Microchemical Journal 137 (2018) 480–484

Contents lists available at ScienceDirect

Microchemical Journal

journal homepage: www.elsevier.com/locate/microc

Nuclear magnetic resonance analysis for treatment decisions: The case of a white sculptural environment by Louise Nevelson

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ARTICLE INFO

Article history:
Received 5 September 2017
Received in revised form 31 October 2017
Accepted 6 December 2017
Available online 07 December 2017

Keywords:
Solid state NMR
Unilateral NMR
Fine arts conservation
Treatment
Cleaning

ABSTRACT

In this work both solid state nuclear magnetic resonance (NMR) and unilateral NMR have been applied to investigate the paint composition and to inform the treatment decision for a white sculptural environment by Louise Nevelson completed in 1977. Within ten years of installation, the sculpture required restoration and was repainted by a restorer. The restoration paint is currently stained, dirty and flaking. The original paint and the restoration paint composition were determined using solid state NMR. The original and the restoration paint were identified as an alkyd and a polyvinyl acetate paint, respectively. Pentaerythritol, a compound from the alkyd paint, was identified in the restoration layer and in some areas as a white powder on the surface of the sculpture. The original alkyd paint seemed to be in better condition than the restoration paint, suggesting that the migrated pentaerythritol had contributed to the degradation of the restoration layer. The free pentaerythritol may be a result of excess in the alkyd paint formulation rather than degradation of the original paint. The analytical study guided the decision to remove the highly degraded restoration paint. Cleaning systems using viscous carriers for the solvents were investigated and potential mechanical changes in the alkyd paint were evaluated using unilateral NMR.

1. Introduction

The Louise Nevelson sculptural environment in Saint Peter's Church in New York City was commissioned by the church in 1977 [1]. From 1986 through 2006 the church hired a restorer who regularly applied layers of paint. This resulted in a thick and uneven surface with restoration paint ultimately covering the entire sculptural surface (Fig. 1a–c). Archival research revealed that Nevelson preferred a clean, white, even surface for her white installations, without dirt and losses.

The original alkyd paint can be distinguished from the restoration paint under both visible light and UV light. In visible light it is a warm yellowish white and the restoration paint is a cool greyish white (Fig. 1d). Under UV light the original fluoresces yellow while the restoration paint is non-fluorescent. The same was observed by looking at paint samples in cross section under magnification using a stereobinocular microscope. The color of the original paint is consistent throughout the cross-section, indicating that the yellowish white is not due to oxidation and degradation at the surface. It was also noticed that some brown stains were visible especially where the two paints meet. In addition, a white efflorescence-like powder was found on the surface in some areas of the sculpture. Solubility tests of the two paint layers found that the original was soluble in acetone, and swelled in benzyl alcohol, whereas the restoration paint was easily soluble in acetone, benzyl alcohol and isopropanol, and was highly hydrophilic, easily swelling and lifting upon exposure to water adjusted to pH 8.5 [2–3].

In this study we used solid state NMR for a detailed analysis of the paint layers. This technique has rarely been used to study works of art although recently some examples can be found in the literature [4–8]. This is partly due to the relatively large sample amount required for analysis (order of 50–100 mg). Recent developments of the techniques such as smaller rotors for faster spinning have significantly reduced the quantity of sample needed for analysis [8]. During the past decade another magnetic resonance technique, unilateral NMR, a type of 1D magnetic resonance imaging (MRI), has found applications for the study of cultural heritage directly related to its non-invasive qualities [9–14]. It

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https://doi.org/10.1016/j.microc.2017.12.004
0026-265X/

