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Scientific Examination for the Investigation of the Painting Technique of Contemporary Mural Paintings: "The Angry Christ" by Alfonso Ossorio in Victorias, Negros Occidental, Philippines

Jem Erika Nique[1]*, Emilio Catelli[1], Zohreh Chahardoli[1], Rocco Mazzeo[1]**

[1]*Microchemistry and Microscopy Art Diagnostic Laboratory (M2ADL). Department of Chemistry "G. Ciamician", University of Bologna-Ravenna Campus, via Guaccimanni, 42, 48121, Ravenna, Italy, * jemerika.nique@studio.unibo.it, ** rocco.mazzeo@unibo.it*

***Abstract* – The Last Judgement, known as "The Angry Christ", is a 60-square-meter contemporary mural painting by Alfonso Ossorio (1916-1990) in Victorias, Negros Occidental, Philippines. The artist was reported to use the penetrative binder Ethyl Silicate 40 (ES40) together with an appropriate palette to withstand the harsh tropical conditions, as recommended by paint chemist Ralph Mayer. A combination of non-destructive and micro-destructive techniques was performed to look into the stratigraphy of the mural painting, characterizing the painting palette, confirming the presence and depth of penetration of the ES40 binder, and clarifying the use of the tempera technique as a restoration intervention. The study also revealed the presence of oxalates and metal carboxylates as a result of degradation of organic materials as well as micro-cracks in the paint film possibly caused by the ES40 binder. The final aim of the scientific investigation study was to provide important insights and information on the materials and degradation products for the difficult conservation-restoration interventions on such type of artworks.**

I. INTRODUCTION

The Last Judgement, popularly known as "The Angry Christ", is a 60-square-meter contemporary mural painting by Alfonso Ossorio completed in 1950 at the St. Joseph the Worker Church in Victorias, Negros Occidental, Philippines (Fig. 1). The modernist church is a result of local and international collaboration including works by Czech-American architect Antonin Raymond, Belgian Catholic social artist Adelaide de Bethune, Filipino-American abstract expressionist artist Alfonso Ossorio, together with local artisans such as Arcadio Anore and Benjamin Valenciano [1]. The church was constructed after the World War II to cope with the post-war needs of the people for proper housing and a spot for worship within the sugar factory-mill complex owned by the Ossorio family [2].

Fig. 1. The Last Judgement "The Angry Christ" by Alfonso Ossorio as photographed by a multi-disciplinary team of experts at the St. Joseph the Worker Church.

The materials applied in "The Angry Christ" mural painting were recommended by Ossorio's technical advisor and paint chemist Ralph Mayer. Due to its penetrative properties, Ethyl Silicate 40 (ES40) was suggested by Mayer to be used as a binder, along with an appropriate palette [3] since they are suitable for the Philippines' harsh tropical conditions. ES40 is a low-viscosity liquid polymer containing a mixture of tetraethoxysilane and polyethoxysilanes, and has high silica content of approximately 41% after undergoing complete hydrolysis [4,5]. It is categorized under Organosilane group which are composed of Silicon atoms with attached inorganic and organic functional groups. The condensation through hydrolysis of the inorganic functional group with an inorganic surface creates a stable polymeric siloxane network [6]. Eventually, tempera painting was used by the multidisciplinary team of experts to restore the parts of the mural which were exhibiting chromatic alterations. Unluckily, the tempera paint caused powdering and fading,

and the areas were further treated with technical-grade alcohol [7]. To check the building's integrity, the multi-disciplinary team of experts in the Philippines conducted several tests, including laser scanning to detect any deterioration in the wall painting. Fortunately, no alarming signs of degradation were evident [7].

Artworks such as mural paintings are intricate in terms of materials composition, and due to this reason, they are prone to complex degradations. Degradation phenomena may involve interactions among pigments and binders media as well as the artwork materials and the surrounding environment [8]. To better understand the complexities of these degradations, it is necessary to conduct extensive research using cutting-edge techniques such as the combination of microscopic and spectroscopic analyses that can be both non-destructive and micro-destructive. Non-destructive techniques are typically performed in situ and do not alter the integrity of the artwork surface; however, they have limitations in terms of the provided stratigraphic information. Micro-destructive techniques, on the other hand, can provide information on the stratigraphy, although can cause minimal physical alteration, due to their sampling requirements [9]. These analyses provide information about the raw components, pigment alteration mechanisms such as phase transformations, deterioration status, and oxidation state [9]. Furthermore, these techniques aid in evaluating the appropriate approach for the conservation and restoration of cultural heritage objects.

