

A technological study on the 17th century raised gilded substrates in three royal palaces of Isfahan, Iran

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Abstract

The raised substrates of gilding decorations, called *lāyachīnī* in Persian, were widely used throughout the Safavid period (1501-1736 AD) in Iran. This paper presents the first analytical data obtained from the *lāyachīnīs* of three seventeenth century royal Safavid buildings (Ālī-Qāpū, Chihil-Sutūn, and Hasht-Bihisht) in Isfahan, Iran, using energy dispersive X-ray spectroscopy, scanning electron microscope, X-ray powder diffraction, and thin layer chromatography. According to the analytical data, different forms of calcium sulfate (dihydrate, β-hemihydrate, and anhydrite), the red iron oxides, and a proteinaceous binder (probably animal glue) are the main constituents of the raised *lāyachīnī* substrates. The results show that a dry mixture of the plaster of Paris and the red iron oxides are mixed with diluted animal glue to obtain a slurry to be applied in several layers, one top of the another, to achieve the raised substrates. This technique is similar to those European raised *pastiglia* substrates although the method of the preparation in the Persian technique is different from the European one.

Introduction

Throughout the 14th century, the raised stucco inscriptions were vastly covered with metallic leaves in Iran (Wilber, 1955). This tradition was continued in the 15th century for decorating stucco ornaments in Iran (Golombek and Wilber, 1988) and Transoxiana (Pugachenkova, 1963). By flourishing arts and crafts in the 17th century, during the Safavid period, the raised gilded decorations consisted of a largely used art in the architectural decorations of the capital city of Isfahan (Savory, 1980). In this

period, the raised gilded decorations were extensively used to decorate public buildings, mansions, palaces, and mosques. All these gildings are executed on a red relief substrate whose recent name is *lāyachīnī*.

Lāyachīnī is literally composed of the two Persian words of *lāya* (layer) and *chīnī* (setting) which means *setting several layers*. The use of this term for describing the raised substrates of gilding decorations in Persian architecture seems to be owed to a similar technique for gilding the leather covers of old books. According to the old medieval Persian texts, *lāyachīnī* is achieved by applying several layers of a runny slurry by a brush on a leather substrate which is successively covered by the gold leaf (Māyil-Hiravī, 1993; Karīmzādīh-Tabrīzī, 1997; Nasīrī-Amīnī, 1978). The term *lāyachīnī* was then acquired by Āqājānī (1980) to describe the red Safavid substrates of the gilded architectural decorations. This paper provides the first analytical data on the Safavid *lāyachīnī* substrates of three 17th century Safavid palaces in Isfahan (Ālī-Qāpū, Chihil-Sutūn, and Hasht-Bihisht), Iran, using energy dispersive X-ray spectroscopy (EDX), scanning electron microscope (SEM), thin layer chromatography (TLC), and X-ray powder diffraction (XRD).

Materials and Methods

Samples

The raised gilded decorations of the three important Safavid palaces of Ālī-Qāpū, Chihil-Sutūn, and Hasht-Bihisht were subjected to our analytical study. The sample of Ālī-Qāpū palace was removed from the music room in the fifth floor of this palace (Figure 1a); that of Chihil-Sutūn palace was obtained from the eastern entrance of the palace (Figure 1b); and the *lāyachīnī* sample of Hasht-Bihisht palace was acquired from the north-western room at the first floor (Figure 1c). According to Hunarfar (1965), the raised *lāyachīnī* substrates of Ālī-Qāpū were executed in ca. 1609 AD, those of Chihil-Sutūn in ca. 1628 AD, and the *lāyachīnīs* of Hasht-Bihisht are dated back to ca. 1669 AD.

Scanning electron microscope and energy dispersive X-ray spectroscopy

SEM micrographs and EDX microanalyses were performed with a Philips XL30 scanning electron microscope equipped with an EDX detector using 0.12 nA, 100 s counting time, and about 10 mm working distance. The samples were coated with gold by physical vapor deposition (PVD), using a sputter coater SCDOOS (Bal-Tec, Canonsburg, PA, USA) in

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order to prevent charging effect. The EDX microanalyses were carried out by scanning a large area of the samples with an accelerating voltage of 20 keV and the obtained data were handled by ZAF software.

