Preliminary Study of the Durability of Nano-silica-based Chromatic Reintegration and Fresco Mock-ups with Lapis Lazuli Exposed to Different Natural Environments

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Abstract. *Wall paintings are susceptible to deterioration when exposed to environmental factors (humidity, solar radiation, polluting gases, etc.) that can lead to alteration forms such as the loss of the pictorial layer. Then, chromatic reintegration treatments are usually carried out. Currently, the most recommended technique it is the application of a mixture of the pigment with a mineral binder. In this study, an aqueous colloidal dispersion of nano-sized silica has been used as a binder since it withstands harsh environmental conditions. The commercial pigment lapis lazuli was selected to paint following the fresco technique and it was also mixed with nano-silica to be applied on a lime mortar base as a reintegration. Mock-ups were studied after 6 months of natural exposure in Vigo (NW Spain) and Granada (S Spain). Their characterization was done by means of colour spectrophotometry, X-ray diffraction, Fourier-transform infrared spectroscopy and scanning electron microscopy with energy dispersive X-ray spectroscopy.*

Keywords. Fresco, wall painting, chromatic reintegration, nano-silica, natural exposure

University of Maribor Press

DOI https://doi.org/10.18690/um.4.2023.55
ISBN 978-961-286-783-6

1 Introduction

The main alteration agents that can affect wall painting, especially when they are outdoor-exposed, are generally moisture and soluble salts [1-4], causing detachment of the painted surface (i.e., lacunae) [3-4]. In this context, chromatic reintegrations aim to fill those paint losses. In the case of outdoor exposed wall paintings, the use of a mineral binder such as silicate mineral dispersions, might be a suitable alternative for its water-repellent properties [4-5], which would ensure withstanding strong weather conditions [4]. Aqueous colloidal dispersion of nano-sized silica should be considered due to its apparent inalterability and high resistance to atmospheric deterioration agents [4-7]. This study aims to determine the physical compatibility of a nano-sized silica-based reintegration with a fresco painting made with a commercial lapis lazuli ($3Na_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot 2Na_2S$) and exposed to different natural environments. The reason for the use of lapis lazuli is the common use of this blue pigment in artistic paintings since the 12th century [8] until the end of the 18th century [2].

2 Materials and Methods

2.1 Materials

A set of three paintings mock-ups (ca. 10 cm×15 cm×2 cm) were prepared conformed by two lime mortar layers reproducing the structure of historical wall paintings according to Old Master recipes [8]. Using a calcitic lime in the form of a paste, slaked under water over more than 20 years, coarse (1-2 mm) and fine silica (0,4-0,8 mm) aggregates and marble powder (<0,7 mm), the first layer was carried out with a 1:3 ratio by volume (lime:aggregate), made with coarse and fine silica aggregates, whilst the last painting layer with a 1:2 ratio by volume with fine silica and marble powder as aggregates. In half of the mock-ups, lapis lazuli (LA hereinafter) was applied following the *fresco* (F) technique. Then, mock-ups were left carbonating for one month under laboratory conditions and the other half was painted with a chromatic reintegration (SB) made of an aqueous colloidal dispersion of nano-sized silica commercially known as Nano Estel. This was diluted with demineralised water in a 1:1 ratio and then mixed with the pigment and applied on the dried surface. One of the mock-ups was left at laboratory conditions (18±5ºC at 60±10% RH) as reference. The other two were outdoor exposed for 6 months under 2 different natural environments. On the one hand in Vigo (V), a coastal city in NW Spain, with high humidity, moderate temperatures, marine influence, and low pollution levels. On the other hand, in the inland city of Granada (G) in S Spain, a dry environment, with extreme temperatures depending on the season and highly polluted.

2.2 Methods

A stereomicroscope (SMZ 1000, Nikon) was used to examine the pigments as well as the textural, structural and chromatic features of the paint mock-ups.

The colour of the paint mock-ups was characterized using CIELAB colour space, measuring L* (lightness), a* and b* (colour coordinates), C^*_{ab} (chroma) and h_{ab} (hue) by means of a Minolta

CM-700d spectrophotometer. $C^* =(a^2+b^2)^{1/2}$ and h_{ab}=arctan(b*/a*), where a* indicates the colour position between red (positive values) and green (negative values) and b* between yellow (positive values) and blue (negative values). A total of five measurements were made for each mock-up, one every 40 days.

The mineralogical composition of the raw pigment and the mock-ups was determined using X-ray diffraction (XRD, XPert PRO PANalytical B.V.). Analyses were performed using Cu-Kα radiation, Ni filter, 45 kV voltage, and 40 mA intensity. The exploration range was 3° to 60° 2θ and the goniometer speed was 0.05° 2θ s1.

The chemical composition was obtained by Fourier-transform infrared spectroscopy (FTIR) in diamond crystal attenuated total reflection (ATR) mode, using a Thermo Nicolet 6700 in the infrared spectral region between 400 cm-1 and 4000 cm-1.

