CHAPTER TEN

Theory *vs* practice: synthesis of white 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 white lead pigment (usually described as basic lead carbonate, $2PbCO_3 \cdot Pb(OH)_2$) following the recipes of ancient Portuguese painting treatises was studied, aiming to clarify the importance of some procedure details and the effect of the experimental parameters. Currently available lead plates and commercial vinegar were used. The recipe reported in Filipe Nunes' treatise (1615), was the starting point of the study and the process was monitored by XRD. Selected samples were also characterized by SEM. The relative importance of temperature, CO_2 atmosphere and H_2O vapour was demonstrated. The pigments obtained presents basic lead carbonate phase but also a large content of other components.

Introduction

Before the 19th century, artists prepared their own materials. Namely, the painters and their apprentices prepared the paint colours from pigments that were purchased from apothecaries shops or made at the painter workshop. The knowledge about the materials and their manufacture was transmitted verbally or through technical treatises.

The study of ancient recipes is important for several reasons, some related to the history of sciences and techniques, some related to the history of art.

Concerning the first subject, the research may inform, for instance, about the technical knowledge possessed by a specific social group in a specific time and place, or the function and importance of the written sources in transmission and diffusion of knowledge. In this context it is essential to verify if the antique recipes are really what we expect, that is, procedures for preparation of certain materials, or if they had another function in a world of secrecy. In relation to the history of art, the recipes show the materials that were available to painters and that can be expected to be found in works of art. This is very useful information both for interpretation of data obtained by chemical analysis of works of art and for selection of compatible materials to be employed in conservation and restoration treatments.

In spite the importance of the study of ancient recipes, the research in this field is scarce, most probably because the interpretation of the ancient technical texts is not straightforward. If in some of these books the experimental information for the pigments' synthesis was complete, in many others only scarce details were given, sometimes with an obscure language. On the other hand, some recipes were written by painters and described their own procedures, while others are assemblages of recipes with different origins, collected by persons having no knowledge about the subject. So, in most of the cases these recipes had errors.

Studies based on ancient recipes can only be successfully handled through an integrated approach based on history of art, history of technology, chemistry and materials science. One of the few examples of this kind of approach is the study developed by M. V. Orna *et al.* focused on the blue pigments mentioned in texts from the 9th to the 16th century.[1] On the other hand, two recent symposiums[2] show that the scientific community has deserved a growing attention to this subject.

In the context of a multidisciplinary project that aims the study of the Portuguese painting treatises from the Middle Ages to 1850, we have studied the treatise on painting wrote by Filipe Nunes, first published, in Lisbon, in 1615.[3] This is a very important book about painting techniques, as demonstrated by the fact that a century and a half after printing, the demand for it leads to a second edition in 1767. In the late 19th century it is still cited by other Portuguese authors of art treatises as an authority in the subject. For different reasons, but also related to its importance, it was reprinted in 1982 and soon after translated to English.[4]

Our work was focused on the preparation of white lead because this was the more important pigment used in easel painting until the mid of the 19th century – since it was the only white colour available until then and, besides its individual use, it was used mixed with all other colours to obtain different tones. Mainly

due to its toxicity, it was gradually replaced by zinc and titanium whites in the 19th and 20th centuries, respectively.[5] Furthermore white lead is a pigment for which the ancient methods of preparation are not well understood.[6]

White lead is usually described as basic lead carbonate, $2PbCO_3 \cdot Pb(OH)_2$, with mineralogical designation of hydrocerussite, but many historic samples contain significant proportions of other phases, namely lead carbonate, $PbCO_3$, cerussite.[7] The procedure for the preparation of white lead described, in Greek, by Theophrastus in the 4th century BC is the ultimately source for many of the recipes founded in the medieval and later texts. According to this recipe, "*lead about the size of a brick is placed in jars over vinegar, and when this acquires a thick mass, which it generally does in ten days, then the jars are opened and a kind of mould is scraped off the lead, and this is done again until it is all used up. The part that is scraped off is ground in a mortar and decanted frequently, and what is finally left at the bottom is white lead*".[8] It is probably that this procedure entered the medieval and later literature through the Latin texts of Vitruvius,[9] dated from the 1st century BC, and Pliny, the Elder,[10] dated from the 1st century AD.[11] Vitruvius point out the importance that the jars are well covered to prevent evaporation, while Pliny, in addition to a similar procedure (that kept the jars sealed up for ten days), mention an alternative procedure were the lead is placed over the vessel with the vinegar. The *Mappae Clavicula*, a well known collection of recipes mostly compiled around 800 AD, among other variants, prescribed that the pot with lead and vinegar should be put in the sun or in another hot place.[12] Instead, according to the monk Theophilus' treatise, dated from about 1122, the recipient, in this case a chest made of oak wood were the vinegar could be replaced by urine, should be put under dung during one month.[13] The use of dung is mentioned in other texts, namely the manuscript of Petrus de S. Audemar, dated from the end of the 13th century or beginning of the 14th century,[14] and the manuscript titled *Segreti per Colori*, dated from 1425-1450,[15] although other later texts, such as those of Pierre Lebru [16]or Watin,[17] do not mention neither a warm place nor dung. In the 17th century, the process, with recourse to horse dung, was optimized and scaled up, and was used in several factories that, until the late 19th century, provided European painters with large quantities of white lead.[18] This optimized version is now described as the Dutch process.

