

CHAPTER ELEVEN

Theory vs practice: synthesis of red lead following ancient recipes

PAULA M. GONÇALVES

JOÃO PIRES

ANA P. CARVALHO

MARIA H. MENDONÇA

Universidade de Lisboa

ANTÓNIO J. CRUZ

Instituto Politécnico de Tomar

Abstract

The synthesis of red lead pigment (chemically lead oxide, Pb_3O_4) was carried out considering different starting lead compounds. The experimental procedure followed was established according to some recipes of ancient painting treatises and the knowledge of the phase transformation of lead oxides. The samples transformation was monitored by X-ray powder diffraction and selected samples were also characterized by scanning electron microscopy. The pure Pb_3O_4 phase was obtained for the transformation of PbO_2 and $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$. Morphological studies revealed that the material obtained from PbO_2 presented the more homogeneous grain size distribution. The transformation of white lead Kremer Pigment resulted in a mixture of Pb_3O_4 (major phase) and cerussite (PbCO_3), leading to a sample with low crystallinity.

Introduction

Since the time when the oldest known paintings were done, at least, red is one of the main colours. In prehistoric paintings red was one of the most employed colours, together with yellow, brown and black. In the Roman civilization the most expensive pigment was red pigment cinnabar, a luxurious and prestigious colour extracted mainly from mines in Spain that, according to Pliny (1st century AD), were the most defended place in the Empire. In the

Renaissance, the cardinals' robes begun to be dyed with the red obtained from the kermes insect, a decision that reinforced the importance of the colour.¹

In the western painting, until the development of the modern colours synthesized in the context of the chemical research, red ochre (essentially, hematite or Fe_2O_3 , obtained from earths), cinnabar (HgS) before the 8th century and, after that, vermillion (an artificial form of cinnabar) were the most employed red pigments. Another pigment with the same colour is red lead or minium (an artificial form of Pb_3O_4), but it was less used in general. However, it had some importance in the specific painting techniques of illumination. The Medieval Latin verb *miniare*, that is, to write with *minium*, was applied to the red initial letters of manuscript chapters. It is from this practice that derives words such as *miniature* (English) and *miniatura* (Portuguese). In Antiquity, however, the name minium was not applied to red lead, but to other red pigments.²

Under the name of sandarach, red lead was first mentioned in the western literature by Vitruvius (1st century BC), who said that it was discovered as the result of an accidental fire to which the white lead pigment ($2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$, obtained from lead) was exposed. According to Pliny, this had happened in Piraeus, Greece. Until the 15th century, when an alternative process arises, through the simple melting and oxidation of lead metal, the preparation of red lead was done precisely by heating of white lead.³

Among the published recipes for preparation of red lead there are two recipes presented by the Portuguese writer Filipe Nunes in its *Art of Painting*, dated from 1615 but with significant influences in the Portuguese technical literature of the following centuries.⁴ In the first recipe, which, according to Nunes, is based in Andrés Laguna's edition (1555) of Pedanius Dioscorides's *Materia Medica* (1st century AD), he prescribed the following: "Form a bed of some very thin sheets of lead in the bottom of a new pot. Then make a layer of ground sulphur, then another of lead, continuing in this way until the pot is filled. Put it on the fire, and mix everything with an iron rod. See that your noses are stopped because the vapour is very harmful". In the second recipe, Nunes said: "Others use white lead in place of sulphur⁵. Covering the vessel very well, leaving only a small hole through which it may breathe, they put it in the oven until is very well burned. This is the best way".⁶

The preparation of red lead by heating of white lead, such as in Nunes' second recipe, is presented in many medieval and later technical sources. For instance, that procedure is mentioned in *Mappae Clavicula* (from about 800, but with additions from the 11th and 12th centuries)⁷ and Theophilus presbyter's treatise (12th century)⁸, although none of these sources present details regarding the employed conditions, with the exception that both recommend that white

lead should be stirred during the heating process. Some details are presented in another source. According to Audemar's *De Coloribus Faciendis* (13th or 14th century), the jar with white lead should be "over de fire for two days and two nights" and the fire should be "of charcoal only without flame". Moreover, "the stirring is the principal cause of the perfect preparation" and "must be repeated four or five times in the space of every two or three hours".⁹ In another recipe, it is said that "the more it is burnt the redder it is, and the less it is burnt the more it retains its former colour, that is, its whiteness or its paleness".¹⁰

In spite of the details presented by Audemar, it is not common to find details regarding red lead in ancient recipes and, consequently, it is probably that the pigment was manufactured differently in different places and time and, as consequence, it is possible that red lead with different composition could have been used. Our main objective was, precisely, to investigate how some experimental conditions could originate materials with different composition.

