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Time-Dependent ATR-FTIR Spectroscopic Studies on Fatty Acid Diffusion and the Formation of Metal Soaps in Oil Paint Model Systems

Lambert Baij^{†,*}, Joen J. Hermans^{†,*}, Katrien Keune, and Piet Iedema

Abstract: The formation of metal soaps (metal complexes of saturated fatty acids) is a serious problem affecting the appearance and structural integrity of many oil paintings. Tailored model systems for aged oil paint and time-dependent attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy were used to study the diffusion of palmitic acid and subsequent metal soap crystallization. The simultaneous presence of free saturated fatty acids and polymer-bound metal carboxylates leads to rapid metal soap crystallization, following a complex mechanism that involves both acid and metal diffusion. Solvent flow, water, and pigments all enhance metal soap crystallization in the model systems. These results contribute to the development of paint cleaning strategies, a better understanding of oil paint degradation, and highlight the potential of time-dependent ATR-FTIR spectroscopy for studying dynamic processes in polymer films.

Traditional oil paints are a mixture of mainly inorganic pigments, a drying oil (triglycerides with a high degree of unsaturation) and a wide variety of possible additives. As the oil binding medium dries and ages through autoxidation reactions, this mixture becomes a complex heterogeneous system of solid particles suspended in a dense polymer matrix. Oil paints are subject to slow deterioration processes that affect the appearance and structural integrity of oil paintings. Factors such as humidity,^[1,2] exposure to solvents,^[3,4] temperature changes, and exposure to light^[5] are known to influence the stability of oil paint. Reactions between pigments or metal-based siccatives and the oil binder can lead to the prominent conservation issue of metal soap formation: complexes of metal ions (usually lead or zinc) and long-

chain saturated fatty acids. These complexes can form large crystalline aggregates that protrude through the paint surface and have been associated to cases of brittleness, transparency, and delamination in oil paint layers.^[6]

An important discovery has been that metal ions (originating from pigments or driers) migrate into the binding medium, where they are distributed throughout the polymerized oil network and associated to carboxylate groups.^[7–9] Such an ionomer medium contains clusters of metal carboxylate groups (identified by a broad ν_a COO⁻ band in infrared (IR) spectra) that, while potentially reactive towards long-chain saturated fatty acids (SFAs), could contribute to the stability of the oil network on the short term.^[8] SFAs can either be formed by partial hydrolysis of the polymerized oil network, or be derived from paint additives such as aluminum stearate.^[10] Our current hypothesis, illustrated in Figure 1, is that the presence of free SFAs leads to the formation of amorphous metal soap complexes. Subsequently, owing to the low solubility of metal soaps in oil,^[11] these complexes will tend to crystallize and form metal-soap aggregates. With FTIR spectroscopy, this crystalline state of metal soaps can be distinguished from amorphous metal carboxylate species by their sharp COO⁻ bands at 1510 cm⁻¹ (Pb) or 1538 cm⁻¹ (Zn).

Linseed oil-based ionomer model systems and time-dependent ATR-FTIR spectroscopy were used to investigate the diffusion of a SFA (palmitic acid) and its reaction with metal carboxylate clusters. ATR-FTIR spectroscopy has proven to be a powerful tool to study dynamic processes in polymer films.^[12–17] Mature oil paint model systems (Zn₂pol and Pb₂pol) were synthesized by co-polymerization of linseed oil (LO) and metal sorbate (2,4-hexadienoate) at 150 °C (Supporting Information). We have confirmed that these

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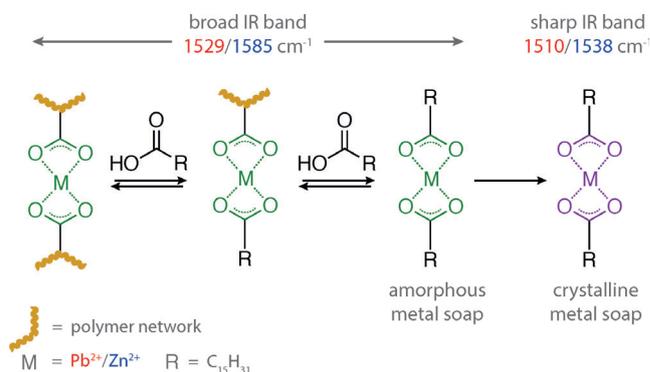


