

Electronic Supplementary Information

An infrared spectroscopic study of the nature of zinc carboxylates in oil paintings

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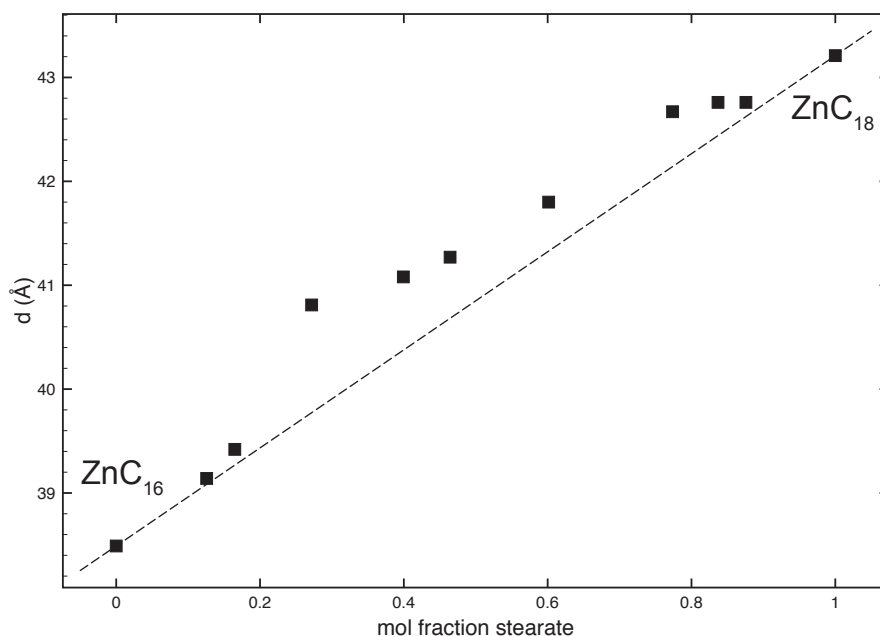


Figure S1: XRD d -spacing of zinc soaps containing a mixture of palmitate and stearate ($\text{ZnC}_{16}\text{C}_{18}$). The dashed line indicates an ideal linear correlation between stearate content and d -spacing. See also [J. Hermans, K. Keune, A. van Loon, M. Stols-Witlox, R. Corkery and P. Iedema, ICOM-CC 17th Triennial Conference Preprints, Melbourne, 15-19 September 2014, Paris, 2014, art. 1603.], for a more detailed discussion of structure in $\text{ZnC}_{16}\text{C}_{18}$ mixtures.

