



Original article

The use of nanostructured fluids for the removal of polymer coatings from a Nuxalk monumental carving – exploring the cleaning mechanism



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ABSTRACT

While undertaking treatment of a monumental Northwest Coast wooden carving at the American Museum of Natural History, conservators encountered a difficult cleaning challenge. The 19th century painted red cedar carving served as a house entry pole in the Nuxalk village of Bella Coola in the province of British Columbia, Canada. The painted surface was weathered by years out of doors in front of the house of Chief Pootlass and obscured by darkened museum-applied coatings and grime acquired during more than 100 years of open display at the museum. The methods used to reduce the grime and cellulose nitrate coating found on the surface overall were not successful when applied to the green painted areas on the bottom of the pole, as it was covered with an additional coating of poly(vinyl acetal) resin. The present work reports on the testing and use of aqueous nanostructured fluids (NSFs) and hydrogels for successfully cleaning these areas, where other methods could not be used safely. There have only been a few published examples of these recently developed cleaning fluids and gels being used on art objects and this is the first known use on this type of material. Further analyses were performed following the cleaning. Micro-reflectance FTIR, optical microscopy, SEM-EDX, and NMR were used to characterize paint and coating samples taken from the carving. In addition, laboratory tests were performed to evaluate the response of poly(vinyl acetal) to a selection of NSFs, providing an understanding of the mechanisms underlying the successful cleaning performed on the pole by the conservators.

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1. Introduction

Cleaning is one of the most complicated and delicate operations in art conservation, generally resulting in irreversible physical or chemical alteration of artworks' surface. The procedure must be controlled and safe, both for the artwork and the conservators' health. A system that selectively targets the unwanted materials is essential to prevent damage to the original components of the work of art. This is easily achieved when the undesired material has a chemical nature distinct from the substrate from which it has to be removed, e.g., the removal of dirt and grime from varnished oil paintings, or organic substances from stones,

metals, or other inorganic materials. However, when the substrate and the material to be removed have similar chemical compositions and solubility parameters, safe and effective removal is more problematic. Organic polymers used as varnishes or consolidants are often chemically similar or identical to paint binders, and thus non-selective cleaning methodologies endanger the original materials. Organic solvents, applied either neat, in a poultice material, or thickened into gel-like pastes, referred to as "solvent gels" [1], are the most common approach in paintings conservation for these types of cleanings. However, organic solvents, even when poulticed or thickened, tend to quickly migrate into layers of the original stratigraphy causing undesired swelling, leaching, and probable harm to the painted surface [2]. Recently-developed aqueous nanostructured fluids (NSFs), such as oil-in-water microemulsions and aqueous swollen micelles, used in conjunction with new

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hydrogels, engineered to meet specific conservation requirements, present a promising alternative. These systems have the potential to be more efficient and controllable (and thus safer) than neat organic solvents or other aqueous systems in poultices, thickeners, or other types of gels.

NSFs include up to 25–30% organic solvents, dispersed or dissolved in an aqueous environment together with one or more surfactants [3–6]. Due to the combined action of the organic solvents and surfactants, and to the presence of a large amount of water, these systems can provide a mild and controlled cleaning action involving swelling/dewetting processes, rather than the solubilization resulting from the application of organic solvent by other methods [7–11]. This cleaning mechanism can be optimal for the removal of polymeric coatings from porous substrates. However, when the selective removal of thin polymer coatings from a delicate painting stratigraphy must be performed, even the application of unconfined NSF shows some limitations; like any unconfined cleaning fluid their penetration cannot be easily controlled. To address this issue, aqueous NSF can be combined with highly retentive hydrogels, creating highly controllable and effective cleaning systems. Confining NSF in hydrogels improves the performance of the cleaning fluid and substantially reduces its penetration. The hydrogels, when properly loaded and applied, hold the cleaning fluids effectively, so that only the surface of the object is wet, not the substrate. This permits application of the NSF to water-sensitive or porous media and substrates, such as acrylic paintings, wood, and paper, which otherwise would have been problematic due to high water content. Moreover, the gel itself does not leave residues, reducing the amount of rinsing required. Advanced hydrogels loaded with NSF and aqueous solutions have been tested on mock-ups and their successful application in treatment of a few artworks has been published, including removal of defacements and overpainting from street art pieces and aged varnish from a painting by Pablo Picasso (“L’Atelier”) [12–19].

The current study documents and evaluates the use of NSF-loaded hydrogels to remove aged coatings from a monumental Northwest Coast painted wood carving in the collection of the American Museum of Natural History (AMNH) in New York (USA). For the first time, conservators have cleaned this kind of artifact using confined NSF, with the aim of exploring the cleaning mechanism of the fluid and studying in laboratory the interaction between the polymer and different NSF.

The pole was carved sometime in the late 1800s by the Nuxalkmc (Nuxalk People), which are indigenous to the Bella Coola valley on the Pacific coast of Canada and was collected and brought to AMNH in 1909. Monumental carvings from the Northwest Coast region, such as this, are often collectively referred to as “totem poles”. However, this terminology is avoided here, as the colonial application of the term “totem” to these carvings is incongruous and ethnographically inaccurate. It originates from a different culture and geographic area: it is an Ojibwe (Anishinaabemowin) term of the Great Lakes region and the Algonguian language family, referring to a clan emblem or individual guardian spirit [20]. The Northwest carvings, on the other hand, generally represent lineage crests and rights, or ancestral narratives associated with particular hereditary chiefs or “houses” [21]. The use of this blanket terminology also conflates several distinct types of carvings, including house frontal poles, interior house posts, mortuary, memorial, and welcome poles and figures [22].

The Nuxalk carving (AMNH 16.1/438) is from the village of Komkotes (Q’umk’uts), located at the mouth of the Bella Coola River (Fig. 1). It stands just over 3.5 m tall, is carved from red cedar, and painted overall with large color fields of white, blue, green, red, and black. It was part of the powerful, vibrant, and colorful display of fully painted house fronts and carvings that greeted all that approached this village. The pole depicts two figures, an



Fig. 1. The Pootlass Entry Pole (16.1/438) ca. 1909 in its original location, on the waterfront of Komkotes village, in British Columbia (Canada). The human figure above the pole was carved separately and is in the collection of the Canadian Museum of History (CMH VII-D-109). Image #46,084, American Museum of Natural History Library.

upper humanoid face and torso with a raven below, its wings parted creating an opening through which one entered the house. It belonged to the house of Chief Sam King Pootlass (Qwalalha). Pootlass meaning, “Plenty for all”, is an important Nuxalk lineage. Chief Sam King’s father was the renowned Big Chief Pootlass, who stood up to the military and logging companies to protect the Nuxalk territories and united the Nuxalkmc and kept them strong following the population displacement and decimation caused by colonization and associated smallpox epidemic.

The wood and polychromy of the entry pole were weathered by more than 20 years of exposure to the elements while in front of Chief Pootlass’ house. The green painted areas on the wings of the raven are the subject of this study. They are located on either side of the entry hole (door) at the bottom of the pole.

