Since the 19th century, the industrial expansion stimulated the development of synthetic pathways to many new materials, including various pigments of the chrome yellow family (PbCrO₄, PbCr₁₋ₓS₄O₄ (0.1 ≤ x ≤ 0.8), (1−x)PbCrO₄·xPbO), cadmium yellow (CdS), emerald green (Cu(C₂H₃O₂)₂·3Cu(AsO₄)₂), and viridian green (Cr₂O₃·2H₂O).

[1] Chrome yellows; nevertheless such information could yield more detailed insights into the sequence of chemical transformations that drive the degradation process, thereby providing additional and/or complementary information with respect to the knowledge already acquired at the micrometer level by synchrotron radiation-based XANES methods.[1,3,13]

The chemical and structural variations in this material were investigated before and after an artificial aging treatment with UVA/Vis light. A microscopic degradation model is proposed that serves to explain all the observed core–shell structures of the pigment particles.

The paint employed for this study was obtained from an oil-paint tube belonging to the Flemish Fauvist Rik Wouters (1882–1913). Artificial aging turns its original bright yellow color deep brown.[1,6] Prior to ageing, cross-sectional TEM samples (3 × 7 × 0.1 μm²) were prepared by means of a focused ion-beam (FIB) technique. [4] These authors contributed equally to this work.

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ion beam (FIB). The same region of the sample was investigated before and after aging in the electron microscope to study at the micro- to nanoscale level the changes induced during the artificial aging step, which is described in more detail in the Supporting Information.[14]

Figure 1a shows a cross-sectional view, obtained by high-angle annular dark field (HAADF) STEM of the topmost 2–3 micrometers of the paint, freshly removed from the 100 year old paint tube; In this Z-contrast image, particles with a size distribution between 20 and 300 nm can be observed inside the oil-based binding matrix (linseed oil). A 3D EELS spectrum image (SI region) was acquired from the region indicated by a green rectangle. In some of the particles, the Cr signal (Cr-L_2,3 edge from 575 eV) is absent from the spectrum (see particle (1), Figure 1b). A few particles show Cr enrichment on the surface (see particle (2), Figure 1b) or in the center (see particle (3), Figure 1b), thus suggesting the phase separation of the material into different core–shell structures. However, the phase-specific identification of the particles is not straightforward, because of the presence of both Cr and O in PbCrO_4 and Cr_2O_3 in this heterogeneous multiphase system. It is, therefore, difficult on the basis of elemental information alone to demonstrate the presence of, for example, Cr_2O_3 in particle (2).

The energy-loss near-edge structure (ELNES) of the core-loss edges of the chemical elements is known to be sensitive to the chemical environment of the element in question.[15–18] Accordingly, the ELNES spectra from the PbCrO_4, PbSO_4, and Cr_2O_3 bulk reference materials all show a unique fingerprint with significant differences at the O-K and Cr-L_2,3 edges (Figure 1c; see the Supporting Information for more details).[14] The above references were chosen according to prior knowledge about the sample. Cr-K edge XANES measurements on the (un)aged paint yielded spectra that could be described well by a linear combination of the XANES spectra of PbCrO_4 and Cr_2O_3, while S-K edge XANES data confirmed the presence of different amounts of sulfur in the sulfate form.[1,3,6,13] The high-energy resolution of monochromated EELS (0.3 eV) enables the different phases in the sample to be identified on the basis of their ELNES fingerprints. This can be done in a much more selective manner than when simple elemental maps such as those of Figure 1b are used for this purpose. A large set of EELS spectra, recorded when scanning the electron probe over the sample, (a so-called hyperspectral image) were fitted to a linear combination of these reference spectra and an averaged spectrum from the matrix. The resulting spectral weight maps represent the local abundance of each phase. The fitted spectra show a very satisfactory degree of similarity with the experimental spectra, thus providing a high confidence in this method and in the chosen references (Figure 1c). The residual between the model and experiment shows no spectral or spatial features, thus indicating that the four reference components used here can adequately describe the spectra at the given noise level. Any further components are estimated to have a weight of less than 3 % in terms of oxygen content for each spectrum in the dataset.

