European Journal of Science and Theology, *February 2021, Vol.17, No.1, 139-148*

INVESTIGATION OF SURFACE PATINAE ON RELIGIOUS MARBLE ARTEFACTS

Luca Lanteri*, Giorgia Agresti and Claudia Pelosi

University of Tuscia, Department of Economics, Engineering, Society and Business Organization (DEIM), Largo dell'Università, 01100, Viterbo, Italy

(Received 30 August 2020, revised 15 October 2020)

Abstract

Religious marble sculptures and architectural elements are often characterised by surface layers used as protective coating and aesthetic finishing, originally applied by the artist or subsequently on the occasion of restoration works. This paper focuses the attention on some cases studies specifically referred to religious marble objects with different kinds of coating: the bust of the Pope Innocenzo X, dated back to the 17th century and attributed to the master Algardi, the 12th capital of *Magister Giulelmus*, the 15th century baptismal font made by Francesco d'Ancona in 1471 and the two bas-reliefs, representing respectively Saint Michael the Archangel and Saint Raphael the Archangel, attributed to Agostino di Duccio, dated back to 15th century. In all cases surface layers can be observed on the marble that constitutes the sculptures and the objects. These layers were sampled and investigated through laboratory techniques, specifically X-ray fluorescence spectroscopy, Fourier transform infrared spectroscopy and optical microscopy in order to characterize the composition and establish if they are original finishing or restoration materials.

Keywords: finishing, FTIR, XRF, microscopy, religious artworks

1. Introduction

Sculptures of interest in cultural heritage were often covered by surface layers that could have various functions. They may be original coatings used with finishing or protective functions, but they could be also restoration materials applied on the occasion of past or recent interventions, often undocumented [1-5]. The superficial patina can also be produced by the faithful who touch the object at specific points for a matter of faith. This frequently occurs, for example, in the case of baptismal fonts or saint sculptures particularly venerated by faithful. The study of these surface layers and patinas is relevant for knowing the conservative history of the artefact and for supporting the restoration [4, 5].

Specifically in the present paper the results of the investigation on the following artworks will be reported and discussed (Figure 1):

1) the marble capital of *Magister Guilelmus* dated back to the 12th century and preserved in the Museum of Colle del Duomo in Viterbo (Italy) [6],

*E-mail: llanteri@unitus.it, tel.: +39 0761357017

2) the 15th century baptismal font in the cathedral of Viterbo, attributed to the workshop of the sculptor Francesco d'Ancona and realized in 1471 [7, 8],
3) the two 15th bas-reliefs representing respectively Saint Michael the Archangel and Saint Raphael the Archangel, attributed to Agostino di Duccio [9, 10],
4) the marble bust of the Pope Innocenzo X dated back to the 17th century and attributed to the Italian Master Alessandro Algardi (1598-1652). The bust is exposed on the Diocesan and City Museum of Acquapendente (Viterbo district, Italy) and was created by the artist probably between 1649 and 1652 [11].

Figure 1. Photographs of the sculptures studied in the paper: (A) the capital of *Magister Giulelmus*, (B) the baptismal font of the Viterbo cathedral, (C) the two bas-reliefs by Agostino di Duccio, (D) the bust of Innocenzo X by Alessandro Algardi.

In all cases, samples of surface materials were taken from the sculptures and analysed in the laboratory by optical microscopy, X-ray fluorescence (XRF) and Fourier transform infrared (FTIR) spectroscopy in order to obtain information about the possible composition and consequently about their functions.

2. Experimental

Micro-samples from the sculptures were taken after carefully on-site observation executed through magnifying lens and portable video-microscope. This preliminary step was useful to address the sampling in order to obtain significant samples for the laboratory analysis.

Sample powders and micro-fragments were observed under stereo Olympus SZ and Zeiss polarizing microscope. This last was equipped with a digital camera Zeiss AxioCam directly connected to a computer for capturing and saving the observed images. In the case of the capital of *Magister Guilelmus* a thin section was obtained from a sample chip, by embedding a micro-fragment in epoxy resin, cutting it by a diamond blade and by polishing the final thin section with ultrafine paper.

After microscope observation, samples were analysed by Fourier transform infrared (FTIR) spectroscopy by using a Nicolet Avatar 360 instrument equipped with a DTGS (Deuterated TriGlycine Sulphate) detector. The FTIR spectrometer operates in the 400-4000 cm^{-1} spectral range with a resolution of 4 cm^{-1}. Sample powders were grounded in agate mortar with potassium bromide (KBr) used also as background material. For each sample 128 scans were acquired in diffuse reflectance modality (DRIFT).