Lead Oxides

Chemically red lead is a lead oxide with lead presented as Pb(II) and Pb(IV). The lead-oxygen phase diagram includes a set of oxide compositions, as it is well known. According to different references¹¹ they have the following compositions: PbO, Pb₃O₄, Pb₁₂O₁₇, Pb₂O₃, among others. In the study of lead oxide decomposition it has been found that the process occurs in the temperature range 330-570 °C, in stages, with the successive decreases of oxygen content, from PbO₂ until PbO.

It is known that lead monoxide has two polymorphous modifications: low temperature form α -PbO (litharge), with tetragonal lattice, stable up to 490-540 °C, and high temperature orthorhombic β -PbO (massicot). Endothermic phase transition $\alpha \rightarrow \beta$ is accompanied with small thermal effect (0.418 kJ mol⁻¹). At room temperature the rate of the reverse $\beta \rightarrow \alpha$ transition is very low and the β -phase can be stored in metastable state over prolonged time. An interesting observation was made when the reverse reaction from PbO to Pb₃O₄ at slow cooling from 600 °C in air was reported. In fact, Clark and Rowan¹² report the formation of distorted 'active' α -PbO after thermal decomposition of lead carbonate and hydroxide and its oxidation to Pb₃O₄ at temperatures below 400 °C.

Experimental

The effect of the experimental conditions on red lead's composition was investigated starting from different materials containing lead and operating at different temperatures and heating times. The compounds used are listed in

Table 1 where some of their characteristics are also presented, as well as their designation in the following text.

Sample	Compound	Colour	Crystal structure
A	PbO (Merck, >99%)	yellow	Orthorhombic
B	PbO (Merck, >99%)	orange	orthorhombic and base centred orthorhombic
C	PbO (M&B, >99%)	orange	orthorhombic and base centred orthorhombic
D	PbO ₂ (M&B, >99%)	Black	Tetragonal and orthorhombic
E	2PbCO ₃ ·Pb(OH) ₂ (M&B, >99%)	White	Rhombohedral
Kremer	White Lead, Kremer Pigment	White	Orthorhombic and rhombohedral

Table 1 – Starting materials used to prepare red lead. (The crystal structures were identified using the files of the International Center for Diffraction Data (ICDD).

A four step procedure was carried out: two calcinations at 400 °C followed by two calcinations at 450 °C, always for 2 hours. Between the treatments the samples were grinded into a fine powder. The samples will be designated by the caption letter correspondent to the starting compound followed by 1, 2, 3 or 4 according with number of heat treatments made. Calcinations were done in a muffle furnace Nabertherm GmbH (Mod. L3/12/P320) equipped with a Controller P320.

The synthesis process was monitored by X-ray powder diffraction (XRD). Patterns were recorded on a Philips PW 1730 diffractometer with automatic data acquisition (APD Phillips (v3.6B) software). CuK α radiation ($\lambda = 1.5406 \text{ \AA}$) was used as incident beam and a graphite-monochromator was employed. Diffractograms were obtained by continuous scanning from 15 to 80 ° 2 θ , with a step size of 0.02 ° 2 θ and a time per step of 0.4 s. The identification of the crystal phases was made using the International Center for Diffraction Data (ICDD) diffraction database.¹³ Morphologic characterization was performed by scanning electron microscopy (SEM) (JEOL, Model JSM –6301F) operated at 25 kV. Samples were coated with gold.

Results and Discussion

The diffractograms presented on Fig. 1 show that the orthorhombic structure of the PbO (ICDD: 38-1477) was not changed upon the heat treatments, and in accordance no colour change was observed.

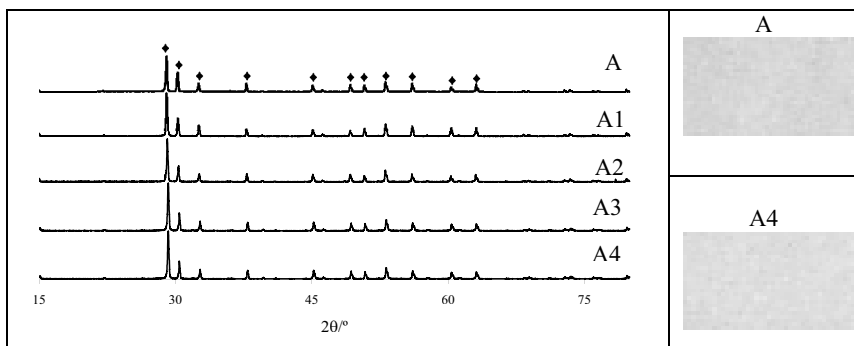


Figure 1 – X-ray diffraction patterns of sample A (PbO from Merck – yellow) and samples obtained after successive calcinations. (♦ - PbO orthorhombic: ICDD 38-1477).

