Mobile nuclear magnetic resonance (NMR) is a flexible technique for nondestructive characterization of water in plants, the physical properties of polymers, moisture in porous walls, or the binder in paintings by relaxation measurements. NMR relaxation data report material properties and therefore can also help to characterize the state of tangible cultural heritage. In this work, we discuss the relaxation behavior in two series of naturally aged paint mock-up samples. First, paints with different pigment concentrations were prepared and investigated in terms of the longitudinal and transverse relaxation-time distributions. We document the evolution of both relaxation-time distributions during the initial drying stage and demonstrate the heightened importance of transverse over longitudinal relaxation measurements. Second, we observe nonlinear dependences of the relaxation times on the pigment concentration in a typical oil binder. Third, in a study of naturally aged paint samples prepared in the years between 1914 and 1951 and subsequently aged under controlled conditions, we explore the possibility of determining the age of paintings using partial least square regression (PLS) by fitting $T_1-T_2$ data with the sample age. Our results suggest some correlation, albeit with significant scatter. Estimating the age of a painting stored under unknown conditions from NMR relaxation data is therefore not feasible, as the cumulative effects of light irradiation, humidity, and biological degradation further obfuscate the chemical and physical impact of aging on the relaxation times in addition to the impact of pigment concentration.

**KEYWORDS**
aging, cultural heritage, drying, NMR-MOUSE, paint, relaxation analysis
oftentimes small devices can be mobile and serve to investigate physical properties in a wide variety of objects and materials\(^6\), where they can be deployed with relative ease. Due to their simplicity, they disseminated rapidly in many areas of research. Historically, permanent-magnet-based relaxometers were developed to test food quality\(^7,\)\(^8\) with table-top instruments and to characterize fluids in porous media\(^9\)-\(^11\) with unilateral stray-field instruments. Nowadays, commercially available sensors detect and classify properties of polymers,\(^5\) skin,\(^6\) or plants.\(^12\)-\(^14\) A more recent use of such compact NMR sensors is to assess the state of cultural heritage, where the nondestructiveness of the investigation benefits the analysis of layered structures in walls or paintings.\(^15,\)\(^16\)

From all the unilateral sensor designs reported in the literature\(^5,\)\(^17\) the NMR-MOUSE (MOBILE Universal Surface Explorer)\(^18\)-\(^20\) is one of the used in most studies. Its thin and planar disk-shaped detection volume is located a few millimeters outside of the magnet casing, allowing the analysis of immobile and arbitrarily sized objects. The sensor consists of an iron yoke carrying two pairs of magnets with opposite polarization. A surface coil placed into a gap between the magnets creates an oscillating magnetic field emanating from the magnets and the surface coil, the detection volume is strongly inhomogeneous, and the excitation is slice selective. Short excitation pulses emitted from the coil for a few microseconds commonly give rise to NMR signal from a layer only 100- to 200-\(\mu\)m thin but usually a centimeter or more in diameter. All signal from this so-called sensitive volume is averaged. Due to the excellent axial resolution, which can be reduced to values of a few micrometers\(^20\) in precision experiments, depth profiles may be recorded by mounting the sensor on a translation stage and retracting it incrementally from its initial position after each measurement.

Contrary to spectroscopy, a signal in relaxometry is characterized only by amplitudes and decay constants, while the oscillation frequencies observed in highly homogeneous magnetic field cannot reliably be measured in a strongly inhomogeneous detection field.\(^5\) Therefore, the NMR relaxation signal is not analyzed by Fourier transformation to extract information on chemical groups. Instead, this modality of NMR quantifies amplitudes and time constants of physical processes by which the macroscopic magnetization relaxes toward the thermodynamic equilibrium state. A distinction is made between longitudinal relaxation where the averaged nuclear magnetization realigns with the applied magnetic field and the usually much faster transverse relaxation in solids, which is caused by a loss of coherence of the magnetization components precessing in the transverse plane. The time constants of these processes are known as \(T_1\) and \(T_2\), respectively. Relaxation times are determined by molecular rotation and translation, as discussed in great detail by Bloembergen et al.\(^21\) For a fluid confined inside a pore, the molecular dynamics are restricted, and the relaxation rates are enhanced. Then, in the fast diffusion limit, \(T_1\) and \(T_2\) are given by Equations 1 and 2:\(^22\)

\[
\frac{1}{T_1} = \frac{1}{T_{1,\text{bulk}}} + \rho_1 \frac{S}{V},
\]

\[
\frac{1}{T_{2,\text{eff}}} = \frac{1}{T_2} + \rho_2 \frac{S}{V} + \frac{D\gamma^2 G^2 t_E^2}{12}.
\]