In the case of the two bas-reliefs by Agostino di Duccio, X-ray fluorescence (XRF) analysis was also performed in order to identify the chemical elements in the coloured areas (yellow and red). A Surface Monitor II (Assing™) was used for XRF analysis, under the following acquisition conditions: Ag tube operating at 40 kV, current 76 μA, acquisition time 60s.

3. Results and discussion

3.1. The capital of Magister Guilelmus in the Museum of Colle del Duomo

Four samples were taken from the capital surface for the laboratory analysis, as shown in the Figure 2. Sample CMG1 contained also e little fragment of the marble constituting the capital. This allowed for obtaining a thin section with the entire stratigraphy, i.e. marble and surface coating (Figure 3).

The constituent material is a medium-wide sized marble (Maximum grain size, MGS, of about 2-3) according to the Moens scale [12]. Both calcite and dolomite (calcium and magnesium carbonates) crystals are present, often characterized with triple points of contact.

On the surface there is a layer of uneven thickness (about 50-200 μm) which, under UV radiation (Figure 3C), shows an intense point-like fluorescence of yellow-orange colour. In this layer there are also black particles. It should be a surface protective (probably wax) to which dirt particles have been adhered.

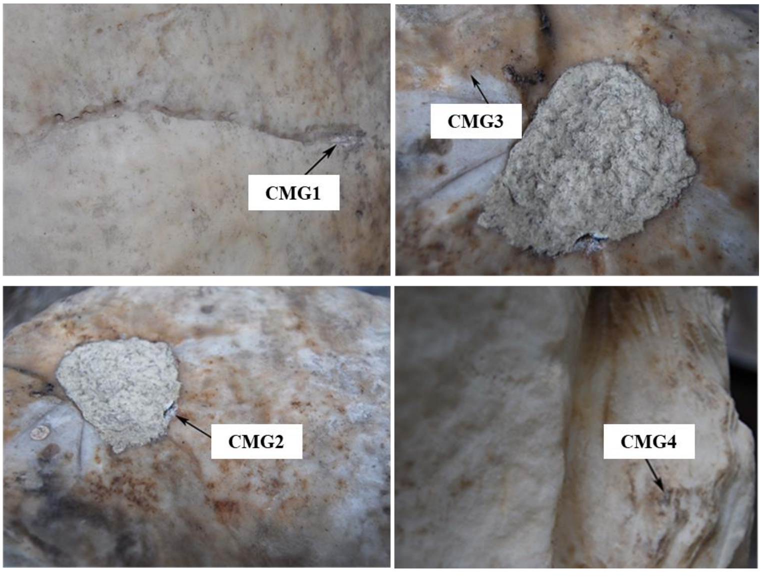

Figure 2. Macro photographs of the capital of *Magister Guilelmus* with the sampling points.

Figure 3. Microphotographs under polarizing microscope of sample CMG1, objective 10x: (A) Parallel polars, (B) crossed polars, (C) UV radiation.

Samples CMG2-4 were examined by FTIR spectroscopy, the results are reported in the Table 1. Sample CMG2 is a sort of stucco made of gypsum and $CaCO_3$ as main materials and an organic resin. This was applied in an undocumented bad intervention.

Samples CMG3 and CMG4 correspond to the surface patina of the capital and they are composed of beeswax. The waxes are recognizable through the FTIR analysis mainly thanks to the very clear and characteristic doublets present at 1473-1463 cm^{-1} and 729-719 cm^{-1}. Natural waxes, such as beeswax, have been widely used in the past as protective of stone surfaces especially for their main characteristic, that is, their strong apolarity and therefore water repellency. However, in addition to yellowing and therefore chromatically altering the stone surface, the waxes retain the dust and foreign material present in the air due to their structure which always remains 'sticky' (low melting point), strongly changing the legibility of the artefact. In the case of the capital of *Magister Guilelmus* an intervention would be necessary for removing the old wax layer that may be substituted with a more appropriate protective [13].

Table 1. Results of the FTIR analysis with the band assignments for the samples taken from the capital of *Magister Guilelmus*.

