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| | Experiment title: Study of the degradation of Cadmium Yellow in historical and historically reconstructed oil paints | Experiment number: HG179 |
| Beamline: ID21 | Date of experiment: from: 06/10/2021 to: 10/10/2021 (1 st exp. session) from: 22/01/2022 to: 24/01/2022 (2 nd exp. session) | Date of report: 01/02/2022 |
| Shifts: 9 (1 st exp. session) 6 (2 nd exp. session) | Local contact(s): Marine Cotte | <i>Received at ESRF:</i> |
| Names and affiliations of applicants (* indicates experimentalists): Marta Ghirardello ^{1,*} , Daniela Comelli ^{1,*} , Lucia Toniolo ¹ , Gianluca Valentini ¹ , Austin Nevin ² , Catherine Patterson ³ , Douglas Maclennan ³ , Letizia Monico ^{4,*} , Vanessa Otero ⁵ (1) Politecnico di Milano, Milano, Italy (2) The Courtauld Institute of Art, London, United Kingdom (3) Getty Conservation Institute, Los Angeles, USA (4) CNR-SCITEC, Perugia, Italy (5) Universidade Nova de Lisboa, Lisbon, Portugal | | |

Context and motivation of the research:

The first experimental session aimed at studying the composition and degradation of Cadmium Yellow (CdY) oil paints in relation to the historical synthesis methods of the pigment [1]. The degradation of this type of paints has been profitably studied through synchrotron radiation techniques, allowing to identify the degradation pathway and some of the factors promoting this process [2-3]. However, it is not still clear why some paints suffer degradation while others are relatively intact. We propose to characterize through μ -XRF/ μ -XANES analyses the chemical speciation and the stratigraphic distribution of compounds in artificially aged CdY model paints prepared with pigments synthesized by different historical methods. This provides a quantitative assessment of the degree of degradation in relation with the manufacturing process and allow to identify which pigment properties, due to the synthesis method, mainly affect paint stability.

The second experimental session was dedicated to the study of the degradation occurred on the passe-partout of the Folio 843 of Leonardo's Codex Atlanticus. The passe-partout shows a darkening phenomenon along the edge of Leonardo's drawing. Preliminary analyses have demonstrated that the degradation is not of micro-biological origin, but is most probably associated to the presence of Hg. The study performed at ID21 aims at defining the chemical speciation of Hg to hypothesize the chemical processes that have induced such type of degradation. This will allow to adopt the appropriate measures of active and preventive conservation for this and other Folios showing the same type of degradation.

Analysed samples:

The model paints were prepared mixing cadmium yellow pigments (synthesized from two different historical recipes and commercially available) with linseed oil, and artificially aged for 45 days under light and at high relative humidity conditions (RH ~80%). Thin sections were prepared to map the distribution of the chemical species through the cross-section.

The passe-partout of the Folio 843 of Leonardo's Codex Atlanticus was cut in three paper samples, belonging to the dark, medium dark and white regions. No further preparation was adopted.

In each experimental section μ XRF maps, fluo-XAS (at S K-edge) maps and single point μ XANES at different elements edge were acquired.

Status of the data processing:

Data were analysed with PyMCA, ATHENA and TXM-Wizard. Quantitative estimation of the compounds through μ XANES measurements and correlation with μ XRD analysis (obtained at ID13) are currently undertaken.

Main results obtained:

Analysis conducted at ID21 on CdY paints shows a clear difference in the degradation of the paintings prepared from different pigments. Indeed, samples prepared from pigments synthesized from Na_2S have a more prominent degradation, with the formation of a thick cadmium sulfate layer on top of sulfide layer. In contrast, reference samples and samples synthesized from H_2S show a very low quantities of cadmium sulfates. Beside the presence of sulfate (due to photo-oxidation of CdS), sulfites were also detected in the degraded samples, as possibly intermediate states of degradation.

Analysis on the passe-partout of Folio 843 of Leonardo's Codex Atlanticus shows the co-localization of Hg and S in the dark and medium-dark regions, suggesting the presence of black mercury sulfide. Sulfide is also detected through μ XANES at S K-edge. No mercury was instead detected in the white paper, allowing to hypothesize that mercury was originally present as antibacterial agent in the glue mixture used for the adhesion of the edge around the Leonardo's drawing, which degraded developing black HgS.

Eventual communication of results (manuscript in preparation, conference...):

The collected data on CdS have been complemented with μ XRD data collected at ID13 and will be published in a paper in preparation. An abstract will be submitted for presentation for ChemCH conference.

Data on Folio 843 of Leonardo's Codex Atlanticus will be complemented with HR-XRD at ID22 and published later.

References:

- [1] Ghirardello, Marta, et al. "An investigation into the synthesis of cadmium sulfide pigments for a better understanding of their reactivity in artworks." *Dyes and Pigments* 186 (2021): 108998.
- [2] Monico, Letizia, et al. "Role of the relative humidity and the Cd/Zn stoichiometry in the photooxidation process of cadmium yellows ($\text{CdS}/\text{Cd}_{1-x}\text{Zn}_x\text{S}$) in oil paintings." *Chemistry—A European Journal* 24.45 (2018): 11584-11593.
- [3] Monico, Letizia, et al. "Probing the chemistry of CdS paints in The Scream by in situ noninvasive spectroscopies and synchrotron radiation x-ray techniques." *Science advances* 6.20 (2020): eaay3514.