Pigment-size effect on the physico-chemical behavior of azurite-tempera dosimeters upon natural and accelerated photo aging

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Abstract
This paper presents the first comprehensive study on the role played by pigment particle size in pigment-binder interactions, and thus susceptibility to aging of azurite-rabbit glue paint dosimeters upon accelerated UV-aging versus outdoor sunlight exposure. A complementary multi-analytical approach, including spectroscopic and surface analytical techniques, was applied to characterize commercial azurite pigments, as well as blank and aged dosimeters. Results show the crucial role played by azurite particle size on protein-copper complex formation, which governed physico-chemical properties of paints and their aging behavior under different light-aging conditions. On UV-aged dosimeters, finer particles promoted stronger binder structural changes, inducing more severe color changes (DE = 6–17). Azurite size also controlled crack formation which was more severe as pigment grain increased due to greater accumulation of binder in inter-pore spaces. Outdoor exposure caused important binder loss (50–60%) and initial transformation of azurite into malachite. Since analyzed pigment composition and particle size differed from manufacturer data, we recommend their characterization prior to use in conservation works and scientific studies. Based on these results, paints made of coarse azurite particles are preferable since they are less prone to color change. Moreover, a small addition of fine-grained pigments might reduce crack development upon aging.

1. Introduction
The increasing interest in historical painting techniques and artist materials over recent decades has led to numerous publications dealing with the use and characterization of traditional painting materials, i.e., in-/organic pigments and organic binders, utilized prior to the 18th century. Research on these materials is key to: i) unravel artistic and technical issues of historic paintings [1–4], ii) establish dating, authorship or forgery of artworks [5–8], iii) understand aging mechanisms [9–13], and thus, iv) promote preventive conservation strategies and suitable conservation/restoration treatments [14–16].

To investigate damage processes, model paint samples (dosimeters or mock-ups), that mimic the composition and structure of real paintings, are often used to evaluate the effects of temperature (T), relative humidity (RH), ultraviolet/visible (UV/Vis) irradiation, and pollutant gases and particles, through in situ and/or accelerated aging tests [10,17–20]. Sunlight is particularly important in promoting physico-chemical reactions on paintings causing fading or darkening [21–23]. Thus, in countries where the incidence of solar light is significant, such as those of the Mediterranean Basin, light-induced decay on paint artworks is an important issue to take into account.

Light-induced damage to a great variety of dyes, pigments and organic binders has been the topic of many investigations over the last decades [23–25]. Only more recently studies have tackled the paintings aging considering the interaction between pigments and binders [10,13,18,19]. For instance, Odlyha et al. [18] examined the effect of accelerated and natural indoor light aging on azurite-egg-yolk tempera dosimeters. They found that azurite induced binder
2.1. Materials and methods

Analytical techniques were applied. Samples an array of complementary spectroscopic and surface commercial azurite pigments were fully characterized. On all materials for their restoration. Prior to aging tests, the selected prevailing degradation mechanisms and the selection of suitable obtained results will serve as the basis for the determination of and Generalife [1,4,7,14] and the wall paintings in the monuments of Granada, including the known worldwide Alhambra results are not easily applicable to wall paintings and polychrome studies mainly focused on photodegradation of pigments and paints under controlled indoor/museum conditions [17,18] and works are not easily applicable to wall paintings and polychrome artworks located in (semi)-open monuments/buildings exposed to the Mediterranean climate. These are part of many important monuments of Granada, including the known worldwide Alhambra and Generalife [1,4,7,14] and the wall paintings in the Carrera del Darro [30]. Their state of conservation varies greatly and the here obtained results will serve as the basis for the determination of prevailing degradation mechanisms and the selection of suitable materials for their restoration. Prior to aging tests, the selected commercial azurite pigments were fully characterized. On all samples an array of complementary spectroscopic and surface analytical techniques were applied.

2. Materials and methods

2.1. Materials

Azurite (Cu₃(CO₃)₂(OH)₂) was the most widely used blue pigment in European paintings from the 15th to the middle of the 17th century [31]. Traditionally, azurite has been used coarsely ground since it becomes pale and unsuitable as a coloring material when very finely ground [32]. In 1997 Michel Price (MP) developed a method for the separation of ground azurite into different pigment sizes corresponding to diverse hues of blue, from a deep rich blue to a pale sky blue [28]. This method consists of consecutive washings in an egg yolk medium, separating different particle sizes based on Stokes’ law. This treatment also confers to azurite protection against acid reactions in oil media by surrounding pigment particles with a protein coating. In 1998 Kremer Pigments GmbH & Co. KG adopted this method to prepare a new range of azurite pigments, called “azurite MP.” These pigments are available in seven grades (according to their average particle size) from a deep royal blue to a pale sky blue.

In this study we analyzed Kremer azurite pigments with different particle sizes which include various “azurite MP” and the “azurite natural standard” (color index PB3077420) (Table 1). Pearls of rabbit glue (Kremer Pigments GmbH & Co. KG, ref. 63028) were used to prepare proteinaceous-based paint dosimeters. The binder was prepared according to traditional recipes. Eight grams of rabbit glue were soaked in 100 ml of deionized water for 24 h, under periodic stirring. Afterward the mixture was heated below 50 °C in a water bath and stirred to obtain a homogeneous mixture. The rabbit glue was cooled to room T (22 °C) until a gel-like consistency was obtained.

2.2. Paint doseimeters preparation

During the Middle Ages and the Renaissance, pigments were ground into particles of properly uniform size to obtain a smooth spreading paint. Afterward the pigments were mixed with the correct amount of binder to make an easily workable paint. Though there are manuscripts, treatises and books with painting recipes [33–35], in practice the precise amount of binder to be mixed with a pigment varied since it depends on the crystal size attained during the pigment grinding.