Western red cedar (*Thuja plicata*) is traditionally used for monumental carving by Nuxalk and other indigenous nations of the Pacific Northwest. The color, texture, and smell of the wood of this pole were consistent with its use and no further analysis was conducted to confirm this identification. The overall condition of the substrate is fair, showing a few breaks, cracks, splintering, and wood loss. The exterior of wood appears softer than the inner part, which is hard and compact. Since arriving at AMNH, the pole has been one of more than 70 monumental wooden carvings on open display in the museum’s historic Northwest Coast Hall for more than 100 years. Before 1995, the Hall had no climate control and the collection was exposed to the full range of widely fluctuating environmental conditions typical of the Northeast United States, including many decades when large floor to ceiling windows lined the hall (Fig. 2). Historically, the presence of an on-site incinerator, coal heating, as well as urban and industrial activities, produced black sooty residues. Although these sources of pollutants have been eliminated or reduced over the years, rapid accumulation of dust continues due to the museum’s high attendance numbers. In addition, dust and grime were compacted and sealed on the fragile painted surfaces by numerous largely undocumented campaigns of cleaning and coating. As a result, soiling was trapped on the surface over, between, and under multiple coating layers.

Beginning in the late 1990s AMNH conservators have undertaken several projects to assess the widespread need for treatment, addressing both structural and surface condition issues, of this important collection [23,24]. Starting in 2017, in conjunction with a complete renovation of the Northwest Coast Hall, a new conservation campaign commenced, focused on cleaning six carvings with



Fig. 2. The Northwest Coast Hall at AMNH, ca. 1919. The image shows monumental carvings installed in the Hall when coal heating and windows were a source for heavy soot deposits. The beak of the Raven of the Pootlass Entry Pole (16.1/438) is visible extending out from the wall on the left (circled in yellow). Image #37,673, American Museum of Natural History Library.

the complex polychromy, including the Pootlass Entry Pole. This project was headed by a team of conservators at the AMNH and included collaborative work with several constituencies. Collaboration with First Nations communities on the Hall renovation included the appointment of Co-Curator Haa'yuups (Ron Hamilton) and nine advisors for individual cultural groups. This provided an opportunity to learn about the cultural context, significance, and history of the pole from co-author Snxakila (Clyde Tallio), orator, ceremonialist, and cultural researcher for the Nuxalk Nation. Conservators and Tallio discussed the condition and planned treatment for the pole and Tallio acted as liaison, communicating this information to others in his community, including the current Chief (Noel) Pootlass (Sixilaaxayc).

Outdoor exposure of the carving weakened the paint, which like all those displayed in the Northwest Hall at AMNH, was covered with multiple layers of grime and non-original darkened coatings, including an overall coating of nitrocellulose (CN). The CN coating on this pole was identified by examination under ultraviolet (UV) illumination and performance of a microchemical test for nitrates [25]. The coating exhibited a similar appearance under UV light to the coating on other carvings in the hall, where the identification of CN had been further confirmed with instrumental analysis (FTIR) [23,24].

CN is characterized by a long history of use in the treatment of art objects, antiquities, and natural science materials in museums [26,27], and it is known to have been used widely on collection materials at the AMNH in the past [24]. CN is unstable, giving rise to dark and yellow films. This degradation process was at least partially responsible for the alteration of the appearance of the painted poles' surface.

The CN was successfully removed from most of the surface using thickened macroemulsions, based on formulations designed by paintings conservators [28,29]. Those employed in this cleaning contained 4 primary components: pH buffered water, a chelator, a water-immiscible solvent, and a viscosity modifier/emulsifying agent. Cleaning solutions were modified to suit the unique sensitivities of the multiple original paints. The pH was buffered to between 6 and 8 using citric or boric acids. At pH 6, the citric acid additionally acted as a chelator; for pH 8 solutions, DPTA was added. Benzyl alcohol, alone or in 2:1 combination with Rhodiasolv Iris (a proprietary dibasic ester), was added in proportions of 2.5 to 10%. Xanthan gum served as both a viscosity modifier

and emulsifying agent. To protect the underlying paint layer, limit penetration, and facilitate the clearance of the emulsion, a volatile Cyclomethicone (D4 or D5) was brushed over the surface prior to the emulsion's application.

However, the lower part of the carving presented an additional polymer coating, identified on other carvings as poly(vinyl acetal) [24], which was not responsive to the viscous cleaning solutions employed successfully elsewhere. The aged and discolored coating had been applied during a previous restoration intervention, over the pre-existing CN layer, and covered an area of fragile green paint.

Conservators attempted to resolve the issue by raising the proportion of solvent in the emulsions to 20%. However, higher solvent content both swelled both the coating and original paint, even in the presence of the cyclomethicone. As a result, the agitation of the surface required by this treatment methodology altered the underlying paint morphology and, thus, this methodology was ruled out. Numerous neat solvents and solvent mixtures with a range of solubility profiles were also tested. Of these, only DMSO and 30:70 (w/w) DMSO/Ethyl acetate mixtures readily dissolved the coating. However, these solvents were not selective, as they readily dissolved the underlying paint. Therefore, they were not considered a viable treatment option. On the other hand, the recently-developed cleaning systems combining NSF's and hydrogels offered the possibility of a more controllable and effective cleaning method.

1.1. Research aim

Three commercial NSF's and two hydrogels were tested in the removal of a stubborn poly(vinyl acetal) aged coating from a Nuxalk carved pole. After some preliminary investigation, the selected system used to successfully clean was Nanorestore Cleaning® Polar Coating S loaded in a Nanorestore Peggy Gel® 6. Small samples were removed from the carving for analysis. FTIR, SEM-EDX and NMR were used to identify the chemical nature of the detrimental coating, the composition of the paint layer and to gain a better understanding of the stratigraphy of the painted surface. In addition, experiments were carried out in the laboratory to better understand the mechanism underlying the good cleaning performances of NSF's on the poly(vinyl acetal) coating.

2. Materials and methods

2.1. Materials used for cleaning tests

2.1.1. Nanostructured cleaning fluids

Three different commercially available NSF's were used in testing: Nanorestore Cleaning® Polar Coating B (hereinafter "NSF B"), Nanorestore Cleaning® Polar Coating S (hereinafter "NSF S"), and Nanorestore Cleaning® Polar Coating G (hereinafter "NSF G"). All of them are amphiphile-based aqueous cleaning fluids specifically designed to remove relatively polar polymeric coatings, and their components are reported in Table 1.

2.1.2. Hydrogels

Two commercial hydrogels were here tested: Nanorestore Gel® Peggy 5 (hereinafter "Peggy 5"), and Nanorestore Gel® Peggy 6 (hereinafter "Peggy 6"). Both Peggy 5 and Peggy 6 are transparent hydrogels based on a poly(vinyl alcohol) polymeric network; they are sold as sheets (approx. 10 cm x 15 cm x 2 mm) loaded with deionized water. These hydrogels were selected because can be loaded with NSF's and were specifically designed to be used on tridimensional surfaces. Peggy 5 is slightly more rigid and water-retentive than Peggy 6, which, consequently, is even more indicated to be used on textured, rough surfaces.

Table 1

NSFs composition. Concentrations are reported in w/w%, according to the information available from technical and safety data sheets.

Component	NSF S	NSF B	NSF G
Water	> 70%	> 60%	> 55%
Surfactant	Anionic (2–4%)	Nonionic (2–4%)	Nonionic (4–7%)
Organic solvents	PeOH (3–9%)	MEK (15–22%)	BuOH (7–10%)
	PC (4–10%)	BuOH (5–10%)	MEK (10–14%)
	EA (4–10%)		PC (4–8%)
			EA (4–8%)

PeOH = 1-Pentanol; PC = Propylene carbonate; EA = Ethyl acetate; BuOH = 2-Butanol; MEK = Methyl ethyl ketone (Butanone); Nonionic surfactant = alcohol ethoxylate.

