

Characterization of calcium sulfate grounds and fillings of applied tin-relief brocades by Raman spectroscopy, Fourier transform infrared spectroscopy, and scanning electron microscopy

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Applied tin-relief brocade (commonly called applied brocade) refers to a decorative painting technique using tin leaf applied over a supporting relief mass (filling) which is glued to the artwork to simulate gold and silver textile brocades. This originated in Germany *ca* 1415–1430 and spread across Europe from the mid-15th century to the mid-16th century. This study focuses on six early 16th century altarpieces in the Basque country in the present province of Guipúzcoa, Spain. Cross sections of the ground and applied brocade were initially examined with optical microscopy and staining tests for proteins and lipids to assess the layering structure and materials present. Further examination with Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy with energy dispersive X-ray spectroscopy identified the inorganic and organic components of the various layers. Raman spectroscopic mapping was used to image the location of phases in selected cross sections. Five altarpieces from Spain had calcium sulfate grounds, whereas one thought to come from Flanders had a calcium carbonate ground. Raman and FTIR spectra showed that the thick, coarse lower ground layer (*yeso grueso*) is anhydrous calcium sulfate (anhydrite) whereas the fine, thin upper ground layer (*yeso fino*) is calcium sulfate dihydrate (gypsum). The filling masses consisted of different mixtures of inorganic (chiefly gypsum or anhydrite but occasionally with other pigments or additives) and organic (protein and/or oil or beeswax) materials. Comparison of the documented historical techniques with the materials found provides insight into local variations of the technique. Copyright © 2010 John Wiley & Sons, Ltd.

Keywords: applied tin-relief brocade; gypsum; anhydrite; beeswax

Introduction

Applied tin-relief brocade is considered one of the most detailed, realistic, and laborious decorative painting techniques used in sculpture and painting outside and inside Spain.^[1] Nevertheless, this technique has been studied very little from either a historical or a technical perspective, particularly within Spain. Although some new studies have been undertaken in the last decade, very few have been published. Together with the poor condition of the diverse examples found, which are often covered with restoration materials, this has resulted in failure to recognize the technique and hence in inappropriate or nonexistent conservation treatments.^[2] Applied tin-relief brocade has been studied and published more outside Spain, both in the antique documentary sources (art treatises,^[3,4] painters' ordinances, and artworks' contracts) and recent specialized publications (journals,^[1,2,5–8] congresses and symposia,^[9–11] books,^[12] and theses^[13]). The discovery in Spain of several altarpieces decorated with applied brocade motifs confirmed the need to establish a corpus of technical information on this technique.^[14] This will help identify new or overlooked examples and develop improved conservation and restoration procedures.

Applied tin-relief brocade has been used on a variety of artworks including wooden altarpieces, wooden sculptures, stone (e.g. limestone) sculptures, wooden reliefs, panel paintings, wall paintings, canvas paintings, and wooden coffered ceilings. Reproductions of applied brocades based on treatises and recent publications have helped in the understanding of the process.^[1,5] The technique can be summarized in the following eight stages, and more detailed descriptions can be found in several references^[1,2,6–10,14–16]:

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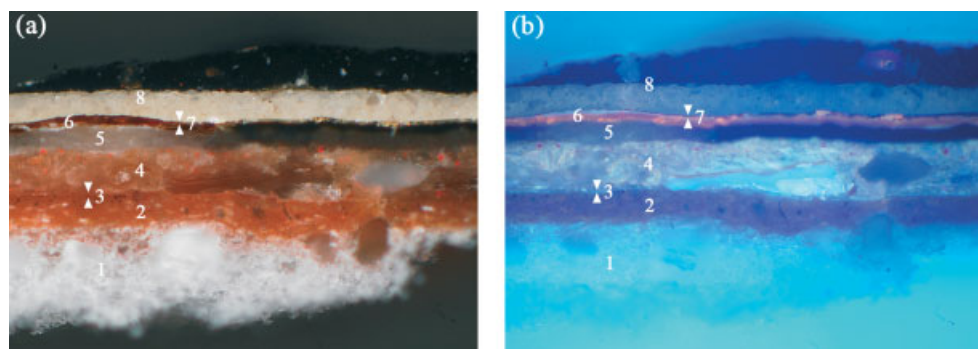


Figure 1. Cross section of a juxtaposed applied tin-relief brocade of the altarpiece of La Santísima Trinidad in the Monastery of Bidaurreta, Oñate: (a) in visible light and (b) in UV light. The numbers correspond to the characteristic layer structure of the technique: 1, ground; 2, imprimatura; 3, adhesive; 4, filling mass; 5, tin leaf; 6, mordant; 7, gold leaf; 8, opaque paint and/or glaze.