The recipe presented for white lead by Filipe Nunes is the oldest known recipe for that pigment in Portuguese technical sources. Based on Andrés Laguna's edition of Dioscorides' treatise on *De Materia Medica*,[19] Nunes said that white lead is made in the very same way that the green pigment verdigris, except that should be used lead instead of copper. About the verdigris, he writes: "*put some very strong vinegar in a crock and place some copper plates across*

the opening (which the vinegar must not reach), and then cover the vessel, leaving no place for it to breathe; let it stand thus for ten days." Specifically about white pigment, he says "*after ten days the vessel is uncovered and the vinegar is poured out, and the sediment that remains is white lead. After being dried and sifted, it is ground on the mulling stone.* […] *All of it is very well ground with vinegar. Then it is formed into loaves which are dried in the sun*".[20]

The present work had two main goals: the first was the preparation of white lead following, as accurate as possible, the recipe presented by Filipe Nunes; and the second was the investigation of the effect of several experimental parameters on the pigment's composition. Currently available materials and common laboratory techniques were employed in order to achieve reproducibility and control of the experimental parameters. The synthesis was monitored by X-ray powder diffraction and, in selected samples the characterization was complemented by scanning electron microscopy. For comparison purposes a commercial white lead pigment (*Kremer Pigmente*) was analyzed.

Experimental

Following Filipe Nunes' recipe, square lead plates (area of around 4 cm^2 and 0.1 cm of thickness) were exposed to vinegar vapours, in a covered recipient, for 10 days at room temperature. Commercial lead plates from Merck were used. Currently available commercial vinegar was employed and its acidity (5% of acidity, in the form of acetic acid) was determined by volumetric analysis with a standard 0.1 mol dm^{-3} sodium hydroxide solution.

As shown in Fig. 1-a, after the exposure to vinegar the lead plates presented a white corrosion product that was recovered by scraping. There was also some white solid deposit on the vinegar recipient that was placed below the lead plates. It was also recovered.

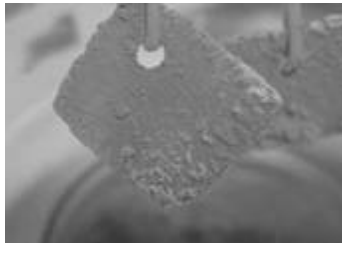


Figure 1 – (a) Plate of lead with the corrosion product formed after 10 days of exposure to vinegar vapours and (b) flask used in the heating treatments.

Since none of these materials had the expected composition of white lead (see Results and Discussion sections) different treatment schemes based on the Filipe Nunes' recipe were investigated. As the treatise only refers that the sample obtained after the exposure to vinegar had to be compressed, embedded in more vinegar and let to dry at sun, several experimental parameters were changed: temperature, time and atmosphere composition (CO_2 and H_2O enriched atmospheres). The details of the different strategies are described in the Results and Discussion sections. The reactions were conducted in closed glass flasks (Fig. 1-b). To create a CO_2 rich atmosphere, the flasks were filled with the gas (99.8 % purity), which was daily renewed. A humid atmosphere was obtained placing a recipient with distilled H_2O inside the flasks. The heating was done in a ventilated oven (Heraeus Instruments UT6120(I)).

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). CuKα radiation (λ= 1.5406 Å) was used as incident beam; a graphite-monochromater was employed. Diffractograms were obtained by continuous scanning from 5º to 50º 2θ, with a step size of 0.02º 2θ and a time per step of 0.4 s. The identification of the crystal phases was made by means of the diffraction data collected by International Center for Diffraction Data (ICDD).[21] Morphologic characterization was performed by scanning electron microscopy (SEM) (JEOL, Model JSM – 6301F) operated at 25 kV. Samples were coated with gold.