A. Research objectives

The studies concerning contemporary mural paintings, particularly *The Angry Christ*, are of great significance and interest, since there is a limited information available regarding this subject, and the materials/techniques employed by the artist are remarkably unique. The main objectives of this study include the enhancement of materials investigation through the clarification of the painting technique used by Ossorio, the confirmation of the use of tempera technique as a restoration intervention, and the characterization of possible physical or chemical degradations. The main goal of this study is to understand the stratigraphy of painting by distinguishing the various layers from one another for appropriate materials characterization, including the examination of presence and depth penetration of the ES40 binder.

II. METHODS AND MATERIALS

A. Samples

Prior to the scientific investigation, direct sampling from the mural painting was conducted by a team of multi-disciplinary experts responsible for the conservation and restoration of mural and mosaics at the St. Joseph the Worker Chapel in Victorias, Negros Occidental, Philippines. The choice of sampling areas was beneath the altar top to avoid recognizable differences from the congregation's sight line. A total of nine (9) samples were chosen as subjects for analyses and were extracted with the paint layer and cement support included. After the extraction of samples, re-cementing was done to the drilled areas and were left to cure before paint were overlaid. Non-destructive techniques were undertaken as preliminary steps for the scientific investigation of the samples. These include Stereomicroscopy (SM) for the photo-documentation of samples [10], and micro-X-ray Fluorescence (μ-XRF) for the identification of the samples' elemental composition [9]. By employing these techniques, it was possible to identify areas that would be subjected to further analyses for the stratigraphic characterization of the samples.

The micro-destructive analyses were carried out to obtain a more in-depth overview and the best possible information regarding the materials used by the Artist as well as the degradation products present. The process involved embedding of prepared samples in Potassium Bromide (KBr) pellet and resin, following the method proposed by Mazzeo et al. [11]. After this, Optical Microscopy (OM) was utilized to observe the stratigraphy of the samples under the visible and UV lights. Micro-Attenuated Total Reflection Fourier Transform Infrared Spectroscopy (μ-ATR FT-IR) was then employed for the compositional analysis on each of the layer of the samples in cross-section. Accordingly, Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy (SEM-EDX) was performed in three (3) samples to obtain the chemical information including the elemental composition and distribution within the paint layers.

B. Microscopic analysis

Stereomicroscopy observation was performed with a Leica MZ6 microscope connected with a digital camera Canon© PowerShot A550 and operated by the Zoombrowser EX software.

An optical microscope Olympus BX51 equipped with an Olympus DP70 scanner camera was used to observe and document cross-section samples, previously prepared following the method reported in [11].

C. X-ray fluorescence (μ-XRF)

The Bruker ArtTAX© μ-XRF was used to detect the key elements of the cement support and paint layers. The analysis was performed directly on selected areas of the fragments. The measurements were undertaken using 30 kV, 700 μA and 100 seconds acquisition time as the principal instrumental parameters. To detect light elements, the measurement was conducted using 17 kV, 1100 μA and 100 seconds acquisition time, together with Helium purging.

D. Micro-attenuated total reflection fourier transform infrared spectroscopy (μ-ATR FT-IR)

The ThermoNicolet iN™10MX equipped with an ATR Germanium crystal and an MCT detector was used to acquire the molecular information on each of the layer of the samples cross-section. The ATR spectra were obtained in the range 4000-675 cm^{-1} with 4 cm^{-1} spectral resolution and 64 co-additions per spectrum. The aperture used was 40μm by 40μm. The OMNIC Picta™ software was used

to process the data.

E. Scanning electron microscopy with energy dispersive x-ray spectroscopy (SEM-EDX)

The Zeiss EP EVO 50 scanning electron microscope combined with Oxford Instruments INCA X-act Penta FET® Precision energy-dispersive X-ray detector (SEM-EDX) were used to investigate the samples in cross-section. Backscattered images and elemental maps were collected on three samples (#5-white, #6-brown and #8-blue) previously selected according to their peculiar features showed under optical microscopy. The elemental map composition was obtained using an acceleration voltage of 25kV and 300-1000 secs lifetime.

