ESRF	**Synchrotron Radiation and Historically Accurate Reconstructions for the preservation of chrome yellow in 19th c. works of art**	**HG-28**
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Report:

OBJECTIVES – PURPOSE

Lead chromate was first discovered and synthesised by the French chemist, Vauquelin, at the beginning of the 19th century. Shortly afterwards, Winsor & Newton (W&N) manufactured yellow lead chromate based artists' materials under the trade names Chrome Yellow and Chrome Deep. In order to better understand the observed darkening of chromate pigments in works of art, we undertook a complete evaluation of 19th c. W&N chrome yellow manufacturing processes from their recipe archive, which allowed us to select the pigment formulations expected to most likely undergo degradation. A set of paint reconstructions (prepared with freshly extracted linseed oil from the same seed lot), were irradiated in a Xenon-light apparatus (λ_{irr}>313 nm). Severe darkening was observed in two reconstructions, Table 1. The degradation process was studied by synchrotron-based techniques, including μXRF, μXANES and μFTIR, Figure 1. The aim of this experiment was to identify the possible degradation produts of Cr^{3+} present in the artificially aged reconstructions, along with naturally aged micro-samples from original works of art by the important Portuguese artist, Amadeo de Souza-Cardoso, shedding light on the factors influencing the degradation process. X-ray fluorescence and particularly μXANES at ID21 were particularly relevant to answer these questions.

EXPERIMENT

A total of 23 samples were analysed during this experiment: 14 micro-samples from Amadeo's paintings, 4 samples from 19th century oil paint tubes and 5 historically accurate reconstructions (HART samples: powders, unaged and artificially aged oil paints). Some of the samples were prepared on site as thin cross-sections using the SES method (Sample Enclosing System). HART samples were analysed with a macro-beam (200 μm) and a micrometric beam (0.3×0.8 μm^2) was used in Amadeo's paintings and the 19th century oil paint tube samples. For all samples, chemical maps and XANES spectra at the Cr-K edge were collected. FTIR maps were acquired for all samples, excluding those already prepared as cross-sections. Data analysis was performed using OMNIC, PyMCA and ATHENA software.

RESULTS

Main results

The preliminary studies of artificially aged paint reconstructions using synchrotron-based techniques, reveals that pigments based on mixed-crystals, CY2, (entitled “Primrose” and “Lemon”) show a higher relative stability than those composed of pure lead chromate in mixture with calcium carbonate and gypsum, CY1 (entitled “Middle”). These results may be explained by the pigment light absorption in the formulation,

which we consider to be lower for the mixed crystals, and by the light effect on fillers such as calcium carbonate.

Table 1. Assessing photodegradation of the paint reconstructions CY1 and CY2.

HART	CY1 (pure lead chromate)		CY2 (mixed-crystals)	
	t_0	t_{1500}	t_0	t_{1500}
				

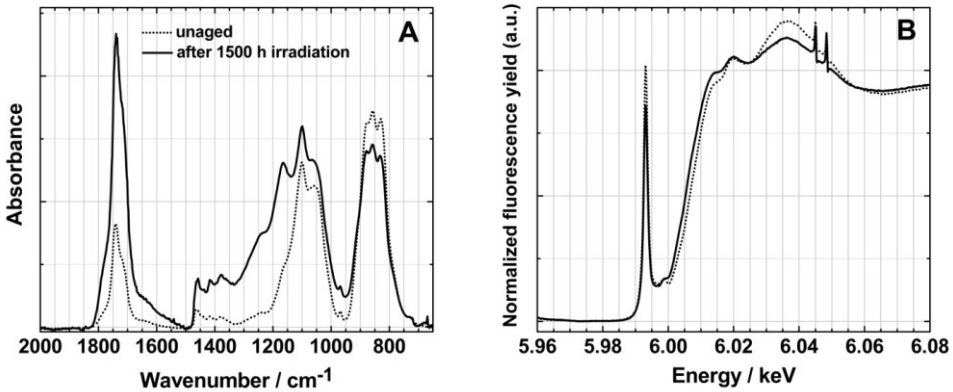

Figure 1. A) FTIR and **B)** XANES spectra of the paint composed of mixed-crystals (CY2) unaged and after 1500 h irradiation.

Both reference material, including the W&N reconstructions, and micro-samples from original paintings were analyzed and the results compared. Synchrotron studies proved particularly useful for assessing the relative photostability of chrome yellow paint systems, based on the ratio Cr^{3+}/Cr^{6+}, which shows a variation with irradiation time (ageing), Figure 1B. Based on these results, we propose to develop a light susceptibility index for the yellow lead chromates [1, 2]. This will allow us to predict the degradation state of a colour, essential to assess the conservation state of a work of art. To this scope, a wider set of irradiated historically accurate paints is currently being studied, and over longer irradiation times.

Amadeo's samples were extensively studied and present excellent preservation with no evidence of colour change [3]. No Cr^{3+} species were detected by μXANES and infrared studies confirmed that the yellow layer was in good general condition with low amounts of carboxilates observed. Due to the very small sample size, we have developed a sample holder to minimize the risk of loss of sample during future synchrotron radiation.

We are hopeful that this ongoing experiment will produce a significant breakthrough in understanding and predicting degradation of this widely used artists' pigment. Our experiments conducted at ID21 provide the foundation work for this study.

Sample preparation

Sample preparation that enables optimal analysis with both μFTIR and μXANES was systematically tested with the collaboration of the ID21 team, particularly Emeline Pouyet. This is a major issue in our studies and the results obtained were crucial for the development of the sample holder for paint samples derived from original artworks, referred above.

OUTPUTS

[1] M. J. Melo, L. Carlyle, M. Vilarigues, V. Otero, M. Cotte, "*Shades of yellow:* a photochemical approach to the preservation of chrome yellows in 19th c. works of art", Poster presentation at the XXV IUPAC Symposium on Photochemistry, 13-18 July 2014, Bordeaux, France.

[2] V. Otero, L. Carlyle, M. Vilarigues, M. Cotte, M. J. Melo, "19th century chrome yellow and chrome deep from Winsor & Newton", in preparation, to be submitted in Oct. 2014.

[3] Results on Amadeo's samples studied at ESRF (ID21) will be included in Cristina Montagner PhD thesis, "Crossing Borders: the brushstroke of a modernist Portuguese painter" (expected completion date, September 2014). A full paper will be also prepared, including the results of the ongoing irradiation of original samples.