Sample	FTIR bands (cm^{-1})	Assignments
CMG2	3544, 3400, 2235, 2140, 1684, 1620, 1155, 1122, 672, 600, 470	Gypsum
	2870, 2513, 1796, 1437, 876, 713	Calcium carbonate
	2951, 2918, 2850, 1733	Organics (esters)
CMG3	2917, 2849, 1722, 1473, 1463, 1378, 1162, 729, 719	Beeswax
CMG4	2917, 2849, 1723, 1473, 1463, 1378, 1265, 1101, 729, 719	Beeswax

Figure 4. The sampling points in the baptismal font of the Viterbo cathedral.

3.2. The 15th century baptismal font in the cathedral of Viterbo

The baptismal font in the cathedral of Saint Lawrence in Viterbo was created in 1471 by the workshop of the sculptor Francesco d'Ancona. This marble artefact exhibited different kinds of surface patinas and also restoration materials applied as protective and grouting. On the occasion of the restoration, performed about five years ago, the surface and grouting materials were sampled for laboratory characterization through FTIR analysis. Seven samples were taken as shown in the Figure 4.

In Table 2 the sample description and the results of FTIR analysis are shown. Samples FB1 and FB2 are mainly composed of beeswax used as protective layer. Samples FB3 and FB4 can be referred to a probable adhesive mixture, but its function is not clear. FB5 is a modern restoration grouting whose composition seems to correspond to the commercial product known as Sintolit [https://www.sintolit.com/marmo/] widely used for repairing marble objects. Sample FB6 contains fatty materials probably associated to the faithful touches.

Table 2. Samples from the baptismal font: description and results of the FTIR analysis.

Sample	Description	Assignments on the base of FTIR results
FB1	Surface protective applied on the upper edge of the baptismal font cup	Beeswax (+++), oxalates (+)
FB2	Reddish surface layer in the edge of the baptismal font cup	Beeswax (+++), oxalates (+)
FB3	Brown glassy material on the upper part of the baptismal font cup edge	Proteins (++), terpene resin (+), oxalates (+), traces of wax or fatty material
FB4	Brown surface layer, probably adhesive	Animal glue (++), oxalates (+), traces of calcium carbonate and wax
FB5	Restoration grouting	Calcium carbonate (++), kaolinite (++), polyester resin (++)
FB6	Brown surface layer on the leg of Saint John the Baptist	Calcium carbonate (++), fatty material (++), oxalates (+), iron oxides (+)
FB7	Brown surface layer on the column of the small temple	Calcium carbonate (++), terpene resin (++), oxalates (+), quartz (tr)

In fact, this part of the baptismal font is usually touched by the faithful that enter in the church and make the sign of the cross with blessed water by dipping their fingers in the baptismal font. For this reason, the leg of Saint John the Baptist has a brown colour. At last, sample FB7 contain a terpene resin. The presence of this resin, found also in sample FB3 can be associated to a surface finishing, probably original.

3.3. The two 15th bas-reliefs representing respectively Saint Michael the Archangel and Saint Raphael the Archangel, attributed to Agostino di Duccio

On the occasion of the master degree thesis by Chiara Abramo [9], three micro-samples were taken from the bas-reliefs surfaces in correspondence of the yellow and red areas (Figure 5). XRF micro-analysis revealed the presence of gold in the yellow areas associated to lead and iron. These last two elements are contained in the ground layer of gold and may be associated to Pb and Fe-based pigments. Due to the presence of lead and iron it can be supposed a mordant technique for gilding. In this kind of technique, lead-based pigments together with ochre and earths were used as siccative agents for linseed oil [14]. The higher counts found in sample BR1 (Pb counts 1019) in respect to those measured in sample BR2 (Pb counts 426) are due to the higher amount of powder. Calcium is the elements of marble constituting the bas-reliefs.

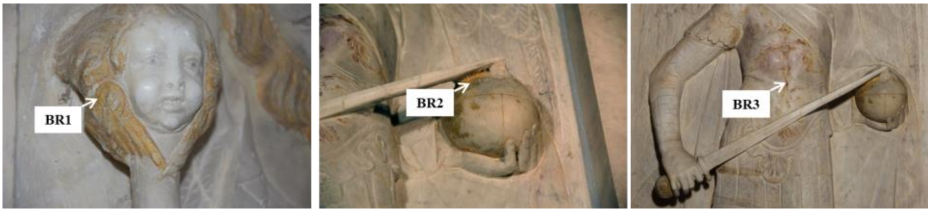

Figure 5. The sampling points in the two bas-reliefs of Acquapendente cathedral.