Results

The indexation of X-ray powder diffraction patterns of the corrosion products of lead after 10 days of exposure to vinegar (Fig. 2), shows that at this step only a mixture of dehydrated and hydrated lead acetate ($Pb(C_2H_3O_2)_2$ ICDD: 18-1738 and $Pb(C_2H_3O_2)_2{\cdot}3H_2O$ ICDD: 14-829, respectively) is observed. The presence of the basic lead carbonate (white lead) was not detected, what is in agreement with the total dissolution of the obtained products in water, also tested. Besides, the powder scraped from the lead plates presents a much higher cristallinity (denoted by well defined peaks) than the powder deposited at the bottom of flask. Regarding these results it is interesting to note that several treatises, like those of Antonio Palomino and José Lopes Baptista de Almada, both published in the first half of the 18th century in Spanish and Portuguese, respectively, expressly state that the lead should not touches the vinegar,[22] although others said that the lead should be immersed in the vinegar.[23]

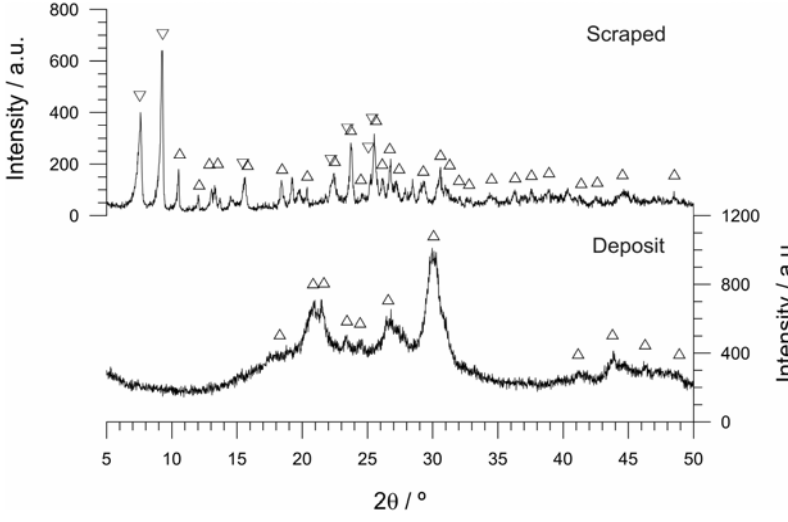


Figure 2 – X-ray diffraction patterns of scraped and deposit obtained after 10 days of exposition of lead to vinegar (△ - hydrated lead acetate; ▽ - lead acetate)

From these results it was obvious that, to obtain the desired white lead pigment subsequent treatments were necessary. Although some recipes do not mention any treatment after scraping other then grinding, according to Nunes and others the powder should dried under the sun. In this context we supposed, as it had already been considered,[24] that this last step could had another effect in addition to the obvious dehydration, namely a reaction with CO_2. The necessity of warming is then evident. About the possible importance of the reaction with CO_2 we can note that the preparation of another white pigment (San Giovanni white) necessarily involves a carbonation reaction that convert $Ca(OH)_2$ to $CaCO_3$, which, according to the treatise wrote in the late 14th century by Cennino Cennini, were achieved by putting the $Ca(OH)_2$ on the roofs in the sun.[25] To check our hypothesis about the importance of the last step mentioned by Nunes, the scraped product (afterwards designated by S) was divided in three sub-samples (S1, S2 and S3), which were submitted to different heating treatments and different atmosphere composition, according to the methodology described in Fig. 3 (scheme 1). As indicated, the temperature chosen to carry out the heating treatment was 35 ºC (a temperature near that of a hot summer day).

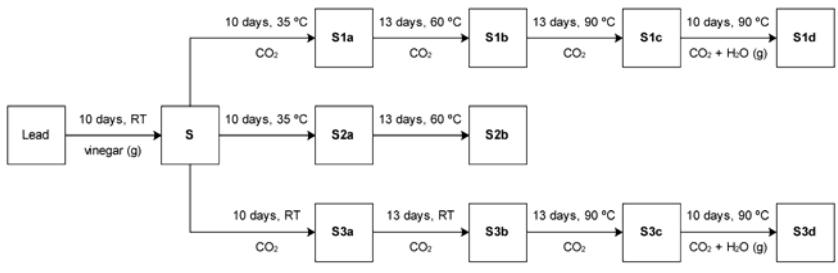


Figure 3 – Experimental conditions applied to the sample scrapped from lead surface after exposure to vinegar for 10 days at room temperature (scheme 1)

After 10 days at 35 ºC in a CO_2 enriched atmosphere, carbonates phases ($PbCO_3$, cerussite, ICDD: 5-417, and $Pb_3(CO_3)_2(OH)_2$, hydrocerussite, ICDD: 13-131 and 28-529) were observed in sample S1a, although the acetate phases have the most intense peaks (Fig. 4-a). In the absence of that atmosphere, sample S2a does not developed any carbonate phase detectable by XRD, pointing out the importance of the CO_2 atmosphere.

The effect of the temperature was also studied. In first place, sample S2a was heated for 13 days at 60 ºC. As no structural modification was observed, no further treatment was made to this sample. In second place, sample S3 was exposed to a CO_2 enriched atmosphere, like sample S1, but at room temperature. Comparing the X-ray patterns of samples S3a and S1a, the same phases were identified. The main difference is that in sample S1a two strong peaks were observed (one attributed to the dehydrated lead acetate and the other to the hydrated form), while in sample S3a only the hydrated lead acetate has originated an intense peak (Fig. 4-c). Sample S1a was then heated at 60 ºC during 13 days, while sample S3a was maintained at room temperature. The XRD pattern obtained for sample S3b was similar to that of sample S3a, except that in sample S3b the principal peak of the dehydrated lead acetate peak is more intense (Fig. 4-b). In the case of sample S1b, the peaks correspondent to hydrated lead acetate had low intensity and the majority of the reflections can be attributed to carbonate phases.

