

## CHAPTER 10 Making red lead from lead white

*Para fazer mui nobre azarcon*

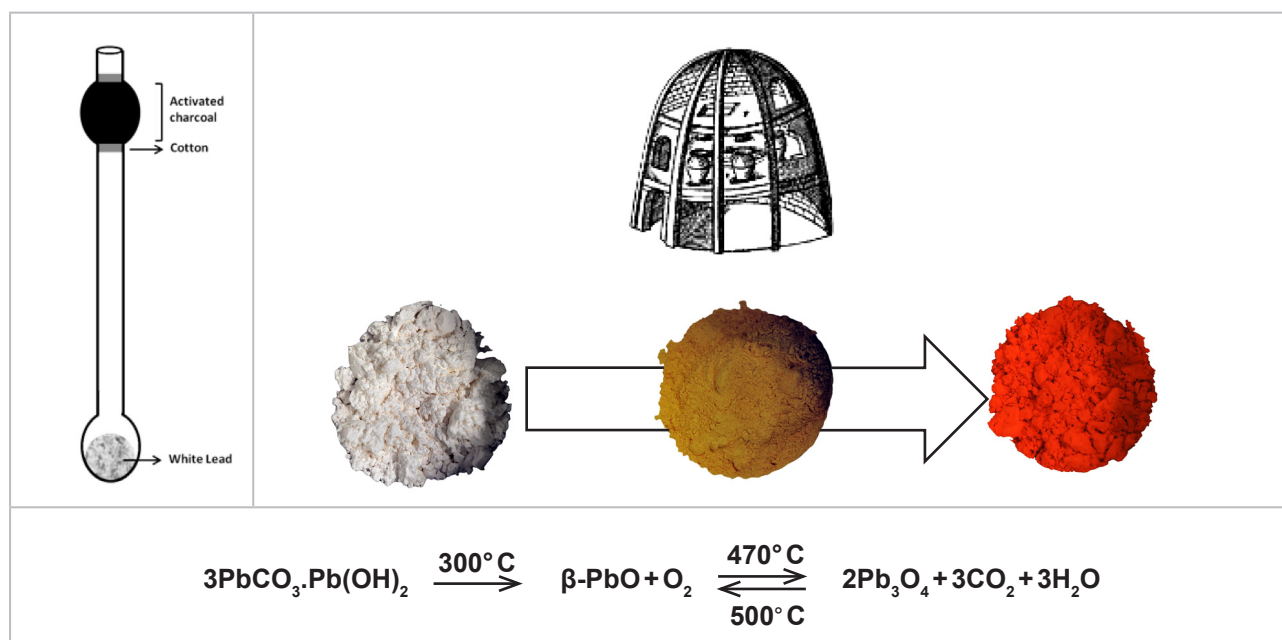


Figure 1 Reaction scheme for red lead synthesis.

'In order to make very fine red lead, take white lead, as much as you wish, and grind it and sift it, and toss it in a broad bowl or bowls. And take it to a glazed furnace, and leave it stand for twenty-two days. And after these days take it out of the furnace, and you will find very good red lead. In this way you will make as much as you wish.' [1]

### Reproduction

In a first experiment, 3 g of lead white were placed in a ceramic crucible in a pre-heated furnace at 300°C. The temperature was slowly increased to 475°C.

After 24 hours of heating, the crucible was cooled to room temperature, and the red lead formed was ground.

If we consider the temperatures inside a medieval glass furnace, 700–1100°C, we may conclude that this experimental procedure could not work, because at these high temperatures the reagents and products will volatilize. It is possible that the author meant in contact but outside the furnace and not inside, so we looked for several possibilities in a homemade glazed furnace and selected a place in which temperature was rather constant at around 470°C. An open glass ampoule with two spherical compartments (separated by 9 cm of tube) was specifically

constructed for the purpose. White lead was put in the bottom compartment, whereas activated charcoal placed between cotton layers (to trap released toxic gases) was put on the second compartment. In 1 day lead white was converted into yellow lead, and after 6 days into red lead

### Rationalisation / Chemical reactions

The heating of lead white ( $\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ ) produces, on a first stage, the orthorhombic form  $\beta\text{-PbO}$  (designated also as massicot), a pale-yellow compound, unstable above 300°C, Fig. 1 [2-7].

On a second stage, the temperature increases until circa 470°C, and through a combustion process, massicot ( $\beta\text{-PbO}$ ) reacts with atmospheric oxygen to produce red lead ( $\text{Pb}_3\text{O}_4$ ), carbon dioxide and hydrogen [2-7].

However, the process can be reverted if the temperature increases to 500°C, leading to the formation of the massicot, again [2-7].

### Key aspects

**Reaction stoichiometry:** Not relevant.

**Transformation of lead white into red lead** is strongly dependent on the complete conversion of the inter-

mediate massicot,  $\beta$ -PbO produced in the first heating step of lead white and on the temperature control of this chemical equilibrium.

**Temperature of reaction:** based on what is known about medieval glazed furnace, the place where the pot was placed in the furnace takes, indeed, a crucial role in the temperature control of the process and, therefore, in the success of the reproduction. One of the advantages of a glazed furnace is that it is always on (night and day), and there will be many available places in its outside wall with high and stable temperatures; an experimented professional could take big advantages of this existing energy.

### Missing / Obscure indications

**heating temperature:** In medieval times a glass furnace worked from 700/800°C till 1100°C [2]. Since it is only mentioned 'take it to a glazed furnace'; it is not known if it should be placed inside or outside the furnace. Possibly at the time a glassmaker would know where to put it, such as in some shelf in the outside wall of the furnace.