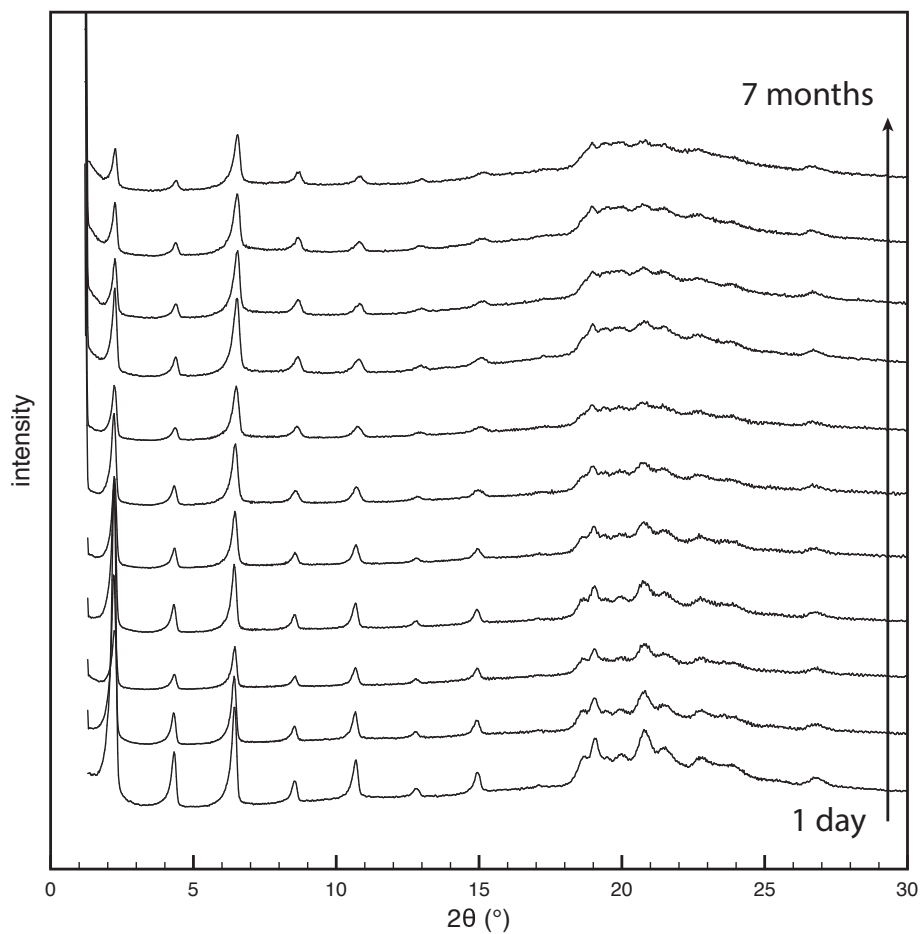


Figure S2: XRD traces of ZnUFA left in air at room temperature for 7 months. The intensity of the series of long spacing peaks ($< 17^\circ$) decreased and broadened slightly, and the peaks resulting from packing of the fatty acid chains ($18 - 25^\circ$) grew weaker. Both these trends indicate a decreasing crystallinity.