1. Engraving the material to be used as the mould, probably wood, metal or stone, to reproduce a textile brocade motif.
2. Placing the tin leaf on top of the mould.
3. Pressing the tin leaf into the mould.
4. Filling the tin leaf with a semi-liquid material. Many mixtures have been described including but not limited to wax, oil, resin, glue, gypsum, and pigments.
5. Lifting the filled tin leaf from the mould.
6. Cutting the brocade motifs, either to give a regular repeating unit which can be combined to give a continuous pattern (*juxtaposed applied brocades*) or as isolated arbitrary motifs (*isolated applied brocades*).
7. Adhering the brocades onto the surface of the artwork, using different combinations of wax, resin, oil, glue, chalk, and pigments.
8. Gilding and painting of the applied brocades. Juxtaposed brocades are normally gilded and painted once the surface of the artwork has been completely covered with brocades, whereas isolated brocades are gilded prior to application onto the artwork and once applied are painted to match the background color of the surface.

This results in a layered structure as follows – from bottom to top – (Fig. 1): 1, ground; 2, imprimatura; 3, adhesive; 4, filling mass; 5, tin leaf; 6, mordant; 7, gold leaf; 8, opaque paint and/or glaze.

Applied tin-relief brocade in Guipúzcoa

This paper presents the results of Raman and Fourier transform infrared (FTIR) study on applied brocades of wooden altarpieces in the Basque province of Guipúzcoa (North of Spain).^[14] This region has several important artworks with applied brocade dated to the late 15th to early 16th century. The profusion of this decoration during this time is attributed to the intense maritime trade between Spain and Central Europe leading to the introduction of Flemish painting practice and techniques.^[17] The altarpieces studied date from *ca* 1500 to 1555 corresponding to the artistic periods of the Late Gothic and Early Renaissance and occur in four towns, together covering the entire geographical area of Guipúzcoa. The six altarpieces studied are (I) the Triptych of La Asunción-Coronación de la Virgen in the Church of La Asunción de Santa María, Rentería (1505–1510); (II) the Triptych of San Antón in the Church of San Pedro, Zumaya (1510–1515); (III) the Altarpiece of La Piedad in the Church of San Miguel, Oñate (1535–1537); (IV) the Altarpiece of San Juan Bautista in the Church of San Miguel, Oñate (*ca* 1530–1555); (V) the Altarpiece of La Santísima

Trinidad in the Monastery of Bidaurreta, Oñate (1531–1533)^[12]; and (VI) the Altarpiece of San Miguel in the Church of Alzaga, Alzaga (*ca* 1530–1550).^[18] An extended protocol of analysis was created to fully understand all aspects of the different types of applied brocades employed. This protocol comprises an *in situ* and analytical study.^[11,14]

Experimental

A range of analytical techniques were employed in the project. All samples were mounted in epoxy resin and polished to provide cross sections,^[11] with analysis performed on the mounted samples. Initial examination was by optical microscopy using a Zeiss Axioscop 2 Mat microscope with reflected light (from a halogen Photo Optic lamp Xenophot 12V 100 W) in dark field and reflected UV light (from an HBO mercury short arc lamp 103 W/2) with a 340–380 nm filter.

Cross-section staining tests were performed for proteins (Amido Black 2)^[19] and lipids (rhodamine B, RHOB).^[20] Amido Black AB2 (AB) is a dark brown powder that stains materials containing protein through chemical reaction. The colors obtained from this stain reaction under normal light range from light blue to dark/intense blue.^[19] RHOB is a bright pink powder that dissolves in lipid-containing materials. Under normal light it stains a bright red; under UV/violet excitation (340–380 nm) it fluoresces a bright orange–red color.^[20] The epoxy resin used to mount the samples is believed not to affect the staining tests used.

