Valencian red imprimaturs since Francisco Ribalta (1565-1628)

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Abstract

The aim of this study was to confirm the use of an admixture of natural earth and a second unusual Al-rich red pigment in the imprimaturs of paintings that date back to 1600-1660, painted by some of the most outstanding Valencian Baroque painters. For this purpose, microsamples excised from six paintings were prepared as cross-sections to be analysed by optical microscopy (OM) and field emission scanning electron microscopy-X-ray microanalysis (FESEM-EDX) combined with Fourier Transform Infrared (FTIR) spectroscopy, microRaman spectroscopy and voltammetry of immobilized microparticles (VIMP). Two possible red pigments, red lake or synthetic Mars red could be used by these painters in red imprimaturs mixed with natural earth pigments. This particular technique, identified for the first time in seventeenth-century Valencian paintings of known authorship, is a novel finding than can help in authentication studies of unknown Baroque paintings.

Keywords: Red lake, Mars red, imprimatur, Valencian painting, oil painting, FESEM-EDX, MicroRaman spectroscopy

1. Introduction

At the beginning of the 16th century, painters from North Italy followed Venetian painters and started using imprimaturs, which varied from the bright and mostly white colour of grounds to warmer colours (ochre, brown, red, grey) [1-2]. This change has been evidenced by the authors in Italian painters from this period, such as Girolano Francesco Maria Mazzola (El Parmigianino) (1503-1540) (Fig. 1S presented as supplementary electronic material) and an anonymous painter from a local Sicilian workshop back in the 17th century (Fig. 2S). This change was introduced into Spain in the late 16th century as confirmed in artistic treatises as that written by Francisco Pacheco (1564-1644), where mention is made to the use of red or brown colours prepared with natural earths and lead pigments (oil siccative) in imprimaturs [3] but also by analyses performed on paintings on canvas of this period. These analyses have confirmed that use of red-brown imprimaturs in paintings on canvas was an extended practice between the Spanish seventeenth painters. A remarkable example is found in Velázquez (1599-1660). Analytical studies of several paintings of this painter have demonstrated that he used a local red earth, *tierra de esquivias*, combined with small amounts of carbon black, in most of his imprimaturs [4,5]. In this context, the occurrence of a change in the artistic technique with an unusual combination of pigments and the possible inclusion of a new pigment is a relevant finding.

Use of red lakes in the East Europe has been abundantly reported in paint layers of easel painting since the twelfth century until the eighteenth century [6-8]. Red lakes are composed of a soluble dye, which is adsorbed in a colloidal substrate. Madder, Brazilwood, cochineal and kermes are the most common dyes used. The substrate is prepared by the reaction between an alkali and alum ($KAl(SO_4)_2{\cdot}12H_2O$) that yield a product of highly variable composition described as hydrated alumina (Al_2O_3 H_2O or Al_2O_3 $3H_2O$) as does not match with any of the crystalline aluminium (oxy)hydroxides or anhydrous oxides. The alkali is a solution of sodium or potassium carbonate depending on the plant source of the water-extracted vegetal ash. Alternatively, lime water prepared from quick lime can be employed. The order of addition of the reagents is determinant for the chemical composition of the substrate. Until the 19th century, the sequence described in the recipes starts with the extraction of the dye from the raw plants or the dyed textiles with an alkali followed by the addition of alum to precipitate the pigment. Addition of alkali to a solution of alum containing the dye is recommended in recipes since the 19th century [6].

The Mars red pigment is a synthetic red oxide whose preparation method is described in detail in several treatises on artists' materials from the mid-19th century as part of the preparation method of setting synthetic pigments known as "Mars colours" [9,10]. Some scientific sources suggest that the industrial preparation process of these pigments began in the late 18th century [10,11] and point out the treatise of the painter Constant de Massoul as the earliest source (1797) [12]. The preparation of these pigments is based on the aqueous precipitation of iron salts. Several manufacture procedures have been described to prepare Mars red. The most widely used one is that based on aqueous precipitation from iron sulphate, although other iron salts can also be used like chloride, nitrate or acetate [13]. This process consists of precipitating iron sulphate ($FeSO_4$) in solution with aluminium sulphate ($Al_2(SO_4)_3$) or alum ($KAl(SO_4)_2{\cdot}12H_2O$), as well as an alkali like sodium carbonate, potassium carbonate, potash or slaked lime (calcium hydroxide) [10,14], which promote the formation of an iron hydroxyde precipitate that is further oxidised in air and results in an iron oxide hydroxyde. Mars yellow is obtained by this procedure and can be subjected to different degrees of calcination to result in a variety of colours, including Mars red.