Hence, in this work the paint dosimeters were prepared according to traditional procedures, used by medieval painters, considering organoleptic parameters. Each pigment was first mixed with deionized water. Then, droplets of prepared rabbit glue were added until an adequate consistency was reached. It was found adequate when droplets formed at the tip of the brush would not fall off easily. Subsequently, several layers of paint mixture were applied by brush to glass slides (76 x 26 x 1 mm). Care was taken that each layer be completely dry before the next was applied. Then, glass slides were cut with a diamond knife into 15 x 15 x 1 mm pieces to conduct the aging tests. To obtain the pure rabbit glue binder dosimeter, the glue paste was directly applied onto the glass slide.

Paint dosimeters are named adding the letter C (which refers to rabbit glue, cola in Spanish) to the pigments label (see Table 1), to clearly differentiate powder pigments from binary (pigment/binder) paint mixtures.

2.3. UV-accelerated aging test

The artificial aging test was performed during 1000 h in a ventilated chamber at 24 ± 3 °C and 25 ± 10% RH. A tubular UV lamp (TL 40W/12 RS SLV/25, Philips Lighting Holding B.V.) was operated continuously during the test. The lamp emits more than 85% of its energy in the UV-B wavelength range with a peak at ~320 nm. Irradiance level was fixed at 765 W/m². Day light was blocked using aluminum foil.

2.4. Outdoor sunlight exposure test

The paint dosimeters were placed vertically in an exterior eave (protected from direct rainfall) of the Granada Cathedral (South Spain), in the historic center of the city where traffic is restricted. Samples faced SW and were exposed for two years to direct sunlight ~5 h in winter and ~10 h in summer, under urban air conditions. It was estimated that the overall sunlight exposure duration was ~5500 h at an irradiance level of ~1090 W·m⁻² [36]. During the exposure, T reached 40 °C in summer and ~3 °C in winter (www.ugr.es/-velilla/meteo-albayzin/resumen.htm, accessed 7.16). The average maximum T in Granada being ~30–35 °C in summer and ~10–15 °C in winter, with diurnal variations up to 20 °C. The average RH was ~40% in summer and ~75% in winter, with average monthly precipitation ranging from ~5 mm in summer to ~40 mm in winter (www.granada.climatetemps.com, accessed 5.16). Data on average concentrations of atmospheric aerosols during winter and summer 2015 are reported in Table 2. Although Granada is a non-industrialized city, concentrations of NO₂, O₃ and particulate matter with 10 μm average size (PM₁₀) in 2015 frequently exceeded the threshold values set by the EU directive 2008/50/EC. The SO₂ concentration was generally below the established limit. Particulate matter is primarily constituted by soil dust (quartz, calcite, dolomite, phyllosilicates, iron oxides/hydroxide), black carbon, secondary inorganic aerosols, and sea salt [14,37].
2.5. Analytical techniques

The azurite pigments, organic binder, and all paint dosimeters (i.e., blank and aged) were analyzed with the following analytical techniques:

A stereomicroscope (SMZ 1000, Nikon) was used to examine the textural, structural and chromatic features of blank and aged paint dosimeters. Granulometry (Mastersizer 2000LF, Malvern Instruments) was performed to verify the particle size of the azurite pigments in the range 0.02 to 1500 µm using laser diffraction. Samples were dispersed in ethanol. Thermogravimetric analysis (TG) was used to quantify both the egg yolk present in the commercial azurite pigments and the rabbit glue binder added to each azurite to prepare the corresponding paint dosimeter. Analyses were performed on a Shimadzu TGA-50H (Shimadzu Corporation) in flowing air (100 ml/min) at a constant heating rate of 10 °C min⁻¹ (25–950 °C). One analysis per sample was performed. The binder content of paint dosimeters was calculated considering the weight loss of the corresponding azurite pigment and the pure binder in the same temperature range. Using X-ray diffraction (X’Pert PRO PANalytical B.V.), the mineralogical composition of azurite pigments and all paint dosimeters was identified. Analyses were performed using Cu-Kα radiation, Ni filter, 45 kV voltage, 40 mA intensity and spinner. The exploration range was 3° to 60° 2θ and goniometer speed 0.05° 2θ s⁻¹. Identification and semi-quantification (~5%) of minerals were carried out using Xpowder [38].

To analyze the micro-texture and chemical composition of pigments and all paint dosimeters, two high-resolution (Schottky-type field emission) scanning electron microscopes (FESEM) coupled to an energy dispersive X-ray spectrometer (EDX) were used. Samples were mounted on Al stubs with double-sided adhesive C tape. The instruments were: i) an Auriga (Carl Zeiss, Germany) joined to an INCA-200 EDX working at 10⁻⁴ Pa vacuum and 2 kV beam accelerating voltage (secondary electron imaging mode; carbon-coated samples); and ii) a variable pressure FESEM (VP-FESEM, Supra 40Vp Carl Zeiss, Germany) equipped with an Aztec 3 EDX and X-Max 50 mm detector. Working conditions were 40–66 Pa vacuum, 15–20 kV (imaging mode) and 20 kV beam accelerating voltage (samples not carbon coated). High-resolution X-ray maps (1024 x 768 pixels) were obtained from selected areas with 100 frames and a dwell time of 10 ms (2.5 h acquisition) using 3 nA filament current and 20 eV/ch resolution. To determine the nature of the crystalline/amorphous phases present in the dosimeters, phase maps were compiled from elemental distribution maps by applying the Find Phases tool implemented in the Aztec 3 version used in this work. This procedure allowed us to highlight the location, morphology and amount of phases present in the

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Table 1

Characteristics of commercial azurite pigments.