As relaxation times are commonly shortened by collisions, both \(T_1\) and \(T_2\) scale with a surface-to-volume ratio \(S/V\), where \(\rho\) is the surface relaxivity. Transverse relaxation additionally contains effects of diffusion-induced signal loss with the self-diffusion coefficient \(D\), the gyromagnetic ratio \(\gamma\), the field gradient \(G\), and the echo time \(t_E\). Due to microscopic and macroscopic gradients in the magnetic field and the inhomogeneity of the stray field emanating from the excitation coil, only an effective value \(T_{2,\text{eff}}\) can be determined for the transverse relaxation. Conventionally, all discussion of \(T_2\) refers to this constant. NMR relaxometry therefore allows direct detection of the self-diffusion coefficient of the NMR-active nucleus, when molecules move through the magnetic gradient-field.

Distributions of these relaxation parameters are obtained when the signal evolves in a multiexponential fashion and is inverted by algorithms referred to as inverse Laplace transformation. This mathematical operation extracts a spectrum of relaxation times from typically exponential basis functions stabilized by some form of regularization. Shorter relaxation times indicate low molecular mobility characteristic of rigid or viscous material. Longer relaxation times are observed in amorphous and rubber elastic materials as well as with low-viscosity fluids. Highest relaxation times commonly occur in liquids.

A painting is composed of material layers that differ in their physical and chemical properties. The visible surface of the painting, where colors and shapes are mixed, consists of the more superficial layers, which include the varnish, pigments embedded in binder applied as paint layers, a ground or preparation layer, and the support material like canvas, wood, glass, or metal. Pigments are either materials of inorganic origin, such as ochres or ultramarine, or they can be derived from natural dyes as lake pigments (e.g., madder lake). Moreover, for modern and contemporary art, there is a great number of synthetic organic pigments (e.g., blue and green copper
phthalocyanine pigments) used as colorants in paints of all qualities. The organic binders (oils, resins, waxes, glue, egg, gums, and many more), which maintain the cohesion of the pigment particles, are related to the painting technique, for example, drying oils for oil paints, and may comprise complex mixtures such as for modern paints. In more recent times, synthetic polymers of industrial manufacture, such as acrylic paints entered the paint market.\textsuperscript{23–26}

The ability of NMR relaxation times to detect material properties has already been shown in several studies dealing with the stratigraphy of oil paintings\textsuperscript{27} as well as the effect of cleaning solvent on the state of the binder layer.\textsuperscript{28} Recently, the potential of unilateral NMR for real-time monitoring the change in binder-material properties\textsuperscript{29} and the diffusion of cleaning agents into paint layers\textsuperscript{30} were discussed.

Organic solvent treatments reduce the relaxation times of binders\textsuperscript{31} by leaching small molecules in a process similar to the loss of plasticizer in polymers\textsuperscript{32} embrittling the binder layer,\textsuperscript{33} thus accelerating the aging process in a way that can be detected and quantified with NMR measurements. A precise explanation of the current state of an artwork, however, can rarely be provided as chemical, biological, and physical effects attributed to aging are cumulative over long periods of time. Moreover, restoration and preservation treatments interfere with the natural aging processes.

Although the propagation of liquids through different layers can easily be tracked with NMR by signal amplitudes, so far, the relaxation behavior is rarely discussed, even though information of the relaxation can be extracted from the same experiment. NMR relaxation times have already been quantified in polymers to reliably determine their elastic properties\textsuperscript{34–36} demonstrating the correlation of the transverse relaxation time with cross-link density. Cross-links in binder are formed by a variety of chemical reactions, which relate to drying and aging.\textsuperscript{32,37} They include predominately autoxidation, hydrolysis, and esterification. They may be enhanced by unpaired electrons of pigments or contaminants and even by biological attack, which produce acids and other metabolites.\textsuperscript{38}

When a painting has visibly aged, the state of binder in paintings must be assessed to decide on how to treat it. The painting is consolidated with specialized adhesives if the binder layer appears brittle or flaky. In such cases, the reduced elasticity of the polymer can be recognized well by their low transverse relaxation times.

