O livro de como se fazen as cores das tintas, in L. U. Afonso (ed.) The Materials of The Image: As Matérias da Imagem, Série Monográfica «Alberto Benveniste» 3.º Volume. Lisboa: Cátedra de Estudos Sefarditas «Alberto Benveniste» da Universidade de Lisboa, 3-27.
– Castro, I. 2010. Notas sobre a língua do Livro de como se fazen as cores (ms. Parma1959) in Afonso, L.U. (ed.) The Materials of the Image. As Matérias da Imagem, Lisboa: Campo da Comunicação, p.87.

2. www.dcr.fct.unl.pt/LivComoFazemCores, e aí seleccionar arquivo digital.

3. O vermelhão é um sulfureto de mercúrio de fórmula química, HgS.

Chapter 15. To make vermilion

Figure 1. Main steps in the reproduction of the process of making 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. [10r.] 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, hand-made 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: 1.047g of mercury and 0.1674g 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.

Rationalization / 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, 3, 4], being thermodynamically stable only for high temperatures, above about 370ºC. The thermodynamic stable form at room temperature is the hexagonal mercury sulphide (vermilion). For more details please see [2-11].

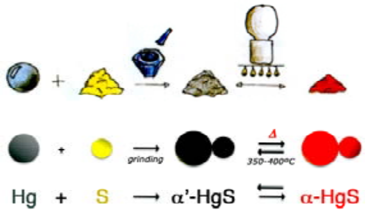


Figure 2. Reaction scheme for vermilion synthesis.

In a second step, metacinnabar is heated at 350-370ºC, 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 [12, 13]. When sublimation occurs, for temperatures higher than 580ºC, a black product, not yet characterized, is formed. This product can be a mixture of meta and hipercinnabar [3].

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 400-450ºC. 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 285ºC for 2h30 and afterwards rising the temperature (heating rate of 15ºC/min) until circa 350ºC 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].

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 620-670ºC. 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.

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.

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

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. Only a black smoke was seen due to the overheating of the bottle (*olha*).

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 the inset temperature control, namely on allowing a controlled heating rate and on maintaining constant temperature inside the *olha*, undoubtedly the two most 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 beautiful instructions 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" not only conveys a beautiful image but it also 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 an organic dye, as found in Santa Cruz 20.

Works cited

[1] - Strolovitch, D. 2005. "Old Portuguese in Hebrew Script: convention, contact, and convivência", PhD Dissertation, Cornell University, 116-184.

[2] - Dickson, F.W. and Tunnel, G. 1959. The stability relations of cinnabar and metacinnabar. American Mineralogist. 44: 471-487.

[3] - Pattrick, R.A.D., Bell, A.M.T. and Vaughan, D.J. 2010. Structural evolution of aqueous mercury sulphide precipitates: energy-dispersive X-ray diffraction studies. Mineralogical Magazine. 74: 85-96.

[4] - Sharma, R.C. and Chang, Y.A. 1993. The Hg-S (Mercury-Sulfur) System. Journal of Phase Equilibria. 14:100-109.

[5] - Melo, M.J. and Miguel, C. 2010. The making of vermilion in medieval Europe - Historically accurate reconstructions from *The book on how to make colours*, in Kroustallis, S. and Del Egido, M. (eds.), Fatto D'Archimia: history and identification of artificial pigments, Madrid: IPCE.

[6] - Miguel, C; Miranda, A.; Lopes, J.A.; Melo, M.J. and Clarke, M. 2011. A Study in Scarlet – vermilion red and colour paint formulations in medieval illumination, in *Preprints of the XVI ICOM-CC Triennial Conference*, Lisbon.

[7] - Miguel, C., Clarke, M., Melo, M.J., Miranda, A. and Oliveira, M. The "book on how one makes colours of all shades in order to illuminate books" Revisited, in "Technology and Interpretation Reflecting the Artist's Process". London: Archetype.