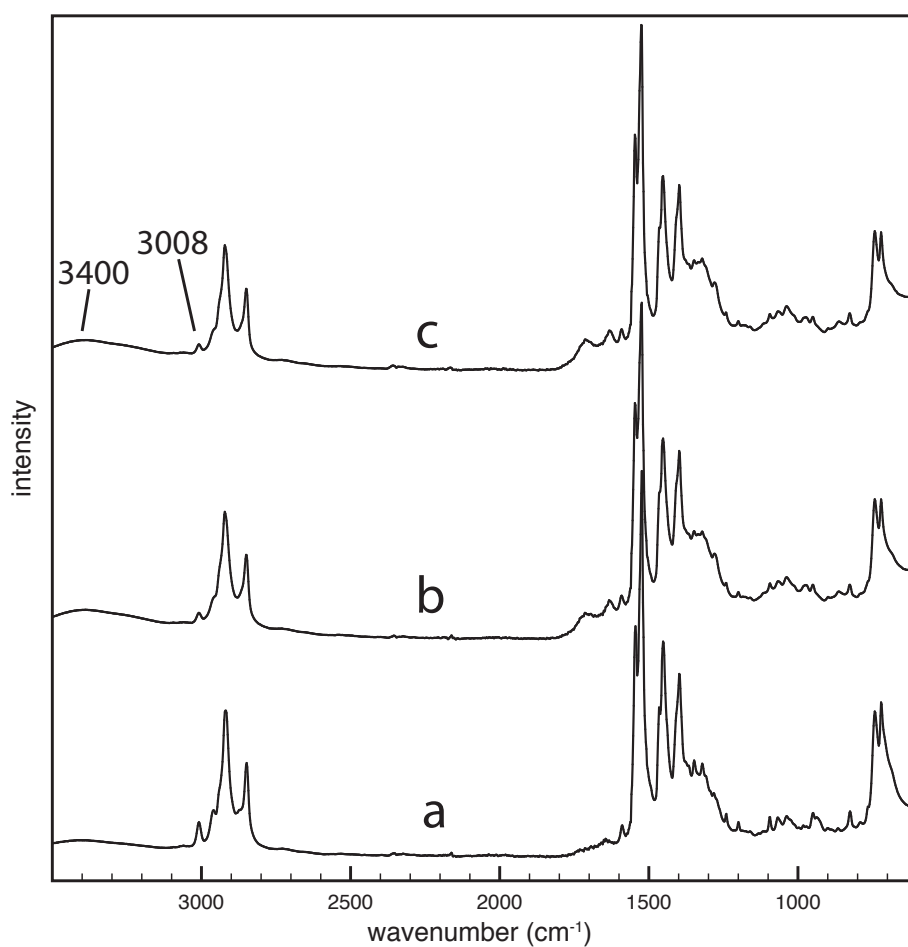


Figure S3: ATR-FTIR spectra of ZnUFA left in air at room temperature for (a) 1 day, (b) 2 months and (c) 5 months. Most important changes are the appearance of a broad -OH band at 3400 cm⁻¹ and the decrease of the C=CH band at 3008 cm⁻¹, both indicating oxidation of double bonds to hydroxyl or hydroperoxyl groups and a degree of cross-linking between fatty acid chains. These changes do not seem to affect the coordination of carboxylate moieties around the zinc atoms, since the COO⁻ bands remain unchanged.

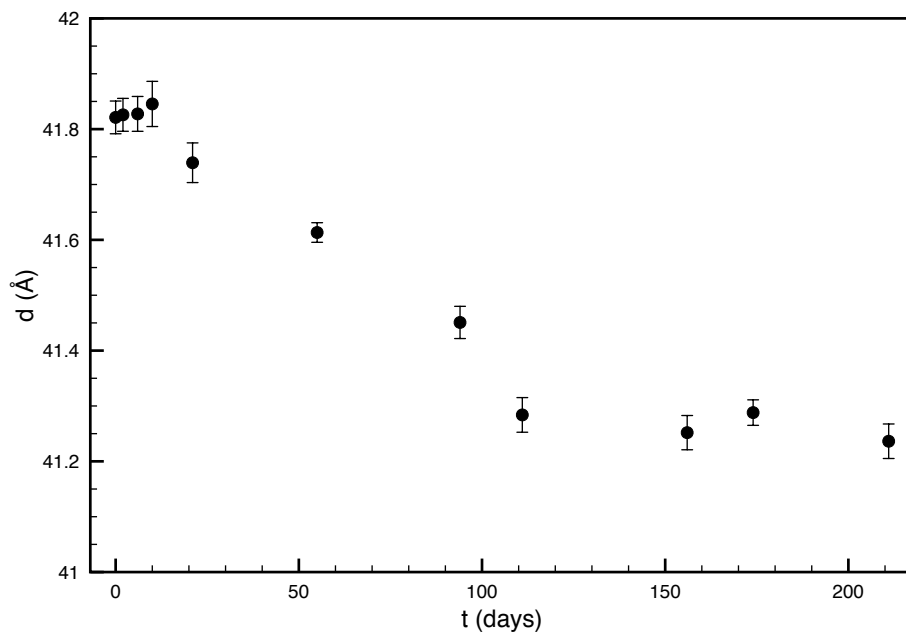


Figure S4: The long spacing of a sample of ZnUFA left in air at room temperature for 211 days. In order to correct for sample displacement, for each XRD trace the value of d of each order of the long spacing (using the appropriate order n) was plotted as function of $\frac{\cos^2 \theta}{\sin \theta}$. The intercept of the linear fit through these points gives the corrected long spacing [see I. Noyan and J. Cohen, *Residual Stress: Measurement by Diffraction and Interpretation*, Springer Verlag, New York, 1987]. The resulting spacings d of ZnUFA show a small but significant decrease over time of about 0.6 Å, probably due to interchain cross-linking. Error bars indicate one standard deviation.