Aged varnish darkens and becomes yellow as it accumulates dirt and dust and must periodically be cleaned or stripped completely. A comparison of the relaxation times in binder layers of two paintings, one of which had never been cleaned whereas the other had been subject of cleaning at least once, has recently revealed an impact of cleaning agents on the binder state.\textsuperscript{28} By monitoring the effects of solvents in a small region of the painting or in mock-up samples of a binder-varnish system, NMR can identify suitable solvents with minimal impact on the binder-material properties.\textsuperscript{29} The noninvasive NMR technique can thus help to understand the impact of aging or cleaning procedures and to optimize conservation treatments, thus aiding the preservation of artworks.

Drying oils, such as linseed oil, contain over 50% polyunsaturated acids and form solid polymer films when exposed to atmospheric O\textsubscript{2}, whereas nondrying oils require additives, which evaporate during the drying process. Besides the type of oil, the type of pigment and additive can vary for different paints. Furthermore, due to properties such as drying speed and yellowing, painters often utilize mixtures of binders (e.g., oil and resin or proteinaceous binders) and siccative agents in a single painting.\textsuperscript{39} Although research has shown how aging affects the relaxation properties of binder, it is yet unclear how combinations of oils, additives, and pigments influence the relaxation times at the onset of drying and in long term.

Relaxation studies with unilateral NMR can provide valuable information about a painting. It has been shown that relaxation can track artificial aging.\textsuperscript{27,40} Although this led to the speculation that the method could also track natural aging and possibly contribute to identifying forgeries,\textsuperscript{15} the extensive study reported here identifies a number of sources other than natural and accelerated aging that affect the relaxation times observed in paint binder. In particular, these are the paint formulation, application, and drying conditions. This work discusses these effects in a study of mock-up samples and a rare set of naturally aged test samples preserved from a period between 1914 and 1951.

2 | EXPERIMENTAL

To investigate drying, 0.137 g of an organic red pigment (Pigment Red 264) obtained from Kremer Pigmente, Germany, were mixed with 0.29-ml linseed oil, and an approximately 0.5-mm-thick film of the paint was applied onto a glass slide using a spatula to approximate uniform thickness of all samples. The measurement was performed immediately after the preparation to follow the early drying process. A second series of mock-up samples concerned the single pigments indigo blue (Natural Blue 1), cobalt green (Pigment Green 50), Bristol yellow (mixed pigment), and zinc white (Pigment White 4), also by Kremer Pigmente, as well as binary and tertiary
mixtures in different concentrations. These samples were stored for two months shielded from direct UV or visible light. Moreover, naturally aged paint samples on hardboard and canvas dated between 1914 and 1951 (Figure 1) were analyzed in view of a correlation of their age with the NMR relaxation times.

$T_1-T_2$ correlation experiments were carried out to detect the changes in the relaxation times during drying and aging. From these two-dimensional datasets, all one-dimensional $T_1$ and $T_2$ data were extracted. A Magritek Kea$^2$ console was used in combination with a PM5 NMR-MOUSE fitted with a 2-mm spacer and operating at a $^1$H NMR frequency 20.14 MHz. For the concentration measurements, an echo time of 40 $\mu$s and a pulse length of 4.25 $\mu$s were chosen for CPMG (Carr-Purcell-Meiboom-Gill\cite{41,42}) excitation and detection following a saturation-recovery sequence and incrementing the magnetization recovery time. Signal was averaged over 2,000 scans with a recycle delay of 1.6 s. For the drying process, the echo time was adjusted to 200 $\mu$s. $T_1$ was determined with 32 magnetization values in the range from 0 to 360 ms. The experiments on the naturally aged mock-up samples were carried out with the same set-up of the MOUSE and pulse length, but the echo time was decreased to 40 $\mu$s. $T_1$ was measured as before. All data were processed with our own MATLAB 2018a code, available from the author upon request.