X-ray powder diffraction

XRD analysed were performed with a Bruker D8 advance X-ray diffractometer, using Cu-K α radiation, 40 kV, and 30 mA and a step size of 1°/2 θ /min in the 4-70° 2 θ range. Semi-quantitative phase analyses were performed based on the ICDD-PDF2 database for X-ray diffraction powder data.

Binder identification and thin layer chromatography

The probable binders of the samples were extracted in water at 80°C for 180 min as suggested by Ronca (1994). The relative amount of the extracted binders was measured by pyrogallol red-molybdate complex method with a Hitachi 726 spectrophotometer at 600 nm (Watanabe et al., 1986). For TLC analysis, aluminum oxide particles (size 5-17 μ m) on aluminum foil were used as the stationary phase and as the mobile phase a solution of acetic acid in ethanol (10/90 v/v) was used. In addi-

tion, the extracted binders were hydrolyzed by a 6M solution of hydrochloric acid (Ronca, 1994; Striegel and Hill, 1996) and a 0.2% w/v solution of ninhydrin in acetone was sprayed on the TLC plates for visualizing the spots.

Results

The identification of the binder

The relative amount of the extracted binders was measured by pyrogallol red-molybdate method (Watanabe *et al.*, 1986). The results showed that in each deciliter of the extracted solutions of Ālī-Qāpū, Chihil-Sutūn, and Hasht-Bihisht samples an amount of 12.4, 11.7, and 2.4 mg protein existed respectively. TLC, however, showed the traces of glycine and, moreover, the presence of proline and hydroxyproline in Ālī-Qāpū and Chihil-Sutūn was positively detected. As it is generally well-known, glycine, proline, and hydroxyproline are the main constituents of collagen which is abundantly found in the composition of natural animal glues (Mills and White, 1999).

Chemical and mineralogical composition of the samples

The results of EDX microanalyses (Table 1) showed that the elemental compositions of Ālī-Qāpū and Chihil-Sutūn samples are close together. However, the chemical composition of Hasht-Bihisht sample is different from the other samples. The deeper red hue of Hasht-Bihisht sample, in comparison with the other samples, may be due to the higher iron content of the sample (16.3 wt%). XRD, moreover, showed three different forms of calcium sulfate (dihydrate, hemihydrate, and anhydrite), iron oxides (hematite, maghemite, and goethite), and feldspars are the main phase components of the three samples (Table 2). The high amount of iron bearing phases in Hasht-Bihisht sample (25.7 wt%), in concordance with EDX results, is the reason of more reddish hue of this sample.

Three forms of calcium sulfate (anhydrite, hemihydrate, and dihydrate), nevertheless, showed more interesting technological features of the samples. As it is generally well-known, in the normal pressures, mineral gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ or dihydrate) is transformed to calcium sulfate hemihydrate ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ or the plaster of Paris) at the temperature range of 45-220°C and it is transformed to anhydrite (CaSO_4) at the temperatures above 300°C. The most stable form among these forms is dihydrate to which the other forms are transformed in the presence of water (Singh and Middendorf, 2007). The presence of all these forms in a same mixture implies a technological fact by which one can hypothesize

that in the process of making the plaster of Paris from gypsum not only calcium sulfate hemihydrate is obtained but also local higher temperatures have resulted to the formation of anhydrite. This is a very probable fact since in the traditional furnaces of making the plaster of Paris, the firing temperature is not properly

controlled and, therefore, anhydrite is a usual byproduct of the plaster of Paris (Sanz-Arauz, 2009). The challengeable issue, nevertheless, is the presence of calcium sulfate hemihydrate and anhydrite in the samples since it should have been previously transformed to the dihydrate form due to the water content of the



Figure 1. The areas from which the samples were obtained: (a) raised lāyachīnīs in the music room at Ālī-Qāpū palace, (b) the eastern entrance of the Chihil-Sutūn palace, and (c) the north-western room at the first floor of Hasht-Bihisht palace.

Table 1. Semi-quantitative microanalyses data of the samples, energy dispersive X-ray spectroscopy results (normalised to 100%).

