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Electronic Supplementary Information

# Ionomer-like structure in mature oil paint binding media

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## Contents

# 1 Composition of SAXS samples

**Table 1:** Overview of the composition of samples for SAXS measurements. LO is linseed oil, So is sorbic acid, MSo is either zinc or lead sorbate, So/LO refers to the molar ratio between sorbate molecules (either as free acid or metal complex) and linseed oil, and COOM/COOH refers to the proportion of total sorbate molecules that is bound to a metal ion (either zinc or lead).

| sample | LO (mg) | So (mg) | MSo (mg) | So/LO | COOM/COOH |
|---|---|---|---|---|---|
| **pSo1** | 200 | 30 | 0 | 1.1 | 0 |
| **pSo2** | 400 | 30 | 0 | 0.6 | 0 |
| **pZnSo1** | 200 | 20 | 12.8 | 1.1 | 0.32 |
| **pZnSo2** | 200 | 10 | 25.6 | 1.1 | 0.64 |
| **pZnSo3** | 200 | 0 | 38.4 | 1.1 | 1.00 |
| **pZnSo4** | 400 | 20 | 12.8 | 0.6 | 0.32 |
| **pZnSo5** | 400 | 10 | 25.6 | 0.6 | 0.64 |
| **pZnSo6** | 400 | 0 | 38.4 | 0.6 | 1.00 |
| **pPbSo1** | 200 | 20 | 19.2 | 1.1 | 0.32 |
| **pPbSo2** | 200 | 10 | 38.3 | 1.1 | 0.64 |
| **pPbSo3** | 200 | 0 | 57.5 | 1.1 | 1.00 |
| **pPbSo4** | 400 | 20 | 19.2 | 0.6 | 0.32 |
| **pPbSo5** | 400 | 10 | 38.3 | 0.6 | 0.64 |
| **pPbSo6** | 400 | 0 | 57.5 | 0.6 | 1.00 |

## 2 ATR-FTIR spectra of custom and commercial ZnO paints

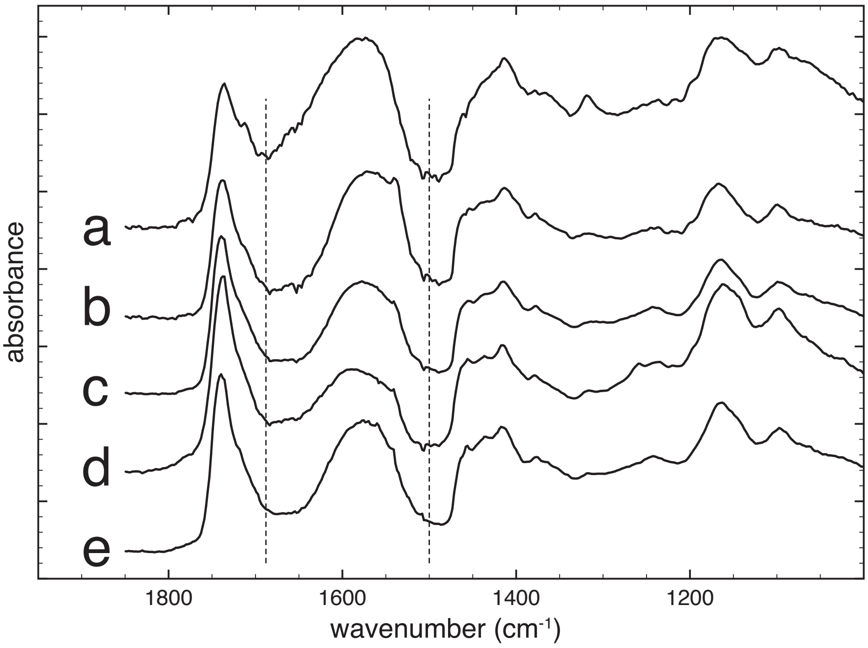


**Figure 1:** ATR-FTIR spectra of various zinc white paints, as reported by Osmond and co-workers in Osmond, et al. (2012). *Appl. Spectrosc.*, 66(10), 1136–1144. (a) Windsor & Newton zinc white in safflower oil, film prepared in 1978, top of film; (b) Windsor & Newton zinc white in safflower oil, film prepared in 1978, underside of film; (c) custom ZnO paint with linseed oil, mixed with litharge, film prepared in 1990, underside of film; (d) custom ZnO paint with boiled linseed oil, film prepared in 1990, top of film; (e) custom ZnO paint with cold-pressed linseed oil, film prepared in 1990, underside of film. Dashed lines indicate the band integration limits used after ester CO band subtraction and spectral processing. See original paper by Osmond and co-workers for further details.

