ELIMINATION OF THE DIRTY CRUST OF WHITE ALTERATED GLAZE FROM EXCAVATED CERAMICS USING THE LASER CLEANING ALTERNATIVE

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ABSTRACT: *The laser technique has been applied to the cleaning process of glazed decorated ceramics from excavation sites. The use of this method arises as the only possible alternative in the process of cleaning pieces with crusts of dirt that are extremely hard and strongly stuck over altered and friable white glaze layers. The study carried out has allowed to fix the optimal laser parameters in the elimination of the dark dirty layer found on several fragments from different periods. The study has been developed with MO and MEB/EDX. The results obtained enabled the optimisation of the laser method that includes different procedures according to the nature of the dirt. In the same way, we have been able to identify the manufacturing technique, the compositions of the vitreous covers, the nature of the crust of dirt and the conservation state of the analysed pieces.*

KEYWORDS: laser, cleaning, art work, glaze, ceramics, archaeological object

INTRODUCTION

The study carried out has consisted in eliminating crusts of dirt strongly stuck over the white opaque deteriorated glaze from ceramics of different periods and excavations. These pieces were Valencian ceramics which came from public institutions. The ceramics had very deteriorated glazes, which were often constituted by thin layers, dull and worn away surfaces without much adherence to the ceramic substratum. The described glazes appear in pieces with a certain production some defect like those in this our study which was carried out on medieval pieces found in a ceramic refuse dump of an ancient factory. Other glazes we also studied had come from correctly executed pieces but had deteriorated over time. An example of such is the Islamic pieces from an excavation carried out in the street Luis Vives of Valencia. In both types of pieces, ageing had caused corrosion and an alteration of the glaze which showed miniature cracks and, in many cases, vitreous flakes or lost areas. This situation has caused dirt and superficial earth deposits of calcareous nature to become incrusted through the cracks to consequently reach a larger scale of contamination and adherence, developing both as carbonated concretions and dirty compact surfaces that even ended up covering the pieces completely (Figure 1).

From our "Instituto de Universitario de Restauración del Patrimonio de la Universidad Politécnica de Valencia" we have felt the need to look for practical solutions for this type of pieces characterised by the dreadful state of conservation of its dirty covers. This search started several years ago from the Investigation Project "Estudio de Restauración e Intervención Conservativa del Patrimonio Cerámico Islámico y Mudejar" subsidised by the Polytechnic University of Valencia. This Project allowed us to search the solutions for very problematic glazes in the cleaning process with complete guarantees of success.

In recent years we have observed the great advance and development of laser technology applied to all fields to not only include stone materials, but also such very diverse materials like metals, textiles, wood, paintings, synthetic polymers, paper, fossils, ceramic and glass, among others. Undoubtedly the biggest bibliographical contribution on the laser technique in the restoration of works of art is on stone materials. Thus, there are numerous studies about cleaning methods (Vergés-Belmin, 2000: 220-273; Rodríguez-Navarro et al, 2003: 65-82; Lanterna and Matteini, 2000: 29-35; Labouré et al, 2000: 21-27) and about optimising the parameters applied to the cleaning of stone façades (Sabatini et al, 2000: 9-19; Armani et al, 2000: 99-104). However there have been very few studies carried out on either architectural façades in terracotta (Oujda et al, 2005: 321-327; Gaspar et al, 2003: 294-302) or on the elimination of inorganic crusts in materials obtained from archaeological excavations (Pouli et al, 2003: 338-342). In recent years several studies have appeared on laser application on glass. In this sense we can find the investigations carried out in Germany on model glasses in an attempt to reproduce the real conditions that are present on historical windows (Fekrsanati et al, 2001a: 253-258; Klein et al, 2000: 287-292; Drewello et al, 2000: 161-171; Fekrsanati et al, 2000: 155-160; Römich and Weinmann, 2000: 151-154; Fekrsanati et al, 2001b: 196-201). Studies on glazed ceramics are difficult to find, like that out on Portuguese tiles from the 18th Century with the purpose of studying the effect of the different wavelengths applied and of optimising the method (Gaspar et al, 2000: 189-200).

EXPERIMENTAL PROCEDURE

The ceramic studied

The selected samples came from two different locations. The pieces from the Islamic Period belong to the archaeological excavation carried out in 2004 in the Luis Vives street of Valencia. This excavation

Figure 1. Ceramic glaze piece of Madinat al-Zahra style, 11th Century. Side with the decoration in green and manganese. Before restoration