Raman spectroscopy was undertaken with a Bruker Senterra system using the 785 and 532 nm lasers. FTIR was used on the cross sections with an attenuated total reflection (ATR) objective. The system used was a Bruker Vertex 70 spectrometer with a Hyperion 3000 microscope. Raman spectroscopic mapping was performed on three cross sections – II9Ab from Zumaya, III14Ca from Oñate (altarpiece of La Piedad), and V6Ba from Oñate (altarpiece of La Santísima Trinidad) – using 785 nm, and a 20× objective to give a 5- μ m spot size. Measurements were taken on a grid with 10 μ m intervals for 30 s at each location. A background with equal acquisition time was subtracted. Specific Raman bands were integrated using the Bruker OPUS software (Version 6.5). The Raman and FTIR spectra were identified by comparison with databases of artists' materials within the Straus Center for Conservation, Harvard Art Museums, the Museum of Fine Arts Boston, University College London, and the IRUG database. Some samples were carbon-coated for scanning electron microscopy with energy dispersive

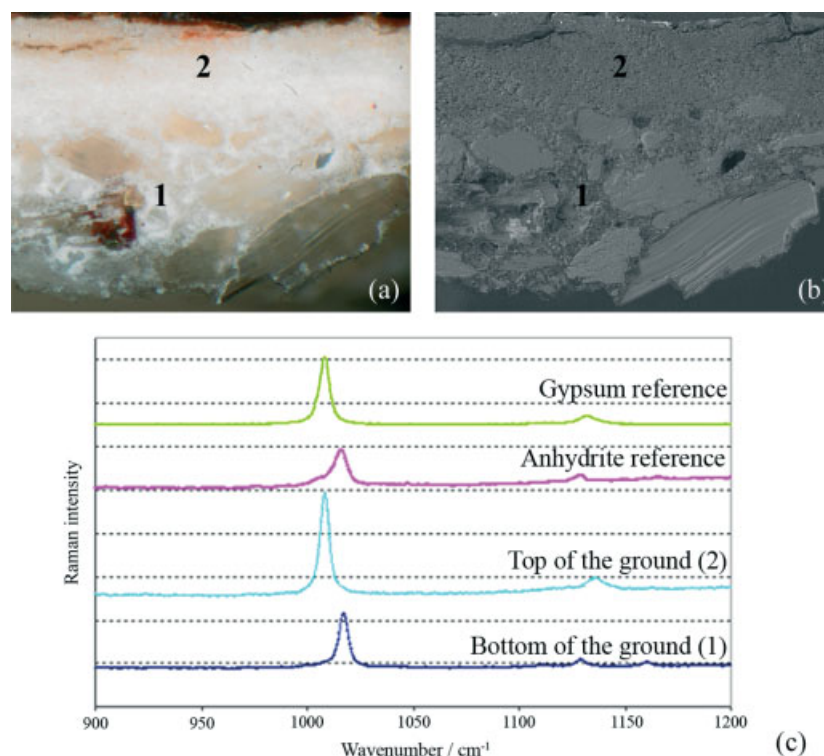


Figure 2. Ground layer of sample III14Ca from an isolated applied tin-relief brocade of the altarpiece of La Piedad, Oñate: (a) cross section in visible light and (b) in SEM where 1 indicates the coarse gesso (*yeso grueso*) and 2 the finer gesso (*yeso fino*); (c) Raman analysis showing anhydrite for the coarse gesso (layer 1) and gypsum for the fine gesso (layer 2).

analysis (SEM-EDS) with a JEOL JSM-640LV SEM operated at 20 kV in the high-vacuum mode.

Results

Raman and FTIR-ATR spectroscopy proved particularly useful for the study of the grounds and the filling materials of the applied tin-relief brocades but gave little information on the other layers and materials, such as the tin leaf and mordant. A full discussion of these other layers and materials can be found elsewhere.^[11,14] Hence, this work concentrates on the findings from the Raman and FTIR-ATR spectroscopy in the grounds and filling masses.

Grounds

Point analyses and vibrational mapping showed that the grounds are predominantly calcium sulfate, the exception being juxtaposed and isolated applied brocades of the triptych of Rentería where calcite, calcium carbonate, was used. In most instances, the calcium sulfate grounds have two clearly distinct areas, both of which can consist of several layers: a lower zone of coarse gesso (*yeso grueso*) and an upper zone of fine gesso (*yeso fino*). Raman and FTIR-ATR spectroscopy of individual grains and Raman spectroscopic mapping of sections from the altarpieces of Zumaya (II9Ba), La Piedad (sample III14Ca), and La Santísima Trinidad (sample V6Ba) showed that the lower coarse gesso, the *yeso grueso*, was predominantly anhydrite (anhydrous calcium sulfate: CaSO₄) with peaks at 416, 497, 607, 625, **1015**, 1127, and 1159 cm⁻¹ in the Raman spectra. In contrast, the upper zone, the *yeso fino*, was predominantly gypsum (calcium sulfate dihydrate: CaSO₄·2H₂O) with peaks at 495, 621, 672, **1009**, and 1141 cm⁻¹ in the Raman

spectra. In both cases, the strongest peak is denoted in bold. There were, however, occasional particles of gypsum in the lower zone and of anhydrite in the upper zone in some instances.