2.1.3. Other

Glacial acetic acid, deionized water, and 10% ammonium hydroxide were used to set the water pH to 7.5. Highly absorbent polyester/polyamide microfilament fabric (Evolon CR), soft polyurethane foam (cosmetic sponges pre-washed to remove unwanted fabrication materials), and polyethylene (PE) plastic film were also used in the cleaning tests.

2.2. Methods used for cleaning tests

The pole was deinstalled from the Northwest Coast Hall (AMNH) and the treatment was performed in the Museum's Anthropology conservation laboratory. The pole was placed horizontally on sawhorses and fume extraction and ventilation were provided.

2.2.1. Preliminary tests

Preliminary tests were performed to determine the optimal application methodology for the removal of the detrimental coatings and soiling while avoiding potential harm to the original green paint. The test area was located at the lower proper left side of the pole. Each test spot was 1 cm² or smaller. A cotton swab soaked with each of the three NSFs was then rolled on the surface for approximately 30 s. After each test, the surface was rinsed to remove any residues with water with an adjusted pH of 7.5, matching the pH of the cleaning solution as closely as possible.

2.2.2. Assessment procedure

The two hydrogels (Peggy 5 and 6) were loaded with the NSFs as follows: small pieces (few cm²) of each gel were cut out from the original sheets and initially soaked in the NSF for two hours. The cleaning fluid was then replaced, and the gels left soaking overnight. This procedure helped to eliminate all water from the gels, ensuring it was loaded with a full concentration of cleaning fluids. Prior the application, the gels were gently pressed on a piece of blotting paper, to eliminate the surface excess liquid. The ability of the two gels to successfully adapt to the surface morphology was assessed visually by placing them on the carving and comparing the cleaning results. The time needed to achieve the swelling of the coatings was assessed by gradually increasing the duration of contact between the surface and the loaded gel from 1 to 10 min. A PE film was placed over the gels, in order to hamper NSFs evaporation. The surface was examined at each interval to assess the effects on the coatings and to ensure there was no visible damage to the original paint. The effectiveness of the gels loaded with the three different NSFs was assessed under visible and UV light, looking at their effect both on the materials targeted for removal (polymer coatings and soiling) and on the underlying original green paint (see SI file for further details). Finally, three different materials commonly used in the AMNH conservation laboratory were tested for removal of the

swollen polymer coatings: cotton swabs (hand-rolled and commercially prepared), a soft polyurethane foam, and a highly absorbent polyester/polyamide microfilament fabric (Evolon CR). Tests were performed with the materials both dry and wet with cleaning fluids or water.

2.3. Materials and methods: samples from the pole

Two small samples (approx. 4–10 mm x 1–4 mm coated wood chips) were collected from the Nuxalk pole; the first (sample "Green") was taken from the green area where the cleaning was performed, while the second (sample "Coating") was taken from a black-painted hidden area where the aged and discolored coating was evidently present. The Coating sample was used to characterize the detrimental polymeric film targeted by the cleaning intervention. The Green sample was used both to characterize the chemical nature of the green paint and to evaluate the result of the cleaning method. Both samples were analyzed by means of micro-reflectance FTIR spectroscopy analyses and optical microscopy. The Green sample was then embedded in an epoxy resin cube, polished to expose the cross-section for SEM-EDX analysis. Finally, the polymeric coating(s) present on the Coating sample were also analyzed by means of NMR measurements.

2.3.1. FTIR spectroscopy

2.3.1.1. Attenuated total reflectance (ATR). ATR measurements were carried out on polyvinyl acetal solid flakes with a Thermo Nicolet Nexus 870 spectrometer equipped with a liquid nitrogen-cooled MCT detector and a single reflection diamond crystal ATR unit. Spectra were recorded in the 4000–650 cm⁻¹ range (128 scans, 4 cm⁻¹ resolution).

2.3.1.2. Micro-reflectance. Microreflectance FTIR analyses were performed on the surface of the two samples collected from the Nuxalk pole: sample "Green" and sample "Coating", and on polyvinyl acetal solid flakes. They were analyzed using a Nexus Fourier transform infrared spectrometer from Nicolet. The instrument was interfaced with OMNIC software and equipped with a microscope for microanalysis. A MCT detector was used to collect the signal in the 4000 – 650 cm⁻¹ range. A gilded surface was used to collect the background signal. The spectra were collected as single-beam files as the sum of 128 scans with a resolution of 4 cm⁻¹. Then, they were divided by the background signal and transformed using the Kubelka–Munk algorithm, which is commonly used to display reflectance spectra, as it applies a scaling factor to the curves in order to obtain data more easily comparable with the absorption spectra.

2.3.2. Nuclear magnetic resonance (NMR)

The Coating sample was immersed in chloroform for 24 h in a closed vial, to extract all the polymeric compounds from the wood splinter. Then the solvent was evaporated and the polymer

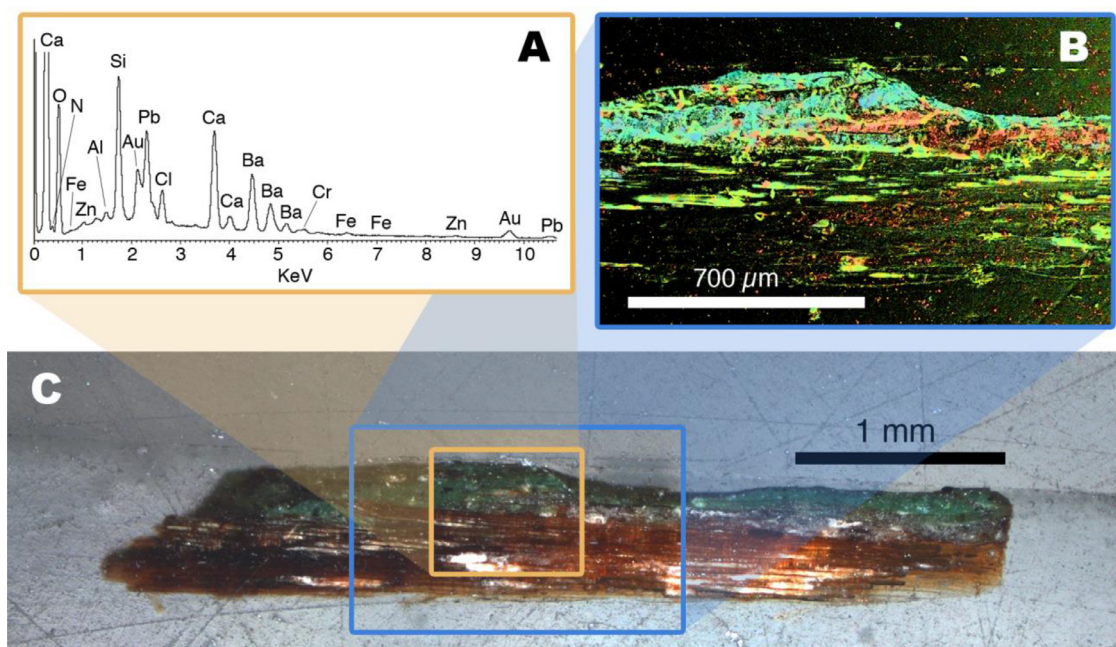


Fig. 3. A) SEM-EDX energy spectrum collected on the section of the Green sample taken from the pole in a green painted area. B) CAMEO™ imaging showing, in false colors, the elemental composition of the sample (scale color ranges from Si (red) to Ba (blue)). C) Micrograph of the Green sample section embedded in epoxy resin.

left in the vial was dissolved in deuterated chloroform. Then, ^1H NMR spectra were recorded with a Varian Mercury Plus 400 spectrometer working at 399.921 MHz. The chemical shifts are reported in ppm and referred to TMS as internal standard. Spectra elaboration was performed with the software MestRe-C 4.3.2.0. DMSO- d_6 (99.8%), purchased from Sigma Aldrich.

