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MURALS, STONE, AND ROCK ART

Old interventions and potential new treatments for Maya mural paintings in Tulum (Mexico)

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ABSTRACT

This paper presents preliminary results from research at the Maya archaeological site of Tulum. A long-term project was initiated in 2010 in order to understand the alteration and decay of the buildings and their interior and exterior mural paintings. The specific area of the research presented here comprises both a review of the site's history of interventions and tests aimed at identifying aged polymers and eliminating them in order to recover the readability of the paintings. Tests were also undertaken to assess the feasibility of cleaning the paintings with oil-in-water microemulsions and of stabilizing the buildings and plasters in the aggressive tropical climate of Tulum. The preliminary results of these tests and analyses are presented here.

INTRODUCTION

The eastern coast of the Yucatan Peninsula, in southern Mexico, contains dozens of Maya archaeological sites dating from between 900–1000 and 1517 CE. At many of these sites, there are remains of mural paintings located in ancient ceremonial buildings, as well as the houses of administrative and high-ranking officials. Some of the most representative paintings can be found at the archaeological site of Tulum (Figure 1). These include anthropomorphic and zoomorphic figures, depicted in what has been called the "codex style" (Figure 2). Figures are usually arranged in horizontal sections, representing different levels of the world in Maya ideology.

In Tulum, paintings are found inside and outside distinctive limestone masonry buildings from this period. The construction techniques that were used generated structural problems, some of which were already apparent in Mayan times. This is evidenced by corrections and thick, superimposed layers of plaster in areas where cracks and deformations had occurred.

The mural paintings were made on lime-based plasters and renders. The main colors were two shades of "Maya blue" (a complex mixture of palygorskite clay and indigo) and coal black. A lighter shade of Maya blue and black were both used as background, whereas figures were outlined in black, with details in a darker shade of blue. The painting technique has been described as tempera (Magaloni 2001), although the light-blue base color has been found to be mixed with lime. The organic binder used for the outlines was probably a tree gum. Historical descriptions of Maya techniques dating from the 16th century describe paint binders based on local tree gums and resins (De la Garza et al. 1983). Several monosaccharides have been identified in the paint layers by gas chromatography/mass spectroscopy (GC/MS) (Magaloni 2001), but species or combinations have not been fully identified through analytical techniques.

HISTORICAL BACKGROUND

The ancient walled city of Tulum was built on a cliff along the coast on the Caribbean Sea. Given its location in a semi-tropical climate, it is exposed to constant sea breezes as well as tropical storms and hurricanes. The main deterioration problems of the mural paintings are therefore mostly caused by water infiltration and the associated presence of soluble salts. The

Figure 1
View of Tulum

Figure 2
Mural paintings from Tulum

Figure 3
Alveolar decay

current condition of mural paintings within the site is also in many ways a result of the history of its past conservation interventions. Tulum was abandoned around the time of contact with Europeans in the 16th century CE, presumably due to the major introduction of European diseases, which decimated the local population. The city, described in 1518 as "a city or town so large that Seville would not have appeared bigger or better" (Díaz 1972), was in a ruined state half a century later, as observed during J. de Grijalva's expedition along the coast of the Yucatan peninsula.

Different stages of alteration and decay can be detected when comparing the existing documentation of the mural paintings from different periods. The most ancient evidence dates back to the first drawings and description of the site made by explorers Stephens and Catherwood between 1841 and 1842 (Stephens 1962). During the second half of the 19th century, there were no explorations of the site. More systematical documentation was only carried out much later, by the Carnegie Institute of Washington, between 1916 and 1922, under the direction of S.K. Lothrop (Lothrop 1924). During this expedition, the first plan of the site was drawn. Lothrop's team realized the first photographs of the paintings, as well as tracings and sketches. At the time of these expeditions, the mural paintings seem to have been in good condition, and visible enough to allow direct tracings on most of them. This careful documentation allowed drawn reconstructions of various mural paintings in Tulum.

INITIAL TREATMENTS

The first documented interventions on the mural paintings, limited to the most significant ones, were carried out by the Mexican Southeastern Scientific Expedition, led by painter and archaeologist M.A. Fernández between 1938 and 1940 (Fernández 1941, 1945a, 1945b; Fernández et al. 1945), who undertook major structural interventions on the main mural paintings of Tulum as well as on the buildings. The treatments on the paintings were quite aggressive and were undertaken with tools and materials that were locally available. To remove calcium carbonate covering the mural paintings, Fernández used either caustic soda diluted in water, or muriatic acid. He also used this acid to remove "remains of a deteriorated varnish" that he believed had been applied by the Carnegie Institution Expedition in 1927. However, no records of the application of any varnish were found in the Carnegie records. Fernández finished his interventions by applying several coats of synthetic materials as varnish, with the intent of isolating and protecting the paintings from exposure to the environment. These synthetic materials included Dulux, a trade name assigned to automotive coatings developed by the DuPont Company in the 1920–30s, and essentially composed of nitrocellulose-based pyroxylin lacquers and alkyd resin enamel.

