Degradation of gold and false golds used as gildings in the cultural heritage of Andalusia, Spain

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Abstract

The causes and degree of alteration of metals such as gold, tin, silver and bronze powders from ornamental implements of Andalusia Cultural Heritage have been studied. The unaltered gold is lost due to the alteration of the material used to adhere the leaf gold on the ceramic. Tin is transformed to romarchite and is lost due to a similar alteration as with the gold leaf adhesive. Silver is altered to Ag$_2$S due to environmental contamination. Part of the bronze powders and silver used in Huercal-Overa altarpiece are altered to atacamite and AgCl, respectively, due to an unsuitable cleaning process.

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1. Research aims

The cultural heritage of Andalusia (Spain) is very important, and several metals such as gold, silver, tin and bronze powders have been used to create ornamental implements. These metals may be altered by reaction with environmental contaminants producing partial or total degradation. The aim of this paper is to study the causes and degree of alteration of these metals.

2. Introduction

For many years, humans have used metals to create both utilitarian and ornamental implements. The most frequently used metals for Cultural Heritage are silver, lead, copper, tin, iron and tin-mercury amalgam, that are easily altered. The use of metal for artifact construction has been known for more than 10,000 years [1]. Tin was one of the metals best known to the ancients. It is soft and malleable, so it is easily beaten into leaf or foil and was used to embellish paintings in its own right or for imitating gold. Theophilus [2] tells how to ornament pictures in books and how to imitate gold by coating it with glair mixed with saffron. Silver leaf was used in mediaeval painting. Cennino Cennini warns against silver for its tendency to tarnish and to blacken [3]. Gold is the most malleable of the metals and may be beaten into leaves of very small thickness. It can be used to cover large surfaces without a high economic cost. There were various ways of making the leaf adhere to the surface but for large areas, a hole or fine red earths were usual [4].

3. Materials and experimental methods

3.1. Materials

The Cathedral of Seville has various porticos decorated with terracotta. The samples were taken from the ceramics of the tympanon (Birth portico, XVth century) (Fig. 1a), the Virgin and Archangel (Pardon portico, XVIIIth century), and St. Peter and St. Paul (Pardon portico) (Fig. 1b). Environmental pollution has altered the surface of the ceramic sculptures, destroying the polychrome, so that only small parts covered by crust or dust remain.

Other samples were taken from the altarpiece of Asuncion Church in the village of Huercal-Overa (Almeria) (Fig. 1c).
This artifact is considered a great altarpiece with high historical-artistic quality. José Ganga Repio made it between 1746 and 1764. The polychromes of architectonic elements and figures of the most inaccessible zone appear, without modifications or additions, in spite of undergoing significant mutilations during the Spanish civil war.

In the ceiling of the Principal Meeting Room of Seville City Hall appear polychromed stone sculptures that have suffered significant alterations. Several samples were taken from these wall paintings (Fig. 1d).

3.2. Experimental methods

Cross-sections were made up following the methods of Khan-dekar [5] and Duran [6]. The cross sections were studied using a stereomicroscope, X-ray diffraction (XRD), scanning electron microscopy (SEM) equipped with an X-ray dispersive energy analyser (EDX), infrared spectroscopy (FTIR) and an olympus BH-2 microscope with Mettler Heating Stage FP 82HT.

4. Experimental data and results

4.1. Gold leaf

Cross-sections were prepared from samples taken from the ceramic statues representing the Virgin and Archangel of Saint Peter portico and the tympanon of Birth portico. Optical microscopy showed that both ceramic statues had been covered with a red-brown layer, followed by a thin metallic layer, and over them layers of polychromy were deposited. Herm et al. [7] have carried out research on polychromy terracotta army of the first emperor Quin Shi Huang. Jimenez de Haro et al. [8] and Perez-Rodriguez et al. [9] described the material and techniques used to make these ceramic statues.

The chemical analysis of the red-brown layer carried out by EDX shows that it is composed of lead (not shown). The XRD study (Fig. 2a) confirms that this layer is composed of hydrocerussite and lead oxide (minium). FTIR study also shows the presence of wax (bands at 2955 cm\(^{-1}\), 2920 cm\(^{-1}\), 1742 cm\(^{-1}\)) (Fig. 2b).

On this red-brown layer, the chemical analysis shows another layer composed of gold. There were various ways of making the leaf adhere to the surface, but for large areas a bole or mix of fine earth was typical. For other ornamentation, wax was used or an aqueous medium and brushed onto the part to be gilded. For panel and wall paintings however, oil mordant was common [10]. In our study, the gold was adhered to the surface using other material constituted by a mixture of hydrocerussite, lead oxide and wax. The use of this material may be due to high temperatures (between 323 and 331 K) during the summer in Seville. Contact thermometers were used to measure the temperature of the ceramics.
Fig. 2. a) X-ray diffraction of red–brown layer (gold is deposited over it) of ceramics [Cer = cerussite, Hy = hydrocerussite, M = minium]; b) IR spectra of red–brown layer (gold is deposited over it) of ceramics; c), d) SEM micrograph of gold layer of ceramics (hyphae growing are shown); e) X-ray diffraction of red–brown layer (tin is deposited over it) [Hy = hydrocerussite, Rom = romarchite].
This temperature may melt the wax or other organic compounds and also may be responsible for expansion of the gold leaf and its tendency to be bent, dented or flexed that has been used to argue against the use of metal for ornamentation. However, the mixture used on the ceramic for gilding is very convenient. Samples were heated in a thermal microscope with heating stage and the high stability of this mixture till very high temperatures has been confirmed.