III. RESULTS AND DISCUSSION

A. Support

The microscopic observation, specifically the optical microscope (OM), reveal a similar preparation layer for all of the samples. The support is made of a whitish matrix with brownish-yellow grains of dimension ranging from a few micrometers to tens of micrometers. Moreover, large transparent crystals >200 micrometers are also visible, sometimes in contact with the paint layers. A representative cross-section describing the above structure is reported in Fig. 2. The µ-XRF elemental composition of the support shows the presence of calcium (Ca), iron (Fe), and silicon (Si) as major elements, and potassium (K) and aluminum (Al) as minor. The molecular analysis undertaken with the µ-ATR FT-IR revealed the presence of calcium carbonate and silicates. Iron, aluminum, and potassium-based compounds, devoid of signals in the infrared region, are due to the corresponding oxides. Particular attention is given to the characterization of the small and large grains. The SEM-EDX reveals that the slight brownish-yellow inclusions mainly comprise of calcium, while the large transparent inclusions are silicon-based crystals. Finally, traces of an organic compound are detected through week CH stretching signals in the infrared region.

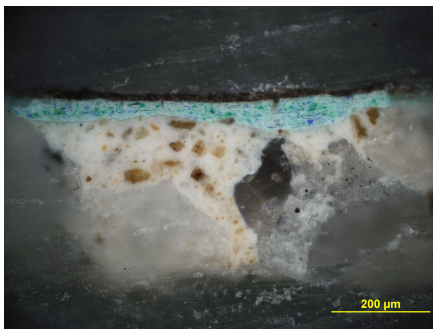

Fig. 2. Cross-section micrograph of sample 6.

B. Pigments in paint layers

All the samples but two show a two-layer paint structure. Table 1 summarizes the list of samples together with the color and morphology observed under optical microscopy of each paint layer.

The combination of µ-XRF and µ-ATR FT-IR analysis, complemented with SEM-EDX investigation, allows us to establish the chemical composition of the pigments used by the artist. Some pigments are applied as a mixture, while others are used pure and applied layer over the other layer. The significant presence of titanium (Ti) in all the paint layers, especially with high signal in the white areas, suggests the use of titanium white (TiO_2). Barium (Ba) is also present overall, pointing to the use of barium sulfate ($BaSO_4$). The distribution of the two elements across the painting stratigraphy are investigated by SEM-EDX among three samples, namely samples 5, 6, and 8. As a result, titanium and barium elemental maps perfectly overlap, suggesting the use of barium sulfate as an aggregate of the white pigment.

The green pigment (sample 1 and 8) is constituted of chromium (Cr), which point to the presence of the pigment chromium oxide. Moreover, the green layer of sample 8 also shows green iron-based particles, indicating the additional use of green earth. Of particular interest is the light green pigment in sample 6 (Fig. 2 and Fig. 3a), an inner layer (layer 2) visible only under the optical microscope, which is clearly the result of a mixture of different blue and green particles in a whitish matrix. The key elements of the layer are barium (Ba), titanium (Ti), chromium (Cr), and cobalt (Co). Barium and titanium belong to the whitish matrix (Fig. 3e, f). Likewise, chromium and cobalt correspond to the green and blue particles, respectively (Fig. 3h and i). The layer is then composed of titanium white and barium sulfate mixed with chromium oxide and smalt. The outer layer of sample 6 contains phosphorus (P) and cobalt (Co), with high overlapping of the two elements in the corresponding elemental maps (Fig. 3g and h). An unusual pigment that contains P and Co together, such as cobalt violet ($Co_3(PO_4)_2$), could be inferred. However, the appearance of the outer layer is not violet-blue but dark brown, raising the question of whether the artist intentionally obtained the color or whether it is a result of a degradation phenomenon [7].

The red pigments, dominant in Ossorio's masterpiece, is found that they were applied singly (sample 5) or mixed with blue particles (samples 2 and 7). In the former case, the pigment is made of cadmium red, identified by cadmium (Cd), sulfur (S), and selenium (Se) elements. In the latter, we suppose an earth-based red pigment (ochre) with cobalt blue-based inclusions due to the simultaneous presence of Fe and Co. Unfortunately, the identification of earth pigments cannot be supported by infrared microscopy as the characteristic silicate-based bands of ochres overlap with those owned by the ethyl silicate binder. In the red-pinkish samples (samples 3 and 9), the presence of Fe, Ti, and Ba suggests the presence of an earth-based red pigment mixed again with titanium white and barium sulfate.

Table 1. Color and morphology of samples' paint layers.