As the temperature seemed to have a significant effect on the synthesis, the two samples were heated at 90 ºC for 13 days, leading to samples S1c and S3c. Sample S1c does not showed any significant difference in relation to sample S1b, which suggest that an equilibrium between the mineralogical phases was achieved (Fig. 4-a and c). In the case of sample S3c, the intense peak due to the hydrated lead acetate disappeared and some similarity between the

diffractogram obtained for samples S3c and S1c was observed. It must be noted that some 17th century texts include instructions for roasting the pigment.[26]

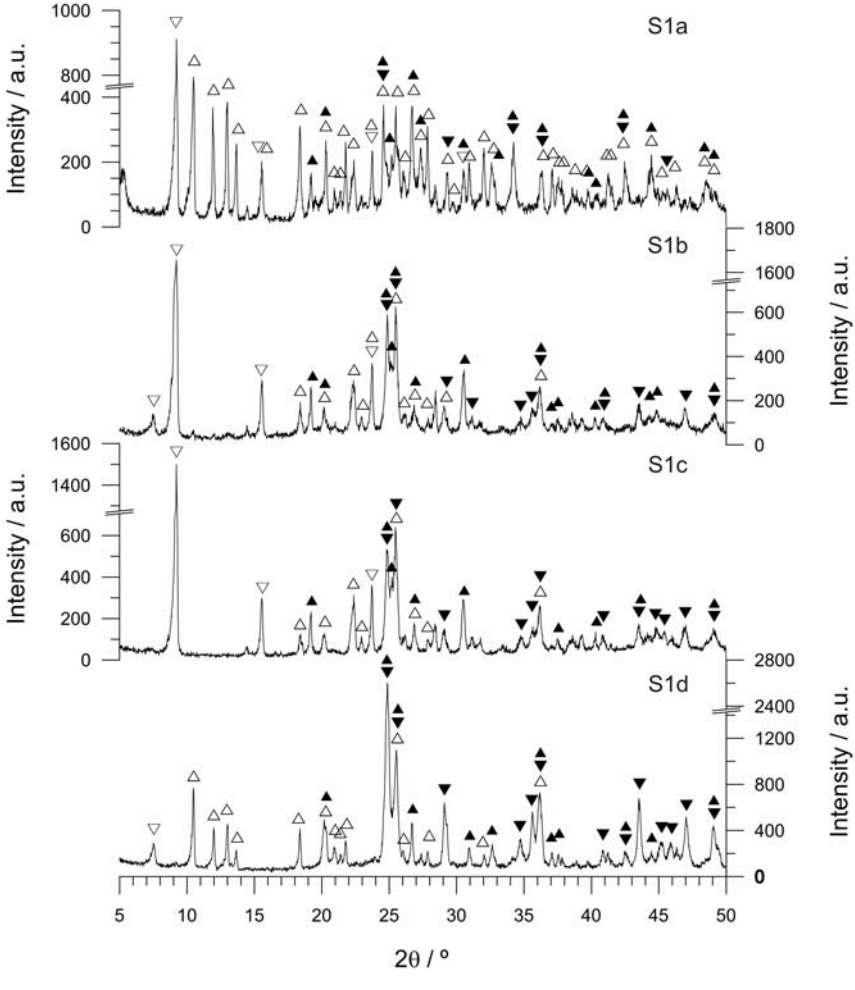


Figure 4 (a) – X-ray diffraction patterns of samples obtained according to scheme 1 (△ - hydrated lead acetate; ▽ - lead acetate; ▲ - basic lead carbonate; ▼ - lead carbonate)

