Introduction

In 1996, the Texas Historical Commission excavated René Robert Cavalier, Sieur de la Salle’s vessel *La Belle*, which had sunk in Matagorda Bay, Texas in 1686. The fine sediments in the bay floor facilitated the preservation of the lower portion of the wooden vessel, its cargo, the personal belongings of its crew, and an assortment of supplies necessary to start a colony in the New World. Among the organic materials recovered were lines from *La Belle*’s rigging and coils of rope that had been stored in its hold. The conservators of *La Belle* have been faced with the formidable task of conserving the large amount of hemp rope recovered from the vessel, which includes segments more than 100 feet (30.5 m) in length. Of particular challenge to the conservators is the vessel’s anchor line which consists of a continuous section of rope over 500 feet (152 m) in length. The diameter of these sections ranges from 6.25 to 6.6 centimeters, after conservation. Although the majority of the recovered rope appeared to be in pristine condition during excavation, microscopic analysis has indicated that most of the fibers are thin and visibly degraded; microbial action and water saturation has caused them to weaken and decay.

Methods

*Silicone Treatment Strategies*

The Texas A&M Archaeological Preservation Research Laboratory technique for stabilizing waterlogged rope with silicone oils involves a displacement of the water trapped in the rope fibers with acetone, followed by the replacement of the acetone with a hydroxyl-ended functional polymer and crosslinker. The polymer-impregnated rope is then cured by exposure to a catalyst which is applied either topically to the rope, or as a vapor. We suggest that the resultant preservation of the treated rope is a result of surface
consolidation, the penetration of hydroxyl-ended polymers with the addition of
crosslinking agents and final treatment with a tin-based catalyst to complete the
polymerization process.

The Frankfurter Method of Rope Preservation

Conservators at the National Museum Conservation Laboratories in Brede, Denmark,
routinely use a technique for conserving waterlogged rope that they refer to as the
Frankfurter Method (Koefoed et al. 1993). This process involves encapsulating
waterlogged rope between sheets of perforated polypropylene film; that are heat sealed to
produce a form-fitting jacket in which each sample remains throughout treatment. The
packaged rope is attached to a piece of Masonite (TM), which acts to support the rope.
The resultant packaged rope is then treated with PEG. Following treatment, the rope is
placed into a large freeze-drying unit, and freeze dried at -20°C Celsius with a 50% relative
humidity. After freeze drying, the rope sample is removed from the Masonite /
polyethylene bag structure and allowed to sit in fresh air. Rope specimens that are treated
with the Frankfurter Method often require additional treatment with applications of
polyurethane in ethylacetate (Koefoed et al. 1993). This is necessary because the rope is
often extremely delicate after processing. Rope treated with the Frankfurter Method
retains its pre-treatment color and the individual fibers (yarns and strands) that comprise
the rope are well preserved. Like other successful treatments for severely deteriorated
waterlogged rope, this process is generally not reversible due to two factors. First, the
application of polyurethane in ethylacetate is generally not reversible. More important
however, is the fact that most treated rope samples are very friable and desiccated after
treatment, making additional treatment difficult.

Treating Waterlogged Rope in a Non-Polar Suspension Medium

Experiments conducted by the National Museum Conservation Laboratories have also
demonstrated that treating waterlogged rope with PEG in a volatile, non-polar solution
such as ether or kerosene enables the individual fibers of the rope to >float= during
treatment, facilitating thorough impregnation of the PEG within the matrix of the rope.
The use of suspension mediums in PEG treatments results in rope specimens which lack
the characteristic matted appearance of rope treated with PEG alone; the resulting rope,
however, is extremely fragile and very susceptible to environmental changes.

Incorporating the Use of Non-Polar Suspension Mediums and Elements of the
Frankfurter Method into >Traditional= Silicone Treatment Strategies
Experiments conducted with silicone oil treatments at the Archaeological Preservation Research Laboratory have demonstrated that treating waterlogged rope that has not been enclosed in some form of permeable material results in a specimen that tends to unravel slightly during treatment. We believed that the polypropylene jacket used in the Frankfurter Method would provide a permeable membrane that facilitates chemical transfer and also acts to protect the physical integrity of the artifact during treatment.