2.3.3. Optical microscopy (OM)

A Reichert Zetopan 353–890 microscope was used to collect micrographs. The instrument was coupled with a Nikon Digital Sight DS-Fi2 camera. The NIS-ELEMENTS software was used to capture and edit images.

2.3.4. Field emission gun-scanning electron microscopy (FEG-SEM)-Energy dispersive X-ray (EDX) analysis

A FEG-SEM SIGMA (Carl Zeiss, Germany) was used to collect the images on the wood samples coming from the pole, using an acceleration potential of 25 kV and a working distance of 8 mm. For the analyses, a gold-metallization of the sample was performed with an Agar Scientific Auto Sputter Coater. The EDX analysis was performed using a X-Act system (Oxford Instruments) equipped with a Silicon Drift Detector and using the app Cameo for the mapping of elements.

2.4. Materials and methods: interaction of poly(vinyl acetal) and NSF

500 μL of a 10% (w/w) solution of a poly(vinyl acetal) commercially known as Alvar® (Monsanto) in EA were evenly distributed on an area of about 2 cm × 6 cm of microscope glass slides, which previously had been thoroughly cleaned with acetone. The thickness of the layer was about 35 μm, assuming that the density of Alvar® is around 1.2 g/cm³, similar to that of poly(vinyl acetate). The film was left drying for a week at room temperature and then immersed in 40 mL of each of the NSFs. The structural evolution of the Alvar® coating was followed by means of pictures taken under visible light

3. Results and discussion

3.1. Materials' characterization

Scientific studies of historic poles are limited, both in terms of investigation of museum-applied coatings and analysis of their painted surfaces. The Canadian Conservation Institute (CCI), Ottawa, has reported the most extensive instrumental analysis of Northwest Coast painted surfaces to date for characterization of pigments and binding media [30]. They analyzed 107 samples of green paint from museum collections of the Northwest Coast. The majority was from the Haida, Tsimshian, and Kwakwaka'wakw nations, with additional samples from the Nuxalk, Heiltsuk, Nuu-chah-nulth, Tlingit, and others. Green earth (celadonite) was the most commonly identified pigment but was not reported in any Nuxalk samples. Chrome green, a mixture of Prussian blue and chrome yellow (lead chromate), the second most commonly found green pigment, was identified on Nuxalk items, including a mask dated to 1893. Recent analysis of green paint samples from a set of Tsimshian house posts at AMNH also identified Prussian Blue but could not confirm the presence or identify of a yellow pigment [23]. A later article, also from CCI, focused on the identification of green earth (celadonite), reported that chrome green was identified in three Nuxalk samples [31].

Micrographs showed that the green paint was applied directly onto the wood (Fig. 3C), while Figs. 3A and 3B report on the elemental composition (obtained through SEM-EDX analyses) of the green paint, which was probably obtained by mixing blue and yellow pigments. According to the presence of both Fe and N, the blue pigment likely is Prussian blue, a ferric ferrocyanide ($\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$). On the other hand, the presence of Zn, Ba, Pb, and Cr could suggest the presence of different yellow pigments, i.e. zinc potassium chromate hydrate ($4\text{ZnCrO}_4 \cdot \text{K}_2\text{O} \cdot 3\text{H}_2\text{O}$), barium chromate (BaCrO_4), and lead chromate (PbCrO_4), which are all known to be used in XIX century [32]. However, no mixtures of Prussian Blue and Zinc Yellow were found in the papers from CCI [30,31], therefore Zn, Pb, and Ba found in the paint from the Pootlass' entry pole are most likely attributable to commonly used fillers in

commercial paints, such as lead white, zinc white, and barium sulfate [30].

It does not appear that any of the samples in the CCI studies were removed from poles or other monumental works, which may have differed in techniques and materials used due to their size and frequent outdoor installation. In addition, while there are a few past accounts of museum-applied coatings found on poles in other collections, none report the scientific analysis of these materials [33], until the recent studies conducted on poles at AMNH [22,23].

Based on macroscopic and microscopic examination of the pole surface, under visible and UV light, at least two different coatings were present on the carving. The first is applied over the entire front surface of the carving including the object of this study, and not on the backside of the pole. It is darkened and yellowed, unevenly applied, thick and drippy in some locations, while thin or absent in others. As noted above, solubility profile and yellow appearance when observed under UV are consistent with a coating, which was found on all the other carvings in the museum hall, and identified as nitrocellulose (CN) by FTIR analyses [24]. The second layer was localized on the lower section of the pole front and backside of the wings, covering red, black, white, and green areas, over the CN layer. This second coating appeared glossier, thicker, and harder than the nitrocellulose coating. Based on its location, appearance, and institutional knowledge of materials historically employed by AMNH staff, it was hypothesized that it was a poly(vinyl acetal). Poly(vinyl acetal) resins, primarily poly(vinyl butyral), were used in conservation from the 1930s until the 1960s [27]. Poly(vinyl acetal) itself is less often reported but has been cited by a few authors as a consolidant or coating for wood and as a filler for ceramics [34]. Moreover, it was employed by paleontologists as a consolidant for fragile fossil material [35,36] and it was classified as an “exceptionally hard and tough” resin.

In order to check this hypothesis, the microreflectance FTIR spectrum collected on the surface of the Coating sample was compared with the spectrum of a commercial poly(vinyl acetal) known as Alvar® and manufactured by Monsanto (see Fig. 4). The similarity between the two spectra clearly confirmed that the detrimental discolored polymer present over the Nuxalk pole lower surface is actually a poly(vinyl acetal). Records of treatment campaigns in the hall where the pole is exhibited, indicate the poly(vinyl acetal) coating might have been applied during the 1960s, when Alvar® was commercially available. Moreover, a poly(vinyl acetal) coating was also identified on the bottom areas of many of the other monumental Northwest Coast carvings conserved at AMNH [24]. The resin was likely applied to lower areas, which were in easy reach of visitors, to protect them from continuous touching or vandalism. This polymer was largely used in the UK and North America during the 1950–60s [34]. As Alvar® was discontinued at the end of the 1960s [35], the polymer sample used for the experiments in the present work was provided by the AMNH Vertebrate Paleontology Preparation Laboratory, where it was quite extensively used on fossil bones, and thus it is at least 60 years old. Dating back to that period, this polymer was produced by the acid-catalyzed acetalization of poly(vinyl alcohol) with acetaldehyde [37]. Looking at the ATR-FTIR spectrum reported in Fig. 5A, it seems that a significant amount of acetate groups is present in the polymer, whose spectrum is indeed very similar to that of poly(vinyl acetate) [38,39]. Apart from the CH stretching peaks at 2928 and 2972 cm^{-1} , there is a strong peak at 1729 cm^{-1} , relative to the C=O stretching of the acetate group. Moreover, a sharp and intense peak at 1234 cm^{-1} is visible, which is usually considered a diagnostic signal for poly(vinyl acetate), and is due to the asymmetric stretching of the C–O group. The peaks at 1428 cm^{-1} and 1371 cm^{-1} are due to the in-plane CH bending; the peak at 1130 cm^{-1} to the out-of-plane CH bending; the peak at 1020 cm^{-1} to the asymmetric