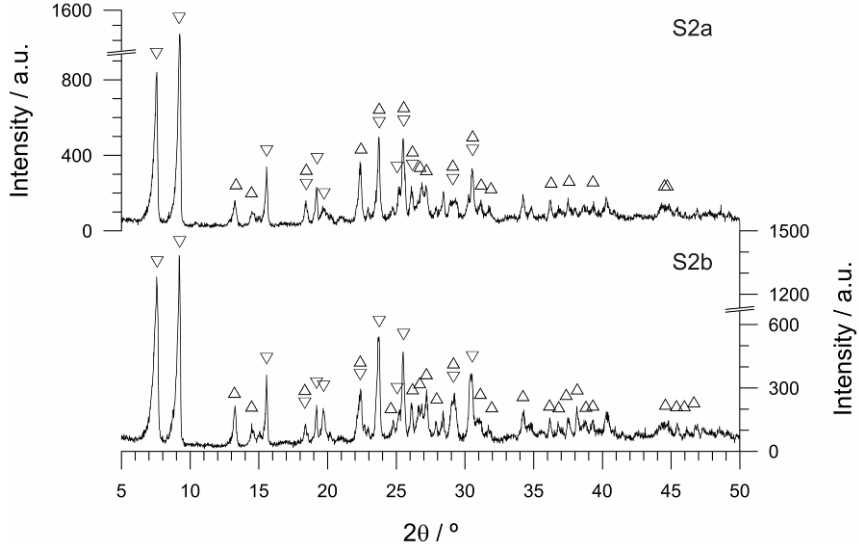


Figure 4 (b) – X-ray diffraction patterns of samples obtained according to scheme 1 (△ - hydrated lead acetate; ▽ - lead acetate; ▲ - basic lead carbonate; ▼ - lead carbonate)

At this point, another variable was introduced in the process, increasing the atmosphere humidity inside the flasks. Thirteen days later, the intensity of the diffraction lines attributed to the carbonates phases had increased and only minor differences between the pattern obtained for S1d and S3d samples were noticed (Fig. 4-a and c).

The relative importance of temperature, CO_2 and H_2O, and the effects of these parameters on the mineralogical composition were further investigated. In first place, metallic lead was exposed to vinegar vapours at temperatures higher than room temperature, according to scheme 2 (Fig. 5). This modification took account of several treatises which state that the flask with lead and vinegar should be put in a warm place. This is referred in the *Mappae Clavicula* and, among others, in two Portuguese treatises dating from the 18th century, one wrote by João Pacheco[27] and the other by an anonymous author.[28] The last one declares that the warm place should be a "*low temperature fire*". A French treatise from the beginning of 19th century recommends that the temperature should not exceeds 35 or 40 ºC, at maximum, except in the final of the process.[29]

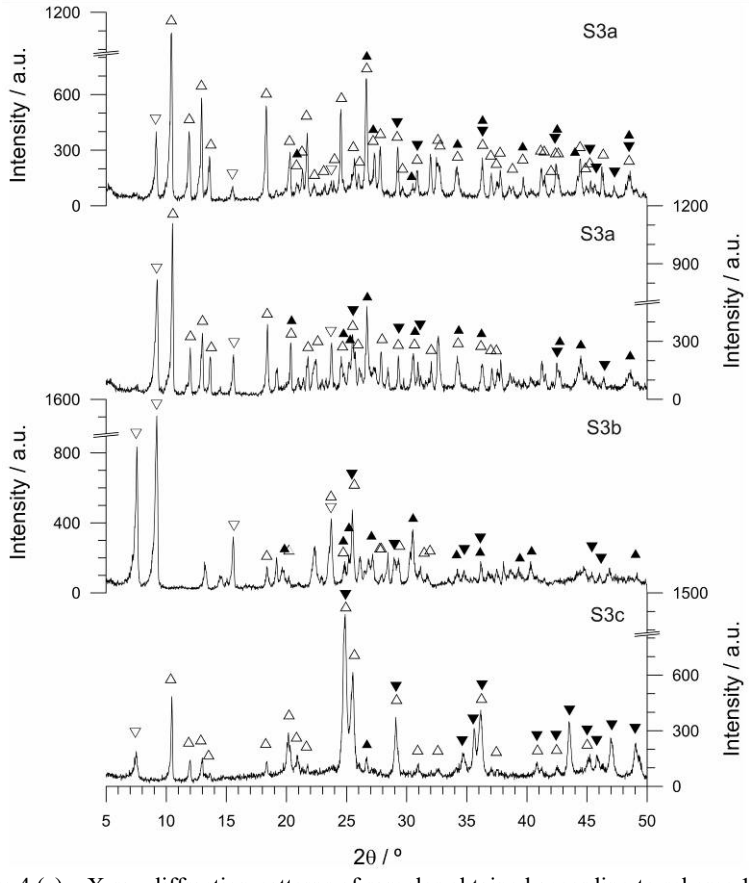


Figure 4 (c) – X-ray diffraction patterns of samples obtained according to scheme 1 (△ - hydrated lead acetate; ▽ - lead acetate; ▲ - basic lead carbonate; ▼ - lead carbonate)

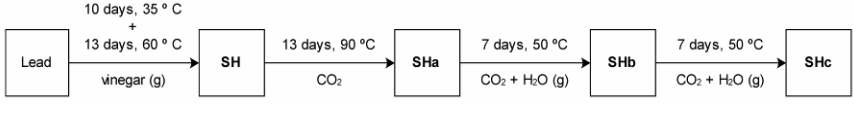


Figure 5 – Experimental conditions applied to the sample scrapped from lead surface after exposure to vinegar at temperature higher than room temperature (scheme 2)

The sample obtained by exposure of the lead to the vinegar vapours according to scheme 2, named SH, present a X-ray diffraction pattern where the dehydrated lead acetate is predominant and where carbonate phases were not detected (Fig. 6). Sample SHa shows that the CO_2 enriched atmosphere, in spite of the higher temperature, was not sufficient to observe an important development of a carbonate phase. Only when a source of H_2O was placed inside the flask the acetate phases were extensively transformed in carbonate phases (samples SHb and SHc). The obtained material is a mixture where, according to the XRD result, the lead carbonate phase is predominant and not the basic lead carbonate. This difference in relation to the expected composition of white lead is reinforced by the comparison with the XRD pattern of a commercial white lead pigment (from Kremer Pigmente) (Fig. 6).