3 | RESULTS

3.1 | Monitoring relaxation in drying oil paint

During drying and aging, physical and chemical processes such as the evaporation of small molecules and the polymerization of binder reduce the mobility of binder molecules, resulting in shorter relaxation times $T_1$ and $T_2$. Monitoring $T_1$ and $T_2$ of the red pigment mock-up sample during drying reveals how both relaxation times decrease following a short induction period. This induction period can be attributed to the initial formation of a surface layer that impacts the hardening of the paint layers underneath. After approximately 100 h, the relaxation times of the binder begin to change on a much longer time scale that is referred to as aging, whereby the essential physicochemical processes of reaction and evaporation of small molecules remain similar to the early drying processes but are significantly slowed down.

Inverse Laplace transformation of the transverse relaxation decays yields more detailed insight (Figure 2). The distributions of longitudinal relaxation times reveal mono-exponential behavior, whereas the distributions of transverse relaxation times suggest more complex
behavior as at least two components are observed. The narrow peak at shorter relaxation times can be attributed primarily to the polymerizing binder molecules. It is essentially discarded in a mono-exponential analysis of the $T_2$ decay. The signal at longer relaxation times is caused by liquid solvent in the binder matrix. During the early stages of drying, signal amplitude is lost by evaporation of small molecules and translational diffusion in the stray field of the sensor. At later times, the remaining liquid molecules become bound to the binder matrix so that their relaxation times are reduced while signal attenuation from diffusion is reduced at the same time. As transverse relaxation is easy to measure, it is well suited to describe the state of the binder and its interaction with liquids. Longitudinal relaxation is more tedious to acquire, in particular for dry paint where low signal is expected, but it may yet be useful when it is correlated with the transverse relaxation time distribution.

### 3.2 Pigment effects on relaxation of binder

To investigate the effects of various pigment types and of the pigment concentration on the relaxation processes observed in naturally aged paint, mock-up samples with different pigments were produced at varying concentrations. The studied pigments are either homogeneous (Pigment White 4 and Natural Blue 1) or are blends of several substances (Pigment Green 50 and Bristol yellow, a mixture of PY 184 and an unknown organic pigment). The mock-up samples were investigated 2 months after preparation. During this time, they were stored at ambient conditions without exposure to UV light. Figure 3 compares the changes in the relaxation times of four different pigments.

The relaxation times observed in mixtures of linseed oil with most types of pigments do not necessarily

![FIGURE 2](https://example.com/fig2.png) Longitudinal and transverse relaxation times $T_1$ (a) and $T_2$ (b) determined by mono-exponential fits and inverse Laplace transformation plotted against the drying time. The data from a mono-exponential fit are superimposed, as it is more stable and seems to be a sufficient measure to describe the changes in $T_1$.

![FIGURE 3](https://example.com/fig3.png) Longitudinal (a) and transverse relaxation times (b) in mock-up samples made with indigo blue (Natural Blue 1), cobalt green (Pigment Green S0), Bristol yellow (mixed pigment), and zinc white (Pigment White 4) diluted in linseed oil.

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**FIGURE 2** Longitudinal and transverse relaxation times $T_1$ (a) and $T_2$ (b) determined by mono-exponential fits and inverse Laplace transformation plotted against the drying time. The data from a mono-exponential fit are superimposed, as it is more stable and seems to be a sufficient measure to describe the changes in $T_1$.

**FIGURE 3** Longitudinal (a) and transverse relaxation times (b) in mock-up samples made with indigo blue (Natural Blue 1), cobalt green (Pigment Green S0), Bristol yellow (mixed pigment), and zinc white (Pigment White 4) diluted in linseed oil.
depend linearly on the pigment concentration. However, the transverse and longitudinal relaxation times commonly decrease or remain constant with pigment concentration. This behavior is well understood in fillers of polymers, where small particles are added to decrease the free volume and increase the firmness of materials.[43] Within a range of concentrations from 85% to 97%, the longitudinal relaxation time is affected most by indigo blue as well as by cobalt green pigments at higher concentrations, whereas transverse relaxation times are affected mostly by zinc white and indigo blue. However, all three of them show a major change of both relaxation times by approximately 30% within the concentration range. Varying the concentration of Bristol yellow has little effect in the investigated range as its initial value is already low.

