The synthesis of new types of lead and zinc soaps: a source of information for the study of oil paint degradation


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JOEN J. HERMANS*
Van ’t Hoff Institute for Molecular Sciences
University of Amsterdam
Amsterdam, The Netherlands
j.j.hermans@uva.nl

KATRIEN KEUNE
Van ’t Hoff Institute for Molecular Sciences
University of Amsterdam
Amsterdam, The Netherlands

ANNELIES VAN LOON
Van ’t Hoff Institute for Molecular Sciences
University of Amsterdam
Amsterdam, The Netherlands
Royal Picture Gallery Mauritshuis
The Hague, The Netherlands

MAARTJE J.N. STOLS-WITLOX
Faculty of Humanities
University of Amsterdam
Amsterdam, The Netherlands

ROBERT W. CORKERY
Royal Institute of Technology (KTH)
Stockholm, Sweden

PIET D. IEDEMA
Van ’t Hoff Institute for Molecular Sciences
University of Amsterdam
Amsterdam, The Netherlands

*Author for correspondence

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ABSTRACT
Lead and zinc soaps are commonly seen as signs of oil paint degradation. The pathway from pigment to metal soaps and their subsequent migration and accumulation are poorly understood, and it is unknown to what extent these processes are influenced by humidity and temperature. In order to understand fully the behavior of metal soaps in paint systems, it is first necessary to characterize the molecular structure of metal soaps in detail. This paper presents the synthesis and structural characterization of three new types of metal soaps: “basic” lead soaps, zinc soaps that incorporate sodium or potassium ions, and metal soaps containing both palmitate and stearate. The results are a first step toward more accurate interpretations in paint sample analysis and a more detailed understanding of oil paint degradation on a molecular scale.

INTRODUCTION
The presence of metal soaps in paint layers is an important issue in oil paint research. Lead and zinc salts of palmitate and stearate are now commonly recognized as signs of paint degradation, since metal soaps play a role in the formation of aggregates, efflorescence, and increased transparency in paint layers (Higgitt et al. 2003, Noble et al. 2005, Keune and Boon 2007). The different steps in the pathway from pigment and binder to metal soap are poorly understood. In addition, it is still an open question whether it is possible to form different varieties of metal soaps that incorporate multiple metals or a mixture of anions. Variations in composition have an effect on the behavior of metal soaps in paint systems. Also, it is essential for the conservation of paintings to know to what extent specific environmental conditions like humidity and temperature promote the formation and migration of metal soaps. The molecular structure of soaps is a potential source of information on the conditions that lead to paint degradation. In order to characterize the molecular structure of metal soaps in detail, it is necessary to start by simplifying the system and to study their formation outside a paint context, investigating the possibility of alternative metal soaps. Once structural knowledge is available and favorable conditions for metal soap formation are well understood, the analysis of samples from works of art can be interpreted more accurately. Moreover, the understanding of internal paint conditions as well as metal soap migration processes will be improved.

This paper introduces the syntheses and analysis of three new types of lead and zinc soaps to the field of conservation: a variety of lead soaps forming on litharge (PbO) particles, soaps containing mixtures of metal ions, and soaps containing mixtures of fatty acids. All soaps are characterized with Fourier transform infrared spectroscopy (FTIR) and powder x-ray diffraction (PXRD).

Lead soap variations
Pure lead soaps synthesized in solution invariably show a sharp infrared absorption band around 1510 cm⁻¹, corresponding to the asymmetric COO stretch vibration (Robinett and Corbeil 2003). In paint samples, FTIR absorption bands attributed to lead soaps are often much broader and the position of the band maximum is shifted to higher wave numbers. An
example of such a shifted broad band is shown in Figure 1, in an FTIR spectrum of a sample of lead white paint from Portrait of a Man by Thomas de Keyser. A partial explanation for this effect is the heterogeneous nature of oil paint: the wide range of molecular species in aged oil paint may result in multiple overlapping absorption bands. However, the variation in infrared absorption could also be caused by differences in the coordination environment around the lead atom. Fatty acids adsorbed on a pigment particle, for instance, may involve multiple coordination modes of carboxylic groups around surface lead ions. Such an effect has been studied for zinc white (ZnO) (Lenz et al. 2009). To investigate similar structural variations, the authors followed the reaction between PbO and palmitic acid in water.