In some samples, the two gesso layers were separated or sealed by a glue layer in order to improve the adhesion of the uppermost fine layer to the coarse lower layer. Figure 2 shows the ground layer of a sample from an isolated applied tin-relief brocade of the altarpiece of La Piedad, Oñate, (sample III14Ca) and the distinction between anhydrite and gypsum. Note the coarse anhydrite particles mixed in with finer anhydrite in the lower ground compared to the uniform fine particle size in the upper gypsum layer. In contrast, the ground in all applied brocades from the altarpiece of Alzaga, in some juxtaposed and isolated brocades from the triptych of Zumaya, and in some juxtaposed applied brocades from the altarpiece of San Juan Bautista in Oñate had only a single zone of calcium sulfate. This zone was identified as anhydrite in samples from the triptych of Zumaya and as anhydrite with occasional gypsum in the altarpiece from Alzaga and San Juan Bautista. Figure 3 shows selected vibrational maps from a cross section of an isolated applied brocade from the altarpiece of La Piedad, Oñate. The maps show a clear distinction between the lower layer of anhydrite and upper layer of gypsum. Similar maps for a sample of applied brocade from the triptych of Zumaya show a single layer of anhydrite in the ground; hence anhydrite underlies the *imprimatura* and filling mass directly in Fig. 4.

Analysis also identified the presence of a layer of earth pigments between the lower layer of coarse gesso and the upper layer of finer gesso in juxtaposed applied brocades of the altarpiece of La Santísima Trinidad. The detection of this layer in the grounds of samples from two embraced figures belonging to the same relief

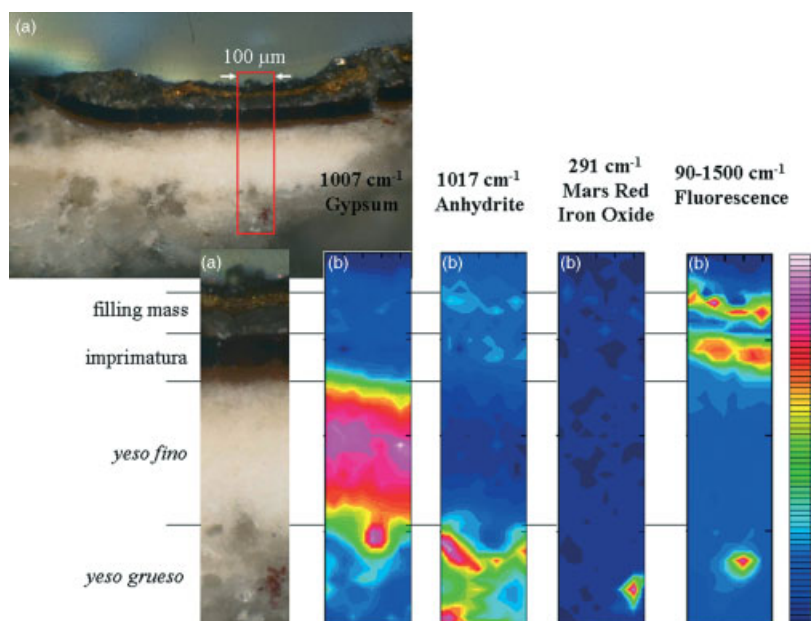


Figure 3. Cross section from applied brocade from the altarpiece of La Piedad, Oñate, (sample III14Ca) showing filling, imprimatura, and ground: (a) optical image; (b) Raman maps for gypsum, anhydrite, iron oxide, and fluorescence. Levels of the phases grade from very low/absent (dark blue) to highest (red–pink).