The spectral abundance maps of PbCrO_4, PbSO_4, and Cr_2O_3 (Figure 2) show their distribution at the nanometer scale in the examined area prior to aging. In general, the spectral signatures of PbCrO_4 and PbSO_4 are observed together, consistent with the presence of solid solution particles of PbCr_1–xS_xO_4. In addition, PbSO_4 can be observed as individual grains with a size of approximately 200 nm (particle (1) in Figure 2); it is also present on the surface of some particles. The Cr_2O_3 phase is mainly present as small particles or at the surface of some of the larger particles. Particle (2) clearly shows a PbSO_4–Cr_2O_3 core–shell structure. The PbCrO_4 phase is never observed to be present in a pure form but only as the core of core–shell structures with PbSO_4 and/or Cr_2O_3 at their surface. Particle (3) shows a three-layered PbCrO_4–PbSO_4–Cr_2O_3 core–shell structure. The insets in Figure 2 show more detailed maps of this particle. The layer thickness of both PbSO_4 and Cr_2O_3 is approximately 20 nm. The small surrounding satellite particles are mainly Cr_2O_3 with a very low amount of PbCrO_4 and PbSO_4. Spherical particle (4) shows a 10 nm Cr_2O_3 layer around a central PbCrO_4 core, while PbSO_4 is absent.

An ex situ experiment was conducted on this sample to evaluate the influence of UVA/Vis light on the same micro-meter-sized region of this material. The results of the STEM-
EELS measurements, performed on the same area before and after 40 days of UVA/Vis aging treatment, are shown in Figure 3; it can be seen in the upper row images that the core–shell structures of some of the particles were already well-defined prior to artificial aging. The corresponding average phase composition comprises \((36/_{\text{C}6}\%\) PbCrO\(_4\), \((36/_{\text{C}6}\%\) PbSO\(_4\), and \((28/_{\text{C}6}\%\) Cr\(_2\)O\(_3\).

After aging, the PbCrO\(_4\) concentration in the same area drops significantly to \((17/_{\text{C}6}\%)\) and the Cr\(_2\)O\(_3\) content increases to \((46/_{\text{C}6}\%)\). These large changes in concentration indicate that the UVA/Vis treatment markedly accelerates the natural aging process; more than half of the PbCrO\(_4\) in this area before the treatment was converted into Cr\(_2\)O\(_3\). The phase images shown in Figure 3 indicate that most of the small PbCrO\(_4\) particles have become completely reduced to Cr\(_2\)O\(_3\) after aging, while a core of PbCrO\(_4\) remains in the larger particles. Both the concentration and distribution of PbSO\(_4\) remains the same before and after aging, thus indicating that either it is not involved in all of the degradation process or acts as a catalyst. Previous S-K edge XANES investigations of model paints\([3,6]\), more recent Cr and S-K edge XANES and XRF analysis of a paint microsample taken from the painting "Falling leaves (Les Alyscamps)" by Van Gogh also support the latter view (see the Supporting Information for further details).

Based on the results shown here and those obtained by other techniques, such as XAS\([1,3,6,13]\) below we attempt to reconstruct the sequence of chemical transformations leading to the darkening of chrome yellow (Figure 4). Originally, we can assume that solid solution particles of pure PbCrO\(_4\) (Figure 4a), pure PbSO\(_4\) (Figure 4c), and PbCr\(_{1/\text{C}0}\)S\(_{1/\text{C}0}\)O\(_4\) (Figure 4b) were present. During the 100 year period prior to the present experiments, some nanograins already spontaneously formed PbCrO\(_{2/\text{C}1}\)–Cr\(_2\)O\(_3\) and PbCr\(_{1/\text{C}0}\)S\(_{1/\text{C}0}\)O\(_4\)–PbSO\(_4\) core–shell structures (Figure 4d,e).