Metal mixtures in soaps

Paintings usually contain combinations of metal-based pigments and driers. In principle, all metals can form complexes with fatty acids, but only lead and zinc soaps are regularly found in paintings. The formation of mixed metal soaps with multiple di- or trivalent metal ions seems unlikely, since the preferred metal soap structure is highly dependent on the coordination behavior of the metal ion (Corkery 1998). However, structures of mixed metal carboxylates containing alkaline metal ions have been reported (Lah et al. 2000, Casado et al. 2011). The effect of sodium and potassium ions on the soap formation on ZnO and PbO particles was studied.

Fatty acid mixtures in soaps

Metal soap aggregates found in paint samples contain predominantly palmitate and stearate salts (Van den Berg 2002). With FTIR, it is impossible to determine whether palmitate and stearate soaps crystallize in separate phases, or whether the molecules are mixed within a single crystalline material. This distinction can be made with PXRD (Barman and Vasudevan 2007). The formation of zinc and lead soaps of palmitate/stearate mixtures was investigated and their crystalline structures studied.

EXPERIMENTAL

Synthesis

Metal soaps were prepared in a double decomposition reaction or by adding a poorly soluble metal oxide to an alkaline fatty acid solution. In a typical double decomposition synthesis, 0.50 g palmitic acid was dissolved in 25 mL demineralized water (70°C) containing a molar excess of triethylamine (TEA). Adding a solution of Pb(NO₃)₂ or Zn(NO₃)₂.6H₂O resulted in immediate precipitation of an insoluble metal soap. In alternative syntheses using PbO (litharge) or ZnO (wurtzite), the metal compounds were added to the solution as finely ground powders. Reactions were stirred for at least 30 minutes. Products were separated by filtration under vacuum, washed with demineralized water, and dried in an oven at 110°C. In reactions with PbO that were followed over time (at least 8 hours), the reaction was performed in a reflux setup to prevent evaporation. Samples taken from the reaction mixture were immediately filtered and dried prior to analysis.
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SCIENTIFIC RESEARCH

ATR-FTIR spectra of dried powders were collected on a Varian 660-IR FT-IR spectrometer using a Pike Technologies diamond GladiATR unit. Spectra were averaged over 15 scans with a spectral resolution of 4 cm⁻¹. Elemental analysis was carried out by Mikroanalytisches Labor Kolbe, Mülheim, Germany, using a combination of the combustion method and AAS. Crystal lattice spacings were measured on a Rigaku MiniFlex II desktop X-ray diffractometer with Cu Kα radiation (λ = 1.54180 Å). Diffractograms were recorded in a 2θ = 1–40° range (5°/min scan rate and 0.05° step size). Samples were prepared by manually pressing finely ground powder in a glass sample holder.

Diffractograms of metal soaps showed multiple (00l) reflection orders of the long spacing (i.e., the distance between metal ion sheets). In order to obtain highly accurate long spacing values, a fitting procedure was applied that corrects for sample displacement and makes use of all detectable reflection orders. The corrected long spacing was calculated by plotting the d-values as a function of cos²θ/sinθ and applying a linear least squares fit. In this method, the intersect of the fitted line with the vertical axis gives the corrected long spacing (Polvino 2011). The standard error in the measured long spacing was typically around 0.1%.

RESULTS AND DISCUSSION

Lead soap variations

PbO reacted readily with palmitate (C₁₆) in aqueous solution to yield lead soaps, as was observed by a color change in the suspension from orange to white. Under reaction conditions with molar Pb:C₁₆ ratios of 1:2 and higher, the double decomposition product Pb(C₁₆)₂ was found. Surprisingly, at Pb:C₁₆ ratios under 1:1, the end product did not correspond to Pb(C₁₆)₂ (Figure 2a and b). In this alternative product, the characteristic asymmetric COO band normally seen at 1506 cm⁻¹ shifts to 1485 cm⁻¹, while the band at 1540 cm⁻¹ remains unchanged. An overview of relevant FTIR bands is given in Table 1.

Elemental analysis suggests that the alternative product is a “basic” lead soap, with a metal layer structure similar to basic lead acetate (Pb₃O₂(CH₃COO)₂.0.5H₂O) (Mauck 2010). In contrast with neutral soaps, where a single sheet of lead ions links the fatty acid chains, basic soaps contain additional Pb₄O tetrahedra in the metal sheet.

The reaction conditions that lead to the formation of basic soap was repeated with basic lead carbonate (lead white, 2PbCO₃.Pb(OH)₂). Characteristic neutral Pb(C₁₆)₂ bands were detected at all C₁₆ concentrations, and no indications of the presence of basic lead soaps were found.