The results obtained with sample B (Fig. 2) show the importance of the crystal structure of the precursor to obtain accomplish phase transformations. In fact, although sample B has the same chemical composition of sample A, that is, both are PbO, structurally they are different. Sample A is a pure orthorhombic phase, but sample B has some fraction of base centred orthorhombic structure (ICDD: 35-1482) which allowed that after the third heating the presence of lead oxide (Pb_3O_4 : ICDD 8-19) was denoted by the appearance of diffraction peaks at 26.5 , 30.9 and 34.1 ° 2θ . The evolution observed was reflected on the change of colour since after the four heating the initial light orange coloration changed to more dark orange.

The results obtained using sample C, a mixture of orthorhombic and base centred orthorhombic phases, are displayed in Fig. 3. On the contrary of what is observed for sample B, in this case the predominant phase is the base centred orthorhombic. This difference seems to be important to promote the structural evolution upon heat treatments, since in this case the presence of lead oxide started to be observed after the first calcination, as pointed out by the small diffraction peak at 26.5 ° 2θ . The sample obtained after the fourth heating (C4) is also structurally different from sample B4 since a larger fraction of Pb_3O_4 is observed. In what concerns the colour evolution there was no significant

alteration since, among all the starting compounds, sample C was the one presenting the more intense orange coloration.

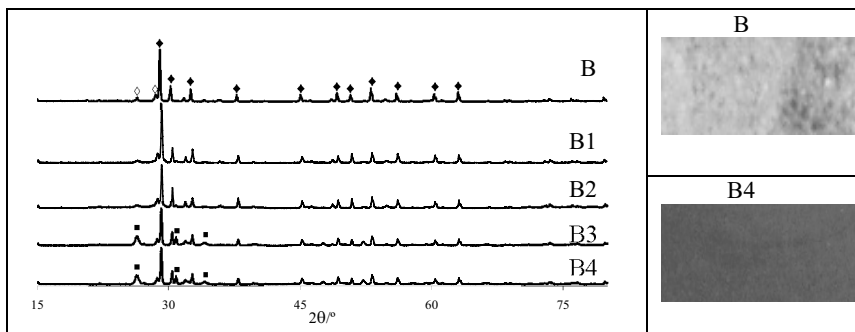


Figure 2 – X-ray diffraction patterns of sample B (PbO from Merck – orange) and samples obtained after successive calcinations. (♦ - PbO orthorhombic: ICDD 38-1477; ◇ - PbO base centred orthorhombic: ICDD 35-1482; ■ - Pb₃O₄: ICDD 8-19).

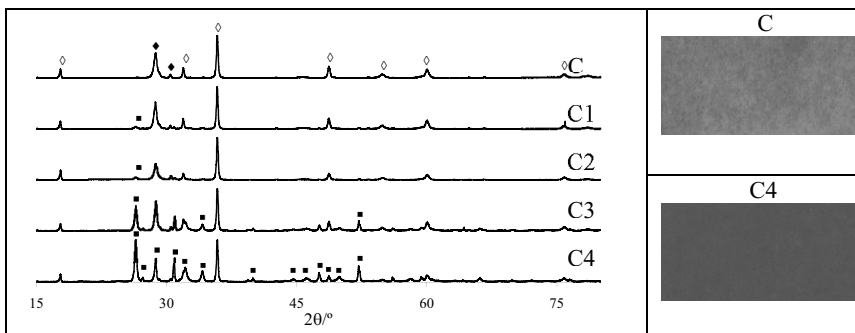


Figure 3 – X-ray diffraction patterns of sample C (PbO from M&B – orange) and samples obtained after successive calcinations. (♦ - PbO orthorhombic: ICDD 38-1477; ◇ - PbO base centred orthorhombic: ICDD 35-1482; ■ - Pb₃O₄: ICDD 8-19).

The last lead oxide essayed was sample D which is chemically different from all the previous compounds, since it is a Pb (IV) compound while the others are Pb(II) oxides. Structurally sample D is a mixture of crystalline phases: tetragonal and orthorhombic. The X-ray powder diffraction patterns of the samples obtained after the successive heatings (Fig. 4) show that structural

changes started from the first calcinations, but the more significant change only occurs when the temperature was increased to 450 °C in the third treatment. In fact, after this treatment Pb_3O_4 is the major phase present and after the fourth treatment is even the only phase detected. These significant structural transformations were reflected in the colour of the samples that changed from black to orange.

