

Review of the use of NMR spectroscopy to investigate structure, reactivity, and dynamics of lead soap formation in paintings

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Abstract

Heavy metal carboxylate or soap formation is a widespread deterioration problem affecting oil paintings and other works of art bearing oil-based media. Lead soaps are prevalent in traditional oil paintings because lead white was the white pigment most frequently chosen by old masters for the paints and in some cases for the ground preparations, until the development of other white pigments from approximately the middle of the 18th century on, and because of the wide use of lead-tin yellow. In the latter part of the 19th century, lead white began to be replaced by zinc white. The factors that influence soap formation have been the focus of intense study starting in the late 1990s. Since 2014, nuclear magnetic resonance (NMR) studies have contributed a unique perspective on the issue by providing chemical, structural, and dynamic information about the species involved in the process, as well as the effects of environmental conditions such as relative humidity and temperature on the kinetics of the reaction(s). In this review, we explore recent insights into soap formation gained through solid-state NMR and single-sided NMR techniques.

KEYWORDS

¹¹⁹Sn, ¹³C, ²⁰⁷Pb, lead-tin yellow, lead white, linseed oil, NMR, paintings, single-sided NMR, soaps

1 | INTRODUCTION

The formation of metal carboxylates (soaps) has been reported in hundreds of oil paintings dating from the 15th to the 20th century.^{1–10} Soaps are the result of reactions between metals in pigments or in other compounds present in the paints, such as driers or other modifiers, and long chain fatty acids originating in the binding medium or coatings. The triggering factors and underlying mechanisms behind the processes are not yet

completely understood. Saponification may manifest itself in a variety of ways, such as by the formation of aggregates and surface crusts, delamination, and/or the increased transparency of the paints. Therefore, these processes affect the visual appearance and structural integrity of affected artworks. Metal soaps, such as those of aluminum, may also be present in commercial paint formulations as additives,^{11,12} but the effect of these compounds has yet to be thoroughly explored. A complete understanding of the dynamics behind the formation and

migration processes is necessary to propose ways to mitigate or prevent the problem.

Vibrational spectroscopy is routinely used for the characterization and identification of the molecular composition of cultural heritage objects because of its ease of use, high sensitivity, and minimal sampling or noninvasive nature.^{13–16} Fourier-transform infrared spectroscopy (FTIR) and Raman spectroscopy, sometimes in combination with chemometrics, have been used extensively in the study of the composition and degradation of binders and other organic artistic materials.^{17–21} The combination of FTIR microscopy and atomic force microscopy (AFM) has been shown to increase resolution, down to the nanoscale.²² FTIR and Raman spectroscopies are commonly used techniques for the identification and characterization of lead soaps in microsamples removed from paintings and in model paint systems.^{10,23–31}

Structural information about carboxylates related to soap formation determined by powder and single-crystal X-ray diffraction has been reported for Pb, Zn, and Cu soaps.^{4,27,32,33} Micro-X-ray fluorescence (XRF) has been particularly useful for analyzing the elemental distribution in Pb soap protrusions. The use of a micron-sized beam in XRF mapping, with scanning of the X-ray photon energy, allows micro-X-ray absorption near-edge structure (micro-XANES) spectroscopy across the Pb-M₄ and M₅ edges that permits differentiation of Pb pigments and Pb soaps.^{9,34,35} Scanning electron microscopy (SEM), in combination with optical microscopy, has been applied to image the characteristic morphology of soap protrusions localized in the stratigraphy of paint cross-sections.³⁶

Chromatographic and/or mass spectrometric techniques, such as gas chromatography–mass spectrometry (GC–MS), pyrolysis–GC–MS, secondary ion mass spectrometry (SIMS), high-performance liquid chromatography (HPLC), direct temperature-resolved mass spectrometry (DTMS), and related methods, have also been utilized in samples removed from works of art and in model paints to identify fatty acids involved in soap formation.^{4,24,25,37,38}

A variety of nuclear magnetic resonance (NMR) techniques have been applied to study cultural heritage materials, because of the unique capability of NMR to provide relatively straightforward molecular characterization of organic materials, particularly with solution-state NMR spectroscopy.^{39–41} Advances in sensitivity and resolution of high-resolution NMR spectroscopy (HR NMR) allow the study of samples on the microgram scale^{42,43}; however, these techniques are not ideal to study artistic materials because of their micro-destructive nature and must be further optimized and

explored for widespread use. As an example, liquid-state NMR spectroscopy has been applied in studies of solvent-extracted components, such as egg yolk, from paint samples.^{44–46}

Solid-state NMR (ssNMR) techniques have been applied to identify paint components and to monitor reaction kinetics in model paint systems. In these complex systems, NMR techniques, to assess water content, average pore size, and porosity distribution in paper and wood samples and to detect CO₂ in natural lapis lazuli, have provided valuable information on cultural heritage samples.^{47–49} ssNMR techniques, as discussed in the following sections, provide valuable information about coordination environments and crystal packing of metal carboxylates implicated in soap formation.

Single-sided NMR studies (e.g., with the NMR-MOUSE[®]) have proved useful in cultural heritage because of their ability to perform in situ, noninvasive analysis of processes such as rotational and translational dynamics, to monitor the penetration depth, the chemical and physical effects of solvents, solutions, and suspensions in various surface-cleaning techniques, as well as to unveil noninvasively the stratigraphy of paintings to establish water distribution in frescoes, stones, and other porous materials that are otherwise difficult to test, and to describe diffusion of water and solvent molecules through paint matrices.^{50–53}

The combination of single-sided, solid-state, and high-resolution NMR techniques provides a powerful, versatile tool for cultural heritage studies. In this review, we focus on the NMR analysis of paints containing one of the two lead-based pigments most frequently implicated in soap formation in traditional oil paintings, lead white, 2PbCO₃·Pb(OH)₂, or lead-tin yellow type I (LTY-I), Pb₂SnO₄, and of the compounds that these pigments form upon saponification. Both have a long history of use as pigments in European paintings, beginning at least in the second quarter of the 15th century.^{54,55} NMR analysis has provided a unique perspective on the structure, reactivity, and dynamics of the reactive species in lead soap formation in these materials.

2 | STRUCTURE OF LEAD SOAPS BY SSNMR SPECTROSCOPY

The most common binder used in traditional oil paintings is linseed oil, a triglyceride. A typical composition (although by no means unique) for linseed oil is reported to be dominated by the C₁₈ acids (stearic, oleic, linoleic, and linolenic) as over half of the fatty-

acid content. The major saturated acid in linseed oil is palmitic acid (PA), approximately 5% of the acids.⁵⁶ In artistic paints, cross-linking of the unsaturated acids binds the pigment particles together and adheres them to the substrates. Free saturated fatty acids, formed by the hydrolysis of the glyceryl triesters, react over time with metal ions such as those in pigments to produce the metal carboxylates (soaps), the production, migration, and aggregation of which are the focus of much study.

