ESRF	**Synchrotron Radiation and Historically Accurate Reconstructions for the preservation of chrome yellow in 19th c. works of art - Part II**	**HG-53**
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Vanessa Otero[a,b*], Leslie Carlyle[a,b], Márcia Vilarigues[a,c*], Marine Cotte[d*] and Maria J. Melo[a,b*]

[a]Faculty of Sciences and Technology, Universidade Nova de Lisboa, 2829-516 Monte da Caparica, Portugal
[b]Department of Conservation and Restoration and REQUIMTE-CQFB.
[c]Department of Conservation and Restoration and VICARTE.
[d]ESRF, Grenoble, France

Report:

OBJECTIVES – PURPOSE

Since their foundation in 1832 Winsor & Newton (W&N) traded on their reputation for high quality durable products. This study was carried out to evaluate whether their yellow lead chromate pigments suffered similar degradation as reported elsewhere [please, see references in our proposal to the works of Janssens, Monico *et al*., 1]. Our research of 19th c. W&N chrome yellow manufacturing processes, enabled us to select the pigment formulations expected to most likely undergo degradation [1]. A set of paint reconstructions together with samples from historic chrome yellow oil paint tubes and μ-samples from paintings of the 19th c. Portuguese artist, Amadeo de Souza-Cardoso, were irradiated in a Xenon-light apparatus (λ_{irr}>320 nm). The photochemical ageing was studied by synchrotron radiation, including μ-XRF, Cr and S K-edge μ-XANES and μ-FTIR, Figure 1. The purpose of this experiment is to develop a *light susceptibility index* to predict the stability of chrome yellow paints using the ratio variation of Cr^{3+}/Cr^{6+} obtained by Cr K-edge μ-XANES, and to get a deeper insight into the degradation processes occuring in chrome yellow paint systems [1, 2]. The combined use of the synchrotron-based techniques show to be indispensable to accomplish these goals.

EXPERIMENT

A total of 32 samples were analysed during this experiment: 4 μ-samples from Amadeo's paintings (2 artificially aged), 3 samples from historic oil paint tubes, 11 historically accurate oil and poly(vinyl acetate) paint reconstructions and 14 PVAc paint references of lead chromate monoclinic and orthorhombic mixed in different proportions with common additives: chalk, gypsum and barytes. Samples with different irradation times were analysed; HART samples by Cr and S K-edge μ-XANES with a macro-beam (200 μm) and a micrometric beam (0.3×0.8 μm^2) was used for μ-samples from Amadeo's, historic oil paint tubes and paint reconstructions. Some of the samples were prepared on site as embedding-free thin cross-sections using the SES method (Sample Enclosing System). μ-FTIR maps of Amadeo's cross-sections were acquired in ATR mode and other samples, mounted as thin cross-sections, were analysed in transmission mode, with a beam size of 8×8 μm^2. Data analysis was performed using OMNIC, PyMCA and ATHENA software.

RESULTS

Main results

By means for Cr K-edge μ-XANES analysis it was possible to establish a *light susceptibility index* for chrome yellow oil paint systems and a first assessment of the stability to light of an early W&N Chrome yellow oil paint tube was made. This suggest that it will be possible to compare the behaviour of original

materials to reference materials produced through reconstructions [1]. A wider set of irradiated historically accurate paints and longer irradiation times is necessary to fully assess the accuracy of the LSI. This experiment is in progress.

Overall, the irradiated historically accurate reconstructions and the samples from Amadeo's paintings displayed high stability to light. In the artificially aged Amadeo's samples (t_{irr} = 5250 h) evidence of Cr^{3+} compounds being formed was found, however, the degradation process is still in an initial stage and longer irradiation times will be required to fully assess the degradation mechanisms. The oil paint which showed the highest color change (ΔE^* = 48.2), after 7750 h of irradiation time, was a reconstruction composed of pure lead chromate with a high extender concentration: 32% of pure monoclinic lead chromate ($PbCrO_4$), 47% of chalk (calcium carbonate, $CaCO_3$) and 21% of gypsum (calcium sulfate dihydrate, $CaSO_4.2H_2O$), Figure 1.