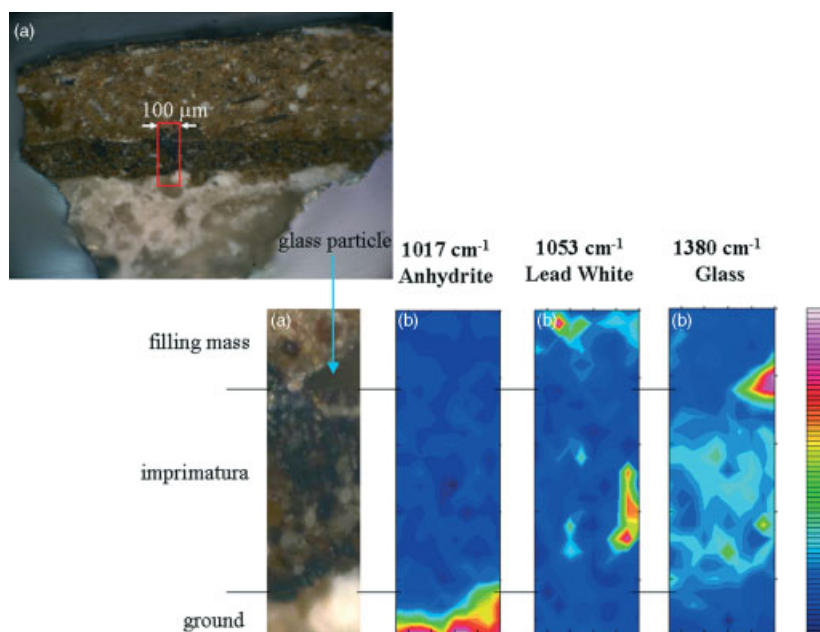


Figure 4. Cross section from applied brocade from the triptych of Zumaya (sample II9Ab) showing filling, imprimatura, and ground: (a) optical image; (b) Raman maps for anhydrite, lead white, and glass. Levels of the phases grade from very low/absent (dark blue) to highest (red–pink).

indicates that the red bole was applied one step too early on top of the initial coarse gesso and then scraped down to resume the correct layer sequence, with some bole remaining. The area was then re-gessoed and re-finished with applied brocades. Dolomite, $\text{CaMg}(\text{CO}_3)_2$, with peaks at 178, 300, 723, and 1097 cm^{-1} in the Raman spectra, was identified as rare particles within the fine gesso of the ground of a juxtaposed applied brocade from the altarpiece of La Santísima Trinidad, Oñate (sample V8Ae). This indicates the use of a different source material from that in the other altarpieces but further studies are required to determine the significance of this differentiation.

FTIR-ATR spectroscopy revealed that the calcium sulfate was normally mixed with a protein-containing material (probably a glue) and an oil. The presence of an oil was concluded on the basis of characteristic bands at 2927, 2855, 1746, 1464, 1237, 1165, 1100 and 722 cm^{-1} . The presence of a protein (probably a glue) was based on the characteristic amide bands at around 1656, 1531, and 1446 cm^{-1} . In one sample from La Piedad, Oñate, both protein and oil were detected in the coarse gesso but only protein was detected in the finer gesso. Although the spectra are not quantitative, they suggest there may be considerable variety in the proportions of oil and protein within the grounds.

Table 1. Ground mixtures found in the applied tin-relief brocades			
Inorganic	Organic	Brocade type	Altarpiece
Calcite, chalk (multiple layers)	Protein and oil	Juxtaposed and isolated	Rentería (I5Ba)
Anhydrite (one layer)	Protein and oil	Juxtaposed and isolated	Alzaga (VI1Ba(2)) and Zumaya (II9Ab)
Anhydrite (some gypsum) (one layer)	Protein and oil	Juxtaposed	San Juan Bautista (Oñate) (IV2Ac)
Coarse anhydrite (one layer) and fine gypsum (one layer)	Protein and oil	Juxtaposed and isolated	Zumaya (II9Ba)
Coarse anhydrite and fine gypsum (multiple layers)	Protein (and oil?)	Juxtaposed	La Santísima Trinidad (Oñate) (V8Ae)
Coarse anhydrite (one layer) and fine gypsum (multiple layers)	Protein and oil	Isolated	La Piedad (Oñate); (III14Ca)
Coarse anhydrite (multiple layers) and fine gypsum (multiple layers)	Protein and oil	Juxtaposed	San Juan Bautista (Oñate) (IV3Ab)
Coarse anhydrite (multiple layers) and fine gypsum (one layer); earth pigments	Oil (and protein?)	Juxtaposed	La Santísima Trinidad (Oñate) (V6Ba)

