

## ABSTRACT:

### Tracking the Chemical Footprints of Artistic Practice: A Multi-Scale Study of Oil-Protein Paint Formulation and Film Formation

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Upon film formation and ageing, natural paint binders such as vegetable oils and proteins undergo extensive cross-linking, becoming insoluble, amorphous, and strongly chemically integrated with pigment particles. However, the chemical speciation, molecular characterization, and structural definition of these systems remain an open challenge, as cross-linked and amorphous organic fractions are largely inaccessible to classical molecular techniques like mass spectrometry. At the same time, the molecular composition, chemical structure, and spatial distribution of paint components are intrinsically linked to paint formulation and artistic practice, governing the chemistry and kinetics of the reactions occurring during film formation and ageing and ultimately influencing the stability and appearance of a painting over time.

Our research focuses on improving the understanding of the molecular features of paint layers as they undergo paint film formation and early ageing. In this context, we have investigated how historical paint formulations involving both oil and protein binders influence paint microstructure, rheology, drying kinetics, and chemical stability. By studying model systems based on historical recipes, we demonstrated that mixing oils and proteins in the same paint layer enables artists to control factors such as paint stiffening, moisture uptake, and brushability at high pigment loadings. Additionally, proteins act as lipid antioxidants, slowing down oil curing and actively participating in the reaction pathways. These effects arise from and depend on the micro- and nanostructural organization of the paint components, which is determined by the artist's practice and paint preparation methods.

To understand these interdependencies, we have examined the rheological properties of paints to assess their flow behavior and have studied their chemical evolution using a multi-analytical approach to track oxidation, cross-linking, and degradation pathways, using a combination of mass spectrometric and thermoanalytical techniques. Finally, we employed a nanoscale imaging technique, specifically atomic force microscopy-based infrared spectroscopy (AFM-IR), to directly investigate the spatial chemical complexity and structural organization of paint layers at the molecular level.

This multi-scale investigation provides new insights into how artistic practice determines the physical and chemical evolution of paint layers over time, paving the way for tracking the chemical footprints of the artistic practices of the Old Masters.

[1] S. Pizzimenti, L. Bernazzani, M. R. Tiné, V. Treil, C. Duce, I. Bonaduce, *ACS Appl. Polym. Mater.*, 3(4), 1912-1922 (2021).

[2] O. Ranquet, C. Duce, E. Bramanti, P. Dietemann, I. Bonaduce, N. Willenbacher, *Nat. Commun.*, 14(1), 1534 (2023).

[3] O. Ranquet, C. Duce, G. Caroti, P. Dietemann, I. Bonaduce, N. Willenbacher, *ACS Appl. Polym. Mater.*, 5(7), 4664-4677 (2023).

[4] R. Georgiou, A. Dazzi, J. Mathurin, C. Duce, P. Dietemann, M. Thoury, I. Bonaduce, *ACS Appl. Mater. Interfaces*, in press (2025).