With scanning electron microscopy, the morphological characterizations of selected samples were made. Fig. 7 shows the electron secondary images obtained for one sample of white lead from Kremer Pigmente and for sample SHc. This last one presents a relatively homogeneous grain size distribution and, although having a different chemical composition, as discussed above, morphologically it is quite alike the commercial pigment. In both cases rhombohedral-like crystals are observed, as it was expected for hydrocerussite and cerussite.

Discussion

Irrespective of temperature, exposure of lead to vinegar vapours in a closed flask for 10 days, as prescribed by Filipe Nunes and authors of other painting treatises, does not lead to formation of lead carbonate phases but only to acetate phases. Although this was already stated in the older literature,[30] recent studies had shown that lead carbonates, namely plumbonacrite (lead oxide carbonate hydroxide) and hydrocerussite, mixed with other phases, may formed when lead is exposed to an atmosphere with acetic vapour concentration inferior to that obtained with a strong vinegar.[31] Our results point out that with strong vinegar, which was generally recommended in the treatises (for instance, in Nunes' treatise), we do not detected any basic carbonate phase by XRD. Our results also show that the last step mentioned by Nunes and others, the exposure of the obtained material to the sun, which apparently have the drying of the pigment as the only objective, could transforms lead acetates into lead carbonates by the mutual action of the temperature, the CO_2 and the H_2O vapour. Considering this step as an integral part of the synthesis procedure, and not only as a drying step, it is possible to obtain white lead through recipes like that of Nunes, contrary to what has been affirmed.[32] According to our results, the pigment obtained this way (samples S1d and S3d) has high content of lead acetates, which decrease

the opacity or hiding power of the pigment and can has deleterious effects on paint.[33] However, due to its solubility, the lead acetates could be removed by wash with water, although we do not found any recipe similar to that of Nunes that mention such procedure. Nevertheless, he says that white lead, after grounded, should be "*placed in little shells and covered with water*".[34] Probably, this should remove some small fraction of the lead acetates.

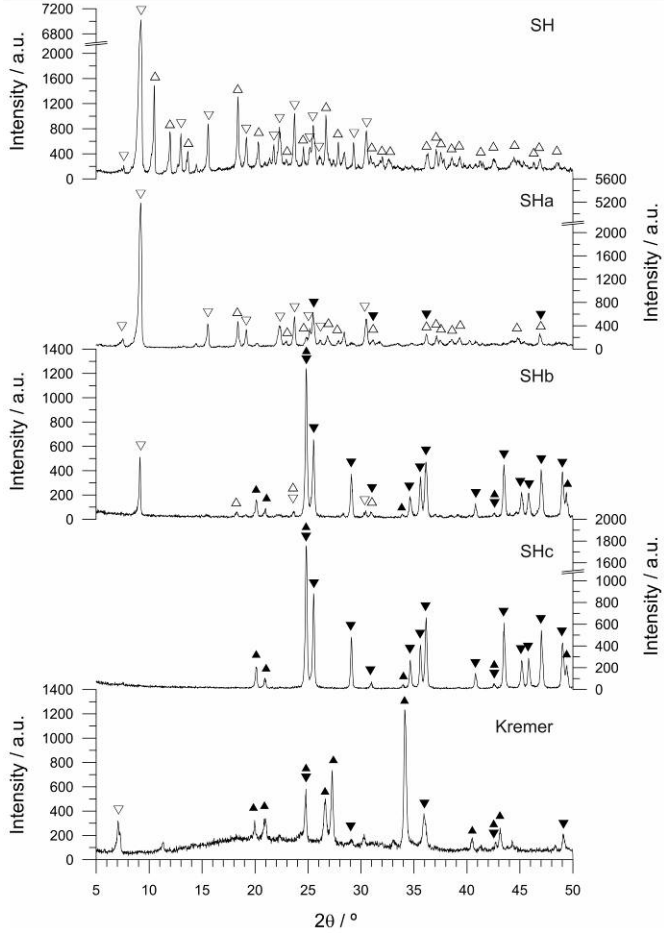
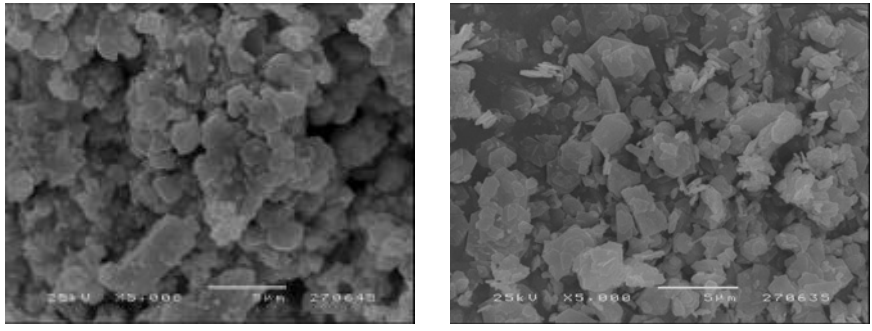
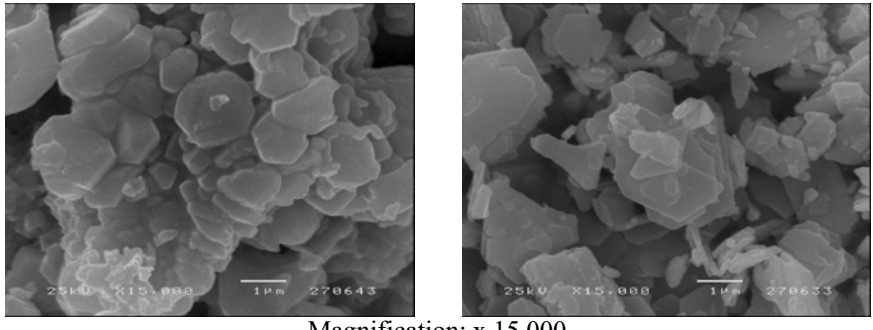