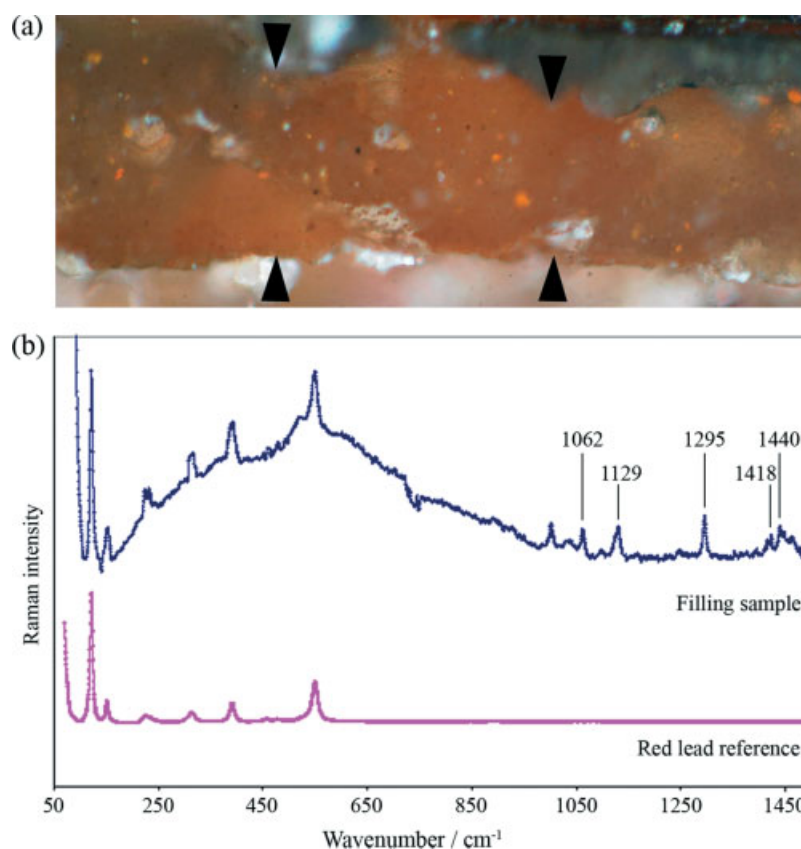


Figure 5. Filling mass of sample III9Gb from an isolated applied tin-relief brocade of the altarpiece of La Piedad, Oñate: (a) cross section of the filling layer in visible light indicated between arrows and (b) Raman spectrum revealing the presence of red lead and beeswax.

The data showed that the ground used for juxtaposed applied brocades was more varied in terms of materials and construction than those of isolated applied brocades (Table 1).

Filling masses

The filling mass supplies consistency to the relief of the brocade patterns and is hence one of the most important layers in this three-dimensional technique. In some instances, the filling materials were purely organic, and most information was obtained

from FTIR-ATR and/or staining. The only organic component clearly identified by Raman spectroscopy was beeswax, as seen in isolated applied brocades of the altarpiece of La Piedad in Oñate in combination with red lead and fibers (Fig. 5). The characteristic peaks for beeswax^[21] at 1062, 1129, 1295, 1418, 1440, 2849, and 2881 cm^{-1} can be seen in this figure. Summation of the fluorescence spectrum in the vibrational maps can be used to show the position of organic-rich layers, as seen in Fig. 3, where two distinct fluorescent layers (the lower corresponding to the top layer of the proteinaceous imprimatura and the upper to the beeswax filling)

Table 2. Filling mixtures found in the applied tin-relief brocades

Filling medium	Particles	Brocade type	Altarpiece
Protein	None	Isolated	Zumaya
Beeswax	None	Juxtaposed and isolated	Rentería (I5Ab), (I5Ba)
Lipid	Red lead	Juxtaposed	Alzaga
Beeswax	Lead white, vermilion, azurite, red iron oxide	Juxtaposed	Zumaya (II9Ba)
Beeswax	Red lead, fibers	Isolated	La Piedad (Oñate) (III9Gb) (III14Ca)
Oil and protein	Anhydrite, lead white	Isolated	Alzaga (VI1Ba(1))
Oil and protein	Gypsum	Juxtaposed	San Juan Bautista (Oñate) (IV3Ab)
Oil and protein	Lead white, red iron oxide	Isolated	Zumaya
Beeswax	Lead white, carbon black, red iron oxide, quartz, soda-lime glass, red lead, azurite	Juxtaposed	Zumaya (II9Ab) (II1Ab)
Protein and oil	Anhydrite	Juxtaposed	San Juan Bautista (Oñate) (IV5Aa(1))
Protein (bottom layer), protein and oil (top layer)	Red iron oxide, gypsum (bottom layer); gypsum (top layer)	Juxtaposed	La Santísima Trinidad (Oñate) (V8Ae) (V6Ba)
Protein (bottom layer); oil and protein (top layer)	Red iron oxide, calcium sulfate (bottom layer); calcium sulfate, red iron oxide, vermilion (top layer)	Juxtaposed	La Santísima Trinidad (Oñate)

are separated by a layer with much lower fluorescence. Many filling masses contained some inorganic particles within the organic matrix, which could be identified by a combination of Raman spectroscopy and SEM-EDS. These phases included red lead, lead white, vermilion, azurite, red earth pigments, calcium sulfate (both anhydrite and gypsum were used but not mixed together), carbon black, quartz, and soda-lime glass. These were combined in a variety of mixtures with different organic phases, resulting in a wide variety of filling mixtures as summarized in Table 2.