Samples	Paint layer	Color and morphology
1	outer	White
	inner	Green with dark green particles
2	outer	White
	inner	Red with blue particles
3	outer	White
	inner	Red-pinkish
4	outer	Yellow
	inner	Light yellow
5	outer	White
	inner	Red
6	outer	Brown with blue particles
	inner	Greenish with blue and green particles
7	outer	Red with blue particles
8	outer	Blue
	inner	Green with dark green particles
9	outer	Red
	inner 2	Light red
	inner 1	Pinkish

The deep blue pigment in the external layer of sample 8 is assigned to ultramarine blue due to the presence of the elements sodium (Na), sulfur (S) and aluminum (Al), and for the absence of other key elements of blue pigments. Ba and Ti white inclusions are detected by SEM-EDX, confirming again that titanium white and barium sulfate were used together.

Cadmium yellow is the color found in the yellow area of sample 4, although the presence of Fe could suggest the additional use of a yellow ochre.

C. Binders in the paint layers

As stated in the literature, the binder used in the wall painting was the ethyl silicate 40 (ES40). The μ-ATR FT-IR characteristic signal of Si-O-Si stretching at 1000-1100 cm^{-1} of silicates is clearly detected in all the paint layers, thus confirming the use of the above compound. To provide an in-depth distribution of the ES40 binder in the paint layer, we carried out the SEM-EDX elemental analysis on the three selected cross-sections, namely samples 5, 6, and 8.

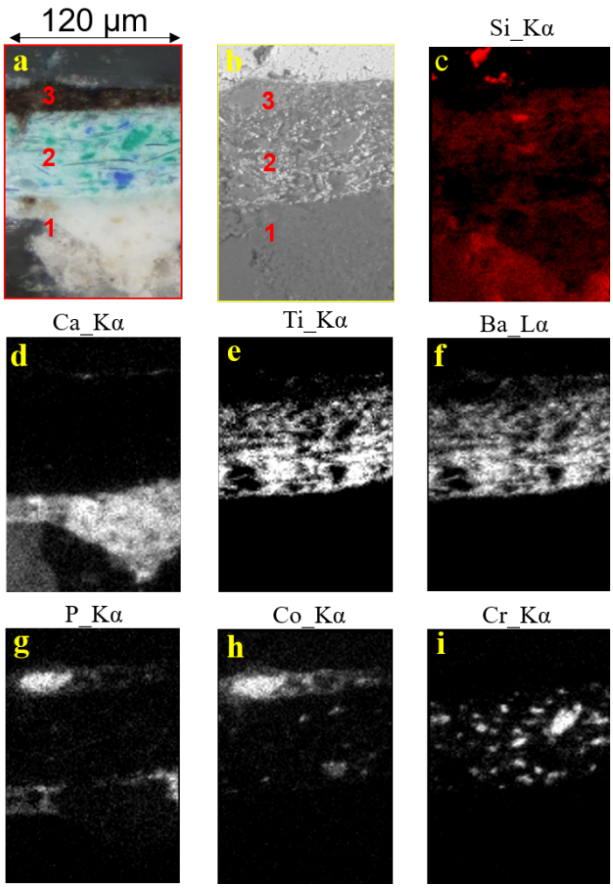

Fig. 3. SEM-EDX Analysis on sample 6: a) Optical microscopy of the investigated area; b) SEM backscattered image c)-i) element distribution maps.

In all the cross-sections, the silicon map clearly shows a high-intensity signal in correspondence with the painting layer, proving the penetration of the compound down to the support (Fig. 3 a,c, Fig. 4a-b, Fig. 4c-d). Unfortunately, due to the presence of silicates in the support, it is not possible to further explore the penetration of the binder below the painting layers.

From historical records, a restoration intervention was carried out using a tempera painting [7]. Micro-ATR FT-IR analysis identified the characteristic infrared bands of organic compounds in the painting layers of samples 1, 3, 7, and 9. Specifically, the ester's C=O stretching (1725-1736 cm^{-1}) and the CH stretching (2800-3000 cm^{-1}) point to a lipidic component. The infrared bands of proteinaceous materials (amide I at 1650 cm^{-1} and amide II at 1550 cm^{-1}) are found with certainty only in sample 9, while the intricate infrared signals in all the other samples could only make assumptions about their presence. The above results show lipidic and proteinaceous-based organic materials present in few samples, possibly due to the restoration intervention [7].

