

Polychromed Silver Bust Reliquaries

Material and Technical Characterization

Bust reliquaries represent an outstanding aspect of the goldsmiths' art starting in the Middle Ages.¹ Among these, polychromed silver ones are very widespread. Remarkable examples are the reliquaries of Saint Peter and Saint Paul from the Lateran Basilica in Rome and the bust of Saint Agata from Catania Cathedral, made by the Siena goldsmith Giovanni di Bartolo between the end of the fourteenth and the beginning of the fifteenth century.² These artworks were probably born in the context of the medieval workshop, where artists specializing in different techniques worked together, creating a stimulating environment for experimentation.³ Bust reliquaries arose from similar wooden objects in the fourteenth century, inspired by the martyrdom of Saint Ursula, and they are meant to keep together the naturalness of the painted «incarnato» and the nobleness of precious metals, enamels and gems. Later on, during the Counter-Reformation, the Catholic Church strongly supported worshipping saints and relics and encouraged the production of reliquaries.⁴ This later production also included reliquaries with painted surfaces, such as the reliquary of Saint Venera in Acireale and Saint Barbara in Paternò, both in Sicily. In later centuries, polychromy applied on silver was often considered not to be original and sometimes it was removed in restoration interventions: this is the case of the bust of Saint Benedict from the Purification Church in Saint-Polycarpe, France.

In this paper, three silver reliquaries, restored at the Opificio delle Pietre Dure in Florence, were examined from a technological and material point of view to gain more information on this particular kind of artwork.

The most ancient one is the reliquary of Saint Ursula, from the Pinacoteca Comunale in Castiglion Fiorentino. The second reliquary is the head of Saint Erasmus, an artwork of Neapolitan manufacture made in the fourteenth century, owned by the Museo Diocesano in Gaeta. These two artefacts exhibit paints on silver. The third one, namely the reliquary of Saint Vittoria from the Museo Diocesano in Agrigento, seems to be different from the other two, as it is made of a copper-based alloy, but our investigation revealed that the upper polychrome layer was laid on a silver substrate.

Methods of investigation

Different analytical techniques, both non-invasive and invasive, were used to identify the materials used for the production of the artefacts.

For the creation of 3D models, an Ametek® Creafom® Go!Scan20® scanner was used with an accuracy up to 0.1 mm, a resolution of 0.2 mm, and a measurement rate of 1.500.000 measures/sec. The scanner uses the Structured Light technique and emits in visible light through a projector. It features a multiple acquisition system in the visible range with three digital cameras with CMOS sensors: two cameras for triangulation of the acquired points and one camera dedicated to the texture information (color from photo recording). The projected series of patterns are acquired by cameras and the dedicated software calculates the deformation of these patterns projected on real surfaces. From deformation, the software generates the 3D cloud of XYZ points. Real time calculation of 3D cloud generates a triangle mesh, a virtual representation of the object surface.

X-ray fluorescence (XRF) measurements for the non-invasive identification of the alloys and of the polychromy were performed by an XGLab Elio portable spectrometer (incidence angle, 90°; spot size 2.5 mm), equipped with a Silicon-Drift Detector (active depth = 500 µm, Take-off angle = 63,5°, Sample-detector distance = 14 mm) and a Rh anode.

Eddy Current techniques were used both for sorting metals and alloys and for measuring coating thickness. For the first, a Sigmascope SMP 10 (Fisher) with ES40 probe at 60 kHz frequency was used. Calibration of the device was verified using a copper certificate standard 101 % IACS. Coating thickness was measured with a Leptoskop 2042 (Karl Deutsch, Germany) equipped with a 1 mm diameter probe (diameter leaning point 12 mm). Eddy Current techniques allow the sorting of alloys and the detection of defects in metals, but also the measurement of the thickness of non-conductive coatings on conductive substrates.⁵ In this study, this technique was very helpful for both aspects, and in particular, it helped identify areas on polychromy with higher thickness. This information allows addressing the sampling of small flakes where it is more likely to find the complete superposition of painting layers. The measurement is quick, easy to interpret, and fully non-invasive; however, limitations are connected to the surface characteristics, since the area being probed needs to be flat, and the measurement will be affected by surface roughness and defects.