# 3 Derivation of maximal COOM/COOR in case of pigment-bound metal carboxylates

With quantitative ATR-FTIR, it is possible to calculate the molar ratio between metal carboxylate bonds (COOM) and ester groups (COOR) in a (model) paint sample. We can calculate the maximum value of this ratio given the hypothesis that all COOM bonds contributing to the broad COOM band in the FTIR spectrum correspond to carboxylates bound to the surface of a pigment particle.

Making the assumption that all pigment particles are approximately spherical and monodisperse, the volume of each pigment particle is

$$V_{\text{part}} = \frac{4}{3}\pi r_{\text{part}}^3 \,, \tag{1}$$

where $r_{\text{part}}$ is the radius of a particle. Since the total volume of pigment is simply $V_{\text{p}} = m_{\text{p}}/\rho_{\text{p}}$ (where $m_{\text{p}}$ and $\rho_{\text{p}}$ are the mass and density of the pigment, respectively), the number of pigment particles $n_{\text{part}}$ can be calculated as

$$n_{\text{part}} = \frac{V_{\text{p}}}{V_{\text{part}}} = \frac{3m_{\text{p}}}{4\rho_{\text{p}}\pi r_{\text{part}}^3} \,. \tag{2}$$

The total available pigment surface area $A_{\text{p}}$ is then given by

$$A_{\text{p}} = 4\pi r_{\text{part}}^2 n_{\text{part}} = \frac{3m_{\text{p}}}{\rho_{\text{p}} r_{\text{part}}} \,. \tag{3}$$

The pigment surface area needed for the adsorption of one carboxylate group is denoted by $A_{\text{COO}}$. In our calculations, we derive a value for this parameter by assuming the dense packing of crystalline palmitic acid for carboxylates on the pigment surface (Moreno, E., et al. (2006). *Acta Cryst.*, C62, o129–o131). This packing is probably an overestimate of the maximum surface coverage of disordered carboxylates on the pigment particles, but is useful as a limiting case. Using the dimensions of the unit cell in crystalline palmitic acid, we find that $A_{\text{COO}} = 23.3$ Å$^2$. The maximum number of COOM bonds $n_{\text{COOM}}$ that can form is

$$n_{\text{COOM}} = \frac{A_{\text{p}}}{A_{\text{COO}}} = \frac{3m_{\text{p}}}{A_{\text{COO}}\rho_{\text{p}} r_{\text{part}}} \,. \tag{4}$$

The number of COOR groups $n_{\text{COOR}}$ in a given mass $m_{\text{LO}}$ of fresh linseed oil (LO) is

$$n_{\text{COOR}} = \frac{3m_{\text{LO}} N_{\text{A}}}{M_{\text{w,LO}}} \,, \tag{5}$$

where $M_{\text{w,LO}}$ is the average molecular mass of linseed oil (876 g mol$^{-1}$), $N_{\text{A}}$ is the Avogadro constant, and the factor 3 represents the fact that each triglyceride in linseed oil contains three COOR moieties.

We now make the additional assumption that every carboxylate group bound to a pigment surface is the result of hydrolysis of a linseed oil ester group, reducing the number of ester groups present in the system once a mixture of pigment and oil has been formed and cured, and further increasing the COOM/COOR ratio within the pigment surface hypothesis. This assumption is highly unlikely since many carboxylate groups will form through oxidation of the unsaturations in linseed oil triglycerides. However, since we do not have quantitative information on the relative concentration of these two types of carboxylate groups (formed through hydrolysis or oxidation), we favor the pigment surface hypothesis and assume all carboxylate groups derive from esters. In this case, the final maximum ratio between COOM and COOR groups in a system of pigment and oil is

