

RESEARCH & TECHNICAL STUDIES

Crude Oil and Archeological Bone and Shell

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Crude oil spills in marine and terrestrial environments are not uncommon, which has in turn created a broad market of products whose purpose is to remove oil. Products such as solvents and surface washing agents are the commonly employed methods for oil-spill clean-up, and studies exist that test the effectiveness of some of these products on various substrates. Unfortunately, the threats crude oil exposure poses to archaeological artifacts and cultural resources are and methods to mitigate such damage have not been widely studied.

The National Center for Preservation Technology and Training (NCPTT) in conjunction with Northwestern State University (NSU) in Natchitoches, Louisiana, has recently concluded a study that began in 2010 and was completed in the summer of 2011 on the effectiveness of five oil-removal products on archeological bone and shell with the intention of cleaning without damaging the material itself. The objectives of the project were to determine the best cleaner for oil removal, to quantify the state of bone and shell samples prior to and after oil application, and to examine the degree of oil removal from samples per cleaner. Crude oil was first applied to the bone and shell samples and then artificially weathered. Following this, cleaners were applied to remove the oil.

Products selected for testing were either common “over-the-counter” cleaners or listed on the EPA product schedule. Five products were tested that included surfactants, surfactants with enzymes, and solvent-based cleaners. Cleaning methods per product were based upon manufacturer's recommendations and instructions. Environmental safety and low toxicity were primary concerns for cleaner selection, as well as how the cleaners might be used under real world conditions. The effectiveness of each cleaner was determined through analysis using the Fourier Transform Infrared Spectroscopy (FTIR) and color measurements.

This examination of the effects and effectiveness of surface oil removal products aims to provide a basis for future studies in crude oil removal from cultural objects and archaeological artifacts.

Methods for Crude Oil Removal from Fort Livingston, Grand Terre Island, Louisiana

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Fort Livingston is located on the western tip of Grand Terre Island, Jefferson Parish, Louisiana. The fort was listed in the National Register of Historic Places in 1974. It has been managed by the Louisiana Office of State Parks since its designation as a State Cultural Area in 1979, and is part of Grand Isle State Park. Construction of the fort began in 1841. The walls

were constructed of tabby faced with brick. The tabby remained exposed in some of the interior spaces. Stairways, lintels, and other trim pieces were made of a fine-grained granite.

The fort and surrounding beaches and wetlands were contaminated with crude oil around the first week of June, 2010. Floating oil slicks arriving at Grand Terre Island reached the fort because the structure is partially submerged in Gulf waters even during low tide. The largest tidal range in the area during that time was approximately two feet, depositing oil onto the brick walls of the fort and on some of the interior spaces that flood during high tide.

Grand Terre Island is only accessible by boat, and there are no sources of power or fresh water on site, presenting unique challenges for the careful removal of crude oil from the structure. Because a portion of the fort now stands in gulf waters, any cleaning products used must be approved for release into seawater. Alternatively all cleaning effluents must be collected and disposed of on the mainland.

Staff from the National Center for Preservation Technology and Training made three site visits to Fort Livingston: June 2010, September 2010, and July 2011. The extent of oil contamination was evaluated, oil samples were collected for further studies in the laboratory, and cleaning tests were performed. A variety of cleaners were tested, including products on the Environmental Protection Agency's National Contingency Plan Product Schedule. In July 2011, testing concentrated on methods using poultices. Results of the site visits will be presented. Additional testing was performed in the laboratory using the same cleaners, and these data will be compared with field testing.

Multi-Layer Atomic Layer Deposition Films as Protective Coatings for Silver Art Objects*

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We present results from a collaborative research program between the University of Maryland and The Walters Art Museum in developing and evaluating multilayer, multifunctional atomic layer deposition (ALD) films for conservation of silver. Tarnishing of silver is a critical problem that is currently dealt with by coating with polymeric coatings such as nitrocellulose or placing objects in specially designed cases containing sulfide absorbers. Use of polymeric coatings is common and if applied carefully can protect an object for 20–30 years in a controlled museum environment. Uneven coating, however, can lead to severe tarnishing and pitting.

Our approach is based upon ALD: an innovative, thermally activated gas phase process for depositing incredibly conformal, very thin, and uniform films on metal (and other) surfaces

regardless of topology. Preliminary studies performed at the Metropolitan Museum of Art in 2006 showed that the tarnishing rates of 70 nm of alumina (Al_2O_3) deposited by ALD performed as well as microns of brush coated nitrocellulose. To validate and improve this process for museum objects, we are exploring multiple compositions and layer structures to optimize barrier performance and optical clarity. Tarnishing is being evaluated via reflectance spectroscopy as well as x-ray photoelectrons spectroscopy (XPS) to measure the amount of sulfur on the surface subsequent to stripping the protective coating after a series of oxidizer exposures. Accelerated aging of test coupons is being performed using both exposure to atmospheres with controlled, elevated concentrations of hydrogen sulfide (H_2S) and increasing the temperature of ALD coated samples under atmospheric levels of H_2S . This is employed to establish the characteristic time scales of diffusion of oxidants through the ALD coated films relative to uncoated and nitrocellulose coated silver. The reversibility of ALD metal oxide coatings is also being evaluated to determine if either the deposition or the removal of thin layers of metal oxides on silver changes the physical characteristics or chemical composition of the silver surface.