Returning to the original question of band broadening in FTIR spectra of lead soaps in paint films, samples were taken over time from the reaction between PbO and C₁₆ where basic soap was formed. Just 15 seconds after the addition of PbO, clear lead soap bands were visible (Figure 2c). Compared to samples of basic PbC₁₆ at longer reaction times, no significant band shifting or broadening was observed. Similarly, samples from the

<table>
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<td>Overview of characteristic FTIR bands (cm⁻¹) and assignments in neutral PbC₁₆ and basic PbC₁₆</td>
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* s = strong, m = medium, w = weak, sh = shoulder

Analysis

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Pb(C_{16})_2 synthesis using 2PbCO₃·Pb(OH)₂ showed sharp FTIR bands throughout the reaction. If there is a pigment surface effect on the band shape, it is expected that at least a small shift and/or broadening can be detected by comparing FTIR spectra taken after 15 seconds, when the soap layer is thin, and spectra corresponding to longer reaction times. Since no correlation was found between the extent of lead soap formation and the FTIR band shape or position, it can be concluded that the band broadening and shift in paint samples is not caused by fatty acids bound to a pigment surface.

An alternative explanation could be that a degree of disorder in metal soap assemblies, not unlikely when metal soaps form in cured linseed oil, disturbs the coordination of carboxylic groups around the lead center. This hypothesis, as well as a full investigation of the reactions of various lead pigments with fatty acids, is beyond the scope of this paper and will be the subject of a forthcoming publication.

It is important for paintings research to be aware that a second type of lead soap with distinct FTIR absorption bands may form on PbO. Preliminary experiments showed that the molar ratio Pb:C_{16} determines the type of lead soap that forms. Regardless of the Pb:C_{16} ratio, however, basic PbC_{16} was detected as an intermediate product. When more is known about the exact conditions that could lead to basic lead soap formation in linseed oil, it may become possible to use an identification of the type of lead soaps in paint samples to determine the extent of metal soap formation, oil hydrolysis, and pigment degradation.

**Metal mixtures in soaps**

ZnO reacted quickly in an aqueous solution of stearic acid (C_{18}) and TEA to yield Zn(C_{18})₂. In this reaction, TEA aids the dissolution of C_{18} in water by deprotonation of the carboxylic group. When TEA was replaced by NaOH, the COO bands in the FTIR spectrum showed marked shifts (Figure 3): the asymmetric stretching COO band is shifted from 1537 to 1595 cm⁻¹, with two smaller bands at 1609 and 1622 cm⁻¹, the COO deformation band shifts to a lower frequency at 677 cm⁻¹, while the symmetric stretching band remains at a similar position (1410 cm⁻¹). The spectrum in Figure 3b corresponds exactly to a ZnNa₂(C_{18})₄ compound reported by Toda et al. (1971). Mixed soaps with zinc and potassium (ZnK₂(C_{18})₄) could be prepared in a similar fashion by using KOH as a base. An overview of all characteristic FTIR bands is given in Table 2.

The crystal structure of long chain zinc/sodium soaps is very likely to be analogous to the structure of Na₂[Zn(C_{6}H₄O₂)$_4$], reported by Lah et al. (2000). In this structure, zinc is tetrahedrally coordinated by carboxylic
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The formation of ZnNa$_2$(C$_{18}$)$_4$ as described by Toda et al. (1971) involves Zn(SCN)$_2$ as a precursor. The synthesis using ZnO described here has not been reported before, and is reproducible under a range of conditions. ZnNa$_2$(C$_{18}$)$_4$ was formed when TEA was used as a base and an excess of NaCl was added just before the addition of ZnO. Alternatively, the soap was synthesized by melting a stoichiometric mixture of powdered NaC$_{18}$ and Zn(C$_{18}$)$_2$ at 160°C. All these reaction pathways could be employed for the synthesis of ZnK$_2$(C$_{18}$)$_4$ as well. However, the incorporation of alkaline metal ions in lead soaps was unsuccessful. In lead soaps, FTIR and XRD analysis showed that sodium and potassium had either no effect on soap formation, or NaC$_{18}$/KC$_{18}$ precipitated as a separate phase.

Of direct relevance to paint research, a mixed metal soap was found to be the major product when a reaction was carried out in untreated cold-pressed linseed oil with ZnO, powdered NaOH or KOH and C$_{18}$. Since ZnNa$_2$(C$_{18}$)$_4$ and ZnK$_2$(C$_{18}$)$_4$ form spontaneously in linseed oil, one can expect to find these soaps in paintings that contain both zinc white and pigments containing sodium or potassium (e.g. ultramarine, cobalt yellow, earth and lake pigments), or in paintings that have undergone conservation treatment with strongly alkaline materials (Stols-Witlox 2011). The detection of a sharp FTIR band around 1595 cm$^{-1}$ in zinc white containing paint layers can be interpreted as a strong indication of the presence of pigments that contain alkaline metals.