D. Degradation phenomena and state of conservation

The presence of micro-cracks in the painting layers of samples 5 and 8 are observed in optical microscopy. As for sample 5 (Fig. 4a), for example, the crack is evident in the inner layer, while the white outer pigment layer partially filled the void. Similar behavior is observed for the other sample (Fig. 4c). Watermarks and cracks on the plaster due to the moist-dry cycles is a typical situation in tropical countries [8]. However, it is difficult to explain the reasons that produced such cracks in this particular case. We suppose the cause could have been derived from the local environmental conditions that may have affected the ethyl silicate curing process.Conversely, the paint film results well attached to the cement support, suggesting a critical role of ethyl silicate in anchoring the paint layers to the silica-based support.

Lipidic materials are one the principal causes of the deterioration of wall paintings as they trigger reactions with the pigment, forming metal oxalate and carboxylates [12]. As expected, calcium oxalates infrared bands are found in the concomitance of the samples where lipidic materials are detected. Surprisingly, zinc carboxylate is found only in sample 9, where a low but present signal of the element zinc is detected. The presence of such metal soaps is of minimal entity; however, particular attention should be paid in the future to monitoring these compounds for the stability of the paint layers.

All the pigments used are found to be particularly stable with the ES40 binder. Ossorio noticed that all the colors stood very well except for one pigment, Cobalt Violet, which turned into an “ugly gray-brown” [3]. This particular pigment is suggested to be present in sample 6, the outer layer. It is reasonable to think that the color of this area might have been violet when it was painted, but a possible degradation mechanism turned it into gray-brown, as described by the artist. Cobalt violet is a very stable pigment, and no particular degradation products are observed from the above techniques. Therefore, a thorough study using further analytical techniques should be undertaken to unveil the nature of the discoloring of the pigment.

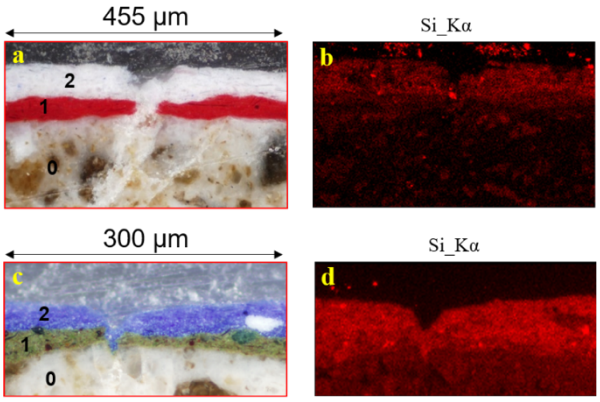

Fig. 4. Cross-sections of samples 5 and 8. a) micrograph of sample 5; b) corresponding Silicon elemental map; c) micrograph of sample 8; and d) corresponding Silicon elemental map.

IV. CONCLUSION

In this study, the previously stated objectives were met as supported by the findings. The clarification of the painting technique used by Ossorio was achieved, including the use of materials recommended by paint chemist Ralph Mayer. From the above results, it can be concluded that Ossorio applied the paint layer directly to the cement, without any priming layer. The SEM-EDX mapping analysis was the most informative, complementary, and conclusive for identifying the pigments since the majority of the components of the mural painting were metal sulfides/oxides.

Lipidic materials and their degradation products, such as calcium oxalates and zinc carboxylates, were observed by the characteristic bands in the µ-ATR FT-IR results. Also, physical deterioration, such as micro-cracks, was found in several samples, but with no critical meaning for the stability of the paint layers, which were well-anchored to the support by the ES40 binder.

The findings of this study were aimed to benefit stakeholders from the Philippines, particularly the multi-disciplinary experts responsible for the mural and mosaics of St. Joseph the Worker Chapel in Victorias, Negros Occidental, Philippines. The information obtained can be utilized to improve their approach on future conservation-restoration campaigns as well as complement their existing scientific documentation. In addition, academics, professionals, and experts in the field can benefit from this study, whether they are interested in understanding the techniques and materials employed by Alfonso Ossorio, the efficiency of the use of ES40 binder, the recommended palette in mural paintings found in tropical countries, or the possible alterations/degradation mechanisms of the materials investigated in this study. Furthermore, future studies can focus on several aspects such as environmental assessments which can be conducted through experimental simulations by creating mock-ups and exposing them to high humidity and temperature, in order to clarify the origin of the micro-cracks found in the samples, which can be due to the painting technique employed or these are initial signs of deterioration. In line with the environmental assessment that can be conducted in the future, the determination of the effect of pollutants and light-induced stability could be added. Lastly, further in-situ molecular analyses can be conducted, including portable FT-IR and micro-Raman analyses, to better understand the situation of the mural painting in situ and monitor the progress of the organic-based deterioration products.

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