Safavid buildings	Elements (Oxide forms)					
	CaO	SO ₃	Fe ₂ O ₃	Al ₂ O ₃	K ₂ O	SiO ₂
Ālī-Qāpū	39.3	42.9	5.1	2.4	0.8	9.4
Chihil-Sutūn	36.5	43.2	6.8	3.7	0.7	9.1
Hasht-Bihisht	29.6	38.1	16.3	5.2	0.9	9.9

Table 2. X-ray powder diffraction results of the phase constituents of the samples.

Phases	Ālī-Qāpū	Chihil-Sutūn	Hasht-Bihisht
Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)	52.9	65.3	28.9
Anhydrite (CaSO_4)	12.8	9.3	11
Hemihydrate ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$)	12.1	2.7	11
Hematite ($\alpha\text{-Fe}_2\text{O}_3$)	10.1	9.3	8.8
Goethite ($\alpha\text{-FeO(OH)}$)	n.d.	n.d.	11
Maghemite ($\gamma\text{-Fe}_2\text{O}_3$)	n.d.	n.d.	5.9
Clinocllore ($\text{Mg,Al}_6(\text{Si,Al})_4\text{O}_{10}(\text{OH})_8$)	12.1	4.2	n.d.
Albite ($\text{NaAlSi}_3\text{O}_8$)	n.d.	n.d.	5.5
Orthoclase (KAlSi_3O_8)	n.d.	9.3	11
Calcite (CaCO_3)	n.d.	n.d.	6.8

n.d., not detected.

binder of the *lāyachīnīs*. It can be concluded that the water content of the binder should not have had enough time in order to transform the hemihydrate and anhydrate forms to the dihydrate form (gypsum). In other words, before transforming calcium sulfate hemihydrate to gypsum, the water was given off from the slurry of the *lāyachīnīs*. On the other hand, the transformation of anhydrite to dihydrate is rather a long time process (Lewry and Williamson, 1994) and, therefore, before transforming anhydrite to gypsum, the water has been given off from the mixture. To sum up, it can be said that the plaster of Paris was not soaked in the water prior to use in the compositions of the *lāyachīnīs*.

SEM micrographs also showed very interesting features of the samples regarding the state of the crystallization of gypsum (Figure 2). First of all, the small crystalline size of the gypsum (in average about 8 μm) suggests that β -hemihydrate, rather than α -hemihydrate, has been used as the primary material in the composition of the *lāyachīnīs* (Singh and Middendorf, 2007). Moreover, the compact structure of the gypsum crystals can be seen in Figure 2 in which dihydrate calcium sulfate are represented as relatively small, needle-shaped, not well-developed, entangled, and disordered crystals. Here, it is obvious that the gypsum crystals are not broken under pressure. On the other hand, the crystals are not well-developed and it seems that they are not fully formed and their process of setting has most probably been aborted before a full setting occurs. On the other hand, it is believed that additives can drastically affect the crystal habit of the different forms of calcium sulfate; that is, they usually enhance crystal growth in specific faces and change interplanar distances (Singh and Middendorf, 2007). The crystalline structure of the samples represented in Figure 2 shows that the habit of the gypsum crystals is not significantly changed due to the existence of the binder (animal glue). Therefore, it can be inferred that the water content of the binder has not remained in the mixture for a long time and, most likely, before it affects the crystal habit of gypsum (dihydrate) its water content was given off from the mixture. As a general result of the aforementioned observations, it could be concluded that β -hemihydrate calcium sulfate (the plaster of Paris) has not been soaked in water prior to use and, furthermore, the water content of the binder has not been able to transform all β -hemihydrate calcium sulfate content to dihydrate crystals because the relative setting time of gypsum has been quite short.