Furthermore, after observing the results of experiments conducted by the National Museum Conservation Laboratories on the use of suspension mediums in the treatment of waterlogged rope with PEG, we anticipated that the use of a suspension medium during the polymerization of waterlogged rope would alleviate the slightly matted appearance commonly observed after silicone oil treatments that do not involve the use of a non-polar suspension medium.

Experimental

The following procedure is but one example of the use of preservation polymers in conservation. For researchers in the field of conservation, exploration with other silicone preservation polymers and crosslinkers is recommended in order to determine the resultant attributes of varying combinations of these invaluable materials.

The majority of rope recovered from La Belle was transported to the Texas A&M University Conservation Research Laboratory, where it is stored in fresh water awaiting treatment. Three samples of rope of similar length were taken from a single continuous coil. Two of these samples were to be treated by the proposed hybrid silicone treatment process (samples Si-1 and Si-2), while the third sample (WL) would be allowed to air-dry at room temperature for a twenty-four hour period.

The samples were rinsed in fresh running water for two days to ensure the removal of soluble salts. The samples were then placed on a sheet of glass for additional manual cleaning. During this process, the samples were positioned beneath a constant, gentle flow of tap water in order to keep the rope wet while debris was flushed from its surfaces. Like the majority of rope from the La Belle assemblage, the samples were partially covered with black and dark brown sulfide stains. These stains resulted from the fact that the cotton cloth in which the rope had been transported from the site to the laboratory had decayed en route. Most of these stains were removed by lightly rubbing the affected areas with a cotton swab. No attempts were made to remove deeply-set stains by chemical means, as it was feared that additional chemical additives would interfere with the conservation process.

The samples that were to undergo silicone treatment were each placed between two sheets of perforated polyethylene film, which is scored with uniform holes that allow water, acetone and silicone oil to freely diffuse (Figure 1). These sheets of polyethylene film were then heat sealed, creating form-fitted, ventilated bags in which the ropes would
remain throughout the initial stages of treatment. Ziploc (TM) brand Vegetable Bags are an ideal source of perforated polyethylene film; they are readily available and easily sealed to form a pouch, using either a heat sealing appliance or a small soldering iron and brown paper.

![Figure 1. Waterlogged rope encased between sheets of Ziploc vegetable bag material prior to water / acetone displacement.](image)

The encased ropes were each placed into a beaker containing 500 milliliters of fresh acetone. At room temperature, a vacuum of 3999.66 Pascal (30 mm) was applied to the samples in acetone to induce rapid displacement of the water with acetone. The samples initially bubbled rapidly as air and acetone were driven from the internal structures of the rope. After approximately twenty minutes, the rapid bubbling ceased and smaller, more infrequent bubbles were observed escaping from the ropes. The samples were then removed from the water-laden acetone and placed into clean beakers containing 500 milliliters of fresh acetone. Each beaker was returned to the vacuum chamber and a vacuum of approximately 5332.88 Pascal (40 mm) was applied. Once the bubbling ceased, the ropes were removed from the vacuum chamber and allowed to sit at ambient pressure and room temperature while the silicone oil /crosslinker solution was prepared.

With the water/acetone exchange process complete, the next phase of treatment was to exchange the acetone with an appropriate silicone oil/crosslinker solution. In this process, the polymer and crosslinker are specifically chosen to produce a desired texture and strength. To maintain flexibility in the treated rope samples, two hydroxyl-ended silicone oils were blended together in a 50:50 solution, by weight. The lighter of the two polymers is a Corcoran Laboratories product known as PR-10, which is a low viscosity hydroxyl-ended fluid. Repeated experimentation indicates that lighter molecular weight silicone oils such as PR-10 tend to penetrate easily into organic materials such as rope; once polymerized, however, they tend to produce a rigid artifact. Corcoran Laboratories PR-12 is a slightly more viscous hydroxyl-ended fluid with a larger molecular weight than PR-10. Because of the porosity of the waterlogged rope, larger molecular weight polymers such as PR-12 are expected to easily permeate the matrix of the rope samples. Due to its increased viscosity, PR-12 acts as a consolidant by keeping loose strands together; furthermore, rope that has been treated with PR-12 tends to be more flexible after treatment than rope treated with smaller molecular weight polymers. A blend of these two silicone oils was used for this experiment to ensure that the finished product maintained a
degree of flexibility as well as internal rigidity and physical strength. Passivation
Crosslinker CR-20, 3% by weight, was added to the PR-10 / PR-12 silicone oil solution.
CR-20 is a highly efficient crosslinker that experience has shown to work well with silane polymers.