<table>
<thead>
<tr>
<th>Kremer pigment reference</th>
<th>Stereomicroscope image of pigments scale: 0.6 mm</th>
<th>Kremer pigment size</th>
<th>Authors azurite reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Azurite MP extra deep. No. 10203 (intense dark blue)</td>
<td><img src="image1" alt="Image" /></td>
<td>80-100 µm</td>
<td>AZ-EC: azurite extra coarse</td>
</tr>
<tr>
<td>Azurite MP, deep. No 10204 (dark blue)</td>
<td><img src="image2" alt="Image" /></td>
<td>63-80 µm</td>
<td>AZ-C: azurite coarse</td>
</tr>
<tr>
<td>Azurite MP, pale. No 10206 (light blue)</td>
<td><img src="image3" alt="Image" /></td>
<td>38-63 µm</td>
<td>AZ-M: azurite medium</td>
</tr>
<tr>
<td>Azurite MP, sky-blue. No K10207 (light greenish blue)</td>
<td><img src="image4" alt="Image" /></td>
<td>&lt;38 µm</td>
<td>AZ-EF: azurite extra fine</td>
</tr>
<tr>
<td>Azurite standard. No 10200 (deep greenish blue)</td>
<td><img src="image5" alt="Image" /></td>
<td>&lt;120 µm</td>
<td>AZ-ST: azurite standard</td>
</tr>
</tbody>
</table>

Table 2

Average air contamination and particulate matter (PM_{10}) concentration (µg·m⁻³) during winter and summer 2015 in the city center of Granada.

<table>
<thead>
<tr>
<th>Dates</th>
<th>SO₂</th>
<th>NO₂</th>
<th>O₃</th>
<th>PM_{10}</th>
</tr>
</thead>
<tbody>
<tr>
<td>15/1/2015-29/1/2015</td>
<td>15.8 ± 6.1</td>
<td>40.2 ± 21.0</td>
<td>31.6 ± 22.7</td>
<td>22.2 ± 14.3</td>
</tr>
<tr>
<td>22/6/2015-8/7/2015</td>
<td>6.9 ± 7.0</td>
<td>29.9 ± 21.7</td>
<td>82.5 ± 31.1</td>
<td>40.6 ± 20.1</td>
</tr>
</tbody>
</table>

Data from [www.juntadeandalucia.es/medioambiente/site/rediam/menuitem, 1.12.16.](#)
paint dosimeters. Linear crack density (mm\(^{-1}\)) was calculated using 0.1 \times 0.095 mm\(^2\) SEM images according to the following equation: crack length (mm)/image size (mm\(^2\)) = linear crack density (mm\(^{-1}\)).

A portable reflectance spectrophotometer (Minolta CM-700D) was used to measure the chromatic features of the paint dosimeters. Color data were collected in SCI (specular component included) and SCE (specular component excluded) modes from 400 to 700 nm at 10 nm intervals for the standard D65 daylight illuminant (color temperature 6504 K) using 10° observer and an 8 mm measuring aperture. Note that the difference between SCI and SCE measurements was <0.2 units for all color parameters, and only the former are reported in this study. Data were expressed in the CIE L\(^*\)a\(^*\)b\(^*\) color system. In the CIE L\(^*\)a\(^*\)b\(^*\) system, L\(^*\) is luminosity which varies from black with a value of 0 to white with a value of 100; a\(^*\) varies from -a\(^*\) (red) to +a\(^*\) (green) and b\(^*\) ranges from -b\(^*\) (yellow) to +b\(^*\) (blue). In the CIE h\(^\circ\)C\(^\circ\)L\(^\circ\) color system each color is represented by three cylindrical coordinates: hue or tone (h\(^\circ\)) which refers to the dominant wavelength, chroma or saturation (C\(^\circ\)) related to the intensity of color, and L\(^\circ\) which is lightness or luminosity of color. The CMC (2:1) version of the color difference formula (i.e., ΔE = √((ΔL\(^\circ\))^2 + (Δa\(^*\))^2 + (Δb\(^*\))^2)) was used to colorimetrically compare dosimeters [39]. In general terms, these differences will be visually perceptible when the values change by more than three units [40]. Average values are based on a minimum of 5 measurements per samples.

A confocal Raman spectrometer (Jasco NRS-5100) fitted with an Olympus microscope and a Peltier-cooled CCD detector (Andor DU 420 OE) was used to recognize the molecular composition of powder pigments, rabbit glue binder and all the paint dosimeters. Samples were observed using the 5X, 20X and 100X objectives. The video camera was used to identify particular locations in the samples, which were excited with lasers at 532 nm (green, Elforlight G4-30: Nd:YAG) and 785 nm (red, Torsana Starbright). The scattered Raman light was collected in a 180° backscattering geometry by a Charge Coupled Device (CCD) after having passed through a 50 μm entrance slit. Spectra were collected with an average resolution of 2 cm\(^{-1}\) within the wavenumber range of 100–3000 cm\(^{-1}\). To improve the signal/noise ratio and avoid laser-induced degradation of samples, a series of recorded spectra \((n = 6–10)\) were collected from each sample spot and averaged, with exposure times from 20 to 30s for green (100% power, Max Power Density W/cm\(^2\) = 6.637 \text{e-1}), and from 30 to 40s for red laser (10% power, Max Power Density W/cm\(^2\) = 8.400 \text{e-2}). To ensure statistical representativity, a minimum of 5 spots were analyzed in each sample.