Fernández (1941) took great time and care in all of the conservation treatments and was convinced these would protect the paintings for a long time, especially because he had also stabilized the buildings. He did what was common practice at the time, and, most importantly, he published the results of his interventions.

The next reported conservation treatments in Tulum were in 1975 (Peralta 1975). These included treatments for the consolidation of the plasters with calcium caseinate mixed with marble powder. In some areas, the paintings were also treated with Paraloid B-72 (3% in xylene), applied over the earlier coatings. Fillings were made with lime mortars mixed with Primal AC33 (10%).

In 1982, the mural paintings were treated with Paraloid B-72 (3% in xylene) and Primal AC33 in water (1:1) (Tapia 1994).

Since 1990, the use of synthetic products on the mural paintings has stopped. However, lime-based fillers, including 5% white cement, were still used in 1990 and 1991 (Cedillo et al. 1990, 1991). Since 1994, all interventions have been carried out exclusively with lime-based products.

CHANGING THE PERSPECTIVE IN TREATMENTS: LOOKING FOR COMPATIBILITY AND RE-TREATABILITY

For the past decades, lime-based products have been used in an attempt to preserve the most representative archaeological mural paintings in Mexico. Although changes in approaches and treatments have not been linear, there has been a conscious effort to undertake research in order to better understand traditional uses of lime.

The often disastrous effects of synthetic materials prompted this review of conservation approaches. Aged synthetic polymer films, sometimes combined with calcium carbonate concretions, have resulted in thick impermeable layers that produce a drastic alteration in the painted surfaces by hindering water movement in masonry. Soluble salts from many sources, including the previous use of Portland and white cement mortars visible in building conservation treatments, and the accumulation of moisture behind the impermeable layers, create detachments, loss of cohesion, or cryptoflorescences in the paint layer and underlying plasters. Moreover, one of the main consequences of polymer degradation is a loss of solubility over time that often makes their removal very difficult, especially when several synthetic materials are overlaid. In the case of Dulux, it was highly insoluble from the outset. These effects have progressively led conservators to limit treatment materials to lime-based products, which are more compatible with the original materials.

In Tulum, these types of decay are aggravated due to the site's location, its climatic conditions, and the deficiency of the built structures that were abandoned and have fallen into a ruined state. The approach used by archaeologists for many years was to stabilize these buildings with Portland cement mortars, but the unfavorable properties of this material (brittleness, high strength, and high thermal expansion coefficient, among others) have not stabilized the buildings, which continue to reveal cracks and fractures on the walls, lintels, and vaults. The paintings are therefore continually exposed to abundant rain infiltration during wet seasons, and to dramatic evaporation during dry seasons.

All of these phenomena, possibly linked to other causes such as composition, techniques, and aging of the materials, have created a series of alteration and decay effects, not all of which are yet fully understood. A very specific form of decay is occurring in Tulum, which is not found as extensively at surrounding sites. It has been described as alveolar decay or Liesegang patterns (Rodriguez-Navarro et al. 2002) and includes the preferential decay of areas of the lime-based plaster, following concentric shapes or lines, in which some lines seem to be case hardened, while the adjacent lines are decayed (Figure 3). In other areas around these losses, the plasters are extremely hard. Analyses and characterization of alveolar decay on mortars and renders are still underway.

The additional complexity at Tulum is the long history of conservation treatments. The mural paintings are extremely altered, with areas that have been attacked by salt efflorescence and cryptoflorescence. In other areas, superimposed layers of calcium carbonate concretions that have encapsulated the various synthetic polymers used in the past have hardened the surface. The aged polymers have also altered the surface colors, with stains varying from white to yellowish to dark gray.

Considering this context, the main question is whether the paintings can be stabilized and cleaned in order to improve their visibility.

NEW APPROACHES TO DECIPHERING AND REVERSING THE EFFECTS OF ANCIENT TREATMENTS

In 2010, an interdisciplinary conservation project entitled East Coast Mural Painting Conservation and Research Project was launched by the National Coordination of Conservation in Mexico (CNCPC-INAH), in order to try and find sustainable conservation solutions for the mural paintings located at nine archaeological sites, including Tulum. One important objective was to retrace the history of interventions at the sites. Data gathered from various libraries and archives was fundamental to understanding the history and evolution of the site. That information was then compared with analytical results from mural painting samples to identify remains of past intervention treatments on the mural paintings and their alteration and decay mechanisms. The laboratory analyses have been part of ongoing PhD research by Y. Jáidar, at the Department of Chemistry and the Research Center for Colloids and Nanoscience (CSGI) at the University of Florence.