After placing the dehydrated ropes in clean beakers, a sufficient amount of the silicone
oil / crosslinker solution was added to each beaker in order to immerse the samples in
solution. Aluminum mesh was securely fixed over the packaged ropes in order to prevent
them from floating to the surface of this viscous mixture. A vacuum of 5332.88 Pascal
(40mm) was applied to the samples in solution for twenty minutes to ensure that the
acetone present in the rope fibers would vaporize rapidly, facilitating a thorough
penetration of silicone oil solution throughout the artifacts. During the initial stages of
vacuum treatment, large bubbles were observed escaping from the ropes. After thirty
minutes this rapid bubbling diminished and sporadic small bubbles were observed rising
from the artifacts.

The packaged ropes were then taken out of the vacuum chamber and allowed to sit in
solution at ambient pressure and room temperature. After sitting for two hours, the
samples were removed from the silicone oil/crosslinker solution and from their perforated
polyethylene bags. The samples were placed on an aluminum screen to allow drainage of
excess free-flowing silicone oil solution. After one hour, the surfaces of the ropes
appeared to be reasonably dry and the artifacts were placed in beakers containing 500
milliliters of fresh CR-20 crosslinker. We have found that immersion in CR-20 after
bulking the samples with a silicone oil/crosslinker solution is helpful in removing
additional silicone oil solution from the external surfaces of the rope. While immersed in
the crosslinker, a soft brush was used to wipe the rope surfaces in order to facilitate
removal of excess silicone oil solution. After five minutes of immersion and surface
preparation, polymerization was initiated by exposing the rope sample to a tin-based
catalyst.

The samples were placed into loose perforated polyethylene bags and the bags were heat-
sealed shut. The sample packages were each suspended with two wooden clothes pins
from wooden dowels. These dowels rested on the top edges of a small vat containing
kerosene with CT-32 tin catalyst, 3% by weight (Figure 2). The open structure of the
mesh bag evenly exposed the surfaces of the rope to the kerosene/catalyst solution. With
the samples suspended in the solution, the vat was placed into a vacuum chamber and a
vacuum of 5332.88 Pascal (40 mm) was applied. After twenty minutes under vacuum, the
valves of the chamber were locked and the rope was left suspended in the solution
overnight. The following morning, the vacuum chamber was returned to ambient pressure
and the samples were removed from the kerosene/catalyst solution.
Figure 2. Rope sample suspended in kerosene / CT-32 solution.

The rope was removed from the perforated polyethylene bags and placed on several paper towels, which absorbed the kerosene/crosslinker and silicone oil solutions from the artifacts. Immediately following removal from the kerosene/crosslinker solution, the surfaces of the cordage were covered with a thin, slippery coating of silicone. After a few minutes of exposure to fresh air, droplets of fully cured polymer were observed on one end of the samples. These were easily removed using a soft, lint-free cloth. After allowing the rope to air-dry in a vented fume hood for twenty-four hours, the surfaces of the samples appeared dry and very natural in texture.

In order to determine the degree of deterioration caused by waterlogging, as well as to compare the results of the silicone-treated rope against an untreated specimen, WL was weighed, measured and allowed to air-dry at room temperature in a vented fume hood for a twenty-four hours (Table 1).
### Table 1. Data for the dried rope sample.