### Comments

**heating temperatures:** From the 1960s to the present, several authors have been proposing different temperatures for the synthesis of red lead, although with minor differences [3-7]. Buxbaum (1998) and Cabral (2001) are the ones that refer the most appropriate temperatures [4,5], according to our experiments.

**location:** Considering the working temperature of a glazed furnace, it is expected that the pot was put in a shelf in the outside wall of the furnace where the temperature could be around 460°C.

**heating time:** it is clear that if the correct temperature for the reaction is reached and maintained constant, the reaction takes place in hours and not days (the recipe refers 'twenty-two days'). However, this would depend on the temperature at which the pot was placed, if lower than 450–470°C than more time would be necessary. The end point could be easily assessed by the colour change. To an experimented professional it would be possible to determine when the final conversion of lead white would have taken place, or at least if a satisfactory colour had been reached. It is not necessary to have a full conversion of lead white into red lead, as the first can act as a filler.

### Red lead in Portuguese medieval illuminations

Red lead is an important colour in 12-13<sup>th</sup> c. Portuguese medieval manuscripts. Red lead was applied as a pure pigment for orange colours or admixed with vermilion to produce reds; calcium carbonate and lead white were added as extenders (as they did not affect the final colour), although the latter could be the result of an incomplete synthesis. In the Lorvão collection, mixtures of vermilion with variable percentages of red lead (from 5% up to 40% wt) were found in the red colours of big size illuminations, from the Apocalypse manuscript (Lorvão 44, ANTT-DGARQ) [8-11].

Red lead was also found in Fernão Vaz Dourado's Atlas, dated from the 16th century, at ANTT-DGARQ [12].

This particular pigment presents some conservation challenges, because of its alteration into the lead sulphide, galena (PbS), which is a black degradation product [10-12]. This phenomenon is evident in the Apocalypse manuscript as well as in the detail from the Fernão Vaz Dourado's Atlas, Figure 2.

### Works cited

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- [6] Gettens, R.J., Stout, G. L. 1966. *Painting Materials*. London: Dover Publications.



Figure 2 Examples of red lead in Portuguese medieval manuscripts, from left to right: Alcobaça 446, f.96v; Lorvão 15, f.11; Fernão Vaz Dourado's Atlas, f.18; Lorvão 44 Apocalypse, f.86.

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[10] Muralha, V.S.F., Miguel, C., Melo, M.J. 2012. 'Micro-Raman study of Medieval Cistercian 12-13th century manuscripts', *Journal of Raman Spectroscopy*, 43: 1737.

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[12] Melo, M.J., Vilarigues, M., Muralha, V.S.F., Castro, R. 2013. 'Fernão Vaz Dourado's colours', *Universal Atlas of Fernão Vaz Dourado*, 168-186. Barcelona: M. Moleiro Editor, S.A.

## Further reading

### Written Sources

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### Other

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**Main collaboration:**

**Reviewer:** António Pires de Matos

## Appendix

### Red lead characterisation: synthesised following.

'The book on how to make colours'

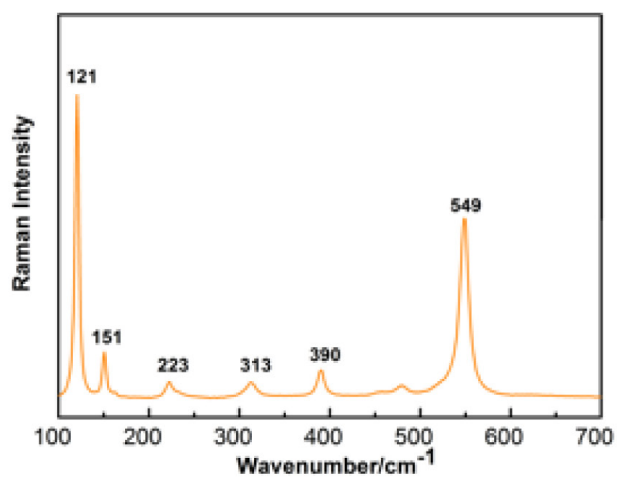


### Colour

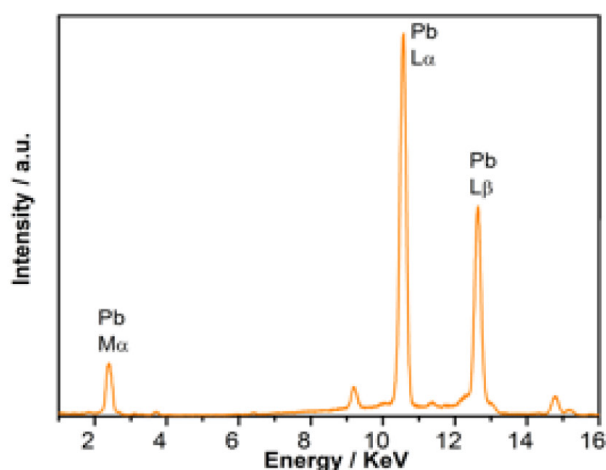
*Table 1* Colour coordinates, Lab\*, for red lead paint reconstructions using two different binders (arabic gum and parchment glue) applied over filter paper and parchment.

Support	Binder	L	a*	b*
Filter paper	Parchment glue	72.25	48.91	63.27
	Arabic gum	72.22	51.07	69.70
Parchment	Parchment glue	71.59	45.72	68.23
	Arabic gum	70.45	47.71	77.31

### Spectroscopic characterisation



*Raman* spectrum acquired with a Labram 300 Jobin Yvon spectrometer. Laser excitation, 632.8nm; 100x objective ULWD; laser power 1.7mW (characteristic bands at 121, 151, 223, 313, 390 and 549 cm<sup>-1</sup>).



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