Silicone Oil and Organic Conservation

Dr. Helen DeWolf
Texas A&M University
Conservation Research Laboratory
2014

Conservation entails a multitude of techniques and technologies. Some of them are very basic and some extraordinarily complex. Most of all conservation is more than cook-book chemistry. There is an art to conservation of artifacts from waterlogged sites and when done well it enables the archaeologist to define those nuances for the story they are trying to tell. The art comes in going the extra step to finish the artifact, to find the maker's marks, to identify patterns and put the pieces together on paper if not reconstruction in reality. The art is to ensure that an artifact has had all of the diagnostic features found recorded and illuminated for the researcher and for the viewer. But the archaeological conservator must also be an archaeologist. We must understand not only the material we are conserving but how it was made, how it was used and what relationship it might have to the rest of the artifacts in the site. As conservators we have the luxury of seeing the artifacts up close for prolonged periods of time. Here the art of conservation is important because we can see patterns of manufacture, of use and in a well-documented site, of deposition. On occasion it is the archaeological conservator that pinpoints elements of the context of a site that the archaeologist misses because we see everything in such detail.

For the most part each artifact must be considered as a unique conservation problem for two basic reasons, because of its life before deposition and because of the conditions after deposition. The manufacture, use and deposition affect an artifacts condition and influence which conservation treatments are considered. The micro-environment while submerged is affected by the amount of salinity, marine organisms, organic material, bacteria, oxygen, temperature, and other materials in close proximity, sedimentation rates, exposure and sedimentation sequences. The complex interplay of all of these elements in varying degrees leads to the condition of the artifact upon excavation. The very act of excavation upsets the micro-environment surrounding the artifact by introducing more oxygen, removing sediments, removing protection and support, water movement/wave action, changing the temperature and even sunlight. All of these can lead to damage and exacerbate the fragility of the artifact. Some of this damage can be irreparable, some is unavoidable and inevitable. The role of the archaeologists on the front lines is to ensure that the site is excavated as carefully, efficiently, quickly, and professionally while doing the least possible damage to the artifacts. It becomes the responsibility of the archaeological conservator to stabilize, document, highlight, record, preserve as much diagnostic information as possible and ultimately (if possible) conserve the artifact for posterity.

Organic artifacts are often composed of a single material (seeds, insects, bone, rope, paper, textiles, leather and in this group we include glass). This makes the conservation process fairly straight forward with a basic controlled dehydration utilizing solvents and a silicone oil polymer bath, draining, cleaning and catalyzed polymerization. Another option is immersion in multiple PEG/water solutions of increasing increments of saturation, and then controlled dehydration or freeze-drying which is not discussed here.

In the case of organic materials, uncontrolled dehydration (drying) begins at the moment the materials are exposed to the atmosphere. Depending on the cellular structure of the organic material this can lead to a rapid movement or wicking of the water inside the cells to the outside surface of the object. The surface tension of this interior water pulls on the degraded cellular structure. As the water leaves there is nothing to support the cell walls thus causing them to collapse. This is the process of shrinking, twisting, cracking, checking, cupping and warping of the material. In the case of wood this process can ultimately lead to a catastrophic failure of the structure of the artifact. This was seen to happen to many wood artifacts with varying results. One example is a 'spirit cask' - where the very thin staves on the top of the cask (exposed) surface of the cask began to change shape in situ, during the excavation. Once this damage has occurred it cannot be reversed, the damage is permanent. Post-conservation it was noted that the distortion of the damaged staves seemed to have been primarily the across the grain and tangentially, longitudinally there was almost no change. This is also true of larger casks where there was virtually no longitudinal change and minimal cross and tangential change depending on the penetration of the corrosion products and damage done during the original wrecking incident, the corrosion process and the excavation. This 'spirit cask' shows of this type of damage cannot be reversed and although reconstructed to the best of our ability it is not 'perfect'.

Dehydration is the key to the conservation process. This is especially true of wood artifacts. The CRL uses water miscible organic solvents progressing from the lower polar (Ethanol) to the higher polar (Acetone) solvent. When we utilize the silicone oil treatment process the initial stages of dehydration are in increments of a maximum of 25%. Beginning with an ethanol/water bath of 25% ETOH in 75% deionized water, then in successive increasing increments of solvent until 100% ETOH is achieved. From