According to the results, the composition of the studied *lāyachīnīs* is entirely different from those used as a substrate for gilding the book covers. Based on old manuscripts, the *lāyachīnīs* used in the decorating book covers consist of burnt copper, natural oils, iron dross, talc, salt (Māyil-Hiravī, 1993; Nasīrī-Amīnī, 1978) which have nothing in common with the substrates used for gilding the architectural

decorations. The only common ingredient between the *lāyachīnīs* used in the architecture and the book covers is animal glue to which is frequently referred in old treatises (Qumī, 2005). It seems that the word *lāyachīnī* in the decoration of architectural elements owes only its name to the technique used in the decorating book covers. The performance of *lāyachīnī*, however, in both uses

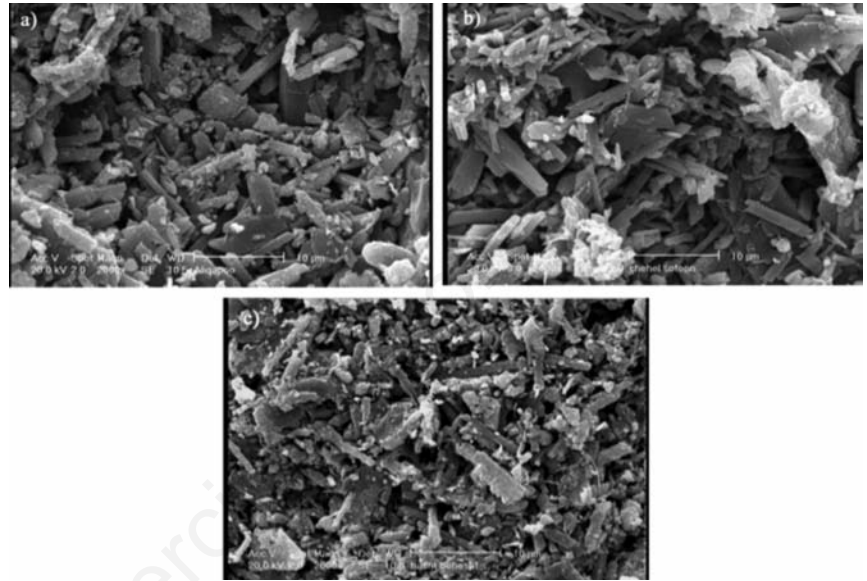


Figure 2. Scanning electron microscope micrographs of the crystalline structure in the *lāyachīnīs* of (a) 'Alī-Qāpū, (b) Chihil-Sutūn, and (c) Hasht-Bihisht palaces.

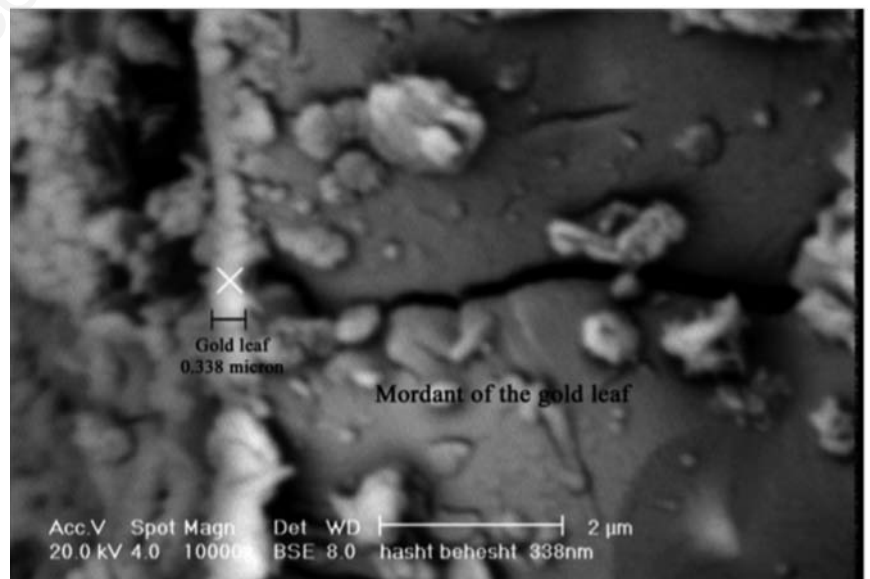


Figure 3. Scanning electron microscope image in backscattered electron mode showing the gold leaf with a thickness of about 0.34 μm on a mordant. *Lāyachīnī* substrate is not given here.

Discussion

is similar: using several layers of a slurry, one on top of the another, in order to make a raised substrate for applying gold leaves.