FTIR-ATR revealed filling masses containing beeswax in samples from the altarpieces of Zumaya, La Piedad Oñate, and Rentería, while those in samples from the altarpieces of Alzaga, La Santísima Trinidad, and San Juan Bautista consisted of mixtures of protein and oil. The identification of the organic components were based on the presence of the characteristic bands for oil and protein listed earlier and for beeswax on the presence of characteristic bands at 2956, 2918, 2850, 1737, 1473, 1462, 1174, 730, and 720 cm^{-1} . However, staining tests suggest that additional combinations may be present in other samples from these altarpieces. Identification of specific proteins and oils would require gas chromatography with mass spectroscopy, which is not possible on mounted samples. In addition, the presence of multiple fine layers within the samples would necessitate careful separation of layers even if scrapings were available.

The vibrational map in Fig. 4 (sample II9Ab) from the triptych of Zumaya includes part of the filling mass and reveals particles of soda-lime glass and lead white within this. Raman analysis of individual particles showed that two lead-containing pigments, i.e. lead white and red lead, were present within the same filling layer of an applied brocade from the triptych of Zumaya (sample II9Ab) (Fig. 6). No red lead particles were seen in the map from this sample due to the dispersed nature of the pigment. The glass particles gave a distinct broad peak around 1380 cm^{-1} with the 785-nm laser but (surprisingly) failed to produce any distinct peaks with the 532-nm laser. Use of a blue laser (e.g. at 488 nm) might give improved spectra but this wavelength was not available.

Discussion

Written sources indicate that the ground is normally applied as a thick, coarse lower ground layer – *yeso grueso* – and a thin, fine upper ground layer – *yeso fino* – (Fig. 2(a) and (b)). However, this study has shown that both gesso layers are not always applied in several layers and in some instances only one layer is observed. The main inorganic materials characterized are calcium carbonate (CaCO_3) and calcium sulfate. The latter is prevalent in Southern European countries, such as Spain,^[22] which explains its identification in five of the six altarpieces, namely, the triptych of Zumaya, the three altarpieces located in Oñate, and the one in Alzaga.

The clear analytical distinction between anhydrite in the lower coarse gesso and gypsum in the upper fine gesso in samples from the altarpieces of Zumaya, La Piedad, and La Santísima Trinidad shows that the grounds for the applied tin-relief brocades of Guipúzcoa agree with previous research, because works by Gomez *et al.* reported the prevalence of anhydrite in the coarse layer (*yeso grueso*) and gypsum in the finer layer (*yeso fino*).^[23,24] The calcium sulfate grounds can consist of a single 57–190 μm layer of anhydrite, up to four layers of coarse anhydrite at the bottom and up to four layers of finer gypsum on the top, or one layer of coarse gesso (varying from 60 to 250 μm in thickness) and one layer of fine gesso (varying from 10 to 76 μm thickness). Since anhydrite is coarser than gypsum, it is reasonable that the former results in thicker layers. FTIR-ATR and staining showed that the binding media usually consisted of a proteinaceous material, most likely animal glue, mixed with oil.

The different layers are usually sealed with a very thin layer of glue but this is not always present on top of the coarse gesso and on top of the uppermost ground layer. RHOB lipid stain showed that lipid, probably oil, was applied in a very thin layer (<1–2 μm) to seal the uppermost ground layer in applied brocades from the triptych of Rentería. This fine layer could not be isolated and individually analyzed by FTIR-ATR. Combined with the presence of a chalk (calcite) rather than calcium sulfate ground, this fits very