<table>
<thead>
<tr>
<th>24 hours Air Drying</th>
<th>2.70g</th>
<th>-77.868%</th>
<th>1.472cm</th>
<th>-2.902%</th>
<th>8.531cm</th>
<th>-12.842%</th>
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</thead>
<tbody>
<tr>
<td>Pre-Treatment</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Post-Treatment</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Texture</td>
<td>soft-mushy</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Integral Strength</td>
<td>fragile</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Color</td>
<td>10YR-2/2 very dark brown &gt; 10YR-2.1 black</td>
<td></td>
<td></td>
<td></td>
<td>5YR-6/2 &gt; 5YR-5\2 pinkish gray</td>
<td></td>
</tr>
</tbody>
</table>

The silicone oil-treated rope samples feel slightly stiff. These samples however, are very stable and aesthetically pleasing. The individual fibers, yarns and strands, of the silicone-treated rope samples were easily distinguishable after treatment and did not become matted and compressed after preservation using silicone oils. The high degree of visible detail in the silicone-treated samples was surprising because these features were indistinguishable in a water-logged state. Furthermore, while it may be impossible to determine the original color of the waterlogged rope, the post-treatment coloration of the silicone-treated samples was acceptable, ranging from a pale to mid brown (Table 2). Figure 3 is a photograph of sample Si-1. Prior to treatment, this sample was loosely twisted. Following treatment, no discernable changes were observed in the twist or physical dimensions of either silicone oil-treated rope sample.

### Table 2. Data for silicone treated rope sample.

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Average</th>
<th>% change</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre Treatment Length / cm</td>
<td>14.308</td>
<td>-1.118</td>
</tr>
<tr>
<td>Post Treatment Length / cm</td>
<td>14.148</td>
<td></td>
</tr>
<tr>
<td>Pre Treatment Width Number 1 / cm</td>
<td>.9280</td>
<td>.922</td>
</tr>
<tr>
<td>Post Treatment Width Number 1 / cm</td>
<td>.9160</td>
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</tr>
<tr>
<td>Pre Treatment Width Number 2 / cm</td>
<td>.9380</td>
<td>.932</td>
</tr>
<tr>
<td>Pre Treatment Width Number 2 / cm</td>
<td>.9250</td>
<td></td>
</tr>
<tr>
<td>Pre Treatment weight / grams</td>
<td>16.597</td>
<td>11.499</td>
</tr>
<tr>
<td>Post Treatment weight / grams</td>
<td></td>
<td>6.4000</td>
</tr>
<tr>
<td>Pre Treatment Color*</td>
<td>10YR-2/2 very dark brown -&gt; 10YR-2.1 black</td>
<td></td>
</tr>
<tr>
<td>Post Treatment Color*</td>
<td>10YR-6/3 pale brown -&gt; 10YR-4/3brown</td>
<td></td>
</tr>
</tbody>
</table>
Pre Treatment Flexibility | limp, almost formless, individual strands indistinguishable
---|---
Post Treatment Flexibility | dry, individual strands visible, slightly stiff


Figure 3. Silicone oil treated rope.

**Post-Treatment Strength**

After one week of air drying, the silicone oil treated rope and the comparably-sized sample of air-dried rope were taken to the Texas Engineering Experiment Station, Testing Machinery and Repair Laboratory at Texas A&M University for tensile strength testing. We believed that these tests would provide us with insight into the strength characteristics of polymer-treated rope. Tensile strength testing was conducted with a 20kip (1 kip = 1000 pounds tensile strength) MTS servo-hydraulic frame, which measures the maximum load breaking point of materials. To more accurately measure the maximum load breaking point of low-potential tensile strength materials such as the fragile treated *La Belle* rope fibers, a 2 kip load cell was mounted into the jaws of the 20 kip machine.

Data control and acquisition was recorded using Gardner Systems software. Time, distance, and pounds force were measured for each sample. In each test, tensile strength testing continued until the sample failed. Rope 1 (*Si-1*), treated with silicone oils, was mounted in the load frame using wedge grips. This sample slipped once during testing. To prevent slippage with the other samples, the second silicone-treated rope sample (*Si-2*) and the freeze-dried sample (*WL*) were mounted into the load frame using wedge grips.
only after being outfitted with epoxy potted ends. This is a more complex mounting process that requires that the ends of the rope be cemented into a cone-shaped epoxy base prior to mounting in the frame. The use of these potted ends eliminated slippage and resulted in more reliable data.