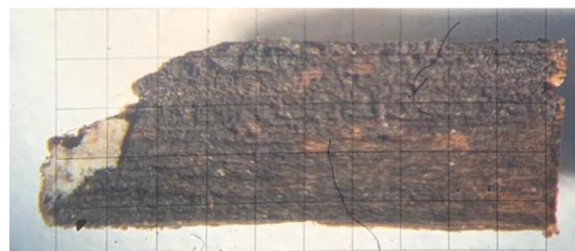
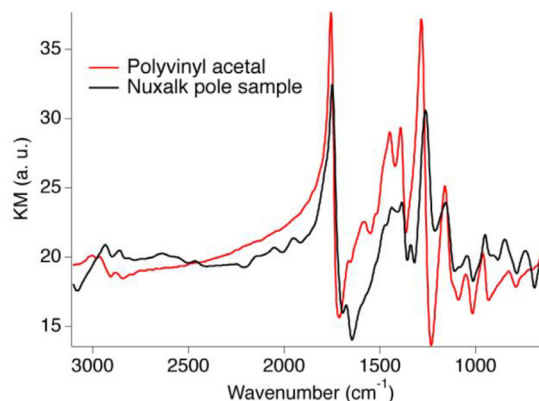


Fig. 4. Bottom: Micrograph of the Coating sample taken from the backside of the Nuxalk pole (squares in the microscope grid are $1 \times 1 \text{ mm}^2$). Top: micro-reflectance FTIR spectrum of polyvinyl acetal (red line) compared with a representative micro-reflectance spectrum collected on the surface of the Coating sample (black line).

CO stretching; the sharp peak at 943 cm^{-1} to the C–C stretching; and the weak signal at 796 cm^{-1} is due to the CH rocking. It is worth saying that most of these absorption bands are also typical of poly(vinyl acetal). Thus, it is hard to say whether this abundance of acetate moieties was originally present in the product, or if they were generated as a consequence of aging, through some degradation mechanism, such as the opening of the acetal cycle [40].

Fig. 5B shows the NMR spectra of Alvar® and of the polymer extracted with chloroform from the Coating sample taken from the Nuxalk pole. The analysis confirms the presence of Alvar® on the wood sample. Similar signals were present in both spectra and, since several of them were overlapped, the attribution was confirmed only thanks to the recording of a two-dimensional 1H-cozy spectrum. The characteristic signals of the vinyl acetate, vinyl alcohol and vinyl acetal units were visible in both NMR spectra at similar chemical shifts. In the 1H-NMR spectra the signals were present at about 1.76 ppm (m, 2H, $\text{CH}_3\text{--COO--CH--CH}_2\text{--}$), 1.93 ppm (m, 3H, $\text{CH}_3\text{--COO--CH--CH}_2\text{--}$) and 4.92 ppm (m, 1H, $\text{CH}_3\text{--COO--CH--CH}_2\text{--}$) attributable to vinyl acetate units. In the NMR spectra of both the samples, the signals of the vinyl alcohol units were present at 1.59 ppm (m, 2H, $\text{HO--CH--CH}_2\text{--}$), 3.56 ppm (m, 1H, $\text{HO--CH--CH}_2\text{--}$) and 4.60 ppm (m, 1H, $\text{HO--CH--CH}_2\text{--}$) while signals at 1.13 ppm (m, 3H, $\text{CH}_3\text{--CH--acetal}$), 1.47 ppm (m, 4H, $\text{--O--CH--CH}_2\text{--}$), 3.73 ppm (m, 2H, $\text{--O--CH--CH}_2\text{--}$) and 4.92 ppm (m, 1H, $\text{CH}_3\text{--CH--acetal}$) were ascribable to the presence of vinyl acetal monomers. These measurements showed that in the area of the pole from which the Coating sample was taken, the backside of the wings (a non-exposed surface of the Nuxalk carving), the nitrocellulose layer was not present.

Heavy soiling was also present overall and previous examination carried out on other poles of the same collection showed that grime and dust particles are present below, between, and within all polymeric coating layers. Moreover, the repeated touching of the surface by visitors over the years left a thick layer of dense, greasy, shiny dark-brown soiling on the lowest areas of the carv-

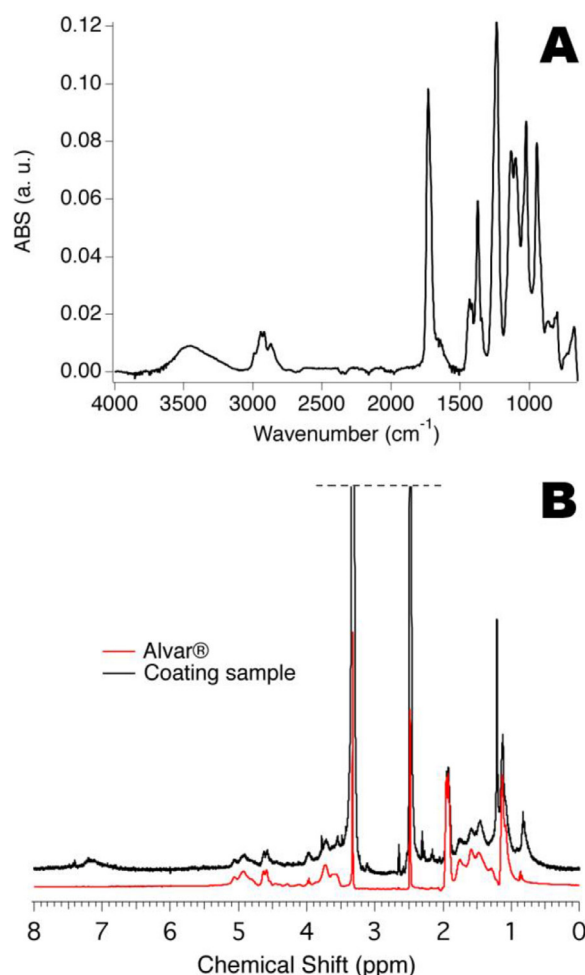


Fig. 5. (A) FTIR-ATR spectrum of the old Alvar® sample that was supplied by the museum; (B) NMR spectrum of the same Alvar® sample (red line); NMR spectrum of the polymer extracted from the Coating sample taken from the Nuxalk pole (black line).

ing. This complex stratigraphy complicated the safe cleaning of the fragile paint below.

3.2. The cleaning intervention

To select the optimal cleaning system for the cleaning of the Nuxalk pole, some small tests were performed on the carving as described in Section 2.2. A cotton swab soaked with each of the three NSF s was rolled on a small area of the artifact surface for about 30 s. All NSF s were able to swell and remove the unwanted coating. The S and G formulations needed less mechanical action, while the coating showed more resistance to the NSF B, requiring a more intense swabbing to achieve the same result. This was attributed to the presence of PC in the S and G NSF s. Since PC has a low volatility (boiling point 242 °C), the polymer swollen by the mixture of solvents included in NSF s S and G tends to dry more slowly than does the NSF B. This, in turn, allows mechanical action with the cotton swab before the coating dries. The NSF s-loaded hydrogels, Peggy 5 and Peggy 6, were then tested on larger areas of the Nuxalk pole. The more flexible gel (Peggy 6) yielded a more even cleaning, as it was better able to conform to the surface, more successfully reaching undercuts in the carving. However, even Peggy 6 gel sheets were unable to efficiently adapt to some irregular areas of the selected surface, resulting in uneven cleaning. This issue was addressed locally, using a different form of the

Table 2

Observations during preliminary cleaning tests performed with the NSF s-loaded Peggy 6 hydrogel.