Samples including metal and polychromy were taken and analysed as flakes, or embedded in polystyrene resin, and examined as cross-sections. The latter were polished with abrasive paper down to P1200 with an average particle diameter of 15.3 µm and observed using a Zeiss Axioplan microscope, with UV and visible light. An EVO® MA 25 Zeiss scanning electron microscope equipped with an Oxford EDS X-MAX 80 mm² microprobe and AZTEC® system with a 20 keV voltage was used (SEM-EDS). Cross-sections were coated with a carbon coating prior to analysing them. FTIR analyses were performed using a Continuum Infrared Microscope linked to a Nicolet Nexus spectrometer, with a spectral resolution of 4 cm⁻¹ (128 scans) in transmittance mode.



Fig. 1
Reliquary bust of Saint Ursula, French production, first half of the 15th century, embossed, chiseled painted and gilded silver, enamels, pearls, stones, glass beads, h. 42.4 cm, Castiglion Fiorentino, Pinacoteca Comunale

Fig. 2
Cross-section of a sample from Saint Ursula, with three overlapping layers with the same composition (lead white with some particles of vermillion)



The Reliquary of Saint Ursula

The reliquary of Saint Ursula (fig. 1) is a complex, multi material artwork in the form of a gilded silver bust with polychromed neck and face,⁶ produced in the Rhine region in the early fifteenth century. On the head is a gilded silver crown with false gems, pearls, and enamels. On the bust, a decoration of lapislazuli can be seen: it was added in the twentieth century during a restoration intervention to cover and hide a shrine to store relics. The surface of the bust is chiselled. On the base, plaques with basse-taille enamels⁷ of French production (Parisian school by Jean Pucelle) are applied.

Both the alloy and the polychromy of the flesh were examined. As for the alloy, the substrate of polychromy, a sample was picked out, embedded in resin and analysed with SEM-EDS. The quantitative analyses show that the alloy is made of 95.9 % of silver and 4.1 % of copper. The fragment shows high porosity and presence of mercury, the latter probably coming from the surrounding gilded areas, although the fragment comes from the painted section of the bust.

The stratigraphy of the polychromy was also examined by taking a sample and embedding it in resin. The combination of optical microscope in visible (fig. 2) and UV light, SEM-EDS and FTIR analyses shows the presence of three different layers, with the same composition of lead white and vermillion. The first upper layer (10–15 μm thickness) and the second one (around 20 μm) seem to be very similar, with the same grain size of lead white,

Fig. 3

Head of Saint Erasmus, Neapolitan production, 14th century, painted silver, h. 24 cm, Gaeta, Museo Diocesano



while the deeper one is thicker (80–100 μm) and has different characteristics (higher granulometry, inhomogeneity). FTIR analyses show the presence of a lipid binder (probably oil).

The presence of several superimposed layers with the same composition may be due to different coats of the original painting or to re-painting. The two upper layers may be two coats of the same painting. The deeper layer might be the original one, with greater thickness. However, no film including deposited dust, is present on top of this layer, as is commonly observed between overlapping layers applied in different times.

The head of Saint Erasmus

The head (fig. 3) was part of a huge artwork that underwent many reassembly interventions, the last one in 1718. In this intervention, the head was mounted on a full body with a new silver dress. Other original parts, in addition to the head, were assembled together on the reliquary, notably a little plaque with the Virgin on a throne and a crosier with *fleur-de-lys* decorations, symbols of the Anjou family.⁸ The reliquary was dismantled and stolen in the 1980s: the only element left was the head, probably because it was not considered precious, owing to the paint that hides the silver substrate.

In fact, the head is completely covered by a layer of paint: on the hair, a black layer is present, while the face is covered by a flesh-tone layer. Lips and eyes are also painted. Some lacunas are present on the face, showing the silver surface underneath.