To understand the processes that produce and distribute soaps in a painting, one must first understand the nature of the soaps themselves and the materials made from them and how those are reflected in the analysis of the materials. Such basic information as structure of pure soap phases has often been missing. It is known that, in the presence of water, salts of fatty acids can form liquid crystalline structures, as has been reported for calcium salts of stearic acid and water.⁵⁷ The structural state of a phase can be addressed by computational methods and/or diffraction methods, but ssNMR methods may also provide structural and crystallographic information on samples as varied as reasonably large proteins and pharmaceutical compounds.⁵⁸ Low solubilities of the metal carboxylates make it extremely difficult, if not impossible, to grow single crystals of these compounds sufficient to obtain X-ray diffraction structures.²⁷ Comparison of experimental NMR results to computationally predicted NMR parameters of proposed structures has aided in using NMR spectroscopy to explain structural features.⁵⁹

²⁰⁷Pb ssNMR spectroscopy provides structural information on the coordination environment of the lead centers in lead soaps; however, acquiring their spectra can be challenging because of sensitivity issues. ²⁰⁷Pb ($I = 1/2$) is 22.6% naturally abundant, and ²⁰⁷Pb chemical shift anisotropies (CSA) may be as large as several thousand ppm, a major issue in the sensitivity problem. Although magic-angle spinning (MAS) may be applied to average the effects of large CSAs in ultra-wideline NMR spectra, particularly, in amorphous materials, extensive manifolds of unresolved spinning sidebands are typically obtained that limit determination of the distribution of NMR parameters such as the chemical shift. Such experimental difficulties are compounded by the limited excitation bandwidths of techniques using square RF pulses. A solution to this issue was proposed by Bhattacharyya and Frydman⁶⁰ with the use of frequency-swept wideband, uniform-rate, and smooth-truncation (WURST) pulses for the excitation and refocusing of wideline spectra. O'Dell and Schurko more recently demonstrated that the sensitivity of this approach could be further enhanced by acquiring a

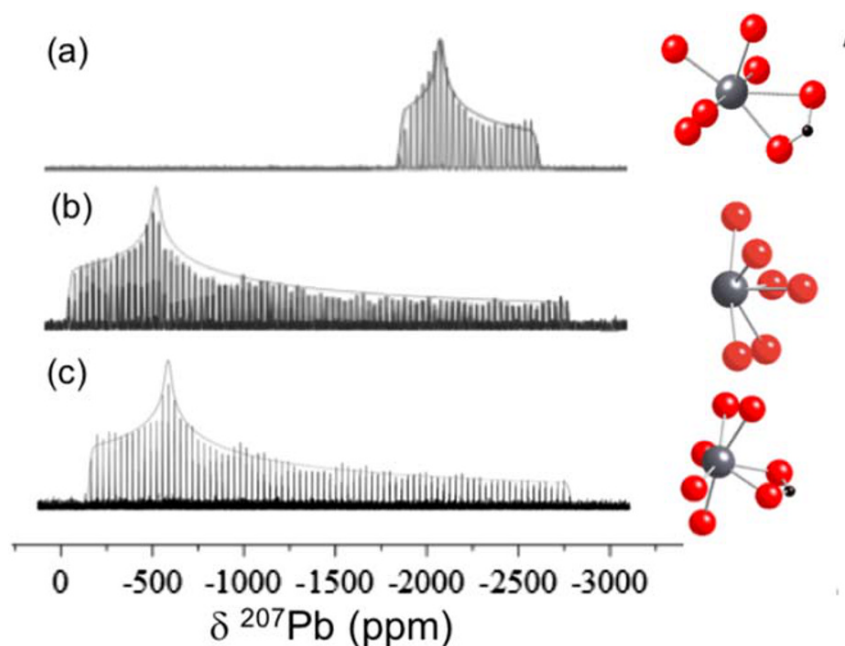
spectrum with a WURST-based Carr–Purcell–Meiboom–Gill (WCPMG) train of echoes.⁶¹ Thus, the analysis of the pure lead soaps with ²⁰⁷Pb NMR spectroscopy has become possible within the last decade.^{27,62–64}

²⁰⁷Pb WURST-CPMG spectra of several lead carboxylates (lead octanoate, lead palmitate [LP], and lead azelate) are shown in Figure 1.²⁷ Previously, Simoni-Livny et al. had indicated the existence of two structural motifs for lead carboxylates, which they named hemi and holodirected.⁶⁵ The ²⁰⁷Pb ssNMR spectra obtained by Catalano et al. demonstrate that the ¹³C and ²⁰⁷Pb ssNMR parameters are indicative of the coordination environment around the lead center in metal carboxylates, in analogy to the proposal of Simoni-Livny et al. In particular, the ¹³C and ²⁰⁷Pb NMR results are consistent with their findings that C₈ and shorter-chain carboxylates exhibit the hemidirected motif, and C₉ and longer-chain carboxylates exhibit the holodirected motif. X-ray diffraction analysis of single crystals of lead octanoate, lead nonanoate, and lead azelate confirm that the local site symmetry in those materials had the expected local structures predicted by the NMR parameters.^{4,27,32,66}

Although none of the coordination environments around the lead centers are perfectly spherically symmetric, the diffraction data display a more nearly symmetric environment around the lead center in the lead nonanoate crystal than in the lead octanoate crystal. This is consistent with the observation of two ²⁰⁷Pb different NMR spans, one “narrow” (~730–750 ppm) and one “wide” (~2,600–2,700 ppm), for these materials. The narrow span indicates a more symmetric environment around the lead center in lead nonanoate, whereas a less symmetric environment around the lead center in lead octanoate and other shorter-chain carboxylates is indicated by the wider span. This correlation is consistent with the disposition of the oxygen ligands in the coordination sphere of the lead found with X-ray diffraction.

²⁰⁷Pb and ¹³C NMR spectra of mixtures of long-chain (C₁₆ and C₁₈) fatty acids relevant to soap formation have also recently been reported.⁶⁷ Kočí et al. carried out powder X-ray diffraction analyses of the materials in conjunction with the NMR spectroscopy. Systematic changes were observed in the position of diffraction lines, as well as in the melting/cooling behavior of the materials as a function of the relative amounts of C₁₆ and C₁₈ components. The ¹³C ssNMR spectra showed changes due to the presence of carbons in disordered phases. The ²⁰⁷Pb NMR spectra obtained for the mixtures were fit with a sum of three components, which the authors attribute to the presence of pure phases and a disordered phase that is formed.

FIGURE 1 The local lead coordination environment and the ^{207}Pb WURST-CPMG spectra for (a) a long-chain carboxylate, lead palmitate, (b) a short chain, lead octanoate and (c) lead azelate



3 | REACTIVITY OF LEAD SOAPS

3.1 | Lead soap formation in paint samples

Proper assignment and interpretation of lead species (both reactants and products) by ssNMR spectroscopy allow investigation of reactions that lead to formation of lead soaps.⁴⁷ ssNMR is quite informative of the dynamics of reactive components, as well as soap formation. For example, a combination of ^{13}C , ^{207}Pb , and ^{119}Sn ssNMR gave in-depth information on the reactivity of LTY-I with PA.⁶³ ^{207}Pb and ^{13}C NMR were also used to study the reactivity of lead white oil paint with PA.⁶¹

Lead white (hydrocerussite), $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$, has a structure described as series of layers of lead carbonate and lead hydroxide.⁶⁸ Early room-temperature ssNMR studies of lead white pigment had only shown lead carbonate impurity to be present in the material.⁶⁹ However, $^{207}\text{Pb}\{^1\text{H}\}$ DNP-BCP (^1H - ^{207}Pb BRAINCP/WURSTCPMG) ssNMR measurements (requiring the sample to be at much lower temperatures) indicated signals from a basic lead carbonate phase in the lead white pigment and signals from the lead hydroxide phase. In agreement with crystallographic data, the spectral fitting revealed the existence of two Pb sites with an intensity ratio of 2:1, corresponding to the carbonate and hydroxide layers in this complex carbonate phase. The comparison suggests that dynamics at room temperature likely suppressed the NMR features of the hydrocerussite phase, revealing only the impurity carbonate phase.⁷⁰