The microtexture and elemental composition of the paint mock-ups was studied with scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX), using a FEI Quanta 200 with backscattered electron (BSE) and secondary electron (SE) detectors. Both the surface of samples and their cross sections were studied under SEM after previous carbon coating.

3 Results and Discussion

Stereomicroscopic observations revealed evident differences in colour between fresco mock-up (LA-F, Fig, 1A) and its counterpart chromatic reintegration (LA-SB, Fig 1D) the latter showing more intense colour. After 6 months exposure, in all the fresco mock-ups (LA-F-V, Fig. 1B and LA-F-G, Fig. 1C) whitish surfaces were detected, whilst brown depositions were observed only in the mock-ups exposed in Granada (LA-F-G, Fig. 1C). No clear differences were detected in the reintegration mock-ups exposed to both outdoor environments (LA-SB-V, Fig. 1E and LA-SB-G, Fig. 1F), compared to the reference ones (LA-SB, Fig. 1D)

Regarding the chromatic study by means of spectrophotometry, when the colour variation (ΔE^*_{ab}) is higher than 3.5 CIELAB units, the human eye can perceive the differences in colour [9]. Fresco mock-ups exposed to Vigo's environment encountered major variations (>3,5 CIELAB units) over 6 months than the samples from Granada, especially the fresco mock-up (LA-F-V).

The mineralogical study of the raw pigment by XRD analysis identified different mineral phases of the sodalite group: lazurite (Na3Ca(Al3Si3O12)S) and sodalite (Na8Al6Si6O24Cl2). Moreover, calcite (CaCO3), diopside (CaMgSi2O6), pyrite (FeS2), albite ((Na,Ca)(Si,Al)4O8), muscovite (KAl2Si3AlO10(OH)2) and wollastonite (CaSiO3) were also found. The same mineralogical composition was obtained after outdoor exposure, apart from a slight increase in the calcite peaks, due to the lime mortar substrate of the mock-ups.

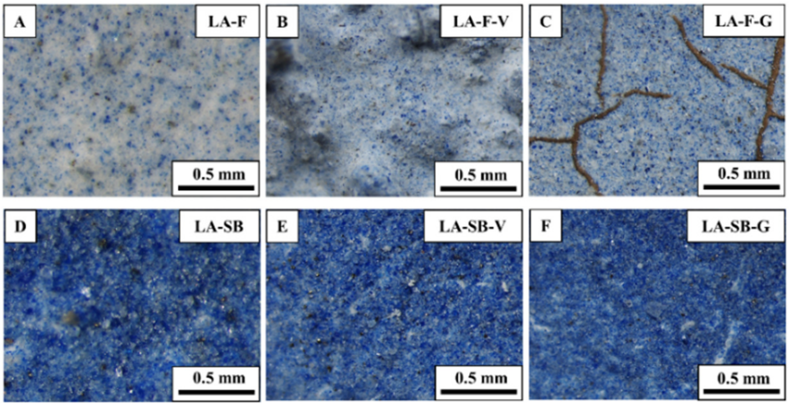

Figure 1. Stereomicrographs of lapis lazuli mock-ups following the fresco technique (A-C) and the nano-sized silica-based reintegration with lapis lazuli (D-F).

FTIR spectra taken on the surface of the exposed samples differ from those obtained on the reference mock-ups (LA-F and LA-SB) only in the wider intensity of the bands at 725, 874 and 1409 cm-1 that correspond to the -CO3 (carbonate) functional group. This can be easily related with the higher amount of calcite obtained also by XRD, especially in the mocks up exposed in Vigo (LA-F-V and LA-SB-V) .LA-SB-V also shows an increase in the bands corresponding to the Si–O stretching (at 425, 663 and 965 cm-1 presumably due to accumulation of silica from the substrate.

The study of the SB mocks up under SEM showed a completely cracked surface before (Fig.3A) and after exposure (Fig.3B). Different particles on the surface of all mock-ups that appear to be neoformations rich in Ca, according to EDS analysis (Fig.3B). On the one hand, in Vigo exposed mock-ups other neoformed phases composed of Na and Cl were also identified (Fig.3B). It could be related to halite (NaCl), a common salt found on heritage materials exposed to marine aerosol [10-12]. On the other hand, the brown deposits observed by stereomicroscopy (Fig.1C) in the fresco mock-ups exposed in Granada were composed of Si, Al, Na, Ca, Mg, P, S, and Fe (Fig. 3C). These elements correspond to those found in airborne particles of Granada according to previous studies [13]. Additionally, in LA-SB-G there was also occasional particles rich in P and calcium Ca (Fig.3D) that can be related to apatite ($Ca_5(PO_4)_3F$), a common impurity found in lapis lazuli pigments [14], probably not eliminated during the purification process of the pigment.