Attenuated Total Reflection – Fourier transform infrared spectroscopy (ATR-FTIR) was performed on powder samples of pigments and binder, as well as on blank and aged dosimeters using a Jasco 6200 (JASCO Analytical Instruments, Japan). The dosimeters were pressed against the ATR diamond crystal window and the infrared (IR) spectra were recorded at a 2 cm\(^{-1}\) resolution over 100 scans from 400 to 4000 cm\(^{-1}\). The ATR correction was applied on selected FTIR spectra using Spectra Manager II software. Results showed no peak shifts as compared to uncorrected FTIR spectra. The results reported here are based on uncorrected ATR-FTIR data.

3. Results and discussion
3.1. Stereomicroscope study of paint dosimeters

The stereomicroscope images revealed that all azurite pigments contained impurities, showing colorless and green colored crystals (Fig. 1), identified as quartz (SiO\(_2\)) and malachite (Cu\(_2\)CO\(_3\)OH\(_2\)) using XRD (see section 3.4). Additionally, a few orange-brown/black crystals were observed and recognized as iron oxides/hydroxides (Fig. 1h) with VP-FEMEM-EDX (see section 3.5). In AZ-ST-C only the larger individual azurite particles could be distinguished, whereas the finer grains were completely covered by egg yolk/rabbit glue, added either during the pigment or the paint preparation. Some large circular pockmarks could be observed on the paint surface, as relics of air bubbles.

After the UV-aging test, dosimeters with the coarser pigments (Fig. 1b, e, h) displayed a whitish glaze with a slight yellowish tint on the surface, which was more pronounced in AZ–M–C. Instead AZ–EF-C (Fig. 1k) suffered severe discoloration towards yellow, while a less significant color change took place on AZ–ST-C (Fig. 1n). Here, part of the organic binder was lost, thus a larger amount of the fine grained azurites was now discernible. Furthermore, some surface micro-pitting was observed which at first might seem surprising considering the low RH conditions (i.e., 25 ± 10% RH) during the artificial UV-aging test. However, in this RH range the amount of water absorbed by the glue changes drastically. Karpowicz [41] reported that below 30% RH, the protein molecule surface was covered only by a monomolecular layer of water. In contrast, above this RH the proteins contained more water, reaching 0.3 – 0.5 g of water per 1 g of protein at 30–90% RH. With this in mind, and considering that the paint dosimeters were at times exposed to RH >30%, a significant increase in moisture content of the glue binder could be expected, which facilitated dissolution processes leading to the formation of micro-pitting on the sample surface.

The two-year outdoor exposure caused binder and pigment loss in all paint dosimeters, being more significant in AZ–EF-C and AZ–ST-C (Fig. 1l). AZ–ST-C revealed a very distinct surface appearance compared with the blank dosimeter (Fig. 1o). Individual pigments were no longer covered by egg yolk/rabbit glue binders, thus morphological features of crystals were perfectly seen. The surface also suffered micro-pitting and formation of fine fissures.

3.2. Particle size analysis of powder pigments

Particles in powder pigments are hardly uniform in size. Results revealed a wider particle size range (Fig. 2, Table 3) as compared to manufacturer’s data (see Table 1). However, it should be said that this technique might detect larger particle sizes, due to the aggregation of smaller particles. Indeed, note that stereomicroscope and SEM observation did not show particles >100 μm. Generally, the finer pigments (AZ–EF and AZ–ST) have wider particle size ranges than the coarser pigments (Fig. 2), especially in the case of AZ–ST which has many particles <10 μm, down to ca. 0.2 μm. Our results agree with the finding of Han et al. [27] who noticed the existence of nanometer-sized particles in diverse historical azurite pigment grades; these were more abundant and finer in size in the smaller particle-size azurites and greatly influence their luminosity.

3.3. Thermogravimetric analysis of pigments and dosimeters

Using TG analyses the egg yolk content added to the azurites during the Michel Price method, as well as the rabbit glue binder added to prepare the paint dosimeters were determined. The former was estimated taking into account the weight loss upon heating from 50 to 200 °C, considering the weight loss of pure egg yolk in the same temperature range (Table 4). Note that weight loss data <50 °C were not considered for calculating the egg yolk content because loss is mainly caused by adsorbed water. Results showed that the egg yolk content was highest in AZ–ST (10.5 wt%) compared with the other pigments (ranging from 2 to 3.5 wt%).

The rabbit glue binder content was calculated from the TG weight loss data (50–950 °C) considering the weight loss of the corresponding pigment and pure binder in the same temperature
Fig. 1. Stereomicroscope photographs of azurite-proteinaceous paint dosimeters: (a, d, g, j, m) blank, (b, e, h, k, n) artificial UV-aged, (c, f, i, l, o) outdoor sunlight exposed.
range. It was found that binder content generally increased with decreasing pigment size (Table 4). However, the calculated amount of rabbit glue binder was unexpectedly low in AZ-ST-C (i.e. 8.4 wt%), considering that this dosimeter is made of the finest particles. Nevertheless, it has to be kept in mind that the AZ-ST pigment already contained a high quantity of egg yolk (10.5 wt%), added during its preparation by the manufacturer; hence the AZ-ST-C dosimeter had the highest amount of total organic media (18 wt%).

After the two-year outdoor exposure, paint dosimeters suffered a decrease in organic content of ~50–60%. Note that this technique did not allow determining whether the reduction was primarily due to egg yolk or rabbit glue loss. No relation was observed between organic content decrease and pigment size.