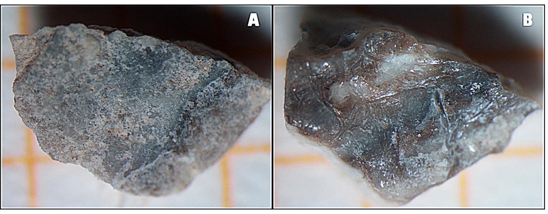
The aim was to evaluate solutions to address some alteration effects and choose the best conservation approaches for the mural paintings. For this specific purpose, several experiments for the removal of synthetic polymers were carried out by using methodologies developed at the CSGI-University of Florence based on nanotechnology (Baglioni and Chelazzi 2013). Specific nanostructured cleaning systems were tested. These systems allow a more controlled removal operation as they act selectively on the polymers, depending on their chemical nature. Aqueous nanostructured systems, such as micelles and microemulsions, have been found to be an effective alternative with respect to traditional organic solvents (Giorgi et al. 2010). In these systems, the volatile organic content is reduced to a few percent, making them safer for users. Preliminary results from the use of these systems, developed within the EU-funded NANOFORART (Nanomaterials for the Conservation and Preservation of Movable and Immovable Artworks) project, are presented here.

The identification of the polymers was carried out by means of Fourier transform infrared (FTIR) spectroscopy. In Tulum, the presence of different layers of aged polymers and the high amount of salts made the characterization of each component extremely difficult. Under an optical microscope, the samples showed a high percentage of salt crystallization on the surface (sulfates, oxalates, and nitrates were identified), and in some areas hard concretions were observed. Additionally, during initial FTIR spectroscopy analysis, salts such as carbonates and gypsum caused an overlap of the absorption bands of the polymer, making identification more complex. A preliminary test to remove the salts mechanically made it possible to observe the polymer film on the sample surface (Figure 4).

Therefore, a specific method of sample preparation based on an extraction and deposition/evaporation sequence was designed to extract the synthetic polymer from the inorganic elements (Domenech-Carbo et al. 2001). The carbonatic fraction was removed with a hydrochloric acid solution (HCl). Then, the residue was mixed with 1 mL chloroform for 48 hours in order to extract the hydrophobic organic components. The remaining component, after solvent evaporation, was deposited on a mortar, to prepare a KBr pellet required for FTIR spectroscopy analysis.

FTIR spectroscopy in transmission mode was used for the analysis. The resulting spectra were compared with references of alkyd resins and cellulose nitrates, resulting in numerous similarities (Figure 5, Table 1).

The characteristic IR absorption bands of cellulose nitrate are reported in Table 1. The intense band at 1630 cm^{-1} can be associated with N–O stretching in cellulose nitrate (e.g., Dulux) (Derrick et al. 1999). After extraction in chloroform, some small peaks associated with alkyd resins were detected. The C=O stretching at 1730 cm^{-1} was evidenced as a shoulder in the 1630 cm^{-1} band; bands at 2959, 2920, and 2851 cm^{-1} were observed together with the $\partial_{\text{in-plane}}$ C–H bands (1470, 1383 cm^{-1}). These peaks confirmed the presence of the alkyd resin used in past conservation treatments.



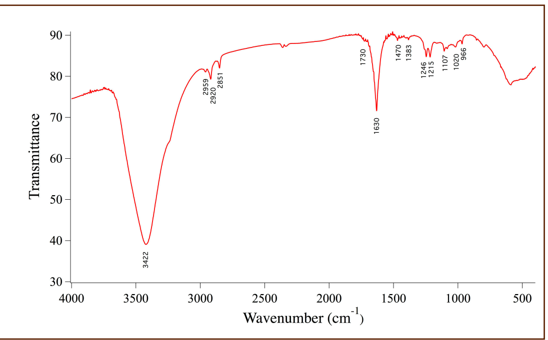


Figure 4
Sample before (A) and after (B) mechanical cleaning of salts, with visible polymer on the sample surface

Figure 5
Spectrum of extraction after removal of calcium carbonate from the sample

IN-SITU CLEANING TEST: MICROEMULSIONS FOR CLEANING

Cleaning tests performed in situ are the initial step in assessing any proposed system. Intervening in real situations, with aged polymers, dirt, and salts, in hostile climatic conditions and involving other factors, shows the real outcome. Cleaning tests were performed using the traditional compress method in one mural painting. The application time was two hours, at the end of which the swollen polymer was gently removed with cotton swabs. Surfactant residues were then rinsed with deionized water.