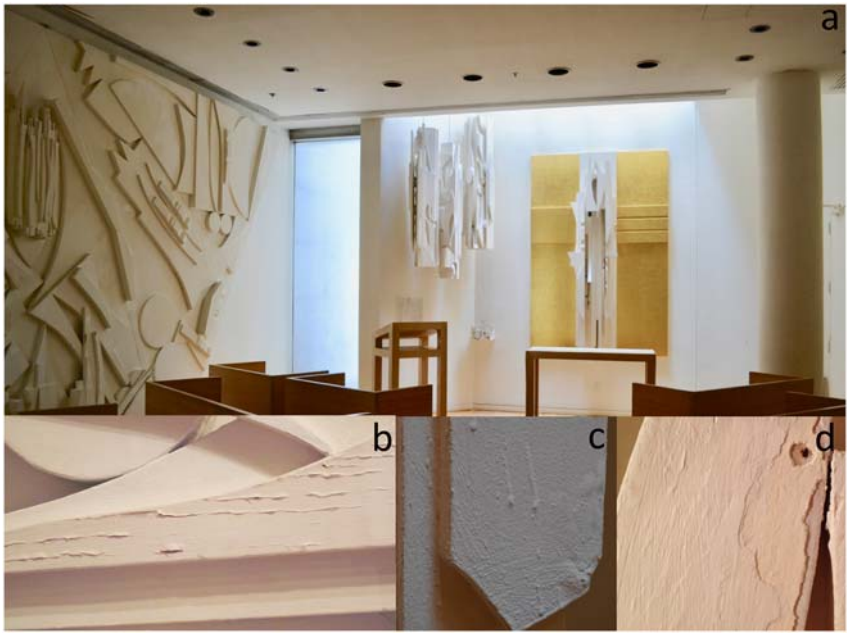

Fig. 1. (a) Part of the Louise Nevelson, *Chapel of the Good Shepherd*, Saint Peter's Church, New York City. (b) Flaking of restoration paint. (c) Thick and uneven surface texture resulting from the restoration paint application. (d) Original alkyd paint is currently yellowish white and restoration paint is greyish white. Photographs by author. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

allows for the measurement of depth profiles, for example of paint layers, without the need for sampling. In the present work we use unilateral NMR to test the effect of various cleaning methods on the original paint and on the restoration paint.

2. Materials and methods

2.1. Sample details

Small pieces of original and restoration paint were collected from flaking areas of the sculptural environment to perform the solid state NMR paint analysis. This flaking separated two layers in some areas. Efflorescence-like powder was collected from the hanging columns next to the altar. Gamblin's PVA Size (Gamblin, Portland, Oregon, USA) was cast out on a glass plate, let to dry, and subsequently scraped off to be used as a solid state NMR reference for polyvinyl acetate. For the unilateral NMR study a fragment (about 50×5 cm^2), that accidentally had broken off the sculpture prior to our study and had been kept by the church, was used without taking further samples. Cleaning tests were performed on four 20×20 mm^2 spots on the fragment using Klucel® M (hydroxypropylcellulose nonionic water-soluble cellulose ether) or polymeric dispersions such as polyvinyl alcohol borate (PVOH-B) as carriers for either isopropanol or pH 8.5 adjusted water. The gel-solvent system was left on the fragment for 10 min before it was wiped off with a dry cotton swap. The unilateral NMR experiments on cleaned spots were done 1 week after treatment or later.

2.2. XRF

X-ray fluorescence (XRF) experiments were carried out using a Bruker Tracer III/VI portable XRF spectrometer with a rhodium tube operating at 40 kV and 1.2 μA.

2.3. Solid state NMR

^{13}C solid state NMR experiments were performed on a Bruker Avance III spectrometer at a magnetic field of 7.0 T (corresponding to a ^{1}H Larmor frequency of 300 MHz). Small paint pieces of original and restoration layer were ground to powder and filled into rotors of 4 mm diameter (volume of 90 μL). Several samples were taken and tested. The sample volume of the original paint and the efflorescence-like powder was confined with Teflon tape as a spacer due to limited sample amount. The rotors were spun at the magic angle (MAS) with a frequency of 5 kHz in a VTN probe at room temperature. Initially the spinning frequency was varied to identify spinning side bands and to avoid them to fall into the regions of interest. ^{1}H-^{13}C cross-polarization experiments (1 ms contact time) were repeated 20 k times with a recycling delay of 3 s. The spectra were referenced to TMS. An exponential window function of 20 Hz has been applied prior to Fourier transform.

2.4. Unilateral NMR

Unilateral NMR depth profiles were performed using an ACT (Aachen Center of Technology) NMR-MOUSE® controlled by a Bruker Minispec console (Bruker, Billerica MA, USA) operating at 18.5 MHz ^{1}H resonance frequency (0.5 T) with a field gradient G of 22.6 Tm^{-1} and 90° and 180° pulses of 4.5 μs. The instrument was equipped with a RF coil creating a sensitive volume of about 10×10 mm^2 times an adjustable thickness, 2.5 mm away from the RF coil [15,18]. The transverse relaxation decays of ^{1}H echoes were measured using the Carr-Purcell-Meiboom-Gill (CPMG) [16,17] pulse sequence with echo times of 30 μs. The acquisition time within the echoes was 20 μs, which corresponds with the given field and gradient to a theoretically achievable resolution of about 50 μm. The sample was moved through the sensitive volume in steps of 50 μm. Due to imperfection of the sample orientation, irregular application of the paint layers, and processing favoring the SNR while compromising resolution the actual resolution is estimated to be rather about 80 μm. The fragment was measured using 256 scans, a recycle delay of 1 s, and 128 echoes.

3. Results and discussion

Portable XRF used on-site identified titanium based white pigment as the colorant in both the original and the restoration paint. Cross-polarization (CP) ^{13}C NMR spectra of the original and the restoration paint layers (Fig. 2) provide enough information to determine the types of paint used. The spectrum of the restoration layer shows four dominating signals indicative of polyvinyl acetate (PVAc) labeled as *1*