In the DNP experiment on a lead white/linseed oil (78/22 wt%) paint film that had been aged 4 years at ambient temperature and relative humidity, soap formation was confirmed by a $^{207}\text{Pb}\{^1\text{H}\}$ DNP-BCP spectrum (Figure 2a). DNP-BCP is an ideal ^{207}Pb ssNMR technique for this application, given that (1) it suppresses the signal from the lead carbonate phase and (2) it selectively enhances the signal from the lead soap.⁶⁹ The spectrum in Figure 2b and the subspectrum in Figure 2c were the first ssNMR ^{207}Pb spectrum to show soap formation in a model paint sample.⁷⁰

LTY-I is prepared by heating a mixture of massicot (PbO) or minium (Pb_3O_4) with tin dioxide, and depending on the conditions, the process may lead to mixtures of the orthorhombic form Pb_2SnO_4 with cubic PbSnO_3 and PbO . The optimum temperatures reported in historic recipes for the synthesis of Pb_2SnO_4 are between 800 and 900°C.⁷¹ Commercial sources report the empirical formula of the pigment as PbSn_xO_y . It is not clear whether these reported ambiguous stoichiometries contain distinct phases or exist in the form of a solid solution and likewise for the pigment used in works of art. Although single crystals of Pb_2SnO_4 have been grown⁷² and powder X-ray diffraction and Raman data have been published,^{73–75} there is scant information on the existence and nature of more complex phases. Yet, these minor components are assumed to react with the free fatty acids in the binding medium of oil paintings because it has been proposed that fatty acids do not react with pure Pb_2SnO_4 to form lead soaps.²⁵

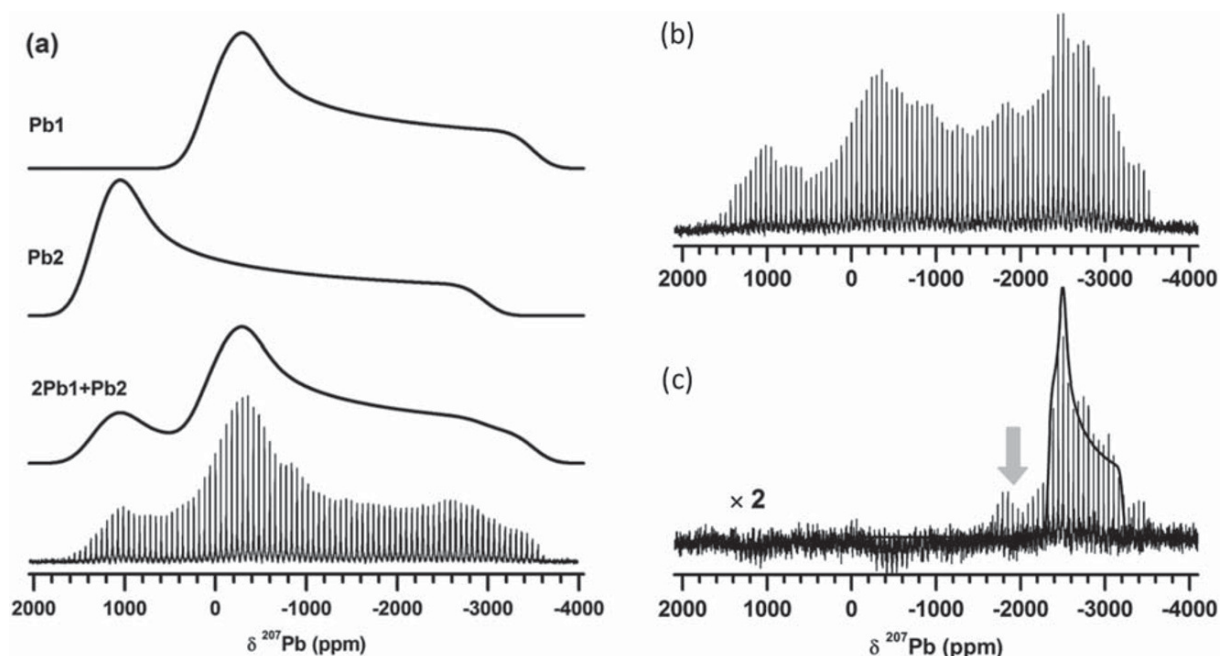


FIGURE 2 (a) $^{207}\text{Pb}\{1\text{H}\}$ DNP-BCP spectrum of lead white (bottom). Simulated decomposition into signals assigned to the two sites and the sum are indicated about the experimental spectrum. (b) The spectrum of a lead white paint sample after sitting at room temperature for 4 years. (c) The spectrum of the sample after subtracting the signals from lead white, revealing the ^{207}Pb signals from the decomposition products. Reproduced with permission from Kobayashi, T.; Perras, F. A.; Murphy, A.; Yao, Y.; Catalano, J.; Centeno, S. A.; Dybowski, C., Zumbulyadis, N.; Pruski, M. *Dalton Trans.* **2017**, 46, 3535–3540

A ^{207}Pb and ^{119}Sn NMR study of an LTY-I commercial pigment samples shows the presence of the main component Pb_2SnO_4 , along with Pb_3O_4 and SnO_2 .⁶³ It was determined that for every mole of Pb_2SnO_4 , there is 0.054 ± 0.011 mol of Pb_3O_4 present in this LTY-I sample by ssNMR spectroscopy. It was also found that for every mole of Pb_2SnO_4 , there was 0.56 ± 0.04 mol of SnO_2 . To determine which species in the mixture were involved in soap formation, paint films made with LTY-I in linseed oil were applied to glass slides and aged for 8 months. The paints were then ground, mixed with PA, and left to react for 3 weeks to allow for soap formation. Spectra taken before and after reaction with PA were compared, and the percentages of all components were reported (Figure 3). Complete soap formation was verified by ^{13}C NMR spectroscopy. ^{119}Sn spectra were acquired using direct excitation with spin-temperature alternation (to minimize ringdown effects) and MAS (STA/MAS) at 5 and 12 kHz to obtain the isotropic chemical shift. The ^{119}Sn NMR spectra in Figure 4 show that the peak for Pb_2SnO_4 relative to that of tin dioxide decreased during the procedure. This change indicates that lead in LTY-1 reacts with PA to form lead soaps. Whether the Pb_2SnO_4 reacts directly with the fatty acid or produces intermediates that react with the PA cannot be determined by these experiments. These results demonstrate how