3.4. XRD of pigments and dosimeters

The diffraction patterns of azurite pigments revealed the presence of mineral phases matching the following Joint Committee on Powder Diffraction Standards (JCPDS): azurite (JCPDS card no 701579), malachite (JCPDS card no 760660) and quartz (JCPDS card no 331161), these last two present as impurities. Semi-quantitative (-5%) XRD analyses (Table 5) showed that the azurite content was highest in AZ-ST (90%) and lowest in AZ-EF (70%). Note that XRD analyses of two different batches of AZ-ST are shown in Table 5, displaying different mineralogical composition, which indicates that quality control for this pigment could be improved. In this work only AZ-ST-1 was used.

XRD analyses showed that no mineralogical changes took place upon UV-aging. Bragg peak positions of sunlight exposed samples did not change either; thus evidence for an azurite to malachite transformation was not detected using this technique. However, XRD patterns of the latter revealed an additional peak at ~3.03 Å indicating the presence (~10 wt%) of calcite (CaCO₃, JCPDS card no 050586), likely due to the deposition of particulate matter on the dosimeters’ surface. Note that Ca and Mg carbonates are among the major mineral phases detected in soil dust in Granada [14,37]. Considering the low reactivity and hygroscopicity of calcite, alteration processes are not likely to be accelerated by its presence. However, it will affect the esthetic perception of the painted surface.

3.5. SEM-EDX of paint dosimeters

SEM-EDX analyses of blank azurite dosimeters revealed the presence of mainly copper (Cu) and in minor amounts silicon (Si), aluminum (Al), iron (Fe), barium (Ba), sulfur (S), calcium (Ca), potassium (K) and titanium (Ti). A general spectrum based on five EDX analyses taken from the AZ-C-C dosimeter is shown in Fig. 3a. Using false-color phase mapping (Fig. 3b) these elements were related...
with the following mineral phases: azurite, quartz, aluminum silicates (ascribed to clay minerals as impurities) [42], barite (BaSO₄), calcite (CaCO₃), iron-bearing oxides/hydroxides, and dolomite (CaMg(CO₃)₂). Mapping also provided information on binder distribution.

SEM images of blank dosimeters revealed that the coarser pigments were covered with a thin rabbit glue binder layer which conferred a smooth, rounded aspect to the originally sharp edges of azurite particles (Fig. 4a, d, g). The relatively large pores between individual azurite particles were filled with binder. In the case of dosimeters prepared with finer pigments (AZ-EF-C and AZ-ST-C), discrete pigment particles could rarely be distinguished, thus the paint appeared as a homogeneous mixture of pigments and binder (Fig. 4j, m). Additionally some drying cracks were observed in AZ-EF-C (Fig. 4).

The artificial UV-aging test caused severe first- and second-order polygonal cracking in the glue binder present in dosimeters prepared with the coarser pigments (Fig. 4b, e, h). In contrast, crack formation was very limited in dosimeters containing the finest pigments (Fig. 4k, n). Cracks were quantified using image analysis (Table 6). Calculated data showed that the linear crack density decreased with decreasing particle size. Quantification could not be done in AZ-ST-C since this paint suffered significant superficial binder loss. AZ-EF-C also suffered some binder loss during UV-irradiation. Consequently in both dosimeters discrete azurite particles were distinguished. Moreover, in AZ-ST-C some micro-pitting was observed which has also been detected in stereomicroscopic images (Fig. 1n).

Crack formation can be attributed to RH fluctuations during the UV-aging test. It can, to a large degree, be correlated with the binder distribution in paint dosimeters. The accumulation of larger amounts of glue in pores of dosimeters prepared with coarse pigments resulted in severe cracking upon UV-aging. Finer pigment particles (φ < 25 μm, present in e.g. AZ-ST-C), in contrast, facilitated a more homogeneous pigment and binder distribution, thus reducing crack development caused by volume changes of the binder. Cracking, causing an increase in the paint’s surface area, further facilitates accelerated chemical and physical attack. Moreover, organic and inorganic particle matter can accumulate in these cracks, enhancing or catalyzing degradation.

After two-year outdoor exposure all paint dosimeters (except AZ-ST-C) suffered severe binder loss. Hence pigments appeared completely uncovered by glue, and thus sharp particle edges, as well as empty pores, could now be observed (Fig. 4l). AZ-ST-C also experienced some superficial binder loss, and likewise, larger azurite particles (~10 μm) are now discernible. However, due to the high organic content of this paint, some egg yolk/rabbit glue were still retained and cemented small azurite particles (i.e., < 1 μm), which formed compact aggregates (Fig. 4o). Overall, SEM did not reveal any alteration of azurite pigments; only the organic binder (egg yolk or rabbit glue) seemed to have been affected by the artificial UV-aging or the long-term outdoor exposure.

### 3.6. Chromatic features of paint dosimeters

Spectrophotometry results revealed that L* and C* of blank dosimeters generally increased with decreasing particle size of azurite pigments (Table 7). The exception was AZ-ST-C which showed the lowest values (L* = 37.12 and C* = 15.82), in spite of its particle size. This behavior was attributed to its high organic content (both egg yolk and rabbit glue). Diminishing crystal size also induced dosimeters to turn more greenish, since a* values vary from 2.59 (AZ-EC-C) to −10.13 (AZ-ST-C). Data also showed that AZ-M-C was the bluest sample (b* = −32.45) while AZ-ST-C was the greenest (a* = −10.13). The particularly high a* value of AZ-ST-C is also attributed to the high organic content, particularly due to the egg yolk amount added during its preparation by the manufacturer. Thus AZ-ST-C is very dissimilar in color parameters to the other dosimeters (see Fig. 1).