Mars red has already been identified in the paint layer of some of the three paintings on canvas of the series entitled *Scenes of the life of Saint Albert* located in the *Our Lady of Carmen* church in Antequera (Málaga, Spain). They were painted by an anonymous painter and date back to the 17th century [14]. The artistic technique described in this analytical study consists of ground gypsum bound with animal glue with upper paint layers that include pigments like natural red ochre, Sienna, lead white, calcite, red lake and Mars red. Nevertheless, this paper mentions neither this pigment being employed in imprimaturs of painting on canvas, nor an adscription of these paintings to a local workshop or foreign painter. Therefore, questions on the use of Mars red during this earlier historic period, such as provenance, authorship and the specific role of this pigment in the artistic technique, still remain.

2.- Research aim

This work presents one part of a broader study conducted to characterise the artistic technique, evolution and mutual influences due to collaborations between some of the most relevant Valencian Renaissance-Baroque painters and/or workshops (ca. 1550- ca. 1670) [15,16]. In an earlier work [16], the authors demonstrated some collaborations and mutual influences among the painters Vicente Castelló, Francisco Ribalta and his son Juan Ribalta, and Jerónimo Rodríguez de Espinosa and his son Jerónimo Jacinto de Espinosa (see Fig. 3S). Mutual influences among painters may have not only affected artistic style, but also materials and the development of new technical procedures to prepare red imprimaturs, which should be justified by the relevant series of changes in artistic techniques that took place during the Renaissance-Baroque period. The conducted research demonstrated that an unusual method or recipe based on a mixture of a local natural earth and a second Al-rich red pigment was frequently used by these Valencian painters to elaborate the bright red oil imprimaturs of their paintings on canvas and panels.

3. Experimental

3.1. Studied samples

Forty-seven samples, including all the paint strata covering each author's complete colour palette of Francisco Ribalta, Vicente Castelló, Juan Ribalta and Jerónimo Jacinto de Espinosa [17-19], were mechanically excised from six selected paintings on canvas adhered to panels and from one panel. Table 1S, provided as electronic Supplementary Material, summarises the main characteristics of the series of studied samples, as well as the identified binders and pigments. The location of sampling points in paintings is shown in Fig. 4S-9S.

3.2. Instrumentation

Optical microscopy (OM), field emission scanning electron microscopy-X-ray microanalysis (FESEM-EDX), FTIR Spectroscopy, microRaman spectroscopy and voltammetry of immobilized microparticles (VIMP) were applied using instrumentation and working conditions described in Table 2S provided as supplementary electronic material.

4. Results

4.1. Optical Microscopy

Figure 1 shows the microphotographs of the six representative cross-sections of the artists' application of red imprimaturs in each studied painting. In five of the six paintings, the authors applied bright red imprimaturs underneath the paint layer (Figs.

1a-e), sometimes accompanied by a darker or ochre one applied beneath (Fig. 1a,b). Figure 1f illustrates a white ground underneath the red imprimatur. This is the only pictorial work of the studied set that was made using a panel as a support. All the imprimaturs exhibit morphologies characterised by heterometric distributions of grain size with an abundant variety of accessory minerals that notably vary in colour and size, and are dispersed in a characteristic cryptocrystalline red clayey matrix of natural earths. A more detailed description of the composition layer by layer of the six samples studied can be found in Table 3S.