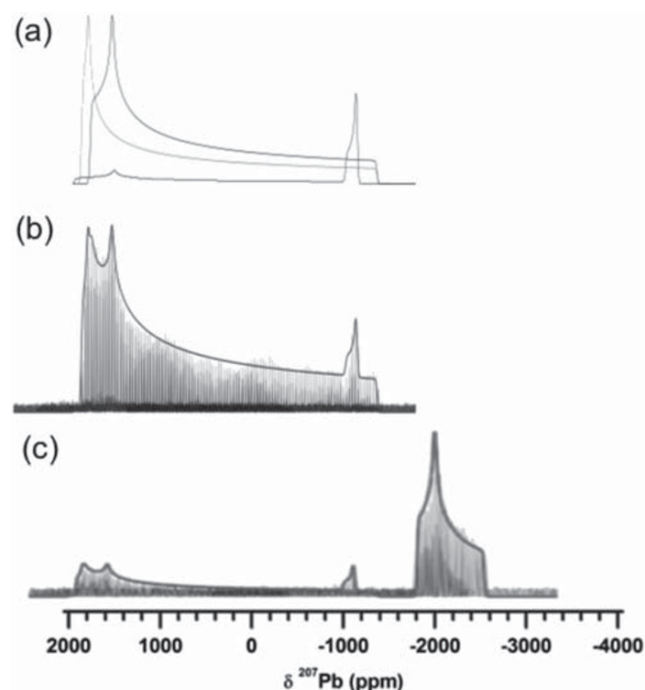


FIGURE 3 (a) Simulated decomposition signals for the two Pb sites in lead-tin yellow and a minimum impurity. (b) ^{207}Pb WURST CPMG spectrum of lead-tin yellow. (c) An aged lead-tin yellow linseed oil paint sample mixed with palmitic acid to form lead palmitate. Reproduced with permission from J. Catalano, A. Murphy, Y. Yao, F. Alkan, N. Zumbulyadis, S. A. Centeno, C. Dybowski, *J. Phys. Chem. A* **2014**, 118, 36, 7952–7958

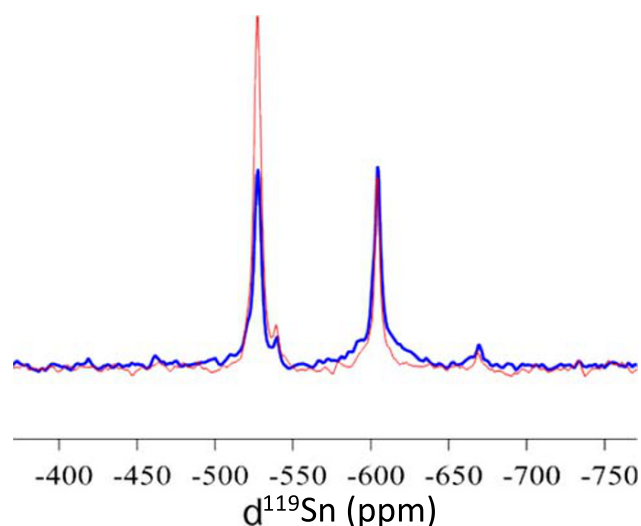


FIGURE 4 ^{119}Sn STA/MAS NMR spectra of LTY-1 before (red) and after reaction (blue) with palmitic acid added to a dried paint film. The difference in relative intensity at -529 ppm from Pb_2SnO_4 in the two spectra demonstrates that Pb_2SnO_4 has been partially consumed as a result of the reaction. Reproduced with permission from Catalano, J.; Murphy, A.; Yao, Y.; Alkan, F.; Zumbulyadis, N.; Centeno, S. A.; Dybowski, C. *J. Phys. Chem. A* **2014**, *118*, 7952–7958

analysis with ssNMR is useful in identifying the amounts of components in a mixture and which species react.

3.2 | ^{13}C NMR study of the effects of relative humidity

The factors that trigger and influence lead soap formation in paints are being extensively investigated with a variety of analytical and physical technologies, as discussed in the introduction. It is widely believed that exposure to water, as specified by the relative humidity, increases the rate of soap formation. In experiments to address this issue, model lead white paint samples aged in the laboratory for 3 years were allowed to

equilibrate, each at a specific relative humidity.⁴⁷ In a separate container, ^{13}C -enriched PA was also equilibrated at the same relative humidity. The two materials were then mixed to create a sample containing ~10% PA by weight, which was immediately placed in a sealed NMR sample rotor. ^{13}C ssNMR spectra were taken at regular intervals over a period of three days. The formation of soap was easily tracked with ^{13}C NMR through the appearance and growth of the doublet of the lead carboxylate as the fatty acid peak decreased (Figure 5). The change in the fractional intensity of the reactant is shown for a number of samples in Figure 6, as a function of time from initial mixing.

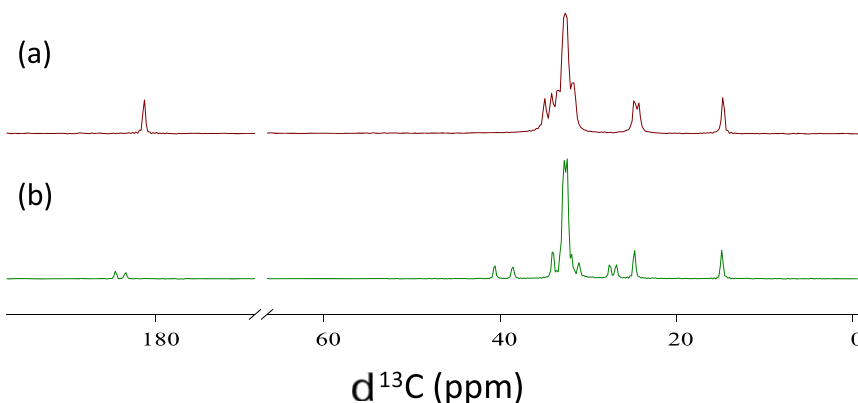
The rate of loss of reactant intensity (and the formation of soap) shown in Figure 6 is a complex function of the time of reaction. To characterize the process, a parameter, T_{50} , was defined at which the reactant signal intensity is reduced to 50% of the total intensity. A plot of T_{50} versus relative humidity is shown in Figure 6b. Although there is significant scatter, it is clear that T_{50} is a function of the relative humidity to which the sample had been exposed. T_{50} is shorter for sample exposed to higher relative humidities, indicating that it does affect the rate of soap formation. A careful examination of Figure 6a shows that rate of loss of intensity is faster at early times but becomes relatively independent of relative humidity at longer times. Future studies and models must be developed to understand this complex reaction.

4 | DYNAMICS

4.1 | Deuterium NMR studies of the local mobility of fatty acid chains

The local rotational mobility of free PA and LP may be a significant factor in the formation of soaps in works of art. The current hypothesis for the formation of metal soap aggregates assumes that free monoacids, primarily

FIGURE 5 ^{13}C MAS ssNMR spectra of (a) palmitic acid and (b) lead palmitate, respectively. Reproduced with permission from J. Catalano, A. Murphy, Y. Yao, N. Zumbulyadis, S. A. Centeno, C. Dybowski, *Metal Soaps in Art: Conservation and Research* **2019**, (Eds. F. Casadio, K. Keune, P. Noble, A. van Loon, E. Hendriks, S. A. Centeno, G. Osmond) Rijksmuseum: Amsterdam, pp. 69–84