When the gold is used for gilding, the material used to adhere on the support (in our case the ceramic) may suffer alternation producing the loss of the gold leaf. SEM micrographs of gold layers of sculptures studied in this paper are shown in Fig. 2c. Hyphae are growing on the red—brown layer breaking the support so the gold layer falls off (Fig. 2d). This type of biodeterioration has been described by Caneva et al. [11]. This alteration process accounts for the small amount of polychromy remaining. The cleaning was not possible to realize using solvents. The remove of the black crusts covering the polychromy by mechanical methods was unsuitable because the crusts were harder than the polychromy, being necessary a previous consolidation [12].

4.2. Tin leaf

Cross-sections were prepared from various samples taken from the ceramic statues representing of St. Peter and St. Paul from the Pardon portico. On the ceramics, a layer made of a mixture of hydrocerussite, lead oxide and wax similar to that in the gold leaf was found. The chemical analysis of the thin metallic layer covering the red—brown layer shows that the metal is tin and not gold. The XRD study of the red—brown and metallic layers are shown in Fig. 2e, showing the presence of romarchite and hydrocerussite (as support of tin layer). In this case, tin was likely used to imitate gold. Tin is better than silver because it does not tarnish and does not black with time. The degradation process is similar to the gold leaf; the red—brown layer is altered and the tin layer falls off.

4.3. Bronze powders

Bronze powders are metal flake pigments made commonly from copper—zinc alloys (brass), but for some powders, copper—tin alloys (bronze) are also used. Cross sections were prepared for some samples taken from the altarpiece of Asunción Church. Two metallic layers appear (Fig. 3a) one on the red—brown color layer and other one on the surface of the cross-section. The chemical analysis of one of the metallic layers shows that it is composed of gold, whereas Cu and Zn constitute another metallic layer.

Numerous shades of colours, ranging from citron yellow to orange, can be made depending upon the alloy composition. In our sample, the alloy was Cu, 85 and Zn, 15 (analysis by SEM) (figure not shown) that was used to imitate yellow gold [13].

The chemical analysis of this sample (cleaned in the past) shows the presence of chloride and the XRD study confirms that atacamite is a present phase (Fig. 3b). Chloride was not present in other samples taken from the same altarpiece (in upper parts) that were not cleaned in the past. The Church is located in a small village from Almeria Mountains, far from the sea, with very low environmental contamination. The presence of chloride only in same samples suggests that the alteration was not produced by environmental contamination and may be due to an unsuitable cleaning process carried out with a product containing chloride. Cleaning and conservation processes of Cu-alloys have been described by Herrera et al. [14].

4.4. Silver leaf

Cross-sections of different samples taken from the “Principal Meeting Room” of Seville City Hall show the use of a metallic layer in the ornamentation of the ceiling. The chemical analysis of these layers shows that they are composed of gold or silver and sometimes by gold alloyed with silver. In layers where silver is present sulphur has also been found and become black occasionally, where the presence of Ag and S is sure following EDX analysis (Fig. 4a). The metallic layer was likely not protected with a good varnish coating or the protection was lost over time [3].

A sample taken from a silver tinted varnish from the altarpiece of Asunción Church, shows another alteration of the silver. The cross-section (Fig. 4b) also shows two metallic layers, one on the red layer (fine red earths) and other one on the surface. The chemical analysis of the internal metallic
layer shows that it is composed of silver. However, the metallic layer of the surface is composed of silver, but also appear chloride ions (Fig. 4c), showing that the silver has been altered, probably due to an unsuitable cleaning process carried out with a product containing chloride. In this case, tensocative agents were used to eliminate superficial dirt [15].

5. Conclusions

Metals used for ornamentation or made artifacts in several monuments of Andalusian Cultural Heritage have been altered or lost. Gold is an unaltered metal, however, the alteration of the material (hydrourousite, minium and wax) used to adhere the metal to the surface of the ceramics from the Porticos of Seville Cathedral has produced the loss of the gold leaf. Tin was oxidized to tin oxide (romarchite) and, similar that in gold leaf, the alteration of the material used to adhere it to the ceramic has led to its loss. Silver used in the polychromed stone sculptures of Sevilla City Hall was tarnished and blackened due to the formation of Ag2S as was expected. Bronze powders and silver used to imitate gold in the Huercal Overa altarpiece have been altered to atacamite and AgCl, respectively, probably due to an unsuitable cleaning process. The bronze powders and silver remain unaltered in the upper parts of the altarpiece, which were not cleaned.

References