In Europe, however, several types of raised substrates were used for gilding decorations spanning the 11th through the 20th century. These raised substrates used to be called with different names such as *pastiglia*, *pastiglia pastillaye*, *yessería*, *relieve en stucco*, *applique relief*, *plasterreliefis* (Mojmir, 1992), *gesso*, *carton pierre*, *papier-mâché*, *carta pesta*, *carta gesso*, *fibrous slab*, *bulk gold*, *pressed on decoration*, *gilder's compo*, *paste compo*, *stucco*, *London composition*, *French composition*, *pâte coulante*, *plaster*, and *composition plaster* (Wetherall, 1991) which are sometimes puzzling to distinguish one from the others. In fact, there is not a unique composition for these raised substrates and based on materials available in the regions where these substrates are found, various ingredients are used in the composition of the raised substrates (Mojmir, 1992). However, the studied *lāyachīnī* substrates are compositionally more similar to those 11th century raised substrates in the southern Europe, especially in Italy, where it was called *pastiglia*. In Italy, from the 13th century onwards, a mixture of anhydrite, animal glue, and a red clay (Armenian bole) were used as the substrate of gold leaves (Bomford *et al.*, 1990). In the Italian raised *pastiglia* substrates, gypsum (*gesso sottile*) was generally soaked in water prior to use as a support of the gold leaf (Cennini, 1933). It is reported that the main components of the 17th and the 18th Italian substrates were red lead, led white, cinnabar, barite, and chrome yellow (Sansone *et al.*, 2010) that are notably different from the Safavid *lāyachīnī*s. There have also been other methods of making the raised substrates of gildings in which different types of materials such as beeswax, drying oils, chalk, pulp paper, lead white, *etc.* were pressed in pre-fabricated molds in order to achieve relief designs (Mojmir, 1992; Sansone *et al.*, 2010; Dunkerton *et al.*, 1991; Richadson, 1991). Concerning the use of the red hue under the gold leaf, it is reported that in Italy, from the 14th century onwards, a red layer of Armenian bole was used on the final stratum of *gesso sottile* to change the visual appearance of the gildings. In these gildings, the reflected red hue of the substrate could conceal the greenish hue of the gold leaf and make a warmer appearance of the gildings (Bomford *et al.*, 1990; Dunkerton *et al.*, 1991), which is recently supported by scientific measurements (Dumazet *et al.*, 2007). It should be noted that the thickness of the gold leaf has a crucial impact on this issue. The thickness by which such a visual effect can be achieved has been about 0.2 μm for the Italian gilded surfaces (Bomford *et al.*, 1990), which is entirely comparable with the thickness of the gold leaf

measured in this study (about 0.34 mm) (Figure 3).

Conclusions

The technological studies presented in this paper showed that the chemical and mineralogical composition of the *lāyachīnī* substrates in Ālī-Qāpū and Chihil-Sutūn palaces is close together which is understandable considering the short time interval between the execution dates of the *lāyachīnī*s of these two monuments (17 years). However, it seems that a period of about forty years after the *lāyachīnī*s of Chihil-Sutūn palace has been long enough to see a change in the proportions of the materials used to create the *lāyachīnī*s of Hasht-Bihisht palace. This paper, moreover, showed that a fine powder of the plaster of Paris, the red iron oxides, and an animal glue have composed the *lāyachīnī*s mixture in the studied monuments. Moreover, according to the crystal morphology of the gypsum content of the *lāyachīnī*s, the setting time of calcium sulfate hemihydrate has not been long. It could be said that in the process of making slurry for producing *lāyachīnī*, calcium sulfate hemihydrate in the combination with anhydrite and red iron oxides were mixed together in order to make a fine powder. Then, this mixture was mixed with the diluted animal glue in water. Afterwards, this slurry has been applied on a rigid and porous ground in several strata in order to make a raised substrate suitable for attaching the gold leaf. The idea of such a technique does not go back further than 15th century in Iran. Although the older prototypes of the *lāyachīnī* substrates could be found in Europe, this article does not aim to attribute the Iranian *lāyachīnī*s to the European raised substrates. This issue could be subject of further studies in the future.

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