Fig. 4
Cross-section of a sample taken from the hair of Saint Erasmus head, showing four re-painting interventions

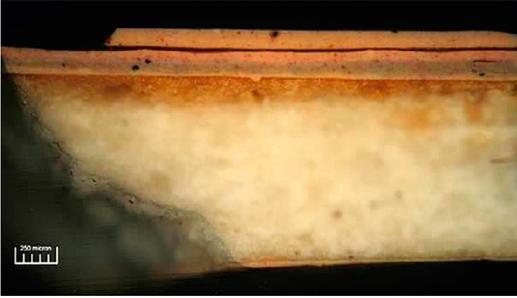


Fig. 5
Cross-section of a sample taken from the face of Saint Erasmus head, showing a thick layer of calcium sulphate bihydrated (gypsum), to re-shape the face



Fig. 6
Cross-section of a sample taken from the neck of Saint Erasmus head, showing a layer of preparation beneath the original painting layer

On the hair, the black painting, whose stratigraphy is very complex, covers the original beautiful fire gilding (fig. 4): the lower layer of the painting, in contact with the metal, is lead-white-based and contains silicates. Another layer based on lead white, 20–30 μm thick, is superimposed on the lower one. These two layers might be the oldest ones. On top of it, a very thick (up to 300 μm of thickness) yellowish layer containing calcium sulphate bihydrated – gypsum – is present; this is covered with a pinkish layer with lead white and vermilion (10–100 μm thick). A further brown layer, containing lead white, iron and black particles, overlaps the pinkish one. The black particles of this layer contain calcium and phosphorus, indicating that the bone black pigment may be present. On the brown layer, a very thin coating containing just organic matter indicates the interruption of the painting sequence with the application of a protective or finishing layer. A layer with lead white and non-homogeneous in thickness follows. This is then overlapped by a further layer containing lead white and umber (20–40 μm thick). Above this, a new preparation layer, with uneven thickness (from few μm to around 60 μm) follows. This preparatory ground contains lead white, and a very thin layer (around 5 μm) of zinc white and umber is superim-

posed on it. It is remarkable that in this single fragment, four different painting interventions are observed. The most noticeable one is the second, featuring the thick gypsum coating. Owing to its thickness, this layer seems to function as preparation for the painting, and as plaster to re-shape the hair.

Lacuna on pink painted surfaces gave us the opportunity to assess its non-homogeneous thickness. In order to investigate the thickness, two different approaches were considered. In the first one, 3D scanning was used to acquire the outside of the face. Since it was not possible to scan the head inside, a silicon mould of the internal surface was created and then the scan of the mould was acquired. The superposition of the two scans gives the overall thickness of both the silver plate (considered homogeneous) and the polychromy: the data processing made it clear that the internal and the external surfaces do not match, and that there is a huge deformation of the silver lamina. In order to restore a correct shape of the face, in certain parts, a thick layer of preparation and a new polychromy were added. A deeper investigation of polychromy thickness was performed using the Eddy Current technique. The measured thickness varies from tens of μm s to around 1 mm (most of the measurements comprised between 200 and 400 μm) with thicker layers on the cheeks, where major alterations of the silver lamina are present. The unevenness of the painting depth confirms that a preparatory ground was applied unevenly to fill concavities created by deformations of silver lamina.

In order to investigate the stratigraphy of the polychromy of the flesh, a fragment was taken from a thick area of one of the cheeks. Examination of a cross-section shows a comprehensive structure (fig. 5): three very thin overlapping layers containing lead white and vermilion form the inner coating. These layers are characterized by different granulometry of the pigment particles and different content of binder, as the UV image of the cross section shows. This inner coating is 15 μm thick and may be considered the original one. On top of that, a very thick layer (around 1 mm) of gypsum can be observed: this is probably the material used to obtain the new shape of the face.