Importantly, the successful preparation of embedded free thin cross-sections of the oil paint reconstruction mentioned above allowed insight into its degradation mechanims through the combined use of SR μ-XRF, chromium and sulfur K-edge μ-XANES and μ-FTIR, Figure 1 [2]. It was possible to detect by μ-XANES not only the reduction of lead chromate Cr^{6+} but also of calcium sulphate S^{6+}, Figure 1B and C. It is suggested that the redox reactions are linked. μ-FTIR imaging disclosed reaction pathways, intermediates and final products that provide a breakthrough in our understanding of the stability of chrome yellow oil paints; this important result is the subject of a communication that we are preparing for submission [2]. Calcium oxalate monohydrate ($CaC_2O_4.H_2O$) was detected by μ-FTIR at the surface and near chalk-rich areas at the interior of the oil paint, and we think that this final product is key for the understanding of the degradation mechanism of chrome yellow in an oil matrix, Figure 1A. Samples from the historic chrome yellow oil paint tubes also show the presence of oxalate compounds (by μ-FTIR), however, its precise identification was not possible for the irradiation times studied. Further investigation will be conducted in order to fully assess the role of metal oxalates in the degradation mechanism of chrome yellow oil paints. Our experiments conducted at ID21 provide the foundation work for this study.

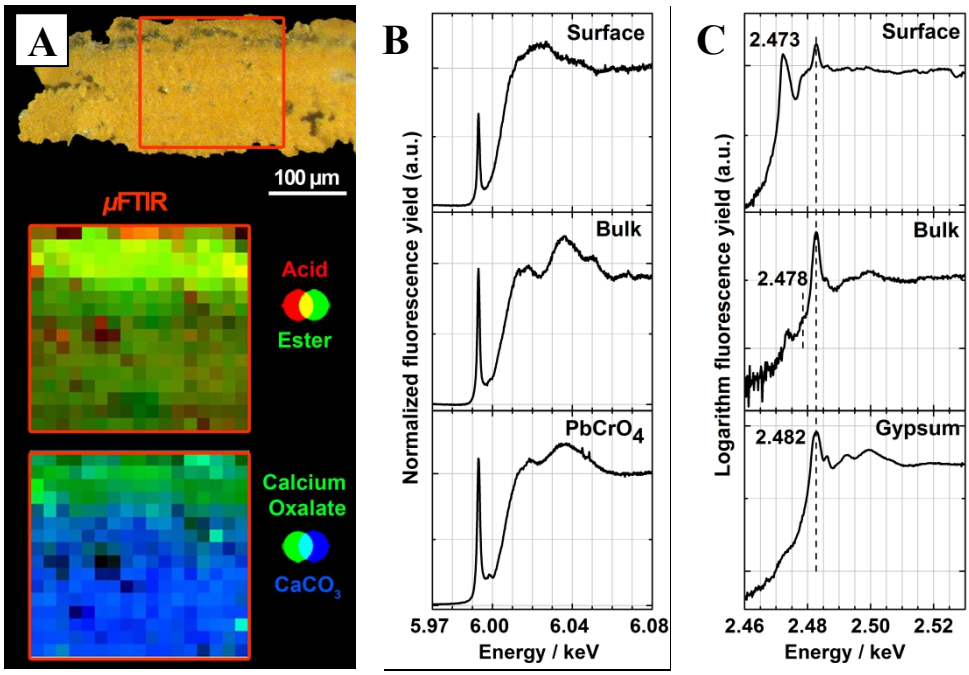

Figure 1. A) SR μ-FTIR chemical maps (160×150 μm^2) of an embedding-free thin cross-section of a chrome yellow oil paint reconstruction composed of pure lead chromate, chalk and gypsum (t_{irr}=7750 h); **B)** Cr K-edge and **C)** S K-edge XANES spectra acquired at the surface and in the bulk.

OUTPUTS

[1] V. Otero, J. V. Pinto, L. Carlyle, M. Vilarigues, M. Cotte, M. J. Melo, "19th century Chrome Yellow and Chrome Deep from Winsor & Newton. *Stud. Conservat.*, accepted, 2015.

[2] Manuscript in preparation. In this forthcoming paper, through the use of SR, we will further the knowledge on the degradation mechanisms of chrome yellow and formation of calcium oxalate, in the presence of calcium carbonate and gypsum.

[3] Results will be included in Vanessa Otero PhD thesis, "Bright colours: historically accurate reconstructions of Amadeo's palette" (expected completion date, March 2016).