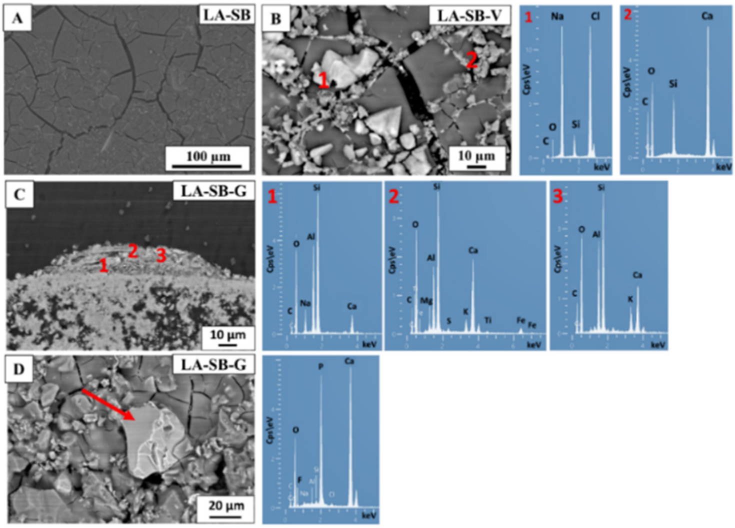

Figure 3. SEM micrograph and EDS spectra in mock-ups from A) reference LA-SB; B) LA-SB-V; C) LA-F-G; and D) LA-SB-G.

4 Conclusions

Comparatively to the fresco mock-ups, their chromatic reintegrations show cracked surfaces and chromatic variations. This might indicate a low compatibility between both techniques. Moreover, paints exposed in Vigo showed more intense alterations and colour changes, especially in fresco mock-ups. Both the frescoes and the chromatic reintegrations show the formation of carbonate deposits on the surface. In addition, in Vigo, sodium chloride salts can also be seen because of the marine aerosol. These formations can induce the slight whitening of the surface. In Granada, brown depositions have been encountered, probably from airborne particles. Nano-silica used as binder for chromatic reintegrations was not as resistant to environmental factors as expected, especially in marine environments.

Acknowledgements

This study was co-funded by Spanish Research Projects PID2020-119838RA-I00, ED431F 2022/07, RYC2020-028902-I.

References

[1] M. Caroselli, S.A. Ruffolo and F. Piqué. “Mortars and plasters—how to manage mortars and plasters conservation”. *Archaeol Anthropol Sci.*, 13(11), pp. 1-20, 2021. DOI: 10.1007/s12520-021-01409-x.

[2] M. Matteini and A. Moles. *Chemistry for restoration. Painting and restoration materials.* Nardini editore, Firenze, Italy, 2016. ISBN-10: 8840444505.

[3] L. Mora, P. Mora and P. Philippot. *La conservazione delle pitture murali.* Compositori, Bologna, Italy, 2002. ISBN-10: 8877942797.

[4] C.G. Venegas and A.L. Barrainkua. *Conservación y restauración de pintura mural.* Editorial Síntesis S.A., Madrid, Spain, 2021. ISBN-10: 8413571391.

[5] V.I. Loganina, S.N. Kislitsyna and Y.B. Mazhitov. “Development of sol-silicate composition for decoration of building walls”. *Case Stud. Constr. Mater.*, 9, e00173, 2018. DOI: 10.1016/j.cscm.2018.e00173.

[6] H. Schmidt, G. Jonschker, S. Goedicke and M. Mennig. “The sol-gel process as a basic technology for nanoparticle-dispersed inorganic-organic composites”. *JSST*, 19(1), pp. 39-51, 2000. DOI: 10.1023/A:1008706003996.

[7] G. Parashar, D. Srivastava and P. Kumar. “Ethyl silicate binders for high performance coatings”. *Prog. Org. Coat.*, 42(1-2), pp. 1-14, 2001. DOI: 10.1016/S0300-9440(01)00128-X.

[8] R. Mayer. *The artist’s handbook of materials and techniques.* Faber and Faber, London, United Kingdom, 1991. ISBN-10: 0571143318.

[9] M. Mokrzycki and M. Tatol. “Colour difference ΔE - A survey*”, Machine Graphic & Vision*, 20, 4, pp. 383-411, 2011.

[10] M. Urosevic, E. Sebastián-Pardo and C. Cardell. “Rough and polished travertine building stone decay evaluated by a marine aerosol ageing test”. *Constr Build Mater.*, 24(8), pp. 1438-1448, 2010. DOI: 10.1016/j.conbuildmat.2010.01.011.

[11] P. Prokos and F. Bala’awi. “Salt weathering in the coastal environment: A thermodynamic approach”, in *Proceedings - 11th International Congress on Deterioration and Conservation of Stone*, Sept. 2008, Torun, Poland, pp. 233-41.

[12] B. Menéndez. “Estimators of the impact of climate change in salt weathering of cultural heritage”. *Geosciences*, 8(11), 401, 2018. DOI: 10.3390/geosciences8110401.

[13] B. Horemans, C. Cardell, L. Bencs, V. Kontozova-Deutsch, K. De Wael and R. Van Grieken. “Evaluation of airborne particles at the Alhambra monument in Granada, Spain”. *Microchem. J.*, 99(2), pp. 429-438, 2011. DOI: 10.1016/j.microc.2011.06.018.