MATURAL CHARACTERIZATION OF EXUDATES FROM BRAZILIAN CONTEMPORARY OIL PAINTING BY FTIR, PY-GC/MS AND SEM-EDS

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ABSTRACT
Contemporary art has employed almost every single synthetic material created by man. Nonetheless, the appeal of oil paint is still present at most public and private collections. Oil paint manufacture has evolved over time along with its formulation and conservation concerns. A reported problem is the formation of exudates on contemporary oil paintings. This work aims to characterize exudates from the Brazilian oil painting “Três pessoas” (1999), by Marina Saleme. Characterization was carried out by Fourier transform infrared spectroscopy, pyrolysis coupled to gas chromatography and mass spectrometry and scanning electron microscopy coupled to energy dispersive x-ray fluorescence spectrometry. Results indicate that exudates are formed by the oxidation of linseed oil and formation of dicarboxylic acids. This process is aided by the formation of zinc stearate in the paint film.

INTRODUCTION
Contemporary art embodies a multitude of materials, such as polymers (polystyrene, polyvinyl acetate), metal alloys, electronic devices (VHS, cassettes, Betamax) and acrylic paints (even fluorescent ones, more recently). Nevertheless, oil paint is still in use. A survey at British Tate Museum showed that 70% of all the twentieth century painting collection is composed of oil (P. Smithen, 2005). Although stability and optical parameters have improved, some problems have surfaced. Several paintings, that now arrive at the studios of restorers for the first time, show efflorescence or exudate formation, that is, material resinous drops which are expelled from the paint layer. The exudate formation in contemporary oil paintings is a worldwide problem, as reported in works from Jean-Paul Riopelle (M. Corbeil et al., 2004), Erik Oldenhof (S. Bayliss et al., 2016) and Mark Rothko (C. Mancusi-Ungaro, 1990). The pioneering works of MOLART and De Mayerno Dutch groups first reported this issue (P. Noble, 2019).

This phenomenon interests not only conservators and museologists, but also gallery owners for the economic impact of the paintings’ deterioration. The drips formed over time above the paint layers alters viewers’ perception greatly and, also, leads to delamination and sticky surfaces. To date, no satisfactory long-term treatment for this issue has been proposed (I.M.A. Bronken et al., 2019). Thus, studies on material characterization of exudates are essential to better understand the causes and perspectives on the conservation of contemporary oil paintings. This work presents the characterization of exudates from the painting “Três pessoas” by Marina Saleme (1999) (Fig. 1), which is part of the contemporary paintings collection at Pinacoteca do Estado de São Paulo museum. Marina Saleme is a renowned Brazilian artist whose work has been exhibited, not only in Brazil, but also in Spain, Colombia and Canada. Throughout her career, Saleme shows a predilection for oil paint abstract diptychs and triptychs, such as the one presented in Figure 1.

Experimental
Paint sample was collected on site with the aid of a scalpel and swabs for the yellow-brown transparent exudate (Fig. 2). Sampling points are highlighted on figure 1 as white circles on the left side of the image. Then, all samples were analyzed on benchtop equipment at the laboratory.
In order to identify the binder, Fourier transform infrared spectroscopy (FTIR) was employed. Pyrolysis coupled with gas chromatography and mass spectrometry (Py-GC/MS) identified the oil type and other organic components in the paint sample. Lastly, scanning electron microscopy coupled with energy dispersive x-ray fluorescence spectroscopy (SEM-EDS) was used to characterize the inorganic elemental composition and particle (extenders) distribution.