Higher order mixtures of pigments appear to exhibit complex trends where relaxation times increase at low pigment concentrations before they drop rapidly at high concentrations (Figure 4). This behavior may be caused by chemical and physical interactions of the molecules from the different pigments as well as separation effects of pigment and oil. Separation would cause lower concentrations of pigment in the oil, due to the formation of emulsions, and enhanced diffusion of the oil.

When the pigment concentration was kept constant at 92 wt.%, the trends observed in the mono-exponential models can further be decomposed by Laplace inversion (Figure 5). Comparing the averages of these peaks, the same sequence of relaxation times $T_1$ and $T_2$ is observed. Most paint layers exhibit a structure of three peaks in the transverse relaxation time distribution, whereas the longitudinal projection can be reduced to a single peak with varying broadness. Within limits, pigment mixtures can be discriminated by the peak position and by the ratio of the peak integrals. The relaxation time distributions observed in the mixtures cannot simply be reconstructed by a linear superposition of their individual distributions, which indicates complex interactions of the pigments and the polymer matrix.

While the cumulative effects of drying and aging often do not permit any assertion about the composition of paints, the results outlined above indicate that colors may be distinguished for paints prepared under laboratory conditions. To demonstrate this, $T_1-T_2$ correlation maps are analyzed for a series of four concentrations of zinc white (Pigment White 4) in linseed oil (Figure 6). The paint mixtures were produced with pigment concentrations from 84 to 94 wt.% and left to dry for two months at ambient conditions before measurement.

As observed by simple mono-exponential fits sufficient to contrast the sample differences, the relaxation properties of paint strongly depend on the pigment concentration. A small increase of $T_1$ along with a stronger decrease of $T_2$ is observable by detailed analysis of the $T_1-T_2$ maps, demonstrating how the distribution of relaxation time evolves toward a structure, which favors three separate peaks. At low pigment concentration, the peak with lowest transverse relaxation times is narrow in the $T_2$ dimension. With rising pigment content, this peak broadens. The longitudinal relaxation time domain yields less information, as only one peak is observed in the $T_1$ dimension. With rising pigment concentration, this peak becomes narrower.
3.3 Naturally aged mock-up samples

All mock-up samples described above were carefully prepared and applied on glass slides for ease of investigation. Real paintings employ a variety of supports and surfaces, including canvas, wood, paper, or cardboard. All layers often undergo natural aging over many years, decades, or centuries before they are first investigated and analyzed with modern methods in the context of conservation and restoration. It is rare for paint samples to survive for periods of time as long as those of paintings. We analyzed historic paint samples from the archives of the Doerner Institut dated between 1914 and 1952.

Although the year of application is written clearly on these samples, there is often little to no documentation concerning their purpose. The presumably didactic and experimental samples contain mostly zinc white and lead white pigments in a variety of binder oils and additives over a ground layer. In a fortunate chain of events, these samples were stored at identical conditions for most of their lifetime.

The principal components (Figure 7a) constructed from $T_1$ to $T_2$ experiments provide a way to analyze the correlation of relaxation times from clusters among plates of the same age. However, as shown above, the average relaxation times do not solely depend on the age and pigment type, but also on the pigment concentration, which is unknown for these samples. Nevertheless, their age may have major impact on the relaxation times and therefore deserves to be further analyzed by means of the more time-consuming two-dimensional $T_1-T_2$ relaxation-correlation experiments that deliver
more detailed information. Constrained by the experimental time available for analysis, however, these samples were only analyzed by mono-exponential fits that provide one $T_1$ and one $T_2$ relaxation time for each sample.