4.2. Field emission scanning electron microscopy-X-ray microanalysis

4.2.1. Ecce Homo and Dream of the Child Jesus

The *Ecce Homo* canvas is adhered to a panel, and has been attributed to Francisco Ribalta. It dates back to 1600-1610, and is the oldest painting in which the use of an Al-rich red pigment in imprimaturs was confirmed. As the cross section of sample EH4 shows, found in Figs. 1a and 2a, the painter prepared the canvas support of this pictorial work by applying an inner dark imprimatur. A red imprimatur is seen over. As evidenced by the X-ray spectra acquired in spot mode in several grains in the cryptocrystalline matrix (Fig. 2b), the red imprimatur seems to be composed of two different red pigments. The first one exhibits a high content in Fe (25.7 wt%), moderate Al (14.5 wt%), S (13.8 wt%) Ca (11.6 wt%) and K (8.5 wt%) and lower content in Si, P, Cl and Pb (less than 5.8 wt%). This composition is in contrast with that other, typical of a natural red earth, found in other grains of the cryptocrystalline red matrix of the imprimatur (Fig 2c) in which the major component is Si (27.3 wt%), followed by moderate content of Al (10.4 wt%) and low amounts of the rest of minor compounds present in clayey minerals. Similarly, a high content in Al (13.7 wt%) accompanied with moderate content in Fe (7.5 wt%), Ca 6.3 wt%) and S (3.9 wt%) was found in grains of the cryptocrystalline matrix of the red imprimatur of the painting on canvas *Dream of the Child Jesus* by Vicente Castelló, that dates back to 1600-1620. Castelló was the son-in-law of Francisco Ribalta and was, therefore, personal and professionally linked with Ribalta's workshop (see sample SNJ1 in Figs. 1b and 10Sa,b).

4.2.2. Saint Peter Crying, Birth of the Virgin Mary and Birth of Saint John

The *Saint Peter Crying* painting on canvas was painted in 1628 by Juan Ribalta, son of Francisco Ribalta. The painting (sample SP3 in Figs. 1c and 3a) was done by applying red imprimatur composed of red earth and an Al-rich red pigment underneath two paint layers, including carbon black and lead white. The Al-rich red pigment exhibited a chemical composition similar to that found in the sample EH4 with Al (9.9 wt%), S (4.6wt%), Si (5.8 wt%), Ca (11.6 wt%) and Fe (20.3 wt%) and lower content in Si, P and K (Fig. 3b). Similar elemental distribution of major and minor components was found in X-ray spectra acquired in grains of Al-rich red pigment present in the imprimaturs of the paintings *Birth of the Virgin Mary* and *Birth of Saint John* that form part of the predella of the *Saint Peter Martyr* Altarpiece of the *San Nicholas of Bari and Saint Peter Martyr* church in Valencia (Spain) (see microphotographs and X-ray spectra of samples NV3 and NSJ2 in Figs. 1d,e, 11Sa,b and 12Sa,b).

4.2.3. Coronation of the Virgin Mary

This artwork is a panel painted in ca. 1660. As Figs. 1f and 4a depict (sample CV3), the painter applied an inner white ground of gypsum bound with animal glue, as confirmed by FTIR spectroscopy (IR spectrum; not shown), and an oil thin red imprimatur over. The outer paint layer is composed mainly of lead white. The X-ray spectra acquired in a grain of Al-rich red pigment present in the imprimatur confirmed its use combined with natural earths (Fig. 4b). Elemental composition includes Al (10.4 wt%), Ca (13.4 wt%) Fe (10.0 wt%), K (3.1 wt%) and S (3.84 wt%) and lower content in Na, Mg, Si, P, Cl. It is noteworthy that the introduction of this technique to make red imprimaturs in the Espinosa family's workshop was thanks to Jerónimo Jacinto de Espinosa. Although his father Jerónimo Rodríguez de Espinosa (1562-1639) also applied a red imprimatur over the white gypsum ground of the panel, he still employed natural earths in this layer, as demonstrated in the panel corresponding to the Altarpiece located in the *Saint John Baptist* church in Muro de Alcoy (Valencia, Spain) painted between 1604-1607 (see Fig. 13S).