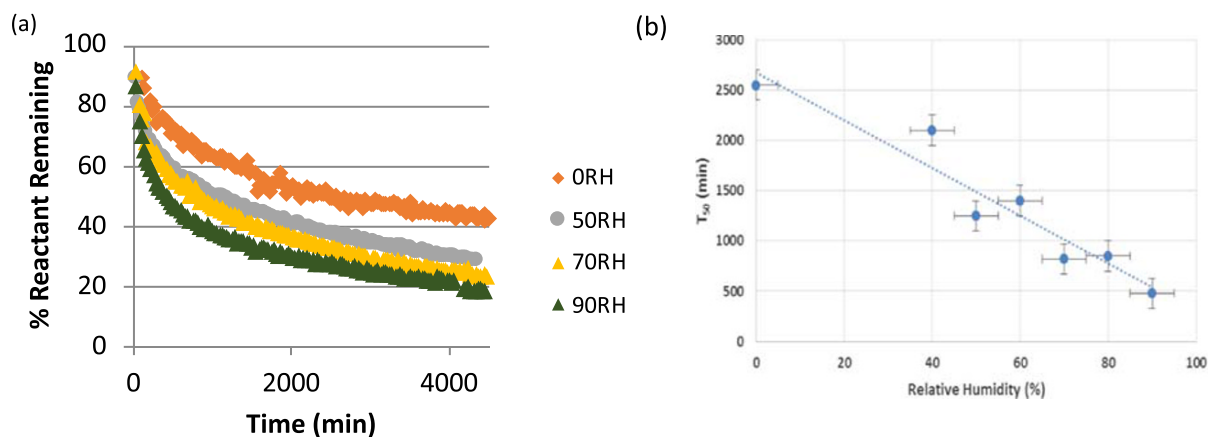


FIGURE 6 (a) Percentage of reactant remaining as a function of time at different relative humidities. The initial rate of soap formation is dependent on the relative humidity. (b) T_{50} versus relative humidity for the formation of lead palmitate from palmitic acid in a lead white paint film. The trend line is presented to aid the eye in following the data and does not represent a prediction of the dependence on humidity. Reproduced with permission from J. Catalano, A. Murphy, Y. Yao, N. Zumbulyadis, S. A. Centeno, C. Dybowski, *Metal Soaps in Art: Conservation and Research* 2019, (Eds. F. Casadio, K. Keune, P. Noble, A. van Loon, E. Hendriks, S. A. Centeno, G. Osmond) Rijksmuseum: Amsterdam, pp. 69–84

palmitic and stearic, formed during the curing of the oil matrix by hydrolysis of the glyceryl esters, migrate to particles of heavy-metal pigments such as basic lead white or LTY-I, where they react to form metal carboxylates. Both translation and rotation are involved in these processes.

Deuterium NMR spectroscopy is well-known to be sensitive to the nature of rotational motions affecting the local nuclear environment. The deuterium NMR response is determined primarily by the coupling of the nuclear quadrupole moment to an electric field gradient

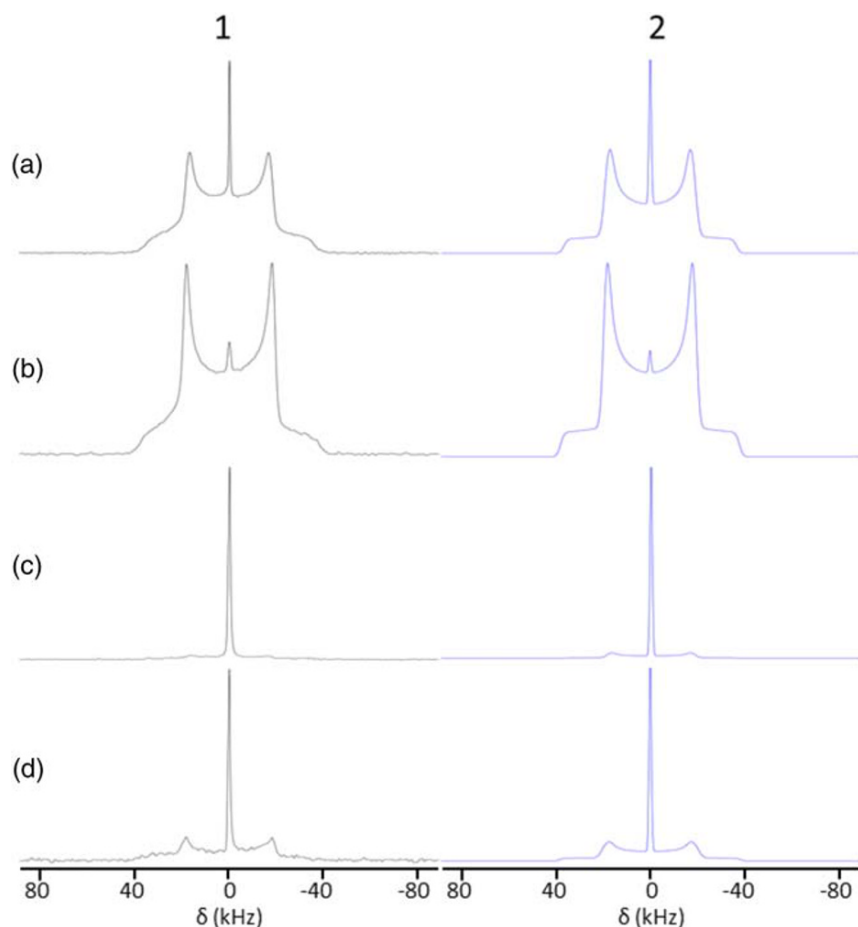


FIGURE 7 ^2H NMR spectra (1) of methyl-labeled palmitic acid and lead palmitate at 295 K next to simulated fits (2). (a) Pure palmitic acid, (b) pure lead palmitate, (c) palmitic acid in linseed oil film, (d) lead palmitate in linseed oil. There are two components to each line shape, as described in the text. Reproduced, with permission, from Catalano, J.; Murphy, A.; Yao, Y.; Zumbulyadis, N.; Centeno, S.; Dybowski, C. *Solid State Nucl. Magn. Reson.* 2018, 89, 21–26

TABLE 1 Static fractions determined from ^2H spectra at 303 K for variously labeled palmitic acid and lead palmitate materials, in the pure state and mixed with linseed oil^a

	LP	PA	LP-linseed	PA-linseed
CD_3	0.99	0.94	0.73	0.34
C_2D_4	1.00	0.92	0.92	0.37
CD_2	1.00	0.80	0.80	0.20

Abbreviations: LP, lead palmitate; PA, palmitic acid.

^aData obtained from results in Catalano et al.⁷⁷

at the nuclear site. For a sample consisting of a random powder, the spectrum consists of a band, the shape of which is determined by the time-averaged coupling of the nucleus to the electric field gradient (determined primarily by the electrons in the bonds to the deuterium nucleus). For example, rapid isotropically random motion of the C–D bond in an organic material results in a sharp resonance, whereas a static C–D bond or an anisotropically moving bond results in a band, whose NMR characteristics are indicative of the rotational mobility.⁷⁶

A series of deuterium NMR studies were conducted on LP and PA, as pure materials and in a linseed oil matrix.⁷⁷ Three isotopic labeling schemes were used to probe dynamics of the fatty acid chain at different positions on the chain (α -carbon (CD_2), the mid-chain methylenes (C_2D_4), and the terminal methyl (CD_3). At temperatures between 250 and 340 K, the spectra of all samples could be described in terms of the superposition of a broad (static) component and a narrow (significantly mobile) component, the fractions of which depend on the temperature and the sample, as indicated in Figure 7 for

the methyl-labeled materials. ^2H spectra of methyl-labeled samples were acquired using the quadrupole-echo pulse sequence, whereas spectra of C_2D_4 - and CD_2 -labeled samples were obtained as spikelet spectra using ^2H MAS techniques.