Figure 2. Ceramic glaze piece of Madinat al-Zahra style, 11th Century. External side. Before restoration

was carried out on the plot of the new headquarters of the "Colegio Oficial de Ingenieros de Caminos, Canales y Puertos de Valencia". This archaeological excavation was directed by Victor Algarra who studied and classified the material finds. The medieval pieces belong to the excavation carried out in 1990 in the Valencia street of the town of Manises. This was directed by Josep Pérez Camps, the director of the Municipal Museum of Ceramic of Manises and by Jaume Coll Conesa, the director of the National Museum of Ceramic and Sumptuary Arts González Martí. In this excavation, a ceramic refuse dump of an ancient factory had been discovered with a lot of discarded pieces of ceramics, generally resulting from faulty production. The excavation was carried out on a large plot measuring 67 x 37 meters. Nowadays it has been constructed on and is located at numbers 24 and 25 of the Valencia street in Manises. Due to the large dimensions of this plot, the work surface was divided into three sectors A, B and C. The ceramic fragments selected to undertake this study all proceed from the A sector, and inside this they belong to level 25, considered to date back to the mid 15th Century. These pieces were presumably discarded by the artisan due to defects during the elaboration process or storage, circumstances that prevented them from being finally completed and sold. Part of this material has been studied and restored at the "Departamento de Conservación y Restauración de Bienes Culturales de la Universidad Politécnica de Valencia". The intervened material includes diverse pieces and ceramic fragments. The pieces selected belong to the collections noted and diverse remains of similar potteries that, given their reduced size, were not classified but were used as practice material. The largest piece is a of a concave source, of the Madinat al-Zahra type, with an incomplete profile, composed of four fragments with a flat base, right lip, and whose decoration is probably epigraphic in green and manganese. It has a semi-circled border with extensive crusts of dirt on the surface and a highly deteriorated glaze (Figures 1-2). The medieval pieces include bowls, jars and non-identified pieces of a reduced size.

Cleaning

The cleaning stage is the most hazardous and delicate of all the restoration processes since it involves an irreversible procedure, so is always necessary to act with extreme care and caution. The previous investigations concerning the cleaning procedures that we have carried out were applied to glazed ceramics, and revealed that the knowledge about the interaction of the laser radiation with the crusts of dirty is very scarce and insufficient.

The objective of this paper has been to determine the particular scope of laser cleaning for these pieces by adopting the same premise as that considered in previous works (Aura et al, 2006: 997-1008), to handle the ceramic with extreme care and, in the same way, to opt for a minimal intervention regarding the pass of time and only eliminating the factors that produce deterioration. For this reason it is highly important to avoid modifying the glazes. The glazes appear to be composed of two layers, an internal healthy layer in contact with the ceramic biscuit, and a superficial altered one. The latter has a laminate structure with miniature cracks in which the dirt has penetrated until a degree of irreversible inlay has taken place (Figure 3). The dirty crusts also appear to be composed of two layers, a superficial layer without the presence of glaze, and an internal one that is yet to be described because it is apparently melted with the glaze because it has encrusted the glaze through the cracks. The irradiation process has only been applied to the crust of superficial dirt to avoid the interaction with the layer of altered glaze that should be respected at all times. However, this is actually an obstacle for the ornamental valuation of the object. Cleaning has been performed at all times under the attentive observation of the process through the optic microscope, thus controlling the result of cleaning with more precision. A binocular magnifying glass has been used, the Nikon model SMZ800, with a zoom of 10X up to 63X, equipped with the digital photographic camera model Nikon COOLPIX950.

Pieces have been irradiated to a frequency of 10 Hz in dry and in humid and with low values energy among 1.5 mJ, 6 mJ and 8.5 mJ, depending on the areas. Cleaning practice sessions have been performed using a laser Q-Switched Nd:YAG, with an energy for pulse variable among 5-30 mJ, with a duration of pulse of 4 ns, frequency repetition of 0-200 Hz and wavelength emission of 1064 nm.

Study by SEM/EDX

From all the analysis methods to study archaeological objects, scanning electron microscopy combined with the spectrometer of rays X (SEM/EDX) is particularly interesting to allow for the simultaneous determination of the chemical composition of the material and its morphological study. The technique offers the possibility of performing a microanalysis of microscopic phases, and is in itself an analysis technique of structures. The electron microscopy used was a JEOL JSM 6300 with a Link-Oxford-Isis microanalysis system, operating with a tension of filament of 20 kV.

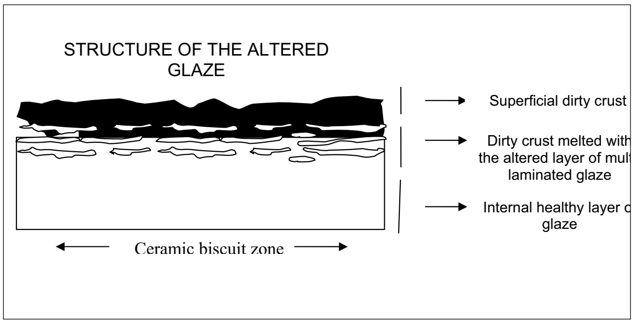

Figure 3. Schematic drawing showing the laminate structure of the altered glaze.

