Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 159 (2016) 117–122

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

# Investigation on the hazing of a Brazilian contemporary painting

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ARTICLE INFO

*Article history:*
Received 20 March 2015
Received in revised form 20 January 2016
Accepted 23 January 2016
Available online 25 January 2016

*Keywords:*
Efflorescence
Blooming
Raman
Preventive conservation
Emmanuel Nassar

ABSTRACT

A whitish crystalline-like coating was observed on the surface of the painting "Incêndio", 1990, produced by Emmanuel Nassar and awarded at the 6th Biennial of Cuenca. This work belongs to the Contemporary Art Museum of the University of São Paulo (MAC-USP) and such coating modified the artwork characteristics, causing an unpleasant effect and compromising its exhibition.
The choice of the proper conservation and restoration strategies involves the understanding of the degradation process, demanding the identification of the chemical compounds formed on the painting surface, as well as of the other components in the painting.
The results here obtained from Raman and optical microscopies, FTIR–ATR, SEM–EDS and GC–MS, revealed that the efflorescence chemical composition is almost only palmitic acid, with minor contents of stearic acid and their methyl esters, and that the paints are composed by chrome yellow, amorphous carbon and toluidine red pigment; an aluminum silicate filler in the black paint applied on the aluminum ground was also detected. Hierarchical Cluster Analyses (HCA) of the Raman spectra also revealed that the concentration of the efflorescence minor components depends on the paint composition.
It was suggested, therefore, that the degradation process resulted from segregation and migration of mainly palmitic acid from the dried paints. Restoration methodologies used in similar cases, as well as factors that contribute to this process, were discussed.



## 1. Introduction

Artworks, like any other material, undergo reactions when interacting with the environment or microenvironment, leading to their degradation [1–6] and causing loss of historical, artistic and cultural values. These reactions can also occur among the artwork chemical compounds, not necessarily involving chemical species present in the environment, such as $O_2$ or pollutants. In anyone of these cases the reactions can be accelerated or inhibited by the presence or absence of, for example, metallic ions or free radicals and/or by temperature, luminosity and relative humidity [7–9].

Considering that cultural heritage has frequently economic and cultural inestimable values, its preservation is of vital importance. To preserve or restore an artwork, or to propose methodologies for this purpose, the understanding of its chemical behavior is necessary and, therefore, the characterization of both artwork [10] and environment [11–13] as well as the knowledge of the chemical and physical degradation processes [1–9] are essential. It is also important to emphasize that it is often during the investigations/characterization of degraded artworks that specific issues arise, making necessary the use of laboratory simulations [1,4,6–8,14–15].

When it comes to conservation and restoration, not only antique artworks but also modern and contemporary artistic objects need to be preserved and restored. Because modern works of art commonly present a wide variety of materials in their composition, they constitute highly complex chemical systems, especially when considering factors like volatiles release during the artwork aging and the possible synergic effects associated with its degradation. Furthermore, even considering the absence of synergistic effects, it is necessary to take into account that each material that constitute the object will present different environmental requirements to be conserved and, as mentioned by Thomas J. S. Learner, "The number of materials that artists have used over the last seventy-five years must be little short of infinite, and for each of those different materials, there is only, at best, limited – and, more usually, nonexistent – knowledge of the ways in which they might alter with age, respond to different environmental conditions, or react to any number of potential conservation treatments" [16].

The Brazilian artist Emmanuel da Cunha Nassar, or Emmanuel Nassar, painter and designer, started his carrier in the 1980's working with acrylic paints on canvas, but since the end of the 80's decade his work became more erudite, incorporating other materials, like brass, wood and bottles. The production appropriated by the artist resulted from materials or signs of a cultural tradition, from the coexistence of

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http://dx.doi.org/10.1016/j.saa.2016.01.035
1386-1425/

several fields and, sometimes, from antagonism, in a way that his works usually refer to something untranslatable to one or another cultural background [17].

Recently, one of Nassar's painting ("Incêndio", 1990, awarded at the 6th Biennial of Cuenca in 1999, Ecuador) belonging to the MAC-USP, developed a coating that completely covered its surface. The whitish coating presented a crystalline-like aspect, which modified the artwork aesthetically and compromised its exhibition. The degraded painting is shown in Fig. 1a and a detail of the affected surface, showing a cleaned area, is shown in Fig. 1b.

Tests performed by the Museum staff showed that even after removal of the coating it rises back again, bringing challenges to the development of methodologies for its conservation and restoration.

Therefore, considering that the choice of the proper conservation and restoration strategies involves the understanding of the degradation process, what demands the identification of the chemical compounds formed on the painting surface, as well as of other components of the painting, this work aimed at investigating the degradation of the painting "Incêndio" through the characterization of the painting components and of the whitish coating formed on its surface. To meet these goals, Raman microscopy, Fourier transform infrared spectroscopy coupled with an attenuated total reflection accessory (FTIR–ATR), gas chromatography coupled with mass spectrometry (GC–MS), scanning electron microscopy coupled with energy dispersive spectrometry (SEM–EDS) and stereomicroscopy were used. A discussion about the observed degradation process and current conservation and restoration methodologies used in similar cases are also presented.