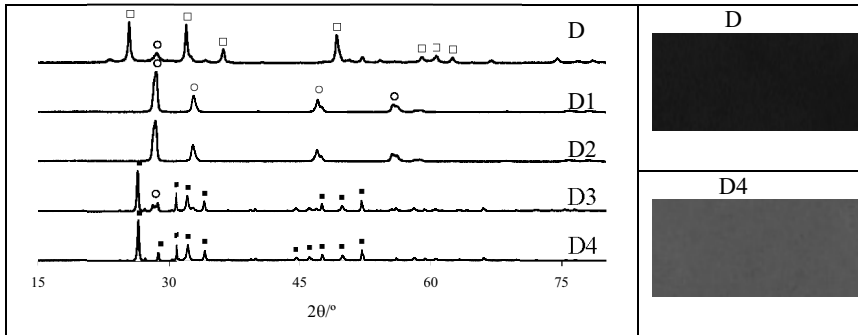


Figure 4 – X-ray diffraction patterns of sample D (PbO_2 from M&B – black) and samples obtained after successive calcinations. (\square - PbO_2 orthorhombic: ICDD 41-1492; \circ - PbO_2 tetragonal: ICDD 37-517; \blacksquare - Pb_3O_4 : ICDD 8-19).

The preparation of red lead from lead basic carbonate was made from sample E and from the white lead pigment commercialized by Kremer Pigment. The diffractograms presented in Fig. 5 correspond to the samples obtained after the 4-step experimental procedure. For comparison, the X-ray powder diffraction patterns of commercial Pb_3O_4 is also presented in Fig. 4. According to the diffractograms, lead oxide Pb_3O_4 is the only phase in the material obtained from $2PbCO_3 \cdot Pb(OH)_2$, while white lead from Kremer Pigment (a mixture of cerussite, $PbCO_3$, and hydrocerussite, $Pb_3(CO_3)_2(OH)_2$) originates a material that reveals diffraction lines of cerussite at around 30, 32, 34 and 48 ° 2θ , besides those of the red lead phase. The presence of cerussite results in a low crystallinity of the obtained material.

The SEM images of samples more structurally alike Pb_3O_4 are presented in Fig. 6. Concerning the grain distribution, it is evident that C4 is the more heterogeneous sample. This finding is in accordance with the previous discussion, since the starting PbO is clearly presented in the XRD pattern of sample C4. Among the others three samples, D4 has the greater homogeneity. The transformation of sample E and white lead from Kremer Pigmente resulted in materials with an intermediate heterogeneity. For these two last samples, no

correlation between the structural results and the morphologic analysis were detected.

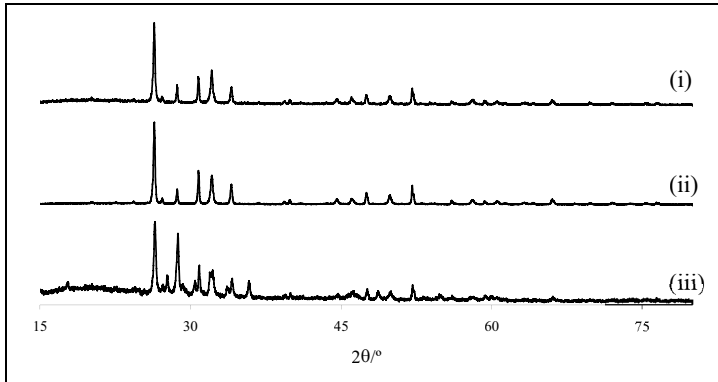


Figure 5 – X-ray diffraction patterns of (i) Pb_3O_4 and samples obtained after heat treatments of (ii) $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ and (iii) white lead pigment from Kremer Pigment.

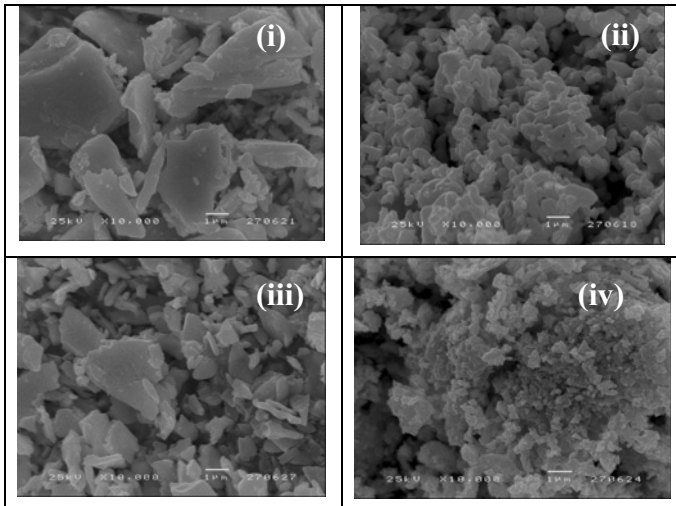


Figure 6 – SEM images of the samples obtained after heat treatments of (i) PbO from M&B – orange; (ii) PbO_2 from M&B – black; (iii) $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ and (iv) white lead pigment from Kremer Pigment.