Tensile strength testing has demonstrated that rope preserved in silicone oil is considerably stronger than rope that has been allowed to air-dry. When tested, the rope section \( WL \) failed at 2.6 lbs tension and the sections of rope treated with silicone oils, labeled \( Si-1 \) and \( Si-2 \), failed at 36.5 lbs and 27.7 lbs respectively. Table 3 lists the data acquired from this tension test. As a result of waterlogging, which deteriorated and weakened individual fibers of the rope, the strands that make up the rope failed at different times in each of the samples. While post-treatment strength may not be an important factor in the decision to conserve rope by a particular method, it is beneficial to know that silicone oil-treated cordage is more internally stable and stronger than rope that is not treated with silicone oil.

**Effectiveness of Incorporating Non-Polar Suspension Mediums and Elements of the Frankfurter Method into Traditional Silicone Treatment Strategies**

The Danish process of using perforated polypropylene film to make a form-fitting jacket within which archaeological rope is treated (an approach most commonly utilized in the Frankfurter Method) worked well when incorporated into our silicone treatment. The polypropylene jacket provided a permeable membrane that facilitated chemical transfer and also acted to protect the physical integrity of the artifacts during treatment. Through experience, we have found that rope treated without being enclosed in some form of permeable material, such as a perforated polyethylene bag, tends to unravel slightly during treatment. Silicone oil-treated rope treated without a non-polar suspension medium such as kerosene usually results in an artifact with a slightly matted appearance. Immersion in a non-polar solution enables the fibers to \( \text{float} \) and facilitates the polymerization of individual fibers. The use of kerosene with a tin-based catalyst works well as a medium for polymerization, but the kerosene/catalyst polymerization medium is not ideal for routine laboratory use due to the flammable nature of kerosene. An additional disadvantage in using a kerosene/catalyst medium for polymerization is that it takes several days for the faint odor of kerosene to be eliminated from the artifact. We fully expect that other volatile solvents will work well in place of kerosene, but these experiments have yet to be conducted.

Experimentation has indicated that CR-20 crosslinker/CT-32 catalyst, 3% by weight, solution is also an effective and safe substitute for the kerosene/catalyst mixture. After removing treated samples from the CR-20/CR-32 catalyst solution, the surfaces of the rope were not slippery, suggesting that more complete catalysis occurred while the sample was in solution. Unlike the kerosene, residual odors associated with this catalyzation medium dissipated in a matter of minutes once the sample was exposed to fresh air.
After silicone oil/crosslinker solutions have been impregnated into organic materials, immersion in CR-20 crosslinker and surface wiping with a cotton swab or a lint-free cloth is an effective way to remove excess polymer from the surfaces of an artifact. In some cases, excess silicone oils have been removed from the surface of rope by immersion in CR-20 crosslinker under a slight vacuum. The process appears to eliminate a great deal of silicone oil solution from within the deep crevices and voids on the surface of the rope.

Obvious benefits of using silicone oils for conserving waterlogged rope include the short treatment duration and the minimum amount of laboratory equipment required for the process; PEG/freeze-drying methods of rope preservation require substantially more time and labor. The silicone oil-treated examples were conserved in less than twenty-four hours. In addition, artifacts treated with silicone oils do not require special curation and, as the data suggests, the dimensional attributes of the artifact are accurately preserved.

As Vera De la Cruz Baltizar observed in her (1996) thesis entitled Plastination as a Consolidation Technique for Archaeological Bone, Waterlogged Leather and Waterlogged Wood, silicone oil treated samples appear to be dimensionally stable with good coloration (Baltazar 1996). Repeated testing of the hybrid silicone-oil treatment described above at the Archaeological Preservation Research Laboratory consistently yields waterlogged rope specimens that are aesthetically pleasing and dimensionally stable.