Given the age of the samples, the experimentally determined average $T_2$ times were analyzed via partial least square regression (PLS)\[44,45\] in view of a possible correlation with the sample age. PLS is a methodology well known in chemometrics and other statistical analyses to mine large datasets and to predict quantities from them. To this end, a model is calibrated by training with a large dataset, for which the quantities under investigation are well defined. To that matter, models were constructed by calibrating with raw $T_1$–$T_2$ data from 45 samples and their known years of production. The data vector of one sample was multiplied with the model vector that was constructed from the age data of the remaining dataset. This process was repeated for all 46 paint samples, ensuring that each training set excluded the data of the paint sample to be tested (Figure 7b). The predictions assigned by the PLS regression roughly follow a linear trend. Even though the scatter of the individual points is high, their average positions follow a trend. The highest variance was found for the dataset from 1917, which according to the records of the Doerner Institut contains lead white and zinc white mixed with different types of linseed oil. As these parameters are varied in the paint samples from all ages, it is unlikely that they are causing the larger spread, but

![Figure 7](image)

**FIGURE 7** First and second principal components of paint samples applied on plates dated 1914 (brown), 1917 (green), 1930 (blue), 1942 (red), and 1951 (yellow) based on $T_1$–$T_2$ relaxation experiments. In favor of an improved overview, a small number of data points is located outside the limits outlined for display of the data correlation (a). The estimated age (b) of the plates calculated via partial least squares extrapolation versus the mean age of manufacture shows an essentially linear trend albeit with large error margins ($R^2 = .68$)

a more detailed description of the samples was not obtainable.

Furthermore, our results on one of the plates indicate that the brand of linseed oil does not have significant impact on the relaxation times. The documentation of the 1951 plate is still well preserved, and these paint samples only differ in the choice of oil used as a binder and include poppy-seed, walnut, and linseed oil and contain only lead and mixed white. The corresponding predictor points however are in close proximity. The effect of aging is underestimated by the statistical evaluation.

Overall, these predictions suggest that the relaxation times of the investigated, naturally aged paint samples show a weak trend following their age, suggesting that even in optimum laboratory settings the paint samples cannot be accurately dated from their relaxation times. Good separation is observed between the oldest and newest paint samples, but the large spread in the 1917 samples discourages NMR-based presumptions of the age, even when the samples share the same history of storage. Moreover, the impact of the individual pigments and binders as well as modern varnish or consolidation materials cannot be evaluated from these experiments. In genuine artworks, the distribution of relaxation times cannot be simply reduced to the age, as aging depends on a multitude of parameters including temperature, humidity, UV irradiation, or any applied conservation treatment. A single event during the long lifetime of the painting may permanently degrade the material properties.
4 | CONCLUSION

Compact NMR sensors like the NMR-MOUSE have been utilized to nondestructively analyze the state of binder in paints. Mock-up samples were prepared and investigated to track the drying of fresh paint and the influence of pigment concentration on the relaxation time. We demonstrate the greater importance of the transverse over the longitudinal relaxation time when monitoring drying processes. Additional information was obtained from $T_1$-$T_2$ correlation experiments, which are far more time consuming than mere $T_2$ analyses. Pigments affect the relaxation behavior in different ways that are determined by their electronic structure, the chemical reactions they cause during the curing of binder, and the manner how they bind to the matrix.

Measurements on mock-up samples with different pigment concentrations in linseed oil report that the pigment concentration can affect the binder relaxation in a nonlinear fashion. Mixtures of multiple pigments exhibit effects on the relaxation times significantly different from those of single pigments. Through Laplace inversion, those mixtures could be somewhat discriminated, however, the lack of linear superposition discourages the ability to predict meaningful data on the age or the authenticity of paintings. Although limited grouping of longitudinal and transverse relaxation times as well as linear behavior in the partial least square regression is observed, the data points scattered widely, and the age of the paint could not be estimated with precision and accuracy meaningful for practical purposes. Moreover, the effect of aging is underestimated in the partial least square regression analysis.

The studies reported here lead to the general conclusion that meaningful data on the age or the authenticity of a painting are difficult to obtain from NMR relaxation measurements, although in special cases they can support dating and authenticity studies executed with other methods. The main difficulty that NMR relaxation studies face is the complex dependence of the relaxation times and their distributions on the composition and the physical and chemical history of the paint. Unless most parameters are well-defined correlations between two are difficult to unravel. To further elucidate the potential of our method, the NMR relaxation times of unknown paints need to be compared with those from paints with well-known pigment composition, concentration, and storage and conservation history.

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