Analysis of spectra such as those in Figure 7 gives the fractional static component for each case, as indicated in Table 1 for either pure materials or materials mixed with linseed oil. The data show that pure LP is static (on the NMR time scale) at the chain end, the middle of the chain, and at the carbon adjacent to the carboxyl carbon. Interestingly, pure PA is also reasonably static along the chain, but there is some mobility at the acid position. For LP in a linseed oil film, the methyl group shows an increase in mobility over the pure material, and there is some lesser increase in mobility of the chain middle and at the carbon adjacent to carboxyl group. However, when PA is intermingled in a linseed oil matrix, at all points along the chain, there is a substantial increase in rotational mobility, indicating the effect of interaction with the linseed oil in its local environment. These data are consistent with a previous study that showed there is a partial melting of the aliphatic chains before the phase change.^{32,78}

These deuterium NMR experiments demonstrate that qualitatively, even though PA and LP mixed with linseed oil are similar to the pure materials in some parts of the material by NMR analysis, portions of the sample in the mixtures are dynamically different from the pure materials. In particular, the existence of molecular rotational mobility in some parts of the sample suggests that fatty acids may have the rotational (and likely translational) freedom to migrate through a linseed oil matrix to

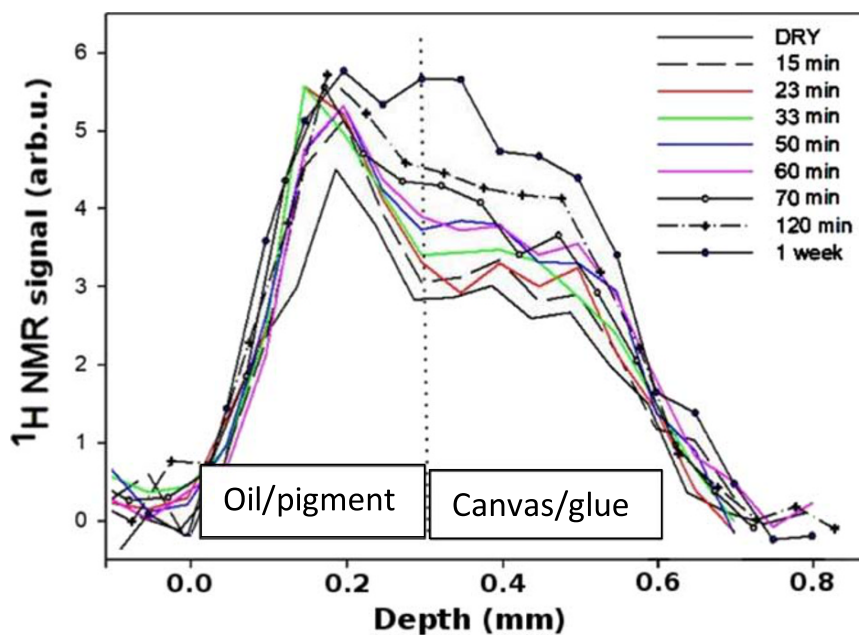


FIGURE 8 ^1H NMR depth profile collected on a lead oil paint canvas sample during water absorption for various absorption times

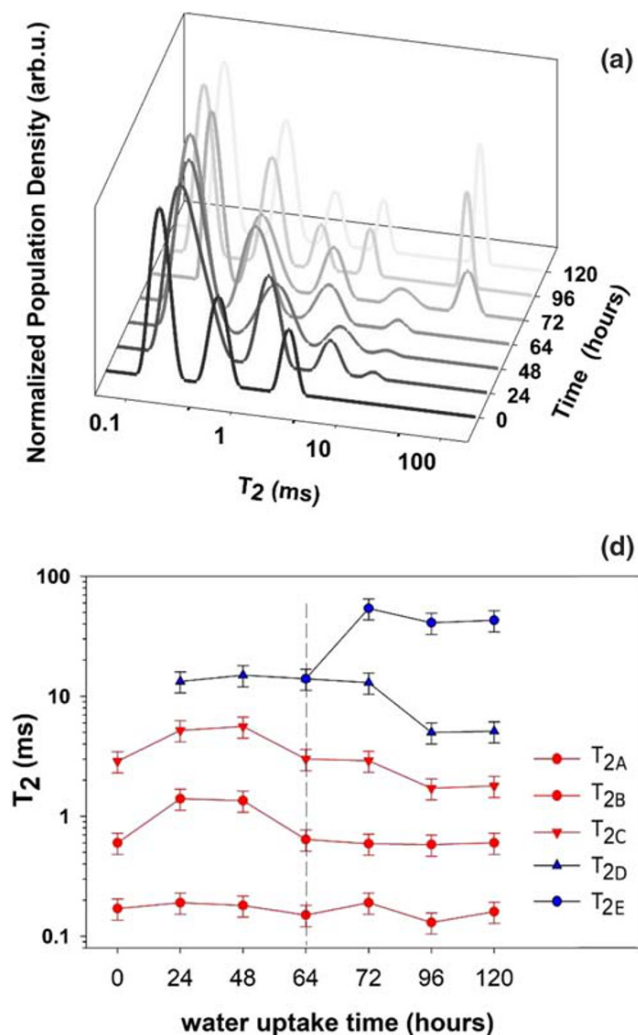


FIGURE 9 (a) Distribution of transverse relaxation times for paint samples as a function of time exposed to water; (b) T_{2A} , T_{2B} , and T_{2C} related to oil paint, and T_{2D} and T_{2E} related to water as a function of time of exposure to water. Reproduced with permission from V. Di Tullio, N. Zumbulyadis, S. A. Centeno, J. Catalano, M. Wagner, C. Dybowski, *ChemPhysChem* **2019**, *20*, 1–8

participate in reaction with pigment species such as lead ions. The fact that a substantial fraction of the molecules in these matrices are isotropically mobile, even at room temperature, implies that reactions in this matrix are probably occurring at temperatures at which materials are stored and displayed.

4.2 | Unilateral NMR studies of the effects of water on lead white paint films

Because the formation of soaps may be activated or driven by diffusion, defining the interaction of water and solvents with paints and the effects of these interactions on diffusion of species in the paint matrix is

fundamental to understanding the processes that underlie the formation reaction. Practically, aqueous and organic-based solutions are often used by restorers to clean the surface of paintings and other works of art. Although these formulations are commonly used in the conservation field, there are few experimental studies that focus on the evaluation of their chemical–physical effects. In recent years, the interest on the potential role of the cleaning treatments as activating agents for degradation has become a field of active study.^{30,79–81} In this framework, unilateral NMR may be considered one of the most useful techniques to evaluate and monitor a cleaning treatment. With unilateral NMR, it is possible to measure the hydrogen depth profile, the relaxation times, and the self-diffusion coefficients of water and solvents within the paint layer in a nondestructive way. Furthermore, these unilateral techniques allow one to monitor molecular dynamics of linseed oil under a variety of experimental conditions, for example, at different temperatures, as a function of humidity cycling, choice of cleaning products, and procedures of conservation.

Here, we report an example of recent analyses of the chemical/physical properties of a model lead linseed oil paint on canvas treated with water, acetone, and ethanol, using unilateral NMR. Water uptake may vary significantly, depending on the materials used by the artist and the state of degradation of the painting. Figure 8 shows ^1H depth profiles obtained with unilateral NMR, collected in a model lead white paint film on canvas during water absorption.