Color changes were more severe in dosimeters exposed to
1000 h of artificial UV radiation as compared to samples after two-year outdoor exposure (Fig. 1). The former samples experienced $\Delta E \approx 10^{17}$ units, which increased with decreasing pigment particle size. This color change was attributed to deterioration of the organic binders added to the azurites, which caused a substantial decrease in $a^*$ and an increase in $b^*$ (i.e., a shift towards green/yellow). However, AZ-ST-C behaved differently and only suffered $\Delta E = 6$ units. In this paint the yellowish color of the original pigment containing ~10% egg yolk, may have partially

<table>
<thead>
<tr>
<th>Paint dosimeter</th>
<th>Linear crack density</th>
</tr>
</thead>
<tbody>
<tr>
<td>AZ-EC-C-UV</td>
<td>88</td>
</tr>
<tr>
<td>AZ-C-C-UV</td>
<td>68</td>
</tr>
<tr>
<td>AZ-M-C-UV</td>
<td>51</td>
</tr>
<tr>
<td>AZ-EF-C-UV</td>
<td>34</td>
</tr>
<tr>
<td>AZ-ST-C-UV</td>
<td>Not available</td>
</tr>
</tbody>
</table>

Fig. 4. SEM photographs of blank (a, d, g, j, m), UV-aged (b, e, h, k, n) and 2-year outdoor exposed (c, f, l, o) azurite-proteinaceous dosimeters.
The UV-aged AZ-C-C dosimeter, and shows clearly that the Raman spectra of the blank and aged AZ-C-C dosimeters attained in the UV-aged dosimeters. Again, AZ-ST-C behaved with decreasing particle size, mostly in AZ-EF-C and AZ-ST-C and a minor increase in b* (towards yellow). Moreover L* increased with particle size, and was induced by a decrease in a* (towards green) shift towards higher wavenumbers is observed in certain azurite masks the azurite Raman bands, displaying lower intensity. Also, a

Dosimeters L* a* b* C* h* ΔL* Δa* Δb* ΔC* Δh* AZ-C-C 33.11 ± 0.22 2.59 ± 0.21 -28.26 ± 0.28 28.38 ± 0.30 275.23 ± 0.38 AZ-C-C-2Y 33.84 ± 0.19 3.52 ± 0.16 -28.94 ± 0.20 28.92 ± 0.23 276.25 ± 0.23 AZ-M-C 37.28 ± 0.20 2.33 ± 0.05 -32.45 ± 0.22 32.54 ± 0.07 274.10 ± 0.07 AZ-EC-C 42.37 ± 0.19 -5.82 ± 0.05 -29.60 ± 0.12 30.17 ± 0.13 258.89 ± 0.13 AZ-ST-C 37.12 ± 0.03 -10.13 ± 0.01 -12.16 ± 0.09 15.82 ± 0.22 230.20 ± 0.22 AZ-EC-C-UV 33.19 ± 0.48 -2.01 ± 0.37 -19.41 ± 0.72 19.51 ± 0.70 264.06 ± 1.19 0.17 ± 0.51 -4.60 ± 0.36 8.88 ± 0.71 -8.89 ± 0.69 10.02 ± 0.73 AZ-C-C-UV 35.55 ± 0.43 -2.88 ± 0.13 -18.52 ± 0.30 18.75 ± 0.31 261.17 ± 0.37 0.93 ± 0.43 -6.10 ± 0.13 11.03 ± 0.29 -10.99 ± 0.29 12.65 ± 0.25 AZ-M-C-UV 38.38 ± 0.86 -5.04 ± 0.12 -17.91 ± 0.33 18.61 ± 0.29 254.29 ± 0.60 1.09 ± 0.86 -7.36 ± 0.12 14.54 ± 0.33 -13.93 ± 0.29 16.36 ± 0.38 AZ-EC-UV 45.04 ± 0.25 -11.77 ± 0.23 -16.37 ± 0.26 18.04 ± 0.17 229.26 ± 0.92 2.67 ± 0.25 -5.96 ± 0.23 15.93 ± 0.26 -12.12 ± 0.17 17.22 ± 0.30 AZ-ST-UV 37.99 ± 0.49 -11.23 ± 0.31 -6.19 ± 0.48 12.83 ± 0.43 208.85 ± 1.66 0.87 ± 0.49 -1.10 ± 0.31 5.97 ± 0.48 -3.00 ± 0.43 6.15 ± 0.47 AZ-EC-C-2Y 35.70 ± 0.25 0.88 ± 0.07 -25.72 ± 0.29 25.74 ± 0.29 271.96 ± 0.17 2.59 ± 0.25 -1.71 ± 0.07 2.54 ± 0.29 -2.64 ± 0.29 4.03 ± 0.14 AZ-C-C-2Y 36.69 ± 0.20 0.60 ± 0.04 -24.55 ± 0.27 24.56 ± 0.27 271.39 ± 0.09 1.99 ± 0.20 -2.64 ± 0.04 4.99 ± 0.27 -5.16 ± 0.27 5.99 ± 0.18 AZ-M-C-2Y 36.56 ± 0.34 0.15 ± 0.13 -27.33 ± 0.55 27.33 ± 0.55 270.31 ± 0.27 -0.72 ± 0.34 -2.18 ± 0.13 5.12 ± 0.55 -5.21 ± 0.55 5.62 ± 0.59 AZ-EC-2Y 47.70 ± 0.43 -6.22 ± 0.04 -29.12 ± 0.66 29.78 ± 0.62 257.94 ± 0.53 5.33 ± 0.43 -0.40 ± 0.14 0.48 ± 0.06 -0.39 ± 0.02 5.40 ± 0.53 AZ-ST-2Y 47.01 ± 0.40 -10.99 ± 0.32 -11.14 ± 0.51 15.65 ± 0.58 225.39 ± 0.53 9.89 ± 0.40 -0.86 ± 0.32 1.02 ± 0.51 -0.17 ± 0.58 10.08 ± 0.39

 masked the green/yellow color change induced by rabbit glue aging.