4.3. FTIR spectroscopy

Figure 14S shows the IR absorption spectrum acquired in the red imprimatur of the *Saint Peter Crying* painting by Juan Ribalta. The main IR absorption bands, assignation and compounds identified in the red imprimatur are shown in Table 4S. The main findings include the identification of characteristic intense bands with maxima at 3390 and 1644 cm^{-1} and 1023 cm^{-1} ascribed to stretching and deformation vibrations of -OH groups and Si-O stretching band from the clayey minerals and quartz in the natural earth pigment and Fe-O stretching band at 539 cm^{-1} ascribed to iron (III) oxide [10]. Bands at 1411(shoulder), 872 and 711 cm^{-1} are associated with calcite, which is present in the natural earth pigment as accompanying minerals of clays. Bands associated to gypsum formed for atmospheric pollution and bands ascribed to the oil binder and its alteration products were also found (cif. Fig. 14S, Table 4S).

4.4. Raman spectroscopy

Raman spectra obtained in the imprimatur layers of the six studied paintings are shown in Fig. 3c, 4c and 10Sc-12Sc,15Sc. The summary of the position of the bands identified together with the assignment of groups is summarized in Table 1. The samples excised from the imprimaturs of the studied painting on canvas exhibited characteristic Raman bands ascribed to iron (III) oxide at 225 and 294, 410, 494 and 606 cm^{-1} [7]. Bands at 177, 207, 225, 294, 372, 450 and 506 cm^{-1} are associated with clays present in natural red earth pigments [20] whereas band at 1051 cm^{-1} is ascribed to lead white probably added by its oil siccative properties [21]. Interestingly, a broad band in the range 1135-1360 cm^{-1}, with maximum at ca 1251 cm^{-1}, is tentatively associated with anthraquinonic dyes [7].

5. Discussion

The analytical results obtained in the six paintings studied indicate that these painters used the same technique for preparing their imprimaturs. This particular technique differs of that used prevalently in this historical period by Spanish painters. Thus, whereas the common imprimatur technique was based on the use of local dark red natural earths such as *tierra de esquivias* and lead white as oil siccative [4], the Valencian painters prepared their imprimaturs as admixtures of a natural red earth pigment and other Al-rich red pigment. This finding is sustained by the different elemental compositions obtained by means of FESEM-EDX in multiple grains of the cryptocrystalline matrix of the imprimaturs. A first chemical compositions is coherent with that of clayey minerals (see X-ray spectrum in Fig. 2c), and a second one (see X-ray spectrum in Fig. 2b) is characterized by its high content in Al and variable amounts of other elements between which predominate S, Fe, Ca and K and at less extent, Si, P, Cl and Pb. This composition is in good agreement with the analysis by Kirby et al [6] of red lakes found in paintings by Italian, Austrian and English painters of this period, characterised by the notable presence of Al and variable amounts of S, K and Ca and traces of Si, Cl and P (quantitative compositions are not provided in [6]). These authors associate these minor elements to residues from the raw dye source (plants or dyed textiles) and from the products used for extracting the dye (an alkali: soda potash or lime) and precipitating the lake (alum) described in recipes dated back before the 19^{th} century. The results obtained here with microRaman spectroscopy point out to the use of a red lake prepared with an anthraquinonic dye. Nevertheless, the origin of the high content of Fe also present in the Al-rich grains remains uncertain. This high Fe content could be associate to the Fe (II) fixed as mordent to the dyed textiles used as raw material of the dye. Thus, dye and mordent should be recovered together in the process of alkali extraction prior to the precipitation of alum to form the red lake [22].

A second hypothesis is based on the prior results of Franquelo et al [14], who identify Mars red in a painting dated back to the 17^{th} century. In this work, Mars red is identified by the profile of emission peaks that exhibits the X-ray spectrum of the paint sample in which the more intense features are Al and S accompanied by moderate lines of K and Fe (neither quantitative elemental compositions are provided in [14], nor Raman spectra of samples). The authors of this study associate this X-ray spectrum to Mars red consisting of Fe_2O_3 accompanied by $Al_2(SO_4)_3$ or alum ($KAl(SO_4)_2 \cdot 12H_2O$) and KOH or alkaline carbonates, all of which are precipitating or washing reagents employed to prepare Mars red. This second hypothesis should agree with the high Fe content found in the Al-rich grains of the Valencian imprimaturs. Nevertheless, no features characteristic of alum or alkali carbonates are recognized in the microRaman spectra.