Above the gypsum layer, a multi-layer system is present: first an accumulation of binding material, then two or three layers (thickness around 150 μm) of lead white with vermilion, with a probable varnish layer delimiting the first application. Two or three layers (thickness around 100 μm) with lead white and vermilion follow. Finally, the upper layer is very thin (5 μm) and contains lithopone (barium sulphate and zinc oxide). Portable XRF analysis confirmed the presence of zinc and barium in the most external layer in several spots on the surface. Cleaning operations of the surface during the conservation treatment led to the disappearance of the signals of these two elements.

A further sample was taken from the neck for comparison (fig. 6). The stratigraphy shows similarities with the previous sample from the cheek, but even differences: for example, the very thick lower layer (more than 500–600 μm) that is not present in the other fragment. This layer includes silicates (probably clay-based pigments) and sulphur, possibly in an organic matrix, and could be related to the preparation for original polychromy, not observed in the sample from the cheek. Another difference is seen in the upper layers, where the presence of titanium could be related to a modern repainting based on titanium white.

Fig. 7

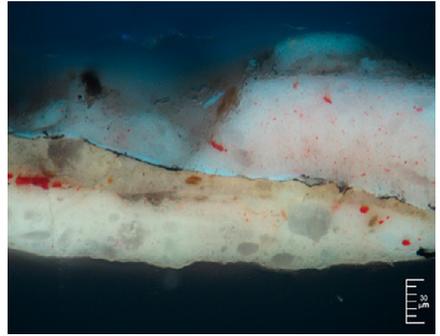
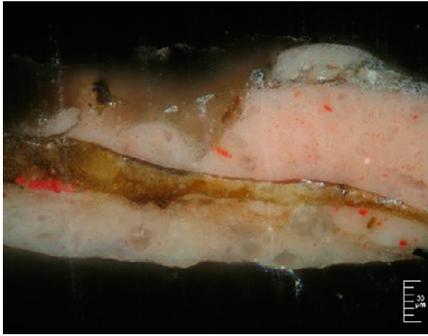
Saint Vittoria, Palermo, 1593, silver, painted copper alloy, gems, h. 50 cm, Agrigento, Museo Diocesano



The Reliquary of Saint Vittoria

The reliquary of Saint Vittoria (fig. 7) is a partially gilded silver bust with gems and some polychrome parts (face, hands). It was made in 1593 by the silversmith Salvatore Lancellata in Palermo, Sicily. A first examination of the alloy under the polychromy was attempted by visual inspection and Eddy Current technique. The reddish/brown tone indicates clearly that polychrome parts do not have a silver substrate but probably a copper alloy. This was confirmed by Eddy Current inspection, revealing values on the head of around 90 % IACS, close to pure copper (101 % IACS), and values on the hands around 25 % IACS, suggesting a copper alloy. XRF analyses were performed on lacunas of paint, both on the head and on the hands. On the head, only the signal of copper was detected, while on the hands zinc was also observed. The different composition of the parts of the reliquary agrees with the observations on the inside of the head. Interestingly, the head was made with two halves of copper laminas, while the hands seem to have been obtained by casting, which needs a lower melting and more fluid metal, such as a copper-zinc alloy.

Since in this case the polychromy is applied on a copper-based substrate, it seems that this reliquary is not to be included in the items featuring polychromy on silver. However, a sample taken from the hand revealed a complex and uncommon stratigraphy (figs. 8 and 9). In fact, the inner layer contains lead carbonate and vermilion to provide a pink base. Superimposed on this base is a thinner layer with lead carbonate and some grains of red lake. This layer is likely to be the last coat of the original paint. On top of it, a thick brownish



Figs. 8 and 9

Cross-sections of a sample of Saint Vittoria observed in visible (left hand) and UV (right hand) light

Evidences of silver leaf are shown in the UV image as tiny black residues.

layer can be observed: it is rich in binder and contains both silicates and lead carbonate. Surprisingly, the cross-section shows that a silver leaf overlaps this layer, which may served as a preparation for the leaf. The presence of silver indicates that, at a certain time in the past, the surface would be completely covered with a silver leaf, with the aim of making the reliquary look more precious and harmonizing the skin parts with the other silver and gilded ones. Later on, a further, new painting layer was applied to make a new polychromy. This is rather thick (around 70 μm) and contains lead white with few vermillion. The same superposition of layers was observed in other fragments taken from other polychromed parts of the bust.

