

Double-Layer Red Lead Hematite-Minium Paint in the Roman City of Italica



Engineering

KEYWORDS : Colour, Microscopy, Archeometry, Paints, Pigments

L. García Sánchez

Department of Materials Science and Metallurgical Engineering, School of Chemistry, Complutense of Madrid University

A. J. Criado Portal

Department of Materials Science and Metallurgical Engineering, School of Chemistry, Complutense of Madrid University

A. J. Criado Martín

Department of Materials Science and Metallurgical Engineering, School of Chemistry, Complutense of Madrid University

ABSTRACT

In this work we have studied a sample of red paint pigment from the Roman city of Italica. The characteristic tone of these samples is most likely determined by the composition and the technique used. The aim of this study is to analyse this sample and establish how the glowing red hue was achieved with haematite and lead minium, and examine the pictorial technique used.

1.- INTRODUCTION

The aim of the following work is to analyse a sample of red paint from the Roman city of Italica; more specifically from the *nova urbs* built during the reign of the Emperor Hadrian (117 to 138) (Figure 1).

Figure 1: Image of the excavations in the ruins of Italica in the *nova urbs*.

This original paint is very technically advanced, and comprises two superimposed coats of hematite and minium in the form of a glaze, whose transparency confers a highly luminous red hue. The first coat of haematite was applied al fresco, and the lead minium coat was done in casein tempera (Doerner, 1975, pp.197-199).

Lead minium was not the genuine minium in classical Rome, but rather natural or artificial cinnabar red (Plinio Segundo el Viejo, Libro XXXIII; Vitrubio Polión, Libro VII); it was however the secondary or false minium which was more economical and much brighter, tending strongly towards an orange tone (Gettens, Feller and Chase, 1993, pp.183-202; Harley, 1982; Gazulla, Rodrigo, Blasco and Orduña, 2013, pp.277-282; Alonso, Capel, Valle-Fuentes, De Pablos, Ortega, Gómez and Respaldiza, 2009, pp.179-186; Báez and San Andrés, 2003, pp.155-172). It is a lead tetroxide (Pb_3O_4) obtained according to Pliny the Elder and Vitruvius (Plinio Segundo el Viejo, Libro XXXIII; Vitrubio Polión, Libro VII) by burning cerussite or white lead: $6 PbCO_3 + O_2 \rightarrow 2 Pb_3O_4 + 6 CO_2$.

The paint analysed shows that on numerous occasions the authentic -cinnabar- minium was replaced with lead minium, which was more economical and had a warmer tone (Doerner, 1975, pp.71-72). Its use in this case is explained by the judgement of the craftsman, who wished to give a heightened tone to the red of the hematite.

Lead minium has one drawback, namely its relative photochemical stability to sunlight, which makes it unsuitable for painting exteriors. The particle size of the paint and vehicle plays a key role in the stability of the colour, and in its association with other pigments. In our case there is a marked compatibility between the lead minium and the hematite.

The choice of vehicles in this red paint was correct: hematite al fresco (limewater) and lead minium with milk casein.

The red paint compounds were studied and identified using x-ray diffraction. We used scanning electron microscopy with an EDS-EDX analytical system for the images of the position of the layers and their characteristics.

2.- EXPERIMENTAL TECHNIQUE

The city of Italica is one of the world's best conserved Roman cities, and has been partially excavated. Excavations are currently taking place in Hadrian's *nova urbs*. Scipio's *retus urbs* lies beneath the town of Santiponce in Seville.

Italica is today a school of archaeology. Its systematic excavation is progressing every year, although at a very uneven rate. These paint samples were collected in the area indicated in Figures 2 and 3.

Figure 2: Image of the outlined area, the focus of the excavation, where the samples of red paint were found.

Figure 3: Image of the street in the *nova urbs*, the focus of the excavation in the area outlined in the previous figure, where the samples were collected.

Various samples were mounted in two-component resin Résine Mécaprex KM-U by Presi and subsequently sanded and polished conventionally with Buehler abrasive paper with a grain of 120, 270, 320 and 600; and a Buehler polishing cloth with alumina α (0.3 μ m) by Buehler (Criado Portal, García, Penco, Criado Martín, Martínez, Chamón and Dietz, 2011, pp.161-168). These operations were done gently and effectively due to the apparently fragile nature of the samples, which were however well embedded in the resin. With no chemical etching, they were dried on a stove at 35°C for two hours.

They were observed through a conventional optical microscope; 20nm thick metallized graphite was deposited on top for one minute for the scanning electron microscopy with incorporated EDS-EDX analysis.

After careful cleaning, the sample components were identified by x-ray diffraction (Figures 4 and 5).

Figure 4: Image of one of the paint samples collected at the excavation.

Figure 5: Image of one of the samples mounted and prepared for study.

3.- RESULTS AND DISCUSSION

This is a complex paint, with the mortar and hematite layers applied al fresco, and the lead minium done in casein tempera.

The process was as follows: first a sand and lime mortar was applied to the wall and while this was still damp, another mortar of lime and very fine sand was applied (Figure 6 and 7).

Figure 6: Macrograph showing the structure of the mortar on which the painting was done.

Figure 7: Detail of the previous image showing the fine mortar layer and the colour layer.

A layer of lime hematite was applied on this plaster while the mortar was still damp. Finally, once both the al fresco mortar and the paint layer were dry, a fine layer of casein glue minium was applied as a glaze. The resulting colour is due to the transparency of the layers, which produce an attractive glowing red tone that cannot be directly achieved with paint (Doerner, 1975, pp.215-218) (Diagram 1).

Diagram 1: Surface reflection on the direct paint. Reflection of the light on several planes in the transparency technique.