The two-year outdoor exposure of dosimeters resulted in \( \Delta E = 4 \)–6 units which could not be correlated with the pigment particle size, and was induced by a decrease in a* (towards green) and a minor increase in b* (towards yellow). Moreover L* increased with decreasing particle size, mostly in AZ-EF-C and AZ-ST-C (values \( \pm \)47); also L* was in most cases slightly higher than that attained in the UV-aged dosimeters. Again, AZ-ST-C behaved differently, experiencing a \( \Delta E = 10 \) units caused by a significant increase in L* which was attributed to the binder/egg yolk loss in the dosimeter’s surface, leaving pigments uncovered. Assuming that color change is mainly caused by binder degradation, the superficial binder loss explains the smaller color change experienced by dosimeters after two-year outdoor exposure, as compared to samples exposed to artificial UV aging where, in general, no important binder loss has been detected.

3.7. Raman analysis

Raman analysis was performed on pigments, binder and dosimeters. Low quality spectra were acquired from pure organic rabbit glue binder with the two laser excitations. Results from azurite-glue dosimeters showed that bands corresponding to this binder – appearing in the region between 2800 and 3000 cm\(^{-1}\) – were only visible in blank dosimeters when spectra were acquired by dosimeters after two-year outdoor exposure, as compared to the green laser, despite the high fluorescence. By contrast, in outdoor aged dosimeters severe binder loss is observed in SEM images, such that uncovered azurite crystals are clearly seen. Thus, the spectra of these dosimeters show the lowest fluorescence and the most intense azurite bands of all dosimeters.

Fig. 5c also reveals that some blue crystals gave spectra where 0.1 cm\(^{-1}\) at 435 cm\(^{-1}\) corresponding to the lattice modes T (CuCO\(_3\); not seen here), and at 1049 and 1097 cm\(^{-1}\) related to the r\(_3\) symmetric stretching modes (of two different CO\(_3\) groups – doubly degenerate mode) [45].

Malachite is a natural impurity present in azurite mineral. Indeed, in this work malachite has been identified with XRD in all pigments (Table 5). Malachite can also be a weathering product of azurite since it is more stable than azurite under atmospheric conditions [46]. That is, azurite is more prone to oxidation processes, and, in the presence of water slowly transforms into malachite. Malachite is a pseudomorph of azurite that holds the same external form as the original azurite crystal, but the unit cells of azurite are gradually replaced by those of malachite. Thus, during this process crystals with intermediate chemical compositions between azurite and malachite can be found, as recognized here.

The Raman spectra acquired from paint dosimeters exposed during two-year to the urban atmosphere of Granada, show a mineral phase intermediate in composition between that of azurite and malachite (Fig. 5c), as also found by Salvadó et al. [47]. We
discount the hypothesis that this intermediate phase was part of the original pigment since it was not found in the blank dosimeters or in the UV-aged ones (Fig. 5). Malachite formation should have been minimal since semi-quantitative XRD analysis (~5%) on two-year aged paints detected no changes compared to the blank dosimeters.

3.8. ATR-FTIR analysis

ATR-FTIR results revealed that the amide I band (carbonyl stretching) and amide II band (N–H bending) of the proteinaceous binder were modified in blank dosimeters. The amide I band at 1627 cm$^{-1}$ shifted to 1640-1645 cm$^{-1}$ when blended with the different azurite grades (Table 8). This band is caused mainly (~80%) by C=O stretching vibrations of the peptide linkages of amino acids [48], and is absent in pure azurite pigments (see AZ-C in Fig. 6). The shift corresponds to a blue shift associated with a frequency increase ($\Delta \nu = 20$ cm$^{-1}$) which indicates increased bond strength of C=O groups (i.e., the bond dissociation strength increases) [49].

The frequency of the amide I band, and thus, the bond strength of C=O groups, is influenced by intra- and intermolecular hydrogen bonding of peptides [50]. When a reduction in hydrogen bonds between N–H and C=O groups of protein chains takes place, the frequency increases subsequently. According to Kong and Yu [48] this shift indicates changes in the secondary structure from β-sheets to random coils. Hence, the decrease in hydrogen bonds in the azurite-glue paints, as compared to pure glue, can be explained by the formation of protein–Cu$^{2+}$ complexes occupying N–H groups of the protein chains, thus reducing sites for hydrogen bonding [19]. Our results agree with the findings of Odlyha et al. [18], who stated that copper catalyzed the oxidation of the egg yolk binder prior to light aging of azurite tempera dosimeters.

FTIR data showed that the amide I band shift was slightly larger in paints prepared with fine grained pigments than with coarser pigments. Although observed differences are small, all pigments followed the same tendency; thus, results suggest that the binder-pigment interaction might have been stronger in the case of fine grained pigments. This seems reasonable considering that smaller pigment particles offer a larger surface area for reaction with amino acids in the glue binder as compared with coarser pigments. On the other hand, the amide II band at 1529 cm$^{-1}$ shifted to 1492-1502 cm$^{-1}$ when blending the binder with the different azurites (Table 8). The observed significant red shift is considered to be a clear indication of the complexation of Cu$^{2+}$ ions with the amide group, a process that reduces the frequency of the bending vibrations of these C–N bonds through the attachment of heavier atoms [51,52].