Conclusions

In this work, three bust reliquaries are shown where some parts (face, neck, hands and hair) feature polychromy on the metal substrate in order to achieve the realism of the flesh and of the hair. In this study, unconventional – for the field of goldsmith art – analytical methods (Eddy Current techniques and 3D-scan) were used, along with more common ones: this approach allowed a non-destructive probing of the thickness of painting layers in different areas, and helped to highlight changes of shape and deformations. The analysis performed on the reliquaries suggests that on this kind of artworks, many different re-paintings overlap. This practice continued until recent times, as shown by the occurrence of modern pigments in upper layers. The presence of many renovations of the surface appear-

ance is clearly related to the devotional value of these objects: their use for processions or other religious events exposed them to serious risks of damage and was followed by the need to restore the original aspect. Due to the complexity of the stratigraphy, it is not always easy to identify the original layer. In cases where the latter was evident, no preparation of the painting was observed and painting layers seem to have been applied directly on the metal substrate. Nevertheless, differences may be present on the same object, like on the Saint Erasmus head where a likely ground layer was observed in the neck but not in the face. In general, the materials used for the flesh are more or less the same in all instances: lipid binder and lead white and vermilion as pigments. Only in one case, were grains of red lake found mixed with lead white.⁹

1 Joseph Braun, *Die Reliquiare des christlichen Kultes und ihre Entwicklung*, Freiberg 1940; Barbara Drake Boehm, *Body-Part Reliquaries. The State of Research 1997*, in: *Gesta* 36 (1997), No. 1, pp. 8–19. **2** Braun 1940; Maria Monica Donato (Ed.), *Opere firmate nell'arte italiana/Medioevo Siena e artisti senesi. Maestri Orafi*, Rome 2013, online: <http://onh.giornale.sns.it> (6.12.2019). **3** Giampaolo Distefano, "Bellissima incarnatura". La policromia dei reliquiari a busto medievali e un caso della loro fortuna nel Cinquecento. Il Memoriale di Girolamo Zanghi per il busto di Santa Vittoria ad Agrigento, in: *Annali di Critica d'Arte* 12 (2016), pp. 59–80. **4** See above. **5** Oliver Bruchwald, Wojciech Frackowiak, Wilfried Reimche, Hans Jürgen Maier, Applications of high frequency Eddy Current technology for Material Characterization of Thin Coatings, in: *Journal of Materials Science and Engineering A* 6 (7–8) (2016), pp. 185–191, online: www.davidpublisher.org/Public/uploads/Contribute/58364f1a1e848.pdf (6.12.2019). **6** Paolo Belluzzo, Cinzia Ortolani, Paolo Torriti, *Busto Reliquiario di Sant "Orsola" in Sacra Mirabilia. Tesori di Castiglion Fiorentino*, Catalogo della Mostra, Roma, Museo Nazionale di Castel Sant'Angelo 2010, Florence 2010. **7** Isabelle Biron, *Emaux sur métal du IXe au XIXe siècle. Histoire, technique et matériaux*, Dijon 2015. **8** Dora Catalano, *Argenti sacri da Napoli e dal Meridione*, in: Benedetta Montevicchi (Ed.), *Sculture Preziose. Oreficeria sacra nel Lazio dal XIII al XVIII secolo*, Rome 2015, pp. 55–65. **9** We would like to acknowledge the Pinacoteca Comunale in Castiglion Fiorentino, the Diocesan Museum of Gaeta and the Diocesan Museum of Agrigento. We are deeply grateful to the conservators of goldsmiths' art Paolo Belluzzo, Martina Fontana, Nicola Ricotta and to Clarice Innocenti and Sandra Rossi, former and current Director of the Goldsmiths' art Conservation department of Opificio delle Pietre Dure.