Application time (min)	NSF B	NSF S	NSF G
1	×	×	×
2	±	±	±
6	±	✓	□
10	±	□	□

× = No change noted. ± = The unwanted coating swells but is not removable. Re-hardens in less than a minute. ✓ = The unwanted coating swells and can be removed without affecting the original green paint. □ = The unwanted coating swells and can be removed, but the original green paint is affected.

Table 3

Observations during tests for removal of coatings swelled and crumbly after application of hydrogel (Peggy 6) loaded with nanostructured fluid (Polar Cleaning S).

Cleansing material	pH-adjusted Water	NSF s	Dry
Cotton swab	×	×	×
Microfilament fabric (Evolon CR®)	×	×	±
Polyurethane foam (cosmetic sponge)	×	×	✓

× = Some original paint is removed. ± = The original paint is not affected, but the swollen coating is hardly removed. ✓ = The original paint is not affected, and the swollen coating is successfully removed.

same gel as described below. Visual observation determined that 6 min of application of the loaded gels was the optimal timing for all three NSF s (see Table 2). When the gel remained on the surface for less than 6 min, the targeted material began to swell but could barely be removed from the surface. Conversely, when it remained for 10 min, the original green paint under the coating was also softened and partially removed with the unwanted polymer film. Table 2 presents the results of the tests performed with all three NSF s loaded into the Peggy 6 hydrogel. NSF S applied for 6 min produce the most effective results, as it yielded an even cleaning without harming the original paint.

This can be easily understood in view of the results of tests performed in the laboratory (see Section 3.3). Among the three NSF s tested, the S formulation offers the best compromise between effectiveness and selectivity. The solvents included in NSF B evaporate too quickly, and the swollen coating re-hardens before the operator has the time to remove it mechanically. On the other hand, NSF G is too aggressive for the delicate stratigraphy of the carving. This concurs with the experiment reported in Section 3.3, where the G formulation showed the fastest interaction with the poly(vinyl acetate) film. Interestingly, in this specific case, the least effective cleaning fluid in the laboratory tests resulted to be the most suited for the real work of art, because it grants a mild, safe, and effective action. This illustrates the complexity of cleaning art, due to the high number of variables at play that cannot be easily predicted.

Finally, three different materials were tested for the removal of the swollen polymeric coating, to identify the best for the final cleaning of the Nuxalk pole Table 3. shows the results of these tests, where the clearing materials were used dry, wet with water, or wet with the NSF s. It was found that wet clearance, even with water, was too aggressive for the original green paint. Dry cotton was found to be too abrasive in some areas, with cotton fibers remaining stuck to the surface. On the other hand, both the monofilament fabric and the polyurethane foam allowed removal of the swollen polymers without harm to the original color, with the polyurethane foam achieving the most effective and even clearance.



Fig. 6. Cleaning of the Nuxalk pole. (A) The pole in its original position (before the cleaning) in the Hall at the ANMH. The red box shows the lower part of the carving selected for the cleaning intervention with the NSF-loaded hydrogels. The comparison shows a detail of the pole before (B) and after (C) the cleaning. (D) A detail taken during cleaning: the left half is cleaned, while on the right the darkened and soiled coatings (composed predominately of poly(vinyl acetal)) and grime are still present. (E) The loaded gels during the application. (F) The white arrow indicates an area where the polymer has swollen becoming crumbly and ready for mechanical removal.

Overall, the tests indicated that removal of the soiled and aged non-original synthetic coatings, poly(vinyl acetal) and, where present, nitrocellulose, from the fragile green paint at the base of the Pootlass entry pole could be accomplished most safely and successfully using the Peggy 6 hydrogel loaded with the NSF S applied for 6 min.

The green paint, an area totaling approximately 2 m² on each side flanking the opening at the base of the pole (see Figs. 6A–C) was then cleaned using the selected system and methodology. Peggy 6 hydrogels were cut into approximately 5 cm × 7 cm pieces. It was observed that smaller cleaning areas slowed down work rate, while trying to clean larger areas was not feasible as the swollen polymers began to re-harden before it was completely removed. The loaded gel was gently pressed against the surface with a gloved hand and massaged to remove any air pockets and let it to come into close contact with the irregular surface of the carving (Fig. 6E). The gel was removed after 6 min, when the outer coating had swelled, become crumbly (Fig. 6F), and could be removed mechanically with a section of dry polyurethane foam (cosmetic sponge).

Where some irregularities were present in the surface morphology, such as gouges, scratches, or deep carving, complete removal of the unwanted coating was unsuccessful, as the gel did not make sufficient contact. In some areas, this could be resolved with the localized reapplication of a loaded gel sheet for a shorter period (1 min). In others, a different form of the same material was used (Peggy 6 Gum) in place of the gel. This material is thicker (approximately 1 cm) than gel sheets and can be shaped with a scalpel to obtain a pointed end. Peggy 6 Gums were loaded with the same cleaning fluid, NSF S, and applied locally for 1 min. As a final step,

the cleaned surface was rinsed to remove any residue. A sheet of gel, which had been soaked in pH 7.5 adjusted water, was applied to the surface for approximately 1–2 min to remove any remaining surfactant residue. Finally, the surface was dried by tapping with a polyurethane foam sponge.

Overall, the cleaning was successful (Figs. 6C and 6D), as it removed most of the targeted material and did not harm the fragile original color, something none of the other previously tested cleaning techniques was able to accomplish.

Fig. 7 shows a micro-reflectance FTIR spectrum collected on the surface of a small wood sample taken from the cleaned area of the pole. Comparison with the spectrum of Alvar®, clearly shows that most of the polymer was removed. The peak visible at 1735 cm⁻¹ and relative to C=O stretching could be due to traces of residual poly(vinyl acetal) or to the binder of the original paint. It was not possible to obtain information about the composition of the green paint's binder from FTIR spectra. The peak at 2092 cm⁻¹ confirms the presence of Prussian blue, as hypothesized according to SEM-EDX results, and the presence of carbonate minerals is also suggested by the combination band (2ν₂ + ν₄) at 2511 cm⁻¹ [41]. However, even if little could be said on the chemical nature of the organic binder, previous analyses performed on other monumental carving at the museum evidenced the presence of drying oils as the likely paint media [24].