Accelerate aging tests and data supplied by Dow Corning Corporation continue to be encouraging regarding the long-term stability of silicone oil-treated artifacts. Eight silicone oil-treated samples were subjected to an extended test in an Accelerated Weathering Machine. The samples were exposed to four months of continuous alternating cycles of six hours at high humidity (95%) and high temperature (45° Celsius) with a UV 340 light, and six hours at a lower humidity (60%) and temperature (20° Celsius) with no light exposure. The tested sample data (including overall dimensions, color and surface integrity) was comparable to data for silicone oil-treated specimens that had not undergone accelerated weathering.

There is no doubt that silicone oil treatments, like treatments that require applications of polyurethane in ethylacetate, are not reversible; this is not to say, however, that rope treated with silicone oil can not be re-treated. In the past, we have re-treated several fragile leather and canvas artifacts preserved with lower centistoke silicone oils, using more viscous polymers to add additional strength and stability. More importantly, waterlogged rope appears to respond well to treatment using silicone oils. While we do not suggest that silicone oil processes are a panacea for all archaeological conservation issues, we suggest that the field of archaeological conservation can benefit from on-going research into silicone oil treatment techniques. Based on experimentation to date, we would concur with Baltazar=s observations that silicone oil preservation is a very promising technique for the consolidation and preservation of many waterlogged materials (Baltazar 1996). The added strength and elasticity characteristics associated with the silicone oil process used for this experiment may have important implications for
the structural well being of some artifacts. Continuing research at the Archaeological Preservation Research Laboratory is focused upon these issues.

**Tensile Strength Data for Rope Samples**

<table>
<thead>
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<th>File</th>
<th>Type</th>
<th>Peak Load (lbs)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rope 1</td>
<td>Si-1</td>
<td>36.5</td>
<td>Wedge grip mounted</td>
</tr>
<tr>
<td>Rope 2</td>
<td>Si-2</td>
<td>27.7</td>
<td>Epoxy potted ends</td>
</tr>
<tr>
<td>Rope 3</td>
<td>WL (air dried)</td>
<td>2.6</td>
<td>Epoxy potted ends</td>
</tr>
</tbody>
</table>

*Figure 4. Rope Si-1 load / displacement data.*
Figure 5. Rope Si-2 load / displacement data.

---

Resources - Materials

<table>
<thead>
<tr>
<th>Resource</th>
<th>Supplier/Contact Information</th>
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<tbody>
<tr>
<td>Kerosene - 1-K, vapor pressure 0.4mm Hg, CAS # 808-20-6</td>
<td>VWR Scientific Corporation, Sugar Land, Texas</td>
</tr>
<tr>
<td>Precision Load Frame System, Model 312.31S</td>
<td>MTS Systems Corp., 1400 Technology Drive, Eden Prairie, MN 55344-9763 (603)937.4000</td>
</tr>
<tr>
<td>-20 kip MTS servo-hydraulic load frame</td>
<td></td>
</tr>
<tr>
<td>-Load resolution limited by software to .1 lbs</td>
<td></td>
</tr>
<tr>
<td>Control and Data Acquisition</td>
<td>Gardner Systems Inc., 3413 W. Fordham Ave., Santa Ana, California 92704-4422 (714)668.9018</td>
</tr>
<tr>
<td>Munsell Soil Color Charts</td>
<td>Macbeth Division of Kollmorgen Corporation, 2441 North Calvert Street, Baltimore, Maryland 21218</td>
</tr>
<tr>
<td>Passivation Polymers</td>
<td>Corcoran Laboratories, 5558 Springknoll Lane, Bay City, Michigan 48706 (517)892.6580</td>
</tr>
<tr>
<td>Testing Machinery and Repair Facility</td>
<td>Division of Texas Engineering Experiment Station, Texas A&amp;M University, College Station, Texas 77843</td>
</tr>
<tr>
<td>Ziploc brand Quart size Vegetable Bags</td>
<td>Dow Chemical Corporation, P.O. Box 68511, Indianapolis, Indiana 46268-0511</td>
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ACKNOWLEDGMENTS

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1993


BALTAZAR, VERA DE LA CRUZ,

1996


Citation Information:

Smith, C. Wayne.