6. Conclusions

Although the study carried out is not conclusive in relation to the identification of the Al-rich red pigment used by the Valencian Baroque painters studied, the performed analyses confirmed that these painters systematically employed a mixture of a natural red earth and a second Al-rich red pigment to enhance the red hue of their imprimaturs.

This unusual imprimatur technique of mixing a natural red earth with other Al-rich red pigment is a relevant finding that suggests that the painters from the Valencian workshops in the late 16th and early 17th centuries developed a particular method for preparing their imprimaturs aimed at improving the chromatic characteristics of this layer by increasing its red hue. This particular technique, identified for the first time in seventeenth-century Valencian paintings of known authorship, can help in authentication studies of unknown Spanish Baroque paintings.

Francisco Ribalta was probably the person who introduced this technique into Valencian workshops when he came to Valencia in 1599, as suggested by the absence of a second red pigment in the imprimaturs of pictorial artworks painted by other Valencian artists before Francisco Ribalta's arrival [13]. Prior to his arrival in Valencia, this painter worked in the Monastery of *Saint Lorentz* in El Escorial (Madrid, Spain) where he was in contact with other outstanding Spanish and Italian painters, such as Juan Fernández Navarrete, trained in Italy, Vecellio di Gregorio Tiziano, Federico Zuccaro, Pellegrino Tibaldi or Luca Cambiaso [10,11]. Perhaps Francisco Ribalta acquired technical knowledge there. Furthermore, the close connections among the studied Valencian painters promoted the use of this combination of red pigments to obtain bright red imprimaturs on not only canvas, but also on panels over gypsum grounds. Nevertheless, the question as if it was an invention of Francisco Ribalta or if other painter to who introduced Francisco Ribalta to use this new technique remains open, and new and more extensive studies are necessary to know the evolution of this artistic technique in Europe during this earlier historic period.

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Table captions

Table 1.- Main Raman bands identified in the red imprimaturs of the samples, assignation and identified compounds.

Figure captions

Figure 1.- Microphotograph (XPL) of the cross-sections obtained from the pictorial samples taken from the six studied paintings, showing the presence of red imprimaturs containing Al-rich red pigment: a) Layer 3 in sample EH4 from *Ecce Homo* by Francisco Ribalta; b) Layer 2 in sample SNJ1 from *Dream of the Child Jesus* by Vicente Castelló; c) Layer 4 in sample SP3 from *Saint Peter Crying* by Juan Ribalta; d) Layer 2 in sample NV3 from *Birth of the Virgin Mary* by Jerónimo Jacinto de Espinosa; e) Layer 2 in sample NSJ2 from *Birth of Saint John* by Jerónimo Jacinto de Espinosa; f) Layer 3 in sample CV3 from *Coronation of the Virgin Mary* by Jerónimo Jacinto de Espinosa. Complete description of the composition of the layers is provided in table 3S in supplementary electronic material.

Figure 2.- a) Backscattered electron image of the cross-section of sample EH4 from *Ecce Homo* by Francisco Ribalta; b) X-ray spectrum acquired in a grain of Al-rich red pigment in the cryptocrystalline matrix of the red imprimatur (dotted lines), inset: averaged elemental content and standard deviation; c) microRaman spectrum obtained in the imprimatur.

Figure 3.- a) Backscattered electron image of the cross-section of sample SP3 from *Saint Peter Crying* by Juan Ribalta; b) X-ray spectrum acquired in a grain of Al-rich red pigment in the cryptocrystalline matrix of the red imprimatur (dotted lines), inset: averaged elemental content and standard deviation; c) microRaman spectrum obtained in the imprimatur.

Figure 4.- a) Backscattered electron image of the cross-section of sample CV3 from *Coronation of the Virgin Mary* by Jerónimo Jacinto de Espinosa; b) X-ray spectrum acquired in a grain of Al-rich red pigment in the cryptocrystalline matrix of the red imprimatur (dotted lines), inset: averaged elemental content and standard deviation; c) microRaman spectrum obtained in the imprimatur.