We verified the composition of the mortar and the pigment with X-ray diffraction (Figure 8): calcite or calcium carbonate, the result of the carbonation of the vehicle, lime base ($\text{Ca}(\text{OH})_2$), mortar and the hematite film. The silica is the sand in the mortar and the hematite (Fe_2O_3) and lead minium (Pb_3O_4) pigments in the paint layer. What the diffractogram does not reveal is the sequence of the layers.

Figure 8: X-ray diffractogram identifying the components of the mortar and the paint layer.

The frontal view of the paint layer on the mortar support is shown in Figures 9a and 9b. The axial section (Figure 5) shows a view of the paint layer using SEM with backscattered electrons (Figure.10)

Figure 9a: Micrograph obtained with scanning electronic microscope of the paint layer viewed from the front.

Figure 9b: Detail of the micrograph in Figure 9 showing the particles of pigment and some quartz aggregates.

Figure 10: Micrograph obtained with scanning electronic microscope with backscattered electrons of the paint layer on the mortar substrate.

There are areas in which the lead minium glaze –due to the effects of deterioration and the fact that the layer is applied on casein tempera– has become detached from the hematite layer (Figure 11).

Figure 11: Image showing how the lead minium glaze has become detached from the hematite layer in some areas.

The EDS-EDX analysis identifies this outer detached layer as mainly lead minium (Figure 12). In the transitional area between the layers, the EDS-EDX analysis reveals that the lead content decreases dramatically and the hematite content increases (Figure 13 and 14).

Figure 12: Identification by EDS-EDX analysis of the detached lead minium glaze.

Figure 13: Identification by EDS-EDX analysis of the intermediate part of the paint showing an increase in the hematite pigment and a decrease in lead minium.

Figure 14: Identification by EDS-EDX analysis of the progressive disappearance of the lead towards the interior of the paint layer.

The presence of phosphorus can be seen in both analyses. This phosphorus comes from the milk casein, which is a phosphoprotein. As we suggested, the lead minium paint layer was done in casein tempera.

4.- SUMMARY AND CONCLUSIONS

This painting is executed with the utmost rigour using a flawless technique. The solution conceived to achieve the effect of colour by means of transparency is centuries ahead of the great painters of the Flemish and Italian schools of the Renaissance. This and subsequent periods are characterised by the technique of building up colour through transparent layers and not by applying the paint directly. Multiple superimposed thin layers penetrated by the light produced –through reflection– an optical effect that cannot be obtained directly with paint. Titian said that in his paintings there was “*svelature, trenta o quaranta*” (Doerner, 1975, pp.311).

The paint in this study is correctly applied on sand and lime mortar with two structures: coarse and fine sand. When damp, the first layer of red haematite paint was applied al fresco (lime-water), and once this layer was absolutely dry, the fine layer of lead minium was done in casein tempera glue (phosphoprotein). The final effect is that the blood red of the hematite (Fe_2O_3) is seen through a layer of reddish-orange lead tetroxide to produce a magnificent shade of vermilion.

REFERENCE

- 1) Alonso, M.P., Capel, F., Valle-Fuentes, F.J., de Pablos, A. Ortega, I., Gómez, B., Respaldiza, M.A. (2009): Caracterización de un vidrio rojo medieval procedente de las vidrieras del Monasterio de las Huelgas de Burgos, Bol. Soc. Esp. Ceram. Vidr., 48 (4): 179-186. | | 2) Báez, M.I., San Andrés, M. (2003): Cinabrio y bermellón: historia de su empleo y preparación. Análisis histórico, Pátina, Época II, nº12: 155-172 | | 3) Criado Portal, A.J., García, L., Penco, F., Criado Martín, A.J., Martínez, J.A., Chamón, J., Dietz, C. (2011): Estudio arqueométrico comparativo de muestras de pinturas con azul egipcio, procedentes de la tumba de Nefertari siglo XIII a.C. y del Balneum, termas romanas, siglos Ia.C., Id.C., Bol. Soc. Esp. Ceram. Vidr., 50 (3): 161-168. | | 4) Doerner, M.(1975): Los materiales de pintura, Editorial Reverté, Barcelona, España, pp. 197-199. | | 5) Doerner, M.(1975): Los materiales de pintura, Editorial Reverté, Barcelona, España, pp. 71-72. | | 6) Doerner, M. (1975): Los materiales de pintura, Editorial Reverté, Barcelona, España, pp. 215-218. | | 7) Doerner, M. (1975): Los materiales de pintura, Editorial Reverté, Barcelona, España, pp. 311. | | 8) Gazulla, M.F., Rodrigo, M., Blasco, E., Orduña, M. (2013): Caracterización química de pigmentos cerámicos a base de sulfoseleniuro de cadmio. Bol. Soc. Esp. Ceram. Vidr., 52 (6): 277-282. | | 9) Gettens, R.J., Feller, R.L., Chase, W.T. (1993): Vermillion and Cinnabar, en A.Roy, Ed., Artist' Pigments. A Handbook of their History and Characteristics, Vol.II, National Gallery of Art, Washington, Oxford University Press, Oxford, pp. 183-202. | | 10) Harley, R.D. (1982): Artist' Pigments c.1600-1835, 2ªEdition, Butterworth Scientific, London. | | 11) Plinio Segundo el Viejo, G.: Historia natural, Libro XXXIII Tratado de los Metales y su Naturaleza, Capítulo VII: Del minio y bermellón. | | 12) Vitrubio Polión, M.: Los diez libros de arquitectura, Libro VII, Capítulo XII: El albayalde, el cardenillo y la sandáraca. |