Screening tests were carried out using some organic solvents as well as several cleaning systems based on oil-in-water microemulsions (Table 2). Microemulsions are thermodynamically stable systems, where the "oil" phase, constituted by one or more organic solvents, is confined to nanosized droplets, formed from the aggregation of surfactants (and often co-surfactants) at the interface of the water and "oil" phase. These droplets possess a very large exchange surface area and show a very high detergency capability because of their structure. The confinement of the "oil" also minimizes the environmental impact of the solvents used.

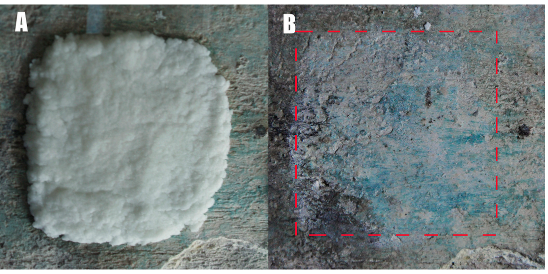
Table 1
Characteristic IR absorption bands of cellulose nitrate

3600–3200 cm^{-1}	O-H stretching band
3100–2800 cm^{-1}	C-H stretching bands
1660–1625 cm^{-1}	N-O stretching band
1285–1270 cm^{-1}	N-O stretching band
1480–1300 cm^{-1}	C-H bending bands
1300–900 cm^{-1}	C-O bending bands
890–800 cm^{-1}	N-O bending band

Table 2

Systems used for the tests (DDAO: surfactant, dodecyldimethylamine oxide; Brij: surfactant, polyethylene glycol dodecyl ether; SDS: surfactant, sodium dodecylsulfate; 1-PeOH, 1-pentanol; DC, diethylcarbonate; XYL, xylene; DN, nitro-diluent; PC, propylene carbonate; EA, ethyl acetate)

System 1: DDAO-DC	H_2O - 90%, DDAO - 5%, DC - 5%
System 2: XYL/MEK	H_2O - 89.8%, Brij 30 - 2.25%, SDS - 2.25%, MEK - 3.8%, XYL - 1.9%
System 3: XYL/DN	H_2O - 86.2%, SDS - 3.9%, 1-PeOH - 6.5%, XYL - 1.8%, DN - 1.6%
System 4: EAPC	H_2O - 73.3 %, SDS - 3.7%, 1-PeOH - 7%, PC - 8%, EA - 8%



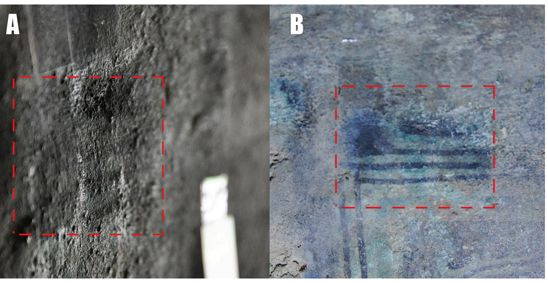


Figure 6

Cleaning tests performed with the DDAO-DC microemulsion on the mural paintings of Tulum: (A) compresses imbibed with the cleaning system; (B) aspect after the cleaning test. The cleaned area is visible, evidently clearer than the surrounding areas

Figure 7

(A) Cleaning tests performed with systems 1 (DDAO-DC) and 3 (XYL/DN) after salt removal with citric acid. (B) The cleaned area is visible; the decorated surface was more easily visible than the surrounding areas

The tests performed provided encouraging results, as the treated area was visibly clearer than the adjacent discolored polymeric coating zones (Figure 6). However, tests also revealed the high dishomogeneity of the paintings. In fact, the same system did not work on all the areas in the same way.

The poor results may also be due to the combination of other factors, including the accumulation of various aged polymers and the high presence of salts on the surface. A test was made to first remove the salt concretions from the surface by applying citric acid compresses for one hour and washing with deionized water and cotton swabs (Figure 7).

The in-situ tests showed that salt removal from the surface should be considered a first step for any future cleaning treatment. This will then allow the removal of the polymer on the mural painting surface with the systems. The most effective of these were system 1 (DDAO-DC) and system 3 (XYL/DN).

FINAL CONSIDERATIONS

Analyzing and understanding past conservation treatments is essential for understanding the problems faced in Tulum. Numerous positive outcomes have resulted from past treatments, but there are also long-term negative effects, including flaking, loss of cohesion, and reduced visibility of the paintings, which are now evident, and must be reversed in order to stabilize the mural paintings and enhance their aesthetic and symbolic values.

The ongoing project at Tulum has already provided new evidence to understand some of the most important causes of deterioration, including both structural problems in the buildings and deterioration effects on the paint layer surface. The research results presented here allowed a better understanding of the complex situation at the surface of the paintings, with mixtures of synthetic polymers, salt deposits, and dust, and hence of the conservation approaches to be undertaken. Preliminary results using a sequence of microemulsion-based cleaning systems specific to different classes of polymers offer the possibility to retrieve a better legibility of the mural paintings.

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