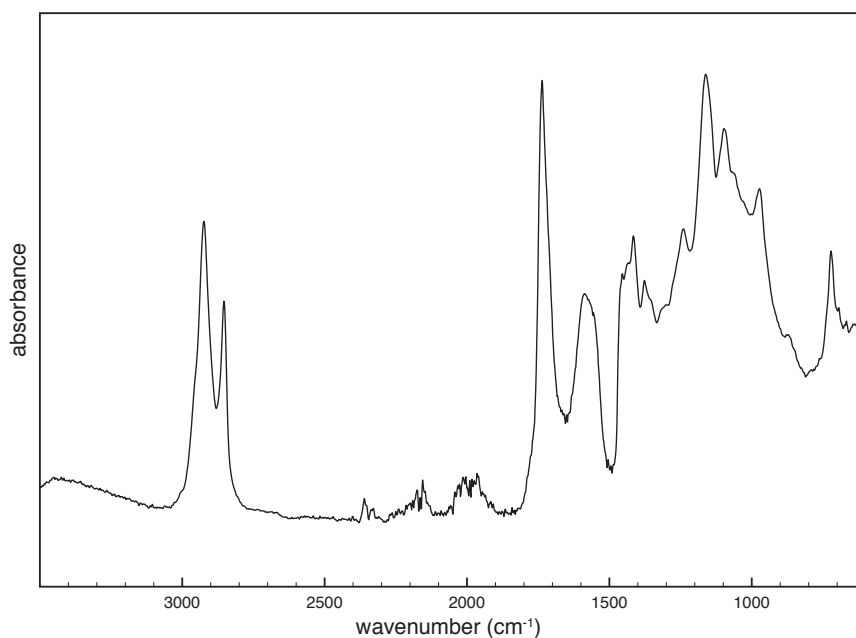


Figure S5: FTIR spectrum of Zn-pol, showing a broad ν_a COO^- band with a maximum at 1585 cm^{-1} . The broad OH band around 3400 cm^{-1} and the absence of a $\text{C}=\text{CH}$ band at 3008 cm^{-1} indicate that full cross-linking/oxidation has taken place.

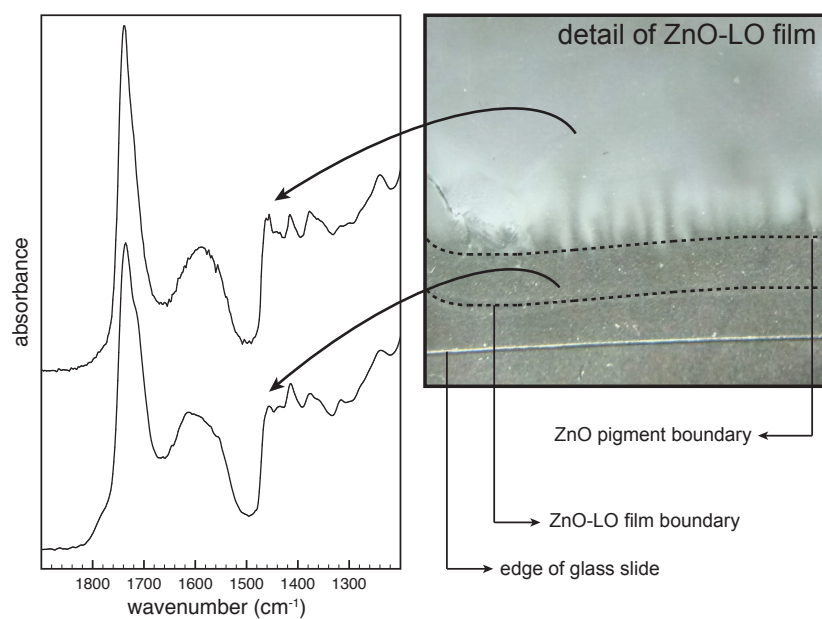


Figure S6: Comparison of FTIR spectra of ZnO-LO. During curing of a thin ZnO-LO film, a transparent ring of polymerized oil containing no ZnO formed on the borders of the paint film. The spectra of both regions showed a strong and broad ν_a COO^- band, indicating that the ZnO pigment plays no role in determining the shape or position of the ν_a COO^- band.