In the dry oil-paint model (at time = 0), the proton depth profile shows layers of the painting model: the canvas bound with animal glue and the overlapped layer made of oil and lead pigments, as the latter is richer in hydrogen. Because the stratigraphy encodes the amplitude of the total ^1H -NMR signal as a function of depth, the thickness of the paint layer is approximately $200 \pm 50 \mu\text{m}$, and from the total extent of signal, the thickness of the glue/canvas layer is approximately $500 \pm 50 \mu\text{m}$.

Water absorption into this material was performed by applying to the surface of the painting a Whatman[®] paper filter saturated with water for 120 min. As shown in Figure 8, the hydrogen content in the material increases as the time of absorption increases. Initially, intensity in the oil/pigment layer increases. After 1 week of water absorption, the ^1H signal depth profile shows increased intensity of protons deeper in the material, including in the canvas/glue region. These results show that at the early stage, absorption of the water occurs by diffusion into and through the paint layer approaching the canvas sized with glue. After 1 week of evaporation, the water

remains trapped in the paint interacting with the water-sensitive cellulose and collagen (i.e., canvas and glue).⁸² Such trapped water can react with linseed oil, generating free fatty acids for soap formation.

To obtain information about the molecular mobility of the cross-linked oil-pigment network and the interaction between the polymer and water molecules, T_{2eff} in a lead oil paint on a glass slide placed in contact with a water source was determined by a procedure similar to that reported for measuring water capillary absorption in other porous materials.⁸³ In all measurements, the multi-exponential decay for the dry sample (at 0 h in Figure 9) had to be fit with at least three components: a short component, T_{2A} , of about 0.2 ms, affecting a majority of the spins (~60% of the protons); an intermediate component, T_{2B} , of about 0.8 ms, affecting ~30% of the protons; and a “long” T_{2C} , of about 4 ms, affecting ~10% of the protons. A reasonable assignment of the shortest component, T_{2A} , is that it arises from protons in the relatively rigid part of the polymeric network. The second component, T_{2B} , may be assigned to protons in a partially constrained environment, for example, methyl groups at the ends of chains. Polymer chains also may have portions possessing relative motional freedom (perhaps moving anisotropically).⁸⁴ The third component, T_{2C} , may be ascribed to

residual fatty acids not fully cross-linked or to fatty acids not linked to the polymeric network that have a higher mobility than those in the rigid matrix and might have an important role as plasticizers.^{85,86}

During absorption, the value of T_{2eff} components assigned to protons associated with the polymerized oil vary depending on the amount of water that the sample has absorbed. For example, in the early stage of absorption, the long component (T_{2C}) associated with the polymer network protons increases but upon longer exposure falls back to its initial value. The intermediate component (T_{2B}) is similar but perhaps less pronounced. The short component is unaffected over 5 days of water uptake. For the first 64 h of absorption, we also could distinguish a fourth component, which we ascribe to water molecules; this long T_{2eff} is of the order of 10 ms.

After 72 h of water absorption, the relaxation profile changes. In these stages, the material exhibits two T_{2eff} values (T_{2D} ~7–10 ms and T_{2E} ~35–50 ms) ascribable to water-associated protons because of their multi-millisecond relaxation times. A reasonable suggestion for these two T_{2eff} components is partially bound (or partially hindered) water and water in a relative freely moving environment, suggestive of the formation of ionic or polar aggregates.

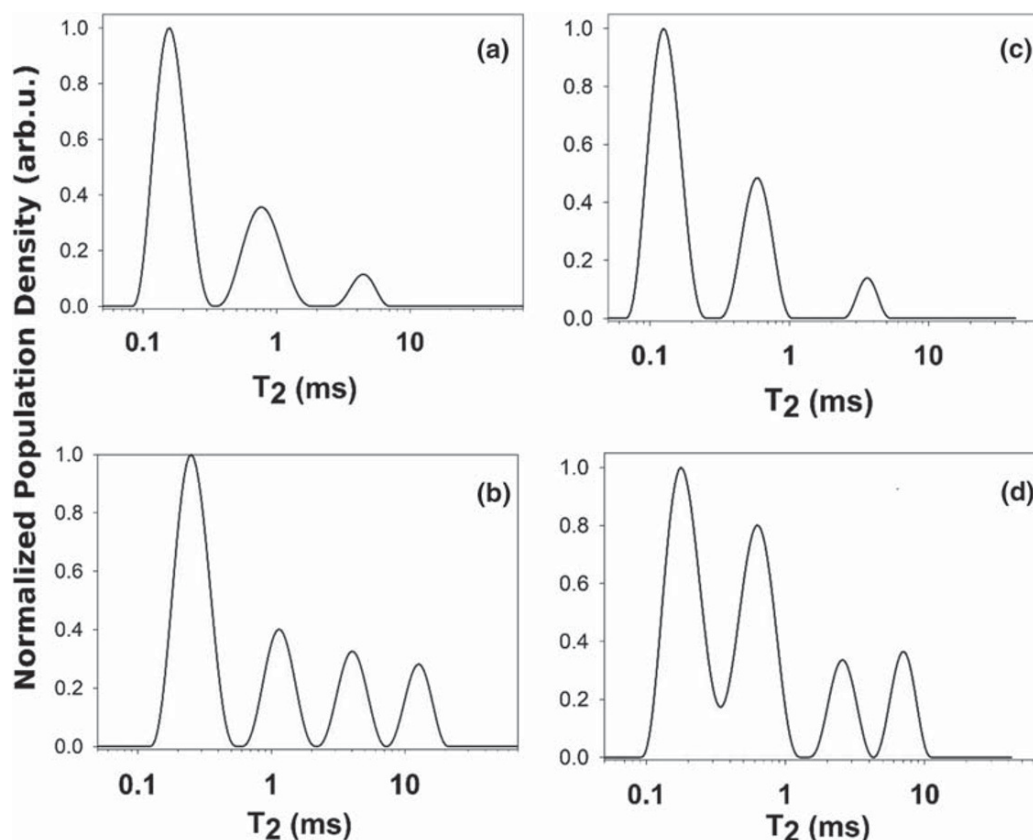


FIGURE 10 Distribution of transverse relaxation times, T_{2eff} , obtained by the UPEN algorithm.⁹² (a) Lead oil paint dry (LOPb-dry1); (b) after treatment with acetone (LOPb-acetone); (c) lead oil paint dry (LOPb-dry2); (d) after treatment with ethanol (LOPb-ethanol)

TABLE 2 T_{2eff} distributions for lead white paint samples exposed to ethanol or acetone

Sample	W_A	T_{2A} (ms)	W_B	T_{2B} (ms)	W_C	T_{2C} (ms)	W_D	T_{2D} (ms)
LOPb-dry1	66%	0.16	28%	0.81	6%	5	-----	-----
LOPb-acetone	30%	0.74	31%	1.16	23%	4	16%	13.8
LOPb-dry2	65%	0.13	28%	0.62	6%	3.7	-----	-----
LOPb-ethanol	45%	0.18	34%	0.64	11%	2.6	10%	7.6

Note: W indicates the weight of each component of T_2 . LOPb sample made of lead white and linseed oil.