Infrared (FTIR) spectra were collected on an Agilent Cary 630, ATR mode, from 4000 to 650 cm\(^{-1}\) and for 32 scans with a resolution of 4 cm\(^{-1}\). The Py-GC/MS instrument used was a Frontier Lab PY-3030D microfurnace pyrolyzer coupled to a Shimadzu Co. GCMS-QP5000 working with SGE BPX5.
column 5% phenyl polysilphenylene-siloxane (30 m x 0.25 μm x 0.25 mm). Pyrolysis was performed at 610 °C for 0.20 min with Py-GC interface at 300 °C and GC-MS interface at 280 °C. The GC oven temperature was 40 °C (held for 2 min.), with a 10 °C min⁻¹ rate and final temperature of 350 °C (2 min). The MS split was 1:150 and the m/z was scanned from 40 to 600 u in electron ionization mode (EI⁺, 70 eV). Spectra were compared to NIST library standards and the works of S. Tsuge et al. (2011) and T. Learner (2004). The TM3000 (Hitachi Co.) scanning electron microscope coupled with a Quantax70 energy dispersive X-ray fluorescence spectrometer (Buker Nano GMBH) was used for SEM-EDS analyses, working at 15 kV and 5.1 mm distance.

RESULTS AND DISCUSSION

According to the artist herself, the preferred medium is oil. Each painting being composed of several layers. The paint binder was identified by FTIR (Fig. 3) with characteristic peaks for νO-H (3398 cm⁻¹), non-aromatic νC-H (2915 and 2851 cm⁻¹), free fatty acids carbonyl νC=O (1707 cm⁻¹) and out of plane νC-H (959 cm⁻¹). Exudate samples were analyzed separately, with characteristic peaks for νO-H (3519 cm⁻¹), non-aromatic νC-H (2977 and 2877 cm⁻¹), free fatty acid νC=O (1711 cm⁻¹), zinc carbonate νZnCOO (1598 cm⁻¹), asymmetric carbonate νCO₂⁻ (1446 cm⁻¹), νC-O (1250 cm⁻¹), symmetric carbonate νCO₂⁻ (1061 cm⁻¹) and δCO₂⁻ (846 cm⁻¹) (D. Banti et al., 2008). Comparing results from paint and exudate, it is possible to observe the presence of several polar species (intense sharp peaks) in exudate, such as free fatty acids (FFA) carbonyl, carboxylates and ester (νC-O). Linseed oil was, then, identified by Py-GC/MS (Fig. 4) using the P/S ratio, i.e. palmitate to stearic acid (P/S = 1.78). The presence of caproic (Cap) and oleic acids (Ole) are noted at 8.5 and 22.7 minutes, respectively. Dicarboxylic acids are also present in paint samples, such as subaric (Sub) and sebacic (Seb), respectively at 10.9 and 11.9.

Results for the exudate sample indicates the presence of palmitate, stearic and oleic acids and dicarboxylic subaric and azelaic acids. Elemental composition was determined by EDS spectrometry (Fig. 5) on paint samples. Al, Si, Ca and Zn were detected, which indicate the presence of kaolin, calcium carbonate (CaCO₃) as extenders. Zinc is present in the paint layer as an oxide (ZnO) white pigment. Exudate (drip) formation is associated to the presence of a mobile polar fraction in the paint film. A fraction of less unsaturated triglycerides fails to anchor on surface particles (I.M.A Bronken et al., 2019). When this occurs on internal layers, paint softening is observed. The presence of dicarboxylic acids is an indicative of degradation (oxidation) of linseed oil binder (F.C. Izzo et al., 2014). Their presence is confirmed by FTIR and Py-GC/MS analyses. Zinc stearate is known to cause cohesion problems in the paint films, although being added to oil paints as hue control. This is a recurrent issue in twentieth century oil paintings (K. Helwig et al., 2014). Micrograph (Fig. 6), at 100 µm scale, indicates high particle-binder ratio, with zinc and calcium as small particles present throughout the paint layer. Aluminum and silicon are present as larger particles of different sizes.

Conclusion

Spectra from FTIR indicated the presence of oil as paint medium and calcium carbonate as extenders, Py-GC/MS indicated the presence of linseed oil and dicarboxylic acids (azelaic, suberic and sebacic) and SEM-EDS indicated the presence of kaolin, calcium carbonate and zinc white. Therefore, results indicate that the exudate formation may be caused by the oxidation of linseed oil leading to the formation of dicarboxylic acids. The presence of zinc white aggravates the problem with formation of a metal stearate. As indicated by A. Sawicka (2014), metal soap protrusions (exudate) can be removed using a pH-controlled metal detergent (EDTA) solution, which reduces light scattering rendering the exudate transparent.

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