[8] - Charnock, J.M., Moyes, L.N., Pattrick, R.A.D., Mosselmans, J.F.W., Vaughan, D.J., and Livens, F.R. 2003. The structural evolution of mercury sulfide precipitate: an XAS and XRD study. American Mineralogist. 88: 1197-1203.

[9] - Munir, Z.A., Kashkooli, I.Y. and Street, G.B. 1973. Sublimation of IIB-VIA compounds. V. Relative thermal stability and heat of transformation of blackmercury sulfide (metacinnabar). High Temperature Science. 5: 8-15.

[10] - Potter II, R.W., and Barnes, H. L. 1978. Phase relations in the binary Hg-S. American Mineralogist. 63: 1143-1152.

[11] - Rodic, D., Spasojevic, V., Bajorek, A. and Onnerud, P. 1996. Similarity of structure properties of $Hg_{1-x}MnxS$ and $Cd_{1-x}MnxS$ (structure properties of Hg-MnS and Cd-MnS). Journal of Magnetism and Magnetic Materials. 152: 159-164.

[12] - Gettens, R., Chase, M., and Feller, R. L. May 1972. Vermillion and Cinnabar. Studies in Conservation. Vol. 17, 2: 45-69.

[13] - Rinse, J. 1928. The vapour pressure, dissociation, and transition point of mercury sulphide. Recueil des Travaux Chimiques des Pays-Bas. 47: 28:32.

Further reading

Written Sources

Blondheim, S. 1928. An old Portuguese work on manuscript illumination. Jewish Quarterly Review. 19: 97-135.

Moreira de Sá, A. 1960. Revista da Faculdade de Letras, 4: 210-223.

Cennini, C. 1960. The Craftsman's Handbook – The Italian "Il libro dell'arte", translated by D.V. Thomson. New York: Dover Publications.

Theophilus. 1979. On Divers Arts. Smith, C.S. and Hawthorne, J.G. (eds). New York: Dover Publications.

Plinio. 1985. Histoire Naturelle, Livre XXXIII. Paris: Belles Lettres.

Merrifield, M.P. 1999. Medieval and Renaissance Treatises on the Art of Painting: original texts with English translations. London: Dover Publications.

Other

Garcia-Moreno, R. and Thomas, N. 2008. Cinnabar or vermilion?, in Art Technology- Sources and Methods. London: Archetype.141-143.

Bruquetas, R. 2010. El bermellón de Almadén: de Plinio a Goya, in Kroustallis, S. and Del Egido, M. (eds.), Fatto D'Archimia: history and identification of artificial pigments, Madrid: IPCE.

Afonso, L.U. 2010. New developments in the study of O livro de como se fazem as cores das tintas, in Afonso, L.U. (ed.) The Materials of the Image. As Matérias da Imagem. Lisboa: Campo da Comunicação. 3-27

Appendix

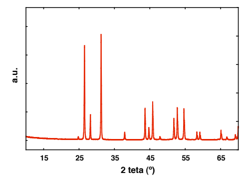
Vermilion characterization. Produced following "The book on how to make colours"

Colour

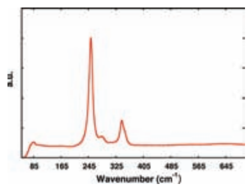
Table 1. Colour coordinates, Lab*, for vermilion paint reconstructions using two different binders (arabic gum and parchment glue) applied over filter paper and parchment.

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

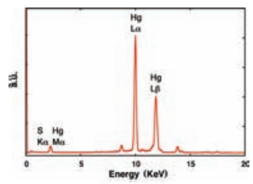
Spectroscopic characterization



XRD diffractogram acquired with a Philips X'Pert diffractometer using monochromatised CuKα radiation.



Raman spectrum acquired with a Labram 300 Jobin Yvon spectrometer with λ_{exc}= 632.8nm; *characteristic bands* @ 253, 285 and 343 cm^{-1}



EDXRF spectrum acquired through ArtTAX spectrometer, with a molybdenum anode.