Figure 1. Hypothetical pathway for the formation of crystalline metal soaps from ionomeric binding media upon exposure to palmitic acid (HPa).^[9] The noted wavenumbers refer to the position of the ν_a COO⁻ vibration band for lead (red) and zinc (blue) complexes. The geometry of the metal carboxylate complexes is only intended as illustration.

systems are representative of mature oil paint in terms of metal carboxylate concentration and structure.^[7–9] We subjected our paint models either to fatty acid in solution or to molten fatty acids, because long-chain fatty acids are solids at room temperature. Both conditions entail a departure from the real conditions in oil paintings to some degree but do allow the studying of essential reaction-diffusion processes.

The model systems were exposed to a solution of palmitic acid (HPa) in acetone in a custom ATR sample cell (Supporting Information, Figure S1) that ensured a constant contact between the samples and the ATR crystal. These experiments provided information on the sequence of several diffusion and reaction processes that happen on much longer timescales in real oil paintings. Figure 2 shows the evolution of IR spectra of Znpol and Pbpol recorded during the first 200 minutes of exposure to a solution of HPA in acetone. The spectra before exposure exhibit clear amorphous metal carboxylate bands in the 1500–1650 cm⁻¹ region. At $t > 0$, IR bands corresponding to acetone appeared within minutes, while the remainder of the spectrum decreased in intensity owing to a decreasing concentration of polymer in the measurement volume. After 10–20 minutes, carboxylate bands associated with crystalline lead palmitate (PbPa₂) and zinc palmitate (ZnPa₂) were detected. In Pbpol, CH₂ pro-

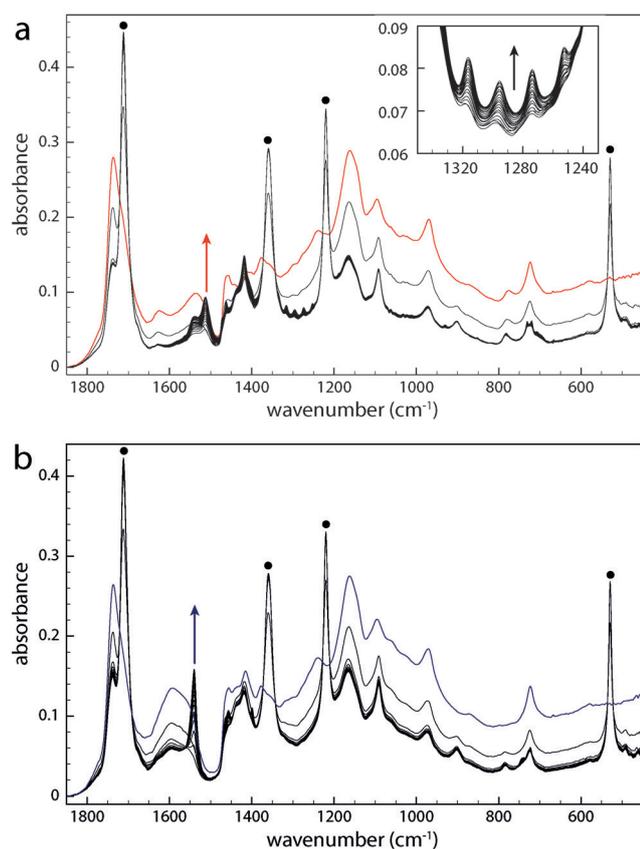


Figure 2. A baseline-corrected selection of IR spectra with 10 min time intervals of a) Pbpol and b) Znpol ionomers of 140–160 μm thickness, recorded during the first 200 minutes of exposure to a solution of HPA in acetone. Spectra at $t = 0$ are highlighted in red and blue for lead and zinc, respectively. Bands associated with acetone are marked by \bullet . Arrows indicate the $\nu_a\text{COO}^-$ vibration of crystalline MPa₂ complexes. The inset in (a) shows the CH₂ progression bands of PbPa₂.

gression bands between 1240–1340 cm⁻¹, associated with packed all-*trans* alkyl chains, were clearly visible. X-ray diffraction measurements on ionomer films after exposure to HPA solution (Supporting Information, Figure S2) confirm the attribution of the sharp $\nu_a\text{COO}^-$ bands appearing in Figure 2 to crystalline metal palmitate (MPa₂) complexes.

