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Supplementary Information

The complete set of irradiated samples is divided into three groups: *a*) 3 late 19th century oil paint tubes from the colourmen W&N and Lefranc; b) *11* historically accurate oil and poly(vinyl acetate) paint reconstructions; and c) *23* PVAc paint references of lead chromate monoclinic, orthorhombic and chromium oxide mixed in different proportions with common additives: chalk, gypsum and barytes (unaged and with different irradiation times). Irradiation was carried out in a CO.FO.ME.GRA accelerated aging apparatus (SolarBox 3000e) equipped with a Xenon-arc light source (λ_{irr} >300 nm) with constant irradiation of 800 W/m² and black standard temperature of 50°C (inside the camera temperature was maintained at approximately 30 °C and RH at 40%).¹ The set of samples was irradiated between 8500h and 11000h (total irradiance = 24451 to 31643 MJ/m²).

Chrome yellow oil paint (CR7) was prepared in 2011 by handgrinding with a glass muller on a glass slab a mixture of 33.3% of untreated linseed oil (HART project seed lot Electra, extracted in 2005²) to pigment by weight. The paint was applied onto a glass slide with a palette knife. The multi analytical characterization of the sample is described elsewhere.³ The irradiated times discussed in this communication for the CR7 oil paint were 7750h (SR-experiment HG-53) and 11000h (SR-experiment HG-80). Embedding-free thin cross-sections of the irradiated chrome yellow oil paint were prepared using the "sample enclosing system" (SES) approach.⁴

SR-based techniques were performed at the X-ray microscopy beamline, ID21, at the European Synchrotron Radiation Facility (ESRF, Grenoble, France).

The first results for the presence of oxalate as key intermediate were acquired for 7750h irradiated samples by SR-FTIR [experiment HG-53, 12-18 March 2015]. To confirm it, samples were further irradiated over 11000h, and SR-XRD beam time was requested to unequivocally provide a molecular structure to the calcium oxalate previously detected by SR-FTIR and confirm the chain of events [experiment HG-80, 13-19 June 2016].

 $\mu FTIR$ analyses were performed using a spectro-microscope based on a commercial instrument composed of a Thermo Nicolet Nexus FTIR bench associated with an Thermo Continumm microscope. In the microscope, two $\times 32$ Schwarzschild objectives were used in a confocal mode and an aperture defines the spot size of the beam. The embedding-free thin cross-sections were mounted horizontally, between two 10 \times 10 \times 0.4 mm³ BaF₂ windows, allowing spectra acquisition in transmission mode. The beam size and step size was 10 \times 10 μ m². Spectra were acquired as a sum of 100 scans, with a spectral resolution of 8 cm⁻¹, over the 4000-750 cm⁻¹ range.

The infrared regions of interest used for μ FTIR mapping were: esters (1755-1720 cm⁻¹), acids (1718-1700 cm⁻¹), calcium oxalate (1340-1300 cm⁻¹) and chalk (1520-1350 cm⁻¹).



Fig. S2 Infrared spectrum between 1800-830 cm⁻¹, obtained on the surface of the chrome yellow oil paint CR7 (artificially aged, t_{irr} = 7 750h) and two reference compounds: KCr(SO₄)₂.12H₂O, CaSO₄.2H₂O; (\blacklozenge) CaSO₄.2H₂O, (\blacklozenge) CaCO₃ and (\diamondsuit) PbCrO₄.

μXRF and **μXANES** experiments were performed in vacuum (10⁻⁶ mbar). The scanning X-ray microscope has a tunable energy ranging from 2.1 to 7.2 keV and is optimized for very low background and low detection limits. A collimated beam of 200 μm diameter and a focused beam of ca. 0.3×0.8 μm² (horizontal×vertical) obtained by means of a Kirkpatrick-Baez mirror system were used for sample irradiation, in macro and micro modes respectively. The XRF excitation is stimulated with a highly monochromatic beam by means of a fixed-exit, double crystal Si(220) monochromator, located upstream of the microscope, and which provides an energy resolution of ΔE/E=810⁻⁵. During the μXRF mapping experiments, the XRF signals were generated by employing a monochromatic primary beam of fixed energy. Two energies were used to map



Fig. S1 SR- μ FTIR mapping for chrome yellow oil paint CR7 (unaged; naturally aged for 2 years and a half).



Fig. S3 Scheme of the three-layer stratigraphy of the chrome yellow oil paint CR7 (artificially aged; t_{irr} = 7 750h).

chromium speciation: 5.993 and 6.1 keV. The former (pre-edge peak) overexcites Cr^{6+} species, while the latter excites almost equally all Cr species.^{2,5}

 μ XANES spectra were acquired by scanning the primary energy around the Cr K-edge (5.96-6.12 keV) with a step size of 0.2 eV. The energy calibration was performed using a metallic Cr foil (maximum of derivative set at 5.989 keV). During the μ XANES energy scans, the position of the primary beam was maintained stable within 0.6 μ m. The Light Susceptibility Index (LSI) of the chrome yellow paints was obtained through their μ -XANES spectra acquired at 5 to 10 different points. Normalization of all XANES spectra were performed by means of ATHENA software and the same energy range and polynomial type of the pre- and post-edge lines were used.^{4,6}

 μ FTIR and μ XRF maps were analysed using the PyMca package.⁷ μ XRD experiments were performed at the new μ XRD endstation, at ID21, in transmission geometry. The primary beam energy was tuned by single fixed monochromatic energy of 8.53 keV and focused down to 0.7×1.0 μ m² (vertical×horizontal). The transmitted diffraction patterns were recorded using a 2D taper FReLoN CCD and the XRF signal was collected using a Ketek 80mm² Silicon Drift Diode. Both μ -XRD and μ -XRF signals were collected in continuous scan (zap) mapping mode. The resulting μ XRD maps were analysed using the XRDUA package.⁸

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