Figure 6. X-ray diffraction patterns of samples obtained according to scheme 2 (△ - hydrated lead acetate; ▽ - lead acetate; ▲ - basic lead carbonate; ▼ - lead carbonate)

SHc white lead *Kremer Pigmente*



Magnification: x 5 000



Magnification: x 15 000

Figure 7 – SEM images of white lead Kremer Pigmente and sample SHc

The complete transformation of the lead acetates into lead carbonates was achieved only at high temperatures (sample SHc). Besides, the pigment obtained in these conditions had the lead carbonate as the main component and not the basic lead carbonate and, consequently, was a *low quality* pigment. As a matter of fact, the proportion between $PbCO_3$ and $Pb(OH)_2$ is very important for painting proposes and should be about 2:1 (molar), as in the case of basic lead carbonate. If the $Pb(OH)_2$ concentration is in excess to that ratio, the opacity of the paint is lessened seriously but if it is lack, as it seems to be the case for the obtained material, the binding-power and working quality of the white lead are impaired.[35] However, in the treatises of Nunes and others nothing suggests that high temperatures, such as those employed in some steps of scheme 2, were

attained and thus it is expect that white lead prepared according to these recipes should instead have a large contents of lead acetates.

Conclusion

An experimental protocol for white lead preparation based on the recipe reported on Filipe Nunes' treatise was established using currently available materials. The results pointed out the importance of the combined action of acetic vapours from vinegar, carbon dioxide atmosphere, water vapour and heating temperature. It was possible to prepare a pigment with the information provided by Nunes and other ancient treatises, but the obtained material presents large content of other components in addition to the basic lead carbonate that is expected for white lead.

Acknowledgments

This work was supported by Fundação para a Ciência e Tecnologia (Portugal) through project POCI/EAT/58065/2004.