As a first step of the transformation, CrO\(_{4/\text{C}0}\) ions (possibly in a partially protonated form, that is, as HCrO\(_{4/\text{C}0}\)) are released by the PbCr\(_{1/\text{C}0}\)S\(_{1/\text{C}0}\)O\(_4\) solid solution into microvolumes of moisture that are present in the voids between the pigment particles and the binding medium\([3,6]\). The greater the sulfate concentration of the solid solution and, therefore the degree to which the PbCrO\(_4\) lattice is distorted, the greater is its solubility\([3]\). As a result of the high standard reduction potential of the HCrO\(_{4/\text{C}0}\)/Cr\(_{3/\text{C}0}\)+ redox couple \((E_0 = 1.21 \text{ V}, \text{pH} 1)\)\([19]\), the solvated chromate ions can act as oxidants of other dissolved chemicals or of solid materials that are in contact with the aqueous solution, such as the organic matter, thereby giving rise to the formation of Cr\(_2\)O\(_3\)\([20,23]\). This insoluble Cr compound will precipitate out at all the available surfaces after the redox reaction. These surfaces include those of the PbCrO\(_4\), PbCr\(_{1/\text{C}0}\)S\(_{1/\text{C}0}\)O\(_4\), and PbSO\(_4\) particles, thereby leading to particles with core–shell structures of the PbCrO\(_{2/\text{C}1}\)–Cr\(_2\)O\(_3\) (Figure 4d), PbCrO\(_{2/\text{C}1}\)–PbSO\(_{4/\text{C}1}\)–Cr\(_2\)O\(_3\) (Figure 4h), and PbSO\(_{4/\text{C}1}\)–Cr\(_2\)O\(_3\) (Figure 4i) type. This transformation gradually depletes the cores of the Cr-containing nanograins so that the original PbCrO\(_4\) particles (Figure 4a) may become Cr\(_2\)O\(_3\) particles (Figure 4g); the depletion of the original PbCr\(_{1/\text{C}0}\)S\(_{1/\text{C}0}\)O\(_4\) particles (Figure 4b) may advance to such an extent that only a PbSO\(_4\) core remains, covered by an outer shell of precipitated Cr\(_2\)O\(_3\) (Figure 4i). These four cases of core–shell structures have been observed in this experiment, while no other structures were present.

![Figure 2](image-url)  
**Figure 2.** Spectral weight maps (phase maps) of PbCrO\(_4\), PbSO\(_4\), and Cr\(_2\)O\(_3\) and their combined color map. The inset is an enlargement of particle (3), clearly showing a PbCrO\(_{2/\text{C}1}\)–PbSO\(_{4/\text{C}1}\)–Cr\(_2\)O\(_3\) core–shell structure. The colors in (d) are scaled to the local maximum concentration of each phase in the imaging area.

![Figure 3](image-url)  
**Figure 3.** Ex situ comparison of the sample before and after aging under UVA/Vis light. A significant amount of PbCrO\(_4\) was additionally reduced to Cr\(_2\)O\(_3\) during the aging process. The systematic error is derived by inducting an experimental spectra variation of ±0.2 eV before fitting.
The speed of the process may vary according to the size of the particles and their composition. Since PbCrO\(_4\) and sulfur-poor PbCr\(_{1-x}\)S\(_x\)O\(_4\) (\(x<0.5\)) are much more stable than the sulfur-rich PbCr\(_{1-x}\)S\(_x\)O\(_4\) (\(x>0.5\)) solid solutions,[6] and thus release significantly less CrO\(_{2}^{2-}\) ions, the alteration affects them to a lesser extent. In our opinion, this supports the validity of the simple model based on the dissolution of chromate ions, a redox reaction at the interface between the solid material and the solution it is in contact with, followed by CrO\(_{2}^{2-}\) precipitation (Figure 4) on the surface of the various particles present in the top layer of the paint.

In conclusion, to better identify the sequence of chemical reactions that are responsible for the degradation of historical chrome yellow pigments, a 100 year old chrome yellow paint sample was investigated down to the nanoscale, before and after artificial aging under UVA/Vis light. The O-K and Cr-L\(_{2,3}\) core-loss edges were acquired in the STEM-EELS mode after artificial aging under UVA/Vis light. The O-K and Cr-L\(_{2,3}\) core-loss edges were acquired in the STEM-EELS mode. By comparing the subtle ELNES features in the spectra to those of references with high spatial and energy resolution. By comparing the subtle ELNES features in the spectra to those of references with high spatial and energy resolution.

Keywords: analytical methods · chrome yellow · electron microscopy · reaction mechanisms · X-ray absorption spectroscopy