One may describe a lead oil paint as an ionomeric polymer network in which water diffusing into and through the hydrophobic matrix is likely to be associated with an initial elastic expansion of the uncross-linked matrix to create to a slightly swollen state, where relaxation would be less efficient. Continued absorption of water, however, would induce dipoles or ionic complexes to form clusters or solvated microscopic aggregates at the polymer/water interface, resulting in shrinkage of the oil network, a behavior commonly seen for many ion-exchange resins and ionomers.^{87–89}

The longest T_{2eff} (i.e., T_{2E}) is assigned to relatively free water moving in the pore structure of the paint. Similar relaxation behavior has been observed in partially saturated rocks in which the distribution of T_{2eff} depends on the water distribution inside the capillary, which, in turn, depends on the pore shape, wettability, and capillary pressure.⁹⁰ As is the case for other porous materials, the effective free volume filled with water can be evaluated from CPMG decays, extrapolating the total amount of protons of water absorbed by the material. For these samples, we find a value of $(5.6 \pm 0.5)\%$ for the effective open porosity, θ_{NMR} , as determined by NMR measurements. The estimation of an effective porosity from NMR data is approximate. Ideally, it should be corroborated by more robust methods. Few studies have been performed to evaluate the porosity of oil paints. Gervais et al. have reported a total porosity of about 15% from X-ray tomography measurements of a sample of a ground preparation layer made of calcium carbonate bound by a proteinaceous medium.⁹¹ The value of $\sim 5.6\%$ obtained by NMR data is somewhat smaller, but the effective porosity determined from NMR measurements is related to the effective volume accessible to water and not to the total porosity. The paints examined here are quite different from the calcium carbonate ground layer examined by Gervais et al. Unfortunately, X-ray tomography cannot distinguish between empty pores and pores filled by polymerized oil.

These relaxation results and their interpretation in terms of the dynamics of water in these lead-pigment paint samples strongly suggest that the system is a porous material with pigment particles dispersed in an ionomeric-like polymer matrix. In a recent study, diffusion

measurements by unilateral NMR and 1H -HRMAS spectroscopy have shown that the water absorbed by the lead-white paint is in a regime of restricted diffusion, which also indicates the presence of a porous-like structure.⁵²

4.3 | Unilateral NMR studies of the effects of organic solvents on lead white paint films

To remove crusts and other deterioration products insoluble in water from a painting, conservators/restorers sometimes use formulations based on organic solvents. Thus, the interaction of common solvents, such as acetone and ethanol, with model paint samples provides a way to analyze the nature of the process of cleaning with them. Analysis of the transverse relaxation time distribution in two lead white paint model samples before and after the application of Whatman[®] paper soaked in acetone for 100 min or ethanol for 180 min has been carried out with the unilateral NMR technique. In both samples, the T_{2eff} distribution in samples before the application of a solvent shows three components of similar values to those found for the samples containing water (Figure 10).

After the application of either solvent by this protocol, a long component, T_{2D} , with values of 13 and 7 ms for acetone- and ethanol-treated samples, respectively, appears. These long components are assigned to protons in the solvent that interact with the polymeric matrix of the paint layer. Because T_{2eff} of the pure bulk solvents is longer⁹³ than found in these samples, it is likely that the solvent molecules are trapped in the pores within the swelled paint matrix. From Table 2, it is also apparent that the presence of solvent also affects the value of the shorter T_{2eff} components, suggesting that the polymeric oil network undergoes a solubilization process along with swelling. Interestingly, the change in T_{2eff} of the fast-relaxing components of the matrix in the paint sample treated with acetone is larger than for the sample treated with ethanol. The intermediate component, T_{2C} , also slightly shortens upon the addition of solvent but not as dramatically as T_{2A} and T_{2B} . The present results are similar to those obtained in the analyses of gels formed with solvents like benzyl alcohol and ethyl lactate.⁸¹

5 | CONCLUSIONS AND OUTLOOK

Artistic paintings are complex systems both in terms of their composition and physical properties and because these may change by the interaction with the environment and aging. The results discussed demonstrate only a few of the variety of ways in which NMR techniques can be used to investigate the structure, reactivity, and dynamics of soaps and other compounds in paint films. The methodology used to analyze artistic materials and others of relevance to the cultural heritage is applicable to other complex, multicomponent systems.

NMR methods are sensitive to local environment and to physical processes. The identification of a species by its NMR signature is perhaps the single most important characteristic that has led to its extensive use in chemistry. The now-common availability of NMR spectroscopic techniques to access a wide variety of nuclei (e.g., ^1H , ^2H , ^{13}C , ^{67}Zn , ^{113}Cd , and ^{119}Sn), particularly in solids and semisolids, allows one to address a wide variety of problems in materials science. In addition, the ability to quantify species in a sample relatively easily is a strength of NMR spectroscopy particularly applicable to complex systems such as paintings.

A limitation of NMR spectroscopy has been its relative insensitivity, as compared with other spectroscopic methods, requiring the investigation of relatively large samples and isotopically enriched. That problem has often restricted the use of NMR spectroscopy in cultural heritage to model systems or to situations in which the amount of material available is not limited. However, advances in magnetic resonance spectroscopy have dramatically improved sensitivity and resolution, permitting the examination of smaller samples or monitoring complex phenomena on a smaller scale. While still being developed, these advanced techniques have already opened new perspectives for the application of NMR to cultural heritage science. The availability of ultra-high magnetic fields has enabled NMR studies of magnetically dilute, low-gamma quadrupolar nuclei without the need for isotopic enrichment.⁹⁴ For example, using these techniques, particularly detection at ultrahigh magnetic field with wide-line techniques such as the WURST-CPMG method, ^{67}Zn NMR spectra of zinc soaps at natural abundance have been acquired to study an analogous soap-formation problem that could not be clearly defined at the lower fields commonly used in NMR.⁹⁵

The issue of sensitivity has also been addressed by technological means. Probe design over the last several decades has decreased noise and optimized signals, but for problems involving limited materials, this improvement may not be sufficient. The cross-polarization technique developed over 40 years ago in which magnetization is

transferred from abundant spins like ^1H to rare spins like ^{13}C is now routine in the study of solids by ^{13}C and many other spins.⁹⁶ The use of HR MAS, whether with cross-polarization or without, in materials science has been discussed by Alam and Jenkins⁴² and recently reviewed in combination with DOSY.⁹⁷ The combination of the two methods, particularly when very high pulsed field gradients are available, allows one to expand the study of slow and complex diffusion processes of multiple species, such as those typically encountered in paint films.

The enhancement of nuclear signals by dynamic nuclear polarization (DNP) is a relatively recent development that has advantages for samples of limited size, as discussed above for ^{207}Pb spectra relevant to lead soap formation.⁷⁰ For problems in which the species of interest lie at a surface, selective enhancement of surface NMR signals is one of the most promising applications of DNP enhancement.^{98,99} This approach, known as DNP surface-enhanced NMR spectroscopy (DNP SENS), uses incipient wetness to impregnate porous or particulate materials with a radical-containing solution to enhance the signals of species in the surface or surface-bound species. It has been recently shown that faster MAS frequencies dramatically help to increase the transverse coherence lifetimes of the surface species, opening new avenues for DNP SENS. DNP-SENS with fast spinning has great potential for the characterization of chemical reactions at the surface of inorganic pigments and the resulting surface-bound species in cultural heritage objects.

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