Upon UV-exposure for 1000 h, the amide I and amide II bands of

<table>
<thead>
<tr>
<th>Dosimeter</th>
<th>Amide I</th>
<th>Amide II</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rabbit Glue</td>
<td>1627</td>
<td>1529</td>
</tr>
<tr>
<td>Rabbit Glue-UV</td>
<td>1628</td>
<td>1531</td>
</tr>
<tr>
<td>Rabbit Glue 2Y</td>
<td>1628</td>
<td>1528</td>
</tr>
<tr>
<td>AZ-EC-C</td>
<td>1640</td>
<td>1498</td>
</tr>
<tr>
<td>AZ-EC-C-UV</td>
<td>1651</td>
<td>1497</td>
</tr>
<tr>
<td>AZ-EC-C-2Y</td>
<td>1653 (vw)</td>
<td>1488</td>
</tr>
<tr>
<td>AZ-C-C</td>
<td>1642</td>
<td>1494</td>
</tr>
<tr>
<td>AZ-C-C-UV</td>
<td>1651</td>
<td>1506</td>
</tr>
<tr>
<td>AZ-C-C-2Y</td>
<td>1653 (vw)</td>
<td>1488</td>
</tr>
<tr>
<td>AZ-M-C</td>
<td>1642</td>
<td>1502</td>
</tr>
<tr>
<td>AZ-M-C-UV</td>
<td>1647</td>
<td>1502</td>
</tr>
<tr>
<td>AZ-M-C-2Y</td>
<td>1656 (vw)</td>
<td>1488</td>
</tr>
<tr>
<td>AZ-EF-C</td>
<td>1645</td>
<td>1492</td>
</tr>
<tr>
<td>AZ-EF-C-UV</td>
<td>1649</td>
<td>1497</td>
</tr>
<tr>
<td>AZ-ST-C</td>
<td>1645</td>
<td>1492</td>
</tr>
<tr>
<td>AZ-ST-C-UV</td>
<td>1651</td>
<td>1488</td>
</tr>
<tr>
<td>AZ-ST-C-2Y</td>
<td>1653 (vw)</td>
<td>1490</td>
</tr>
</tbody>
</table>

vw – very weak.

Fig. 5. Raman spectra (green laser) of blank, UV-aged and sunlight-aged AZ-C-C dosimeters. T – torsion, M – malachite, Az – azurite. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
the pure rabbit glue dosimeters did not suffer any important shift (Table 8). Thus, the spectra of the blank and UV-aged glue samples are quite similar (Fig. 7). However, changes in the intensity ratio of bands at ~1028 and ~1076 cm⁻¹, associated with C=O bonds occurred, indicating a modification of the conformational structure of the rabbit glue binder.

The amide I band appearing in the paint dosimeters suffered a shift to higher frequencies (Table 8, Fig. 6), which indicates a decrease in hydrogen bonding due to the UV irradiation. This suggests that the presence of azurite induced the breaking of hydrogen bonds since the position of the amide I band in pure glue did not change. The shift was more noticeable in paint dosimeters made of larger particle size. Note that the breaking of hydrogen bonds will influence the glue’s adhesive power and elasticity negatively [53]. These results are in agreement with findings by Ghezzi et al. [54], who also detected changes in the glue’s behavior.
upon mixing with azurite pigment. According to these authors, the glue-azurite mixture showed less thermal stability than pure glue, which they attributed to conformational changes. In azurite paint dosimeters the amide I band and the band at ~3300 cm$^{-1}$ corresponding to N–H stretching did not change significantly as compared with the blank paint dosimeters (Fig. 6). This suggests that binder loss was limited in paint dosimeters exposed to 1000 h UV radiation, as observed in SEM images.

The two-year outdoor test caused a significant alteration of the rabbit glue binder in the paint dosimeters, as shown by a drastic decrease or even absence of several bands related to peptide linkage (the amide I band and the band at ~3300 cm$^{-1}$) (Fig. 6). These results agree with the stereomicroscopic and SEM observations (Fig. 4c, f, i, l, o) and TG results, revealing a severe binder loss in outdoor-exposed dosimeters, which could be attributed to dissolution caused by condensation. Nonetheless, the shifts detected in the very low intensity amide I bands in outdoor-aged dosimeters were in most cases similar to those detected in the UV-aged dosimeters (Table 8), even though the light exposure duration and irradiance level were significantly higher during the two-year outdoor exposure.

4. Conclusions

Particle size influenced the binder distribution in azurite tempera dosimeters, which controlled crack formation in paints during accelerated UV-aging. Paints made of coarse pigments were especially prone to crack formation. Thus we conclude that mixing these pigments with a small quantity of fine-grained azurites (i.e., AZ-EF) would be beneficial to avoid crack formation. Finer grains can fill pore spaces between coarse pigments, preventing large accumulations of rabbit glue, and thus reducing binder volume changes caused by RH and/or T variations. However, the amount added must be kept to a minimum in order to preserve the color properties and limit binder-pigment interactions since, as revealed by FTIR data, interactions were stronger in fine-grained azurite paints leading to conformational structural changes of the binder. Changes in the binder structure are most likely responsible for the color variation towards yellow/green of the UV-aged paints, which was more severe as the pigment particle size decreased, since the binder demand increased.

Overall, color changes of paint dosimeters were related to binder degradation. Although color variations perceptible to human eye were found in all light-aged paints, they were lower in outdoor exposed dosimeters due to binder loss exposing unaltered azurite crystals. However, the identified transformation of azurite into malachite in paints exposed outdoors might add to the color change upon long-term exposure, as well as deposition of calcite particles from soil dust.

Experimental results also show the importance of a detailed characterization of painting materials prior to scientific investigations or applications in conservation treatments. Until now little has been published in this respect, although optical, chemical and physical properties might vary significantly with impurities or quality variations among different batches of pigments or binders, which will influence pigment-binder interactions, and thus, the paint aging behavior. These aspects deserve special consideration since they will have important implications in the outcome of aging studies and also affect the durability of conservation treatments of (wall)paintings.

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