Integrated band areas corresponding to acetone, PbPa₂, and ZnPa₂ are shown in Figure 3, which clearly illustrate the sequence of diffusing species detected at the bottom of the

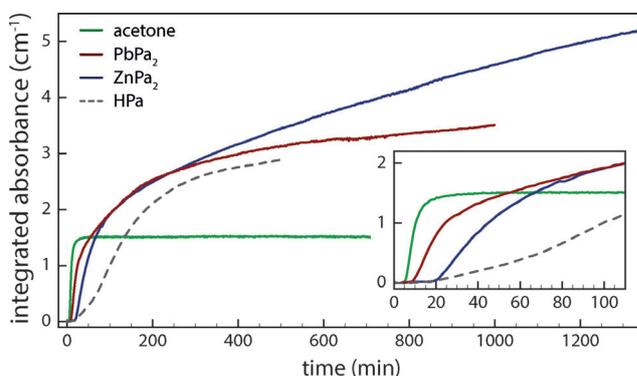


Figure 3. Profiles of IR band areas corresponding to acetone (529 cm⁻¹), PbPa₂ (1510 cm⁻¹), and ZnPa₂ (1538 cm⁻¹) in Pbpol and Znpol ionomers during exposure to a solution of HPA in acetone (56 mm). The diffusion profile of molten HPA (1710 cm⁻¹) was recorded at 70 °C in a polymerized linseed oil film (pLO).

film. To obtain accurate areas of the crystalline MPa₂ bands, a custom spectral processing algorithm was applied to subtract contribution of the overlapping broad metal carboxylate band (see the Supporting Information, Figure S3 for details). After 30 minutes, the concentration of acetone reached a constant value in the measurement volume (penetration depth^[18] d_p varies from 0.5 to 3.5 μm from 3500 to 500 cm⁻¹). IR bands of PbPa₂ and ZnPa₂ were detected just minutes after acetone was first observed. The shape of the profiles and the time at which species are first detected (delay time τ_d) give valuable information on the reaction and diffusion processes taking place.

To investigate the effect of the presence of metal ions on HPA diffusion, we compared reactive and unreactive films (that is, linseed oil without metal ions, see Supporting Information). Films of pure polymerized linseed oil (pLO) were exposed to molten HPA at 70 °C while monitoring the $\nu_a\text{COOH}$ band at 1710 cm⁻¹ (see the Supporting Information, Figure S3 for the integration method). The diffusion profile of molten HPA (dashed line in Figure 3) was described well with a simple Fickian diffusion model,^[18] yielding a diffusion coefficient $D = 1.15 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ (Supporting Information, Figure S4).

The fast formation of MPa₂ complexes in the measurement volume demonstrates that metal soap crystallization starts directly after HPA reaches the bottom of the film, indicating that the presence of free SFAs in ionomeric binding media is enough to cause spontaneous metal soap crystallization. Consequently, any process that may increase the free SFA concentration in a paint (for example, ester hydrolysis or

wax-resin lining of paintings^[19]), is expected to have a significant effect on the metal soap formation rate. Comparing the profiles of Pbpol and Znpol (Figure 3), PbPa₂ had a τ_d of approximately 10 min, while for ZnPa₂ τ_d = 20 min. Interestingly, τ_d for molten HPA in the unreactive pLO was greater than the delay time of crystalline MPa₂ complexes in reactive ionomer systems. This observation indicates that the initial HPA diffusion rate is strongly increased by the simultaneous flow of acetone in the same direction. Moreover, the MPa₂ concentration profile keeps increasing slowly on long time-scales, unlike the diffusion profiles of acetone or other solvents.^[17]