3.3. Investigation on the cleaning mechanism

After the intervention on the pole, experiments were carried out in the laboratory, in order to understand the cleaning mechanism through which the poly(vinyl acetal) coating was removed,

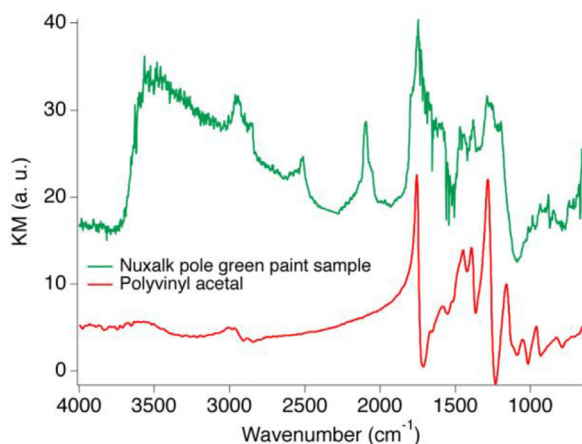


Fig. 7. Micro-reflectance FTIR spectrum of polyvinyl acetal (red line) compared with a representative micro-reflectance spectrum collected on the surface of the green paint sample (CLEAN) taken from the cleaned area of the Nuxalk pole (green line).

using NSF. According to its chemical composition and to its similarity with a poly(vinyl acetate), Alvar® was expected to be solubilized by medium-highly polar organic solvents, such as ketones or esters. To confirm this hypothesis, some solubility tests were performed using the organic solvents included in the NSFs selected for the cleaning, namely: MEK, EA, PC, BuOH, and PeOH. Approximately 10 mg of Alvar® were immersed in 4 mL of each solvent in a sealed vial. The vials were left unmoved until the equilibrium was reached (a few hours for MEK and EA; a couple of days for the remaining solvents). The experiments confirmed what expected: MEK and EA are excellent solvents for poly(vinyl acetate); PC provides some significant swelling of the polymer; BuOH and PeOH, on the other hand, induce very limited swelling. According to these results, all the selected NSFs presented some potential effectiveness in the removal of the poly(vinyl acetate) coating, since the presence of good solvents in the formulation is a prerequisite for the swelling and mobilization of polymer chains, as it was evidenced by previous studies [8,9].

In order to test this, an experiment (see Section 2.4) was then carried out by immersing Alvar®-coated glass slides in the three NSFs and following the behavior of the polymer layer by means of pictures taken under visible light (see Fig. 8). After an initial swelling of the coating, observed in all cases and evidenced by a diffuse whitening of the polymer layer, a dewetting process took place, similarly to what was already observed for several different polymers, cast on glass from solutions, and interacting with NSFs [8–11]. Dewetting is defined as the inverse process of a fluid's spreading on a surface and occurs whenever a liquid film, due to some instability, breaks and withdraws from a substrate to form separate droplets [42–44]. Polymers, in this context, can be considered as very viscous fluids, and can dewet from surfaces in certain conditions. Dewetting is thermodynamically driven by the balance between interfacial energies, described by the spreading parameter, S , which, for a polymer coating laid on glass and immersed in a liquid, is defined as:

$$S = \gamma_{LG} - \gamma_{PL} - \gamma_{PG} \quad (1)$$

where γ_{LG} is the interfacial tension between the liquid and glass surface, γ_{PL} is the interfacial tension between the polymer and the liquid, and γ_{PG} is the interfacial tension between the polymer and the glass. When $S < 0$, dewetting is energetically favored, which means that the system's configuration with separate polymer droplets has a lower free energy than the coherent film configuration. Thin films (< 100 nm) in this condition are usually unstable, and undergo a spontaneous spinodal dewetting pro-

cess with the simultaneous formation of a holes' pattern with a given correlation length, which is connected to the capillary waves and the thickness of the polymer [42]. On the other hand, thick films (from below $1 \mu\text{m}$ to a few hundreds of μm) are typically metastable, which means that dewetting is thermodynamically favored but kinetically inhibited by the presence of some potential barrier [44–46]. Once this threshold is overcome, for instance by increasing the temperature, dewetting is initiated and isolated holes appear in the film, following a “nucleation and growth” process, which leads to the formation of a Voronoi pattern of polymer rims, and, ultimately, to the rupture of these rims to form separate polymer droplets.

In the case of a hydrophobic polymer laid on a hydrophilic surface and immersed in an aqueous fluid, as in the experiment reported in Fig. 8, the balance between interfacial energies usually yields a negative S , that is to say that dewetting is thermodynamically favored. However, a $35 \mu\text{m}$ thick Alvar® film, with a glass transition temperature of about 80°C [47], represents the typical case of a system in a metastable configuration. At room temperature in air, dewetting is inhibited and does not take place. Conversely, when the coated glass slides are immersed in the NSFs, the concomitant presence of good solvents for the polymer and surfactants has the effect of increasing the mobility of macromolecular chains and decreasing polymer/liquid and liquid/glass interfacial tensions, thus lowering the energy barrier and initiating polymer dewetting. The observed process took place following the nucleation and growth mechanism, as easily foreseen for thick films, and evident isolated holes began to be visible after less than 10 min of polymer/NSF interaction. Even if the interaction mechanism overall was the same for the three cleaning fluids, some significant differences could be noticed in the kinetics of the process. NSF G showed the fastest dewetting, while NSF S was evidently slower. This is due both to the different surfactant included in the formulations (it was shown that anionic surfactants are less efficient than nonionics in promoting dewetting [11,48]), and to the different organic solvents included in the three systems. In fact, as expected from the solubility experiments, the NSFs including the highest amounts of good solvents induce faster dewetting of Alvar® from glass. Another interesting feature observed was that, starting from 120 min of polymer/NSF interaction in the case of NSF B, Alvar® droplets began to spontaneously detach from the glass surface. Conversely, this did not happen for the other two NSFs. This behavior was already observed for other polymer/NSF couples [49] and is simply due to the relative density of the swollen polymer droplets with respect to the surrounding liquid phase. PC has a density of 1.2 g/cm^3 (higher than water); thus, in the case of both NSF S and G, which include PC in their formulation, swollen polymer droplets are formed, which have a higher density than the aqueous bulk phase and, consequently, tend to remain stuck to the glass surface. This has little to do with cleaning effectiveness because in real cases the art object to be cleaned is not usually immersed at the bottom of a cleaning fluid pool, where such an effect could take place. However, this is the reason why the glass slide immersed in the NSF B seems to be almost perfectly clean after 6 h (360 min), while the glass slides immersed in NSF S and in NSF G are still covered by bigger or smaller droplets of swollen poly(vinyl acetate).

The removal process observed during the cleaning of the pole appeared different from dewetting observed in laboratory experiments. However, this was easily predictable in view of some considerations. As said, dewetting is driven by the energetic balance described by Eq. (1). It is clear, then, that if one of the three phases at play in the system is changed, the spreading parameter, S , also changes. Thus, laboratory experiments here reported are significantly different from the cleaning of the Nuxalk pole. Even assuming that the coating is the same (and this is not entirely true, be-