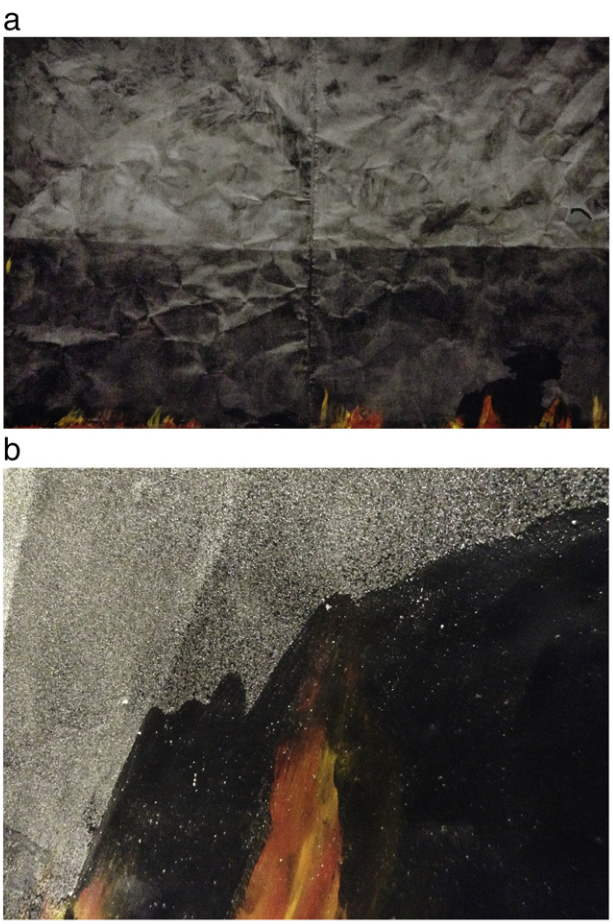


**Fig. 1.** Painting "Incêndio", by Emmanuel Nassar, 1990, produced with synthetic enamel on metal (130 × 200 cm), belonging to MAC-USP and awarded at the 6th Biennial of Cuenca in 1999, Ecuador. Fig.1a shows the whole painting covered by a whitish coating and Fig.1b shows a detail of the painting, with a cleaned area.

## 2. Experimental

### 2.1. Material and methods

The investigated artwork ("Incêndio", 1990, Fig.1) is a 130 × 200 cm painting and was produced using synthetic enamel on metal by the Brazilian artist Emmanuel Nassar. No further details on the paints used are available.

Microsamples (*ca.* 0.5 mm) of the efflorescence material were removed with a scalpel blade from black, red and yellow colored regions and stored in Eppendorf tubes. All the samples were collected by the Museum staff and, in order to obtain representative results, 3 microsamples were collected from each color, resulting in a total of 9 microsamples.

Raman, FTIR–ATR, SEM–EDS and GC–MS were used to characterize the efflorescence, which was initially inspected using a stereomicroscope. Therefore, three different methodologies were applied: non-invasive and non-destructive (Raman microscopy and stereomicroscopic analyses), invasive but non-destructive (FTIR–ATR and SEM–EDS) and invasive and destructive (GC–MS). For the GC–MS analysis, a microsample removed from a black region of the painting was dissolved in a small volume of dichloromethane/methanol mixture (2:1, *v*/*v*); such procedure is similar to other previously used for the extraction of archeological pastes [18] and for the separation of binder/metal oxides mixtures in aging studies [7]. SEM–EDS analyses were conducted in an efflorescence microsample collected from a black region and Raman and FTIR–ATR analyses were conducted for all the 9 microsamples. For SEM–EDS, the efflorescence microsample was supported on a carbon tape. Raman spectra of the efflorescence material were also investigated by hierarchical cluster analysis (HCA), to check possible differences in chemical composition among the samples collected from distinct regions of the painting.

In order to characterize the artwork pigments, Raman spectra were obtained directly from untreated microsamples (also collected with a scalpel blade), without any previous manipulation.

The filler was characterized by SEM–EDS, under the investigation of cross sections of microsamples containing black, red and yellow paints. The cross sections were prepared using scalpel blades and mounted on copper tape.

The metallic screen on which the paints were applied was characterized by SEM–EDS, also investigating a microsample removed with a scalpel blade.

Palmitic and stearic acids (Sigma Aldrich, ≥99% and ≥98.5%, respectively) were used as spectroscopic standards in the samples characterization.

### 2.2. Equipments

Raman spectra (*ca.* five spectra for each microsample) were obtained with a Renishaw inVia Reflex fitted with a Peltier cooled CCD camera (Renishaw, 600 × 400 pixels) and coupled to a Leica Microscope (DM2500 M). The spectra were produced using a 785 nm laser line (diode laser, Renishaw) which was focused onto the samples by a ×50 Leica objective (NA 0.75), or by a ×20 Leica objective (NA 0.40); the laser power was kept in values that avoided samples degradation (between 0.06 mW and 12.0 mW). In all the cases, a visual inspection of the samples after the analysis was performed to ensure that the sample was not affected by the laser illumination.

FTIR–ATR spectra (4 $cm^{-1}$ resolution) were obtained using a Bruker Alpha equipment (KBr optics and DTGS detector) coupled to an ATR accessory (Platinum, diamond crystal, single bounce).

GC–MS analysis was conducted using a Shimadzu 14B/QP5050A equipment with quadrupole analyzer. A BPX5 non polar column (30 m long and 0.25 mm internal diameter) was used and the temperature program started at 60 °C and reached 280 °C with a heating rate of 8 °C/min. Total elution time was 38 min (27.5 min for sample elution