*Work supported by a National Science Foundation SCIART grant, # DMR1041809

Progress in the Investigation of Silicone Rubbers and their Residues

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Silicone rubber molds are often used to cast and reproduce objects and artifacts. These molds are frequently used in conservation because of their ability to capture high levels of detail, making them very useful for examining surface topography of objects. Paired with scanning electron microscopy or other imaging techniques, impressions taken with silicone rubbers can often reveal technological details, such as tool marks, which can help to reveal the processes of an object's manufacture. In the past two decades, conservators have begun to notice that silicone rubbers leave behind a residue, locally discoloring the surface of the object where the impression was made. Residues can sometimes be seen in the form of pieces of cured silicon rubber, trapped within interstices or recesses, but more problematic are components of the silicone rubbers which may be either absorbed by the surface or left on it as a film. These can cause permanent staining of the surface, as well as changes in the surface properties. Some research exists on the characterization of silicone rubbers, the identification of their residues and their mitigation on surface of objects. However, new silicone rubbers have since been commercialized and used in conservation without having been systematically tested for their safe use on historical objects. The current study focuses on an in-

depth chemical analysis of eight of these silicone rubbers, and identifies potential residues left behind by them. The silicone rubbers investigated include President Jet Light Body (Coltène), Extrude XP (Kerr Corporation), Elite Double 8 (Zhermack), Elite HD+ Maxi Putty Soft Fast (Zhermack), Elite HD Plus Putty Normal (Zhermack), Silastic J RTV (Dow Corning), HS II (Dow Corning) and P-4 (Silicones, Inc.). Bulk samples of each of these molds were prepared by casting the silicone rubber on different substrates: glass slides, slides coated for analysis in the mid-infrared region, and limestone. The bulk samples were analyzed by mass spectrometry using evolved gas analysis (EGA) to obtain information on the volatility of components within the mold. Then, gas chromatography mass spectrometry (GC-MS) techniques including pyrolysis gas chromatography mass spectrometry (Py-GCMS) were used to clarify the composition of the individual silicone rubbers and verify the solubility of components in the cured molds. The composition of the bulk and surfaces of the silicone rubbers were also compared by attenuated total reflection Fourier transform infrared (ATR-FTIR) microscopy. The residues left behind on the different substrates were studied by FTIR and GC-MS techniques. The study shows that all silicone rubbers investigated leave siloxanes residues to varying extents. Among the tested silicone rubbers President Jet Light Body leaves the least amount of residue. Although non-polar solvents would be suitable to solubilize the residues, the use of a suitable barrier prior to their application on art objects would be recommended, as the masses of polysiloxanes left on the surface may be too high to allow for their complete removal with a solvent or poultices.

Quantitative XRF Methodology for Examination of Cultural Heritage Artifacts on Paper

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X-ray fluorescence spectroscopy (XRF) is probably the most widely used non-invasive method of analysis for determining elemental composition in cultural heritage artifacts. Elemental composition provides key information for deciphering material identity, as well as treatment history. As commonly applied to paper-based collection items, results are strictly qualitative. Therefore, it is worthwhile to develop quantitative XRF methodology, which may enhance our understanding of the artifact, not only in terms of its material identity, but also its condition.

The difficulty of developing a quantitative XRF method for organic substrates such as paper arises in part from variations in scattering of x-rays in light element matrices and in the lack of appropriate and readily available calibration standards. This paper discusses these issues, and compares and contrasts various

calibration methods developed and tested at the Library of Congress using papers or films doped with minor and trace elements of interest and a Bruker TracerTurbo portable ED-XRF instrument. Different calibration methods have been validated or discounted based on inspection of the raw data and analytical results obtained by inductively coupled plasma-mass spectroscopy (ICP-MS) conducted in collaboration with scientists at the University of Missouri.

Quantitative XRF results from analysis of various artifacts at the Library of Congress will be presented, including: 18th-century historic papers from Fabriano, Italy; text and maps in a 1513 hand-colored edition of Ptolemy's *Geographia*; and various 19th-century American manuscripts. Discussion of the results will focus on the value that quantitative elemental information brings to our understanding of these artifacts, particularly in terms of inherent quality and treatment history. In addition, it will be shown that a quantitative XRF methodology can be an important aid to condition assessment through easy identification of dangerous levels of transition metals, such as from manufacture or potentially after exposure to floods.