$$\left[\frac{[\mathrm{COOM}]}{[\mathrm{COOR}]}\right]_{\mathrm{max}} = \frac{n_{\mathrm{COOM}}}{n_{\mathrm{COOR}} - n_{\mathrm{COOM}}} = m_{\mathrm{p}} \left( A_{\mathrm{COO}} \rho_{\mathrm{p}} r_{\mathrm{part}} \left[ \frac{m_{\mathrm{LO}} N_{\mathrm{A}}}{M_{\mathrm{w,LO}}} - \frac{m_{\mathrm{p}}}{A_{\mathrm{COO}} \rho_{\mathrm{p}} r_{\mathrm{part}}} \right] \right)^{-1} . \tag{6}$$

Finally, defining a weight ratio pigment to oil $R_{\mathrm{wt}} = m_{\mathrm{p}}/m_{\mathrm{LO}}$, replacing particle radii with diameters and some reorganization, the relation between the maximum COOM/COOR ratio and the pigment particle size and concentration as follows:

$$\left[\frac{[\mathrm{COOM}]}{[\mathrm{COOR}]}\right]_{\mathrm{max}} = R_{\mathrm{wt}} \left( \frac{\rho_{\mathrm{p}} N_{\mathrm{A}} A_{\mathrm{COO}} d_{\mathrm{part}}}{2 M_{\mathrm{w,LO}}} - R_{\mathrm{wt}} \right)^{-1} . \tag{7}$$

This equation is plotted as function of particle size for a number of pigment concentrations in the main article, showing that for realistic particle sizes and pigment concentrations the maximum COOM/COOR ratio does not come close to experimental values obtained from model paints of ZnO in linseed oil.

# 4 ATR-FTIR spectra of zinc and lead ionomer samples

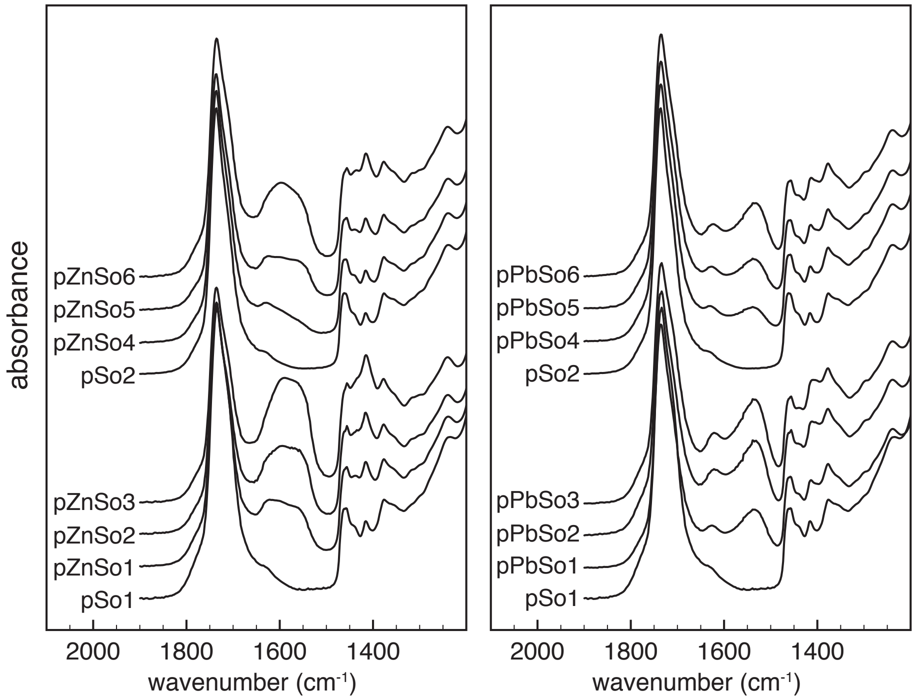


**Figure 2:** ATR-FTIR spectra of (left) zinc and (right) lead ionomer samples used for the SAXS measurements discussed in the main article. Spectra were basline corrected and normalized to the $CH_2$ vibration band at 2925 $cm^{-1}$. Sample codes correspond to the compositions noted in Table S1.