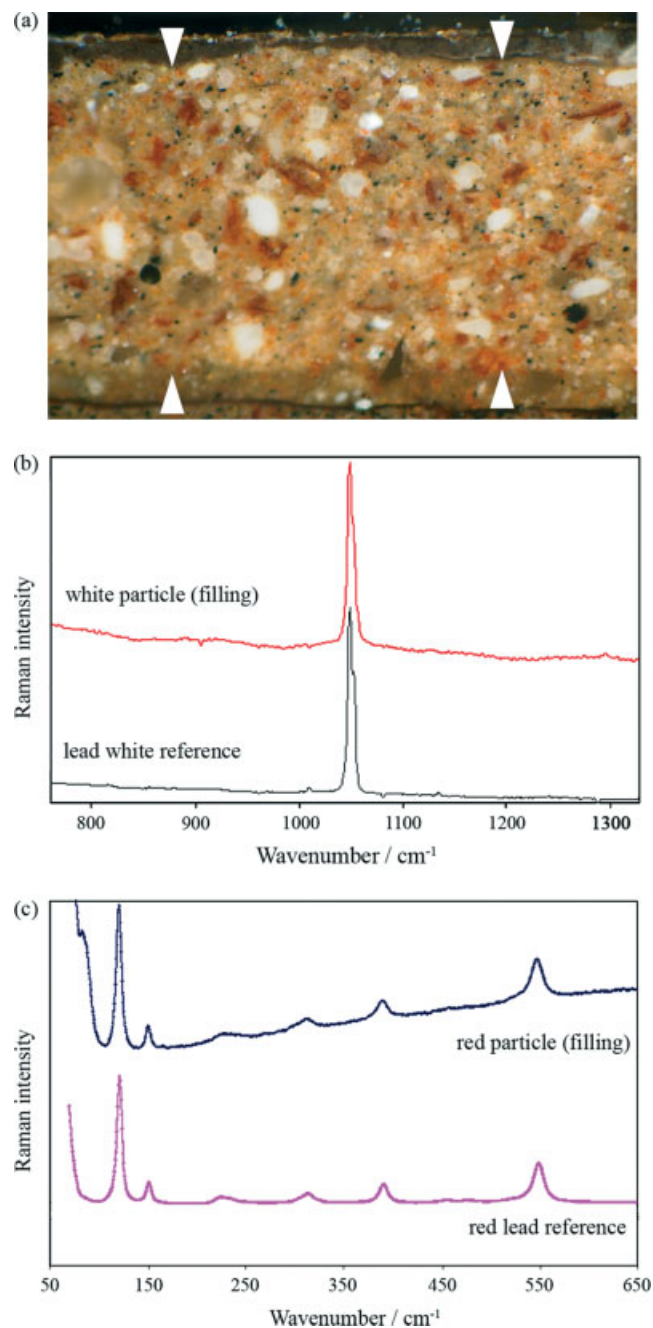


Figure 6. Filling layer of sample II9Ab from a juxtaposed applied tin-relief brocade of the triptych of San Antón, Zumaya: (a) cross section of the filling in visible light indicated between arrows; and Raman spectra identifying (b) lead white and (c) red lead in the composition of the filling mass.

well with primitive Flemish grounds made of calcium carbonate (very common in Northern European artworks) and glue sealed with a mixture of oil and resin.^[25] This observation reinforces the historically reported Flemish origin of the triptych of Rentería.^[26,27]

Fillings can be categorized into those with beeswax and those with a mixture of protein and oil. The presence of both types of fillings in the triptych of Zumaya differs from the findings of Nadolny,^[13] who did not find both types within the same piece of artwork outside Spain. Various pigments were added to the fillings to speed up the drying of these relatively thick masses and give some color.^[1] These pigments included lead white,

gypsum, anhydrite, (the last two more common in Spain than calcium carbonate), red iron oxide, red lead, vermilion, azurite, carbon black, quartz, and soda-lime glass. Beeswax fillings generally contained more pigments than the other fillings. Hence, all the above-cited pigments (except gypsum and anhydrite) have been recognized within the beeswax masses, whereas only gypsum, anhydrite, vermilion, lead white, and red iron oxide have been found in the other filling layers. Most filling masses consist of one layer up to 150 μm . The exceptions are the double-layer fillings discovered in the applied tin-relief brocades of the altarpiece of La Santísima Trinidad, which have layers that are only 40 μm thick (Table 2).

The presence of different components and combinations in the various analyzed samples derives from the professional evolution and experimentation of the artisans. Hence, the artistic proceedings employed in the painting workshops of Europe in the 15th and 16th centuries are supported through a very long artistic tradition, which has resulted in the use of very stable and largely proven material components. The artisans' knowledge of the materials and techniques has contributed to the good conservation of the applied brocades over the centuries. The only alteration detected is visible discoloration of some tin leaf due to oxidation in the presence of air. However, tin leaves decorated and covered with a paint layer are perfectly conserved.

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