The observed concentration profiles offer a better understanding of the reaction and diffusion of free SFAs, solvents (cleaning agents) as well as the possible transport of network-bound metal ions in oil paintings. The idea that the investigated systems contain multiple diffusion processes seems to be confirmed by the presence of a fast and slow regime (Figure 4). One explanation for these two regimes is a decreasing HPA diffusion rate as the local concentration of crystalline MPa₂ increases and fills up the free volume in the polymer network. Alternatively, if there is a slow migration process of metal ions at play, the fast regime of MPa₂ crystallization can be interpreted as the consumption of network-bound metal carboxylates initially present in the measurement volume. The slow regime would then be caused by M²⁺ migration, causing crystalline metal soaps to keep forming at the bottom of the sample even when the initial concentration of metal ions in the measurement volume has been consumed. In this scenario, metal soaps would need to show preferential crystallization near the polymer/ATR-crystal interface. Such an accumulation process is also suggested by the intensity of the ZnPa₂ band in films after long exposure to HPA solutions (Supporting Information, Figure S5). The intensity of this band is far greater in Znpol after reaction than in a mixture of ZnPa₂ and linseed oil with the same Zn²⁺ content. Interestingly, even though one would expect metal ions to migrate towards the top of the film (where HPA arrives first), these measurements suggest that

M²⁺ ions from outside the measurement volume have migrated towards the bottom of the film instead.

The effect of acetone flow on the diffusion of HPA was investigated by carrying out reaction-diffusion experiments in which HPA was only introduced after the sample film was first fully saturated with acetone (Figure 4a,b). While the MPa₂ profile shape was unaffected, the pre-swollen films did show a significantly increased τ_d . This delay supports the notion that the rapid initial diffusion of HPA and subsequent crystallization of MPa₂ shown in Figure 3 is indeed caused by the initial acetone flow.

In all of the experiments, τ_d was approximately twice as long in Znpol compared to Pbpol. Previous research demonstrated that crystallization from the melt is a faster process for PbPa₂ than for ZnPa₂,^[11] which offers an explanation for the earlier detection of PbPa₂. Significant differences in the diffusion rate of HPA in the two ionomers are not expected, because the diffusion constants of a wide range of solvents were approximately equal in Znpol and Pbpol.^[17]

In studies of oil paint ageing, water has always been suspected of causing a broad range of degradation phenomena, primarily through hydrolysis of the triacylglyceride ester bonds. We studied the effect of water on the reaction-diffusion processes by removing as much water from the system as possible. The dotted curves in Figure 4a,b show the MPa₂ profiles recorded on films that were dried overnight in vacuum at 100 °C, using dry acetone that was freshly distilled over B₂O₃. Both for Znpol and Pbpol, τ_d was similar to the non-dried runs. However, the subsequent rate of MPa₂ formation was slower and the final conversion was much lower, especially for Znpol. This result demonstrates that even low concentrations of water in the system have a profound effect on the rate of metal soap formation. Rather than promoting metal soap formation by generation of free SFAs through ester hydrolysis, here water increases the rate of MPa₂ formation when free SFAs are introduced to the system. We hypothesize that water lowers the activation energy for metal ion transfer between carboxylate groups, thereby increasing the metal ion migration rate through the