Notes

[1] Mary V. Orna, Manfred J.D. Low, Norbert S. Baer, “Synthetic blue pigments: ninth to sixteenth centuries. I. Literature”, *Studies in Conservation* 25 (2) (1980) 53-63; Mary V. Orna, Manfred J.D. Low, Maureen M. Julian, “Synthetic blue pigments: ninth to sixteenth centuries. II. 'Silver blue'”, *Studies in Conservation* 30 (4) (1985) 155-160.
[2] Mark Clarke, Joyce H. Townsend, Ad Stijnman (ed.), *Art of the Past - Sources and Reconstructions* (London, 2005); Stefanos Kroustallis, Joyce H. Townsend, Elena Cenalmor Bruquetas, Ad Stijnman, Margarita San Andres Moya (ed.), *Art Technology - Sources and Methods* (London, 2008).
[3] Filipe Nunes, *Arte da Pintura, Symmetria e Perspectiva* (fac-simile da edição de 1615 com um estudo introdutório de Leontina Ventura) (Porto, 1982).
[4] Zahira Veliz (ed.), *Artists' Techniques in Golden Age Spain. Six treatises in translation* (Cambridge, 1986).
[5] G. Fortunato, A. Ritter, D. Fabian, "Old Masters' lead white pigments: investigations of paintings from the 16th to the 17th century using high precision lead isotope abundance ratios", *Analyst* 130 (2005) 898-906.
[6] Dan A. Ciomartan, Robin J. H. Clark, Lachlan J. McDonald, Marianne Odlyha, "Studies on the thermal decomposition of basic lead(II) carbonate by Fourier-transform Raman spectroscopy, X-ray diffraction and thermal analysis", *Journal of the Chemical Society. Dalton Transactions* 18 (1996), 3639-3645.
[7] Rutherford J. Gettens, Hermann Kühn, W. T. Chase, “Lead white”, in A. Roy (ed.), *Artists' Pigments. A handbook of their history and characteristics. Volume 2* (Washington, 1993) 67-81; P. Martinetto, M. Anne, E. Dooryhée, P. Walter, G. Tsoucaris, “Unveiling the stricture of ancient lead pigments. Example of 'lead white'”, in G. Tsoucaris, J. Lipkowski (ed.), *Molecular and Structural Archaeology: Cosmetic and Therapeutic Chemicals* (Dordrecht, 2003), 113-118.
[8] E. R. Caley, J. F. C. Richards, *Theophrastus on Stone* (Columbus, 1956).
[9] M. Hicky Morgan (ed.), *Vitruvius. The Ten Books on Architecture* (New York, 1960).
[10] H. Rackham, *Pliny. Natural History. Books 33-35* (Cambridge-London, 1952).
[11] N. Eastaugh, V. Walsh, T. Chaplin, R. Siddall, *Pigment Compendium. A Dictionary of Historical Pigments* (Oxford, 2004).
[12] S. Smith, J. G. Hawthorne, “Mappae Clavicula. A litlle key to the world of medieval techniques”, *Transactions of the American Philosophical Society* 64 (4) (1974), 3-128.
[13] J. G. Hawthorne, C. S.Smith, Theophilus, *On Divers Arts. The Foremost Medieval Treatise on Painting, Glassmaking and Metalwork* (New York, 1979).
[14] M. P. Merrifield, *Medieval and Renaissance Treatises on the Arts of Painting* (New York, 1999).
[15] Merrifield, *Medieval and Renaissance Treatises.*
[16] Merrifield, *Medieval and Renaissance Treatises.*
[17] Watin, *L' Art du Peintre*, *Doreur, Vernisseur*, 2nd ed. (Paris, 1773).
[18] R. D. Harley, *Artists' Pigments. c. 1600-1835. A Study in English Documentary Sources*, 2nd ed. (London, 2001); W. Eastaugh, S. Chaplin, *Pigment Compendium.*

[19] A. Laguna, *Pedacio Dioscorides Anazarbeo, Acerca de la Materia Medicinal, y de los Venenos Mortiferos* (Salamanca, 1563).
[20] Veliz, *Artists' Techniques in Golden Age Spain.*
[21] *International Center for Diffraction Data,* Power Diffraction File Alphabetical Index (PA, 1988).
[22] A. Palomino Velasco, El Museo Pictorico, y Escala Optica. vol. 2 (Madrid: Viuda de Juan Garcia Infançon, 1724); J. L. B. Almada,; Prendas da Adolescencia, ou Adolescencia Prendada com as Prendas, Artes, e Curiosidades mais Uteis, Deliciosas, e Estimadas em todo o Mundo (Lisboa: Off. de Francisco da Silva, 1749).
[23] Harley, *Artists' Pigments.*
[24] Harley, *Artists' Pigments.*
[25] F. Frezzato, *Cennino Cennini. Il Libro dell'Arte* (Vicenza: Neri Pozza Editore, 2003).
[26] Harley, *Artists' Pigments.*
[27] J. Pacheco, *Divertimento Erudito para os Curiosos de Noticias Historicas, Escolasticas, Politicas, Naturaes, Sagradas, e Profanas*, vol. II (Lisboa: Officina de Antonio de Sousa da Sylva, 1738).
[28] *Segredos Necessários para os Officios, Artes, e Manufacturas*, vol. II (Lisboa: Offic. de Simão Thaddeo Ferreira, 1794).
[29] J. F. L. Mérimée, *De la Peinture à l'Huile* (Paris: Mme Huzard, 1830).
[30] W. H. Pulsifer, *Notes for a History of Lead* (New York: D. Van Nostrand, 1888); C. D. Holley, *The Lead and Zinc Pigments* (New York, 1909).
[31] J. Tétreault, J. Sirois, E. Stamatopoulou, Studies in Conservation vol. 43 (1998) 17-32.
[32] Holley, *Lead and Zinc Pigments*; Tétreault, Sirois, Stamatopoulou (1998).
[33] Tétreault, Sirois, Stamatopoulou (1998).
[34] Veliz, *Artists' Techniques in Golden Age Spain.*
[35] A. H. Church, *The Chemistry of Paints and Painting* (London, 1915).