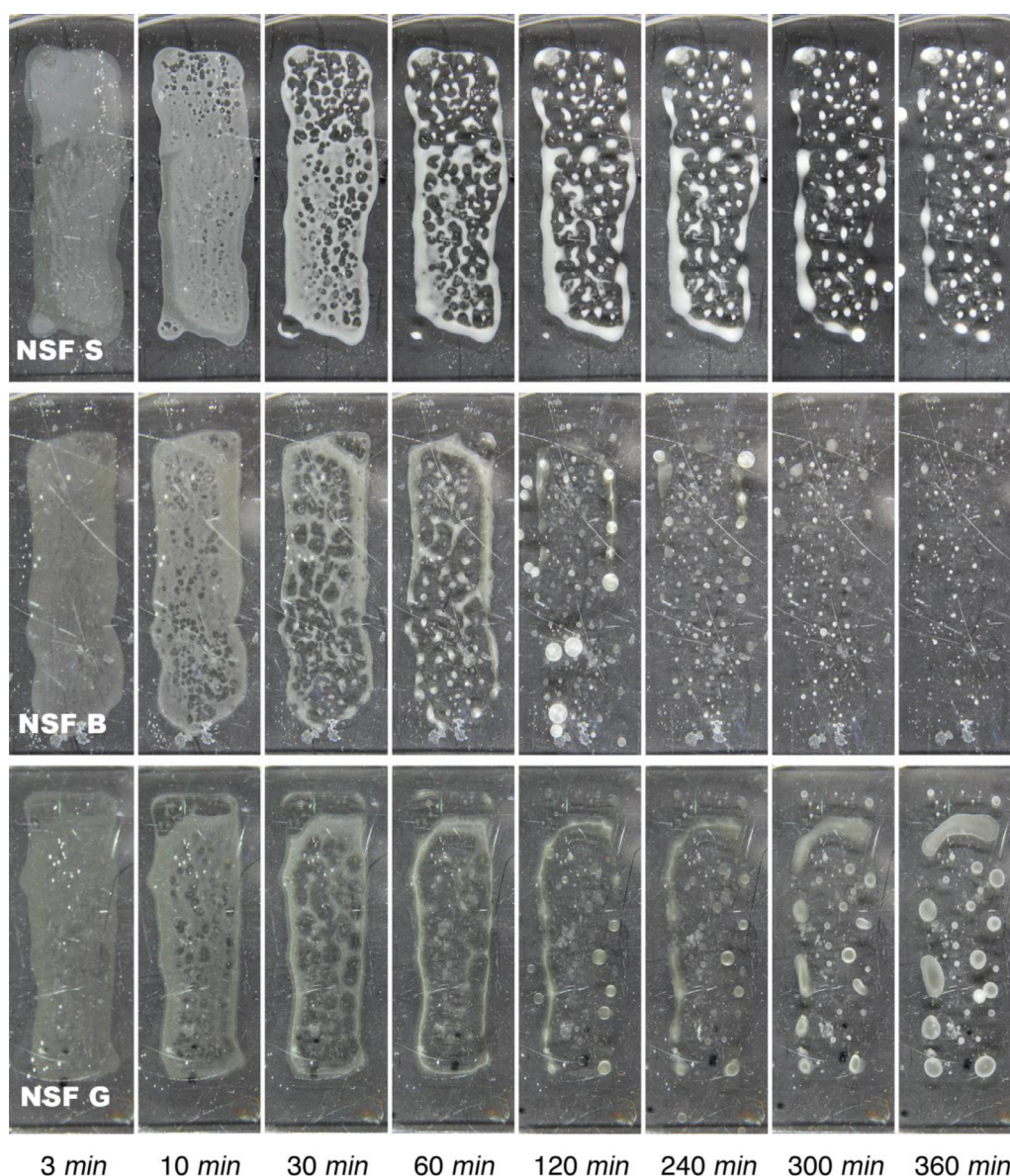


Fig. 8. Photographic observation of Alvar®-coated glass slides immersed in the three selected NSFs up to 6 h (after 24 h the situation was the same, indicating that the systems had reached the equilibrium). Dewetting of the polymer film is evident in all the cases, even if some differences were found in the kinetics of the process.

cause the poly(vinyl acetal) film on the pole is aged, soiled and possibly mixed with other polymers or contaminants), and neglecting the fact that in the actual cleaning the NSF is confined in a hydrogel, which introduces different interactions with the polymer surface, a major change occurs in the solid substrate, switching from glass to a paint layer. The polymer/glass, γ_{PG} , interfacial energy included in Eq. (1) is then substituted by the polymer/paint interfacial energy, which is likely lower, as the two materials are more alike. Also, the liquid/glass, γ_{LG} , interfacial energy is replaced by the liquid (NSF)/paint, which, conversely, is higher because the green paint, based on drying oils [24], should be more hydrophobic than glass. It is then clear, even from a rough estimation, that S in the case of the Nuxalk pole cleaning is surely higher than for the experiments reported in Fig. 8. If S is increased so much that it becomes positive, dewetting becomes thermodynamically disfavored. Also, if it stays negative, there are other factors that complicate things, the main one being the application time of the cleaning system. 6 min of interaction between a small amount of NSF

and the polymer coating is probably not sufficient to initiate the nucleation of holes, which leads to dewetting (see Fig. 8). However, if time were increased, the swelling of the underlying paint layer would have also occurred. This would have changed again the interfacial energies at play and, again, probably disfavoring dewetting, because the polymer coating and the paint layer would have established stronger interactions with one another. This said, the swelling of the poly(vinyl acetal) coating observed on the Nuxalk pole was enough to ease its mechanical removal in a controllable and safe way.

4. Conclusion

The complex issue of selective cleaning, encountered during the conservation of the monumental carving at the American Museum of Natural History, is presented in this work. The original painted surface of the wood pole was covered by a thick and multilayered polymeric coating, which was soiled, aged, and darkened. It required removal to increase readability and more accurately and

respectfully, present this treasure of the Pootlass lineage and the Nuxalk nation in the renovated Northwest Coast Hall. The original green paint was analyzed and was found to be a mixture of Prussian blue and a yellow pigment, possibly chrome yellow (lead chromate). The detrimental coating was shown to be composed predominately of poly(vinyl acetal), a hard and tough polymer with a solubility profile similar to poly(vinyl acetate), laid over a layer of nitrocellulose. A series of cleaning methodologies, macroemulsions and free solvents, were previously tested with unsatisfactory results; thus a recently proposed novel approach, based on retentive hydrogels loaded with nanostructured aqueous fluids, was used as an alternative, achieving an effective, safe, and controllable cleaning. In investigations performed after the cleaning, the solubility of poly(vinyl acetal) was tested and butanone (MEK) and ethyl acetate (EA) were identified as good solvents, while propylene carbonate (PC) induces significant swelling. The polymer film was then subjected to the action of several unconfined NSF, all of which induced its dewetting from glass slides, but with different kinetics (NSF G was the fastest, followed by NSF B, and finally by NSF S, which appeared least effective). The difference in kinetics is easily understood by considering the composition of each NSF. A greater quantity of good solvents sped up the dewetting process, as did the presence of a nonionic surfactant, which was found to be generally more efficient than anionics in inducing dewetting. Preliminary cleaning tests were carried out on small areas of the Nuxalk pole, and NSF S was found to achieve the gentlest and most effective cleaning action. The optimal cleaning methodology was also determined: a 6 min application of NSF S confined in the Peggy 6 hydrogel, followed by clearance of the swollen polymers with a dry polyurethane foam sponge. After testing, the cleaning of the large green painted areas of the pole was performed with the selected approach. Most of the darkened multilayered coating was safely removed without harming the original green paint. The polymer did not reach a full dewetting state upon the action of the NSF. This is explained by the different interfacial energies at play in the laboratory experiments performed on a glass substrate. In this case, controlled swelling, and subsequent mechanical removal of the outer polymer layers was enough to achieve effective cleaning action. These results nicely illustrate the complex physical chemistry principles behind a common cleaning issue faced by art conservators, and helped demonstrate the efficacy of NSFs loaded into flexible and retentive hydrogels as an alternative to more traditional methodologies for the controllable removal of unwanted polymer coatings.

Authors contributions

SALC and RG conceived the research; SALC, SALD, and RG designed the research; SALC, SALD, MB, and RG performed research; MB and RG analysed data; SALC and MB wrote the paper. CT provided essential cultural knowledge and guidance. SALD, MN, CT revised the paper. All authors read and approved the final manuscript.

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Availability of data and materials

All the available data have been included in the article.

Ethics approval and consent to participate

Not applicable.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:[10.1016/j.culher.2022.02.002](https://doi.org/10.1016/j.culher.2022.02.002).

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