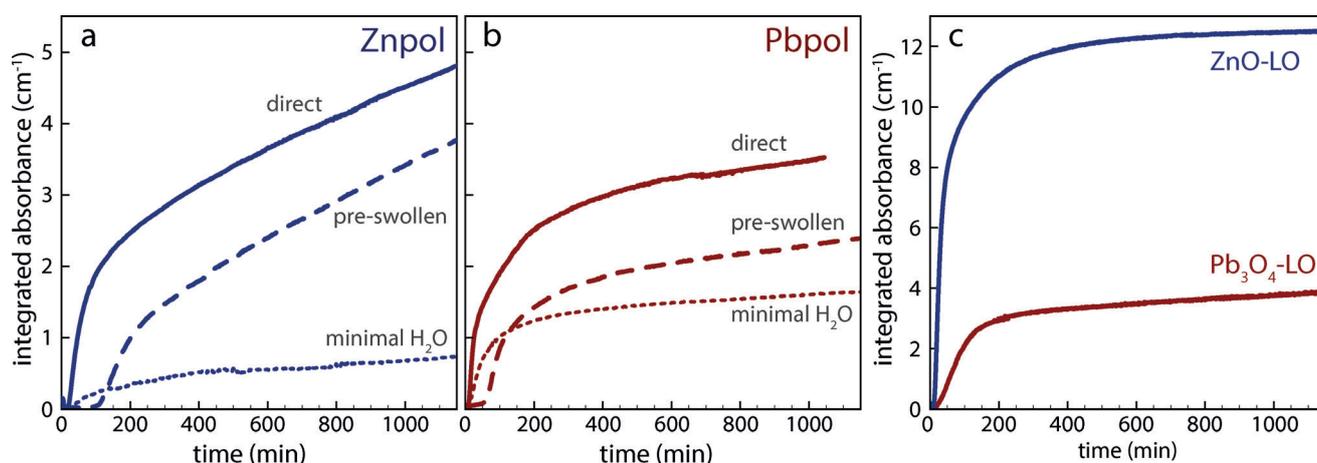


Figure 4. MPa₂ concentration profiles in a) Znpol and b) Pbpol ionomers, comparing experiments with direct exposure to a HPA solution (—), pre-swelling with acetone (-----), or removal of most of the water in the system (•••••). The pre-swollen curves were shifted horizontally to place $t=0$ at the moment of HPA addition. c) MPa₂ profiles in paint films pigmented with ZnO (blue curve) or Pb₃O₄ (red curve).

polymer network and the consumption of metal ions by free SFAs. Such an effect has been demonstrated in perfluorosulfonated ionomer membranes.^[20]

We compared the unpigmented ionomer systems ZnPOL and PbPOL with complete paint models consisting of zinc oxide (ZnO) or minium (Pb₃O₄) in linseed oil, dried at 60 °C for one week (denoted ZnO-LO and Pb₃O₄-LO, respectively). Both these paint models showed broad COO⁻ bands in FTIR spectra that are nearly identical in both shape and intensity to ZnPOL and PbPOL systems (Supporting Information, Figure S6), indicating the formation of ionomeric binding media.^[8] Figure 4c shows the crystalline MPa₂ profiles for ZnO-LO and Pb₃O₄-LO during exposure to HPA solution. The pigmented films showed very fast MPa₂ crystallization on short timescales. The concentration of ZnPa₂ in the ZnO-LO system reached a constant level after approximately 600 minutes, while the concentration of PbPa₂ was still increasing in the PbPOL system after 1000 minutes.

It is apparent that pigmentation strongly affects the metal soap formation process. Though the intensities of the initial broad COO⁻ bands in ZnO-LO and Pb₃O₄-LO were very similar to those in ZnPOL and PbPOL, the initial slope of the profiles and the band intensities after 1000 minutes were, especially in the case of ZnO-LO, greater in the case of pigmented films (compare Figure 4a–c). Two effects can explain these differences. First, in the case of ZnO-LO, it is evident that ZnO particles are consumed as the total concentration of COOH groups increases when HPA flows into the system and metal soaps form. Second, the pigment surface could act as a suitable nucleation site for MPa₂. It is conceivable that both factors are in effect to different degrees in Pb₃O₄-LO and ZnO-LO, explaining the differences in their profile shapes. If Pb₃O₄ is less prone to degradation than ZnO, this higher stability could result in a slower release of Pb²⁺ during the measurement and an overall profile shape that is largely governed by slow transport of Pb²⁺ ions that were already present in the binding medium at the start of the experiment.

All of the effects discussed here highlight the complexity of the metal soap crystallization process in ionomeric binding media. Time-dependent ATR-FTIR spectroscopy is a powerful method to study such complex processes with high chemical specificity. Our current results have shown that:

- the presence of free SFAs leads to rapid metal soap crystallization in ionomeric binding media;
- solvents can displace reactive molecules such as HPA in a paint system (for example, from the surface to the interior of paint layers);
- low water concentrations strongly influence the crystallization rate of metal soaps;
- metal soap crystallization can lead to the breakdown of pigments.

Future work will be directed at the development of computational models to simulate the reaction-diffusion system and FTIR microscopy measurements^[21] on reacting ionomer systems to study heterogeneity in metal soap concentrations across the depth of the paint films.

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Conflict of interest

The authors declare no conflict of interest.

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