Table 3. Results of the FTIR analysis with the band assignments for the samples taken from the bas-relifs by Agostino di Duccio.

Sample	FTIR bands (cm^{-1})	Assignments
BR1	3557, 1621, 1117, 673, 607, 471	Gypsum (+)
	2512, 1791, 1424, 878, 712	Calcium carbonate (++)
	2924, 2855, 1732	Organics (siccative oil, ++)
	1653, 1323, 787	Oxalates (++)
BR2	3541, 3391, 1159, 1116, 671, 602	Gypsum (+)
	2516, 1799, 1438, 878, 714	Calcium carbonate (++)
	2928, 2855, 1733	Organics (siccative oil, ++)
	1653, 1323, 781	Oxalates (++)
	3694, 1041, 914, 542	Silicates and iron compounds (+)
BR3	3547, 3399, 1122, 669, 608, 473	Gypsum (+)
	2982, 2874, 2515, 1796, 1441, 877, 713	Calcium Carbonate (+++)
	2922	Traces of organics
	1652, 1326, 777	Oxalates (++)
	1034, 536	Silicates and iron compounds (+)

The results of FTIR analysis on the three samples are summarized in the Table 3. In samples BR1 and BR2 the presence of siccative oil confirms the use of a mordant to allow the adhesion of the gold on the marble. Gypsum was detected in all samples suggesting the possible use of this material for restoration work on the bas-reliefs. Oxalates are associated to alteration of organic compounds applied as possible protective or finishing on the surface of the sculpture. The production of oxalates on inorganic substrate may be associated also to micro-organisms metabolism [15, 16]. At last, silicates and iron oxides can be associated to earths and ochre used in the polychromies of the bas-reliefs.

The materials found in the samples from the two bas-reliefs suggest that originally they were painted; even no documentary sources are available to definitively support this hypothesis [9].

3.4. The 17th marble bust of the Pope Innocenzo X attributed to Alessandro Algardi

The marble bust of the Pope Innocenzo X is currently exposed in the Museum of Acquapendente (Viterbo district, Italy) and was created by the Italian master Alessandro Algardi. The piece was originally located in a niche in the façade of the Acquapendente cathedral [11]. From there it was removed after the Second World War, because the façade of the cathedral was seriously damaged during bombing and it was positioned inside the church. Finally, in 1970, it was definitively moved in the Museum. On that occasion a gypsum copy was performed by a local sculptor and it was positioned inside the cathedral [11].

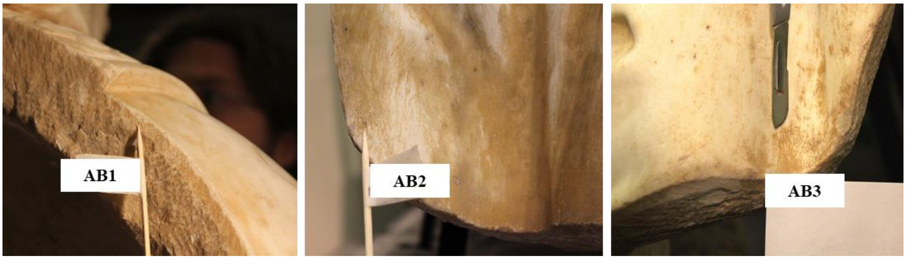

Figure 6. The sampling points from the marble bust of Alessandro Algardi.

Table 4. Results of the FTIR analysis with the band assignments for the samples taken from the marble bust of Innocenzo X by Algardi.

Sample	FTIR bands (cm^{-1})	Assignments
AB1	3322, 2963, 2930, 2868, 1766, 1714, 1453, 1376, 1234, 1163, 1077, 1022, 532, 465	Terpene resin, probably mastic (+++), traces of iron oxides
AB2	3396, 3292, 2969, 2936, 2872, 1766, 1713, 1453, 1376, 1321, 1238, 1167, 1131, 1022, 669, 603, 536, 465	Terpene resin, probably mastic (++), oxalates (++), traces of iron oxides and sulphates
AB3	3401, 2985, 2925, 2878, 2515, 2144, 1796, 1650, 1445, 1326, 1125, 1034, 877, 780, 713, 670, 604	Calcium carbonate (++), oxalates (++), gypsum (+), traces of organics

In May 2015, a restoration was carried out on the bust by the students of the course PFP1 (Conservation and Restoration of Cultural heritage - stone materials section) of University of Tuscia aimed at removing some undesirable surface materials. On that occasion, three micro-samples were taken from the bust for laboratory analysis performed through FTIR spectroscopy (Figure 6).