Conclusions

The results obtained in the present study point out the importance of the starting compound for the preparation of red lead. Actually pure lead oxide phase was obtained only for the transformation of PbO_2 and $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$. The presence of red lead phase was also observed for PbO starting materials presenting a mixture of structural phases. When the use of white lead Kremer Pigment was considered, red lead was the main crystal phase present, although the lead carbonate phase remains present, what is reflected in the crystallinity of the sample.

Acknowledgments

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Notes

¹ P. Ball, *Bright Earth. Art and the Invention of Color* (Chicago, 2001); António J. Cruz, *As Cores dos Artistas. História e Ciência dos Pigmentos Utilizados em Pintura* (Lisboa, 2004); F. Delamare, B. Guineau, *Colour. Making and Using Dyes and Pigments* (London: Thames and Hudson, 2000); A. Varichon, *Colors. What they mean and how to make them* (New York, 2006).

² E. West FitzHugh, *Red Lead and Minium*, in *Artists' Pigments. A handbook of their history and characteristics* Vol. 1, ed. R. L. Feller (Washington, 1986).

³ Cruz, *As Cores dos Artistas*; FitzHugh, *Red Lead and Minium*.

⁴ Filipe Nunes, *Arte Poetica, e da Pintura, e Symmetria, com Princípios da Perspectiva* (Lisboa: Pedro Crasbeeck, 1615).

⁵ Although in the English translation presented here, done by Veliz, it is said “Others use white lead in place of lead sheets”, Nunes, in the original Portuguese text, said “Outros em lugar de enxofre põem Alvayade” [Nunes, 1615, p. 66v], that is, what it is replaced by white lead it is not the lead sheets but the sulphur. Therefore, we corrected the Veliz’s translation.

⁶ Zahira Veliz, *Artists' Techniques in Golden Age Spain. Six Treatises in Translation* (Cambridge, 1986).

⁷ C. S. Smith, J. G. Hawthorne, “Mappae Clavicula. A little key to the world of medieval techniques”, *Transactions of the American Philosophical Society* 64 (4) (1974), 3-128.

⁸ Theophilus, *On Divers Arts. The Foremost Medieval Treatise on Painting, Glassmaking and Metalwork*, ed. J. G. Hawthorne and C. S. Smith (New York, 1979).

⁹ M. P. Merrifield (ed.), *Medieval and Renaissance Treatises on the Arts of Painting* (New York, 1999).

¹⁰ Merrifield, *Medieval and Renaissance Treatises*

¹¹ E. M. Otto, “Equilibrium pressures of oxygen over oxides of lead at various temperatures”, *Journal of the Electrochemical Society* 113 (6) (1966), 525-527; G. L. Clark, N. C. Schieltz, T. T. Quirke, “A new study of the preparation and properties of the higher oxides of lead”, *Journal of the American Chemical Society* 59 (11) (1937), 2305-2308; G. L. Clark, W. P. Tyler, “Studies on lead oxides.II. Hydrous, normal and active lead monoxides”, *Journal of the American Chemical Society* 61 (1) (1939) 58-65; G. L. Clark, R. Rowan, “Studies on lead oxides.IV. Polymorphic transitions by grinding, distortion and catalytic activity in PbO”, *Journal of the American Chemical Society* 63 (5) (1941), 1302-1305; G. L. Clark, R. Rowan, “Studies on lead oxides.V. Further experiments on compounds of the type $PbO_{n(n=1\text{ to }2)}$ ”, *Journal of the American Chemical Society* 63 (5) (1941), 1305-1310; K. Gavrichev, A. Bolshakov, D. Kondakov, S. Denisov, *Thermal Transformations of Lead Oxides* *Journal of Thermal Analysis and Calorimetry* 92 (3) (2008), 857-863.

¹² Clark, Rowan, (1941) 1302-1305; Clark, Rowan, (1941) 1305-1310.

¹³ *International Center for Diffraction Data, Power Diffraction File Alphabetical Index* (PA, 1988).