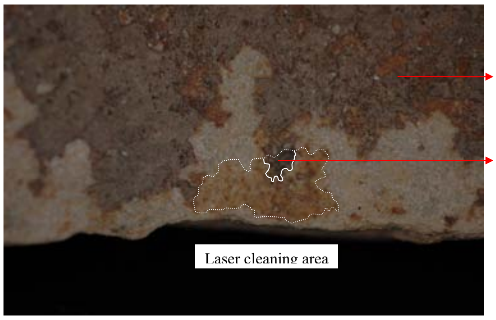

Figure 4. Image detail of a laser cleaning area. In this area, it has been opted to respect the layer of altered glass with incrusted dirt after eliminating the most external crust layer of dirt. Some particular areas of resistant dirt are appreciated which we were unable to eliminate.

Zona	SiO2	Al2O3	CaO	MgO	FeO	SnO2	PbO	Na2O	K2O	TiO2
Bizcocho	42,22	14,57	30,46	2,37	4,21	-	-	1,49	1,71	1,67
C. reverso	39,30	6,84	6,83	1,36	2,21	-	37,92	1,03	4,06	0,46

Table 1. Average results of the chemical analysis composition of the Islamic pieces by MEB/EDX (% in oxides)

RESULTS AND DISCUSSION

Initial cleaning

We carried out a gradual and controllable cleaning, beginning with an elimination stage from concretions with a scalpel either by making superficial abrasions or attempting to remove flakes or dirt with a minimal leverage force. The results obtained by abrasion did not run well because concretions showed great hardness. However the best result was obtained by this second technique applied to the base of the concretions and it was possible to eliminate 15% of the total dirty surfaces. Other alternative abrasion methods, like the one with a Dremel apparatus, or erosion methods were discarded because the concretion constituted a very thin layer and a risk of deteriorating the glazes existed. Different chemical cleaning methods were also carried out but none dealt with the dirt layers satisfactorily. Finally, the laser cleaning method was selected because it produced the photo decomposition of superficial layers, which proved to be selective, controllable, effective and safe.

Laser cleaning

The methodology of work employed has allowed us to determine good cleaning conditions and to establish the parameters that ensure an innocuous intervention on the white vitreous cover. The test carried out on the ceramic biscuit (corresponding to areas of vitreous cover, flaked), using the lowest parameters, did not permit a selective cleaning, and dissuaded us to employ laser cleaning in these areas. In this sense, a density of energy of 0.08 J/cm2 used for the cleaning procedure carried out on the ceramic biscuits has not discriminated among the concretions to eliminate the ceramic support.

The irradiation results carried out at a fluency of 0.35 J/cm2, performed in humid conditions, demonstrated a high capacity of cleaning the glazing areas (Figure 4). A fluency of 0.5 J/cm2 was used in the more resistant dirty layers.

SEM/EDX characterisation

The study carried out by SEM/EDX has shown the deterioration of ceramic glazes. The glazes appear with corrosion on the superficial layers which may be observed through an extensive network of multilaminated miniature cracks and layers. After applying the laser, this altered layer of glass remained intact to prove that at a physical level, i.e., chemical, the laser only eliminated the external crust of dirt and not the layer of dirty that had melted with the glazes through the miniature cracks. The study has also allowed us to determine the chemical composition of both the ceramic biscuit and the white vitreous covers (Tables 1).

CONCLUSIONS

The irradiation results carried out on the different areas of the various pieces has demonstrated the high capacity of radiation laser to discriminate between the crusts of dirt and the layers of altered glazes. Conversely, the ceramic biscuits present a more noticeable sensitivity to the radiation laser used and cleaning with the practice parameters did not provide the same results. The characterisation of the crusts of dirt has identified compact, resistant, strongly stuck concretions with a grade of irreversible inlay through the glazes. The possibility to work with low fluencies has allowed the appearance of these pieces to improve thanks to the meticulous and extensive work under the Optic Microscope. The irradiation process has only been applied to the most superficial dirt, avoiding the interaction with the layer of altered glaze that should be respected at all times, although it is an obstacle for the aesthetic aspect and the valuation of ceramic objects.

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Versión española

TÍTULO: ***Eliminación de la suciedad del esmalte blanco alterado de las cerámicas excavadas usando la alternativa de la limpieza por láser***

RESUMEN: *La técnica del láser se ha aplicado en el proceso de limpieza de cerámica vidriada y decorada procedente de excavaciones. El uso de este método se presenta como la única alternativa posible en el proceso de limpieza de piezas con capas de suciedad de gran dureza y fuertemente adheridas. El estudio realizado ha permitido fijar los parámetros óptimos del láser en la eliminación de la costra de suciedad sobre varios fragmentos de diversos períodos. La investigación se ha desarrollado con MO y MEB/EDX. Los resultados obtenidos permiten la optimización del método del láser que incluye diversos procedimientos según la naturaleza de la suciedad. Del mismo modo, se ha podido identificar la técnica de fabricación, las composiciones de las cubiertas vítreas, la naturaleza de la costra de suciedad y el estado de conservación de las piezas analizadas.*

PALABRAS CLAVE: *láser, limpieza, obra de arte, esmalte, cerámica, objeto arqueológico*