Fatty acid mixtures in soaps

Soaps containing both palmitate and stearate in varying ratios were prepared by double decomposition. Identical products were found when reactions were carried out in linseed oil.

The diffraction patterns of Zn((C$_{16}$)$_{(1-x)}$(C$_{18}$)$_{x}$)$_2$ and Pb((C$_{16}$)$_{(1-x)}$(C$_{18}$)$_{x}$)$_2$ (0<x<1) showed one set of (00l) reflections for all compositions, yielding unique long spacings $d$ in between the values for pure palmitate and pure stearate soaps (Figure 5). The absence of a second set of reflections signifies that palmitate and stearate are mixed within each crystalline particle.

If the fatty acids are randomly distributed in the crystallites, forming a so-called solid solution, the long spacings should grow linearly with increasing molar fraction of stearate $x$. In an ideal case, the measured long spacing is described by $d = (1-x)d_{C_{16}} + xd_{C_{18}}$. For such a linear relationship, a degree of flexibility in the layers is required to accommodate molecular chains of different length (Barman and Vasudevan 2007). Figure 5 shows that in both lead and zinc soaps, the long spacing $d$ deviates from the linear trend towards higher values. This deviation means that the alkyl chains in the metal soap crystal structure are fairly rigid, and that the positions of the alkyl chains and the metal ions are not easily adapted when palmitate is mixed in the structure (Lee et al. 1989). A consequence of this rigidity could be that small voids are left in the crystal structure of C$_{16}$/C$_{18}$ soaps where opposing fatty acid chains meet.
In the FTIR spectra of Pb((C16)(1-x)(C18)x)2 soaps (Figure 6), the progression bands in the 1150–1370 cm\(^{-1}\) region arise from the coupling of different -CH\(_2\) vibration modes in all-trans alkyl chains. The number of bands and their position depend on the length of the carbon chain; pure Pb(C18)\(_2\) shows ten clear bands while pure Pb(C16)\(_2\) has nine. In mixed Pb((C16)(1-x)(C18)x)2 soaps, the intensities of the bands associated with stearate and palmitate are directly proportional to the molar stearate fraction x. The straightness and rigidity of the stearate chains that were inferred from PXRD analysis are also confirmed by the progression bands in Figure 6; in all C16/C18 soaps a full series of progression bands was observed, indicating a neat all-trans chain configuration.

Both FTIR and PXRD analysis are frequently applied to paint cross sections. Provided that a sample contains sufficiently large metal soap aggregates, FTIR microscopy and μ-XRD can be used to determine palmitate-stearate ratios in metal soaps. For example, comparison of the FTIR spectrum of a lead soap inclusion from The Avenue at Middelharnis by Hobbema (Plater 2003) with the spectra in Figure 6 shows that the inclusion contains 25–40% stearate.

Mixing stearate and palmitate in metal soaps can affect solubility and migration behavior. Therefore, the consequences of fatty acid mixing in metal soaps needs to be considered in future studies into the behavior of metal soaps in oil paints and the effects of conservation treatments.

CONCLUSION

Three new types of metal soaps have been synthesized that were not described previously in relation to oil paint systems: basic lead soaps, zinc soaps incorporating sodium or potassium, and soaps containing fatty acids of different length. Soaps containing zinc and sodium form spontaneously in linseed oil, and palmitate/stearate soaps have been found in oil paint samples described in the literature. The next step will be to focus on investigating the properties of these new soaps that are relevant to
conservation practice, such as their solubility, melting point, and mobility in paint systems.

Generally, these studies show that metal soaps cannot be viewed simply as molecules, i.e., two fatty acids bound to a metal ion. Large variations exist beyond the molecular level in the crystalline or disordered structure of metal soap complexes, and these variations are of crucial importance in the study of metal soap formation and migration.

The reactions involved in metal soap formation will continue to be studied. As the next step toward improving our knowledge of metal-soap-related paint degradation, oil paint model systems are being developed in which the formation, migration, and crystallization of metal soaps can be followed. Simultaneously, it will be essential to correlate laboratory experiments to the chemical processes in reconstructed paints prepared according to historical recipes, and, ultimately, to the reactions that have occurred in real paintings.

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