A synthesis of FTIR analysis is reported in the Table 4. The terpene resin was used as a release agent for the construction of the first copy of the marble bust. High amount of oxalates have been detected in the yellow patina. The surface of the bust appears abraded probably due to an intervention for removing the resin and the materials used to obtain the copy.

4. Conclusions

In this paper a study of surface materials on four marble artefacts was reported. In two cases, i.e. the baptismal font in the cathedral of Viterbo and the bust of Innocenzo X, the study was performed on the occasion of the restoration to support the cleaning operations and the comprehension of the conservative history of the artworks.

In all cases different materials were found on the surfaces, such as beeswax, used as protective and hydrophobicizing agent, and terpene resins used as adhesive and release agent. Oxalates were also found on the surfaces of the marble sculptures. These compounds probably originated from the reaction of oxalic acid, produced by micro-organisms, with the calcium carbonate of the substrate or by degradation of organics used in the past as surface treatment.

Only in the case of the two bas-reliefs, a possible original polychromy was observed. The investigation of samples taken from yellow and red areas revealed the presence of mordant gilding and of iron based pigments respectively, suggesting that originally the bas-reliefs were probably painted.

In conclusion, the analysis of surface materials in the marble artefacts revealed useful to know the conservation history of the artworks and to support the restoration activities in two of them.

References

[1] M. Franzini and C. Gratziu, Bollettino d'Arte, **Suppl. 35-36** (1986) 10-15.
[2] K. Ulens, L. Moens, R. Dams and P. De Paepe, Sci. Total Environ., **158** (1994) 63-69.
[3] C. Pardini and P. Tiano (eds.), *Le patine: genesi, significato, conservazione*, Nardini Editore, Firenze, 2005.
[4] D. Pinna, M. Galeotti and A. Rizzo, Heritage Science, **3(7)** (2015) 1-13.
[5] C. Pelosi, D. Fodaro, L. Sforzini, C. Falcucci and P. Baraldi, Stud. Conserv., **62(5)** (2017) 266.
[6] S. Sindoni and C. Sorrentino, Eur. J. Sci. Theol., **16(3)** (2020) 187-196.
[7] A. Scriattoli, *Viterbo nei suoi monumenti*, Stabilimento F.lli Capaccini, Roma, 1915, 139-140.
[8] Mons. S. del Ciuco, *La Cattedrale di Viterbo*, Futura, Viterbo, 1986, 32-38, 106-108.
[9] L. Lanteri and C. Abramo, Eur. J. Sci. Theol., **14(1)** (2018) 173-180.
[10] G. Cuccini, *Agostino di Duccio. Itinerari di un esilio*, Guerra Edizioni Edel, Perugia, 1990, 14-18.
[11] P.M. Fossati, L'Acquapendente. Bollettino della biblioteca comunale, **1** (1987) 1-10.

[12] L. Moens, P. Roos, J. De Rudder, P. De Paepe, J. Van Hende and M. Waelkens, *A multimethod approach to the identification of white marbles used in antique artifacts*, in *Classical Marble: Geochemistry, Technology, Trade*, N. Herz & M. Waelkens (eds.), NATO ASI Series E, vol. 153, Kluwer Academic Publishers, Dordrecht, 243-250.

[13] M.F. La Russa, S.A. Ruffolo, N. Rovella, C.M. Belfiore, P. Pogliani, C. Pelosi, M. Andaloro and G.M. Crisci, Period. Mineral., **83(2)** (2014) 187.

[14] M. Matteini, *The gilding techniques in the ancient sacred art*, Proc. of the 6th European Symposium on Religious Art, Restoration & Conservation, O.A. Cuzman, R. Manganelli del Fà & P. Tiano (eds.), Nardini Editore, Firenze, 2014, V-VIII.

[15] L. Zucconi, M. Gagliardi, D. Isola, S. Onofri, M.C. Andaloro, C. Pelosi, P. Pogliani and L. Selbmann, Int. Biodeter. Biodegr., **70** (2012) 40.

[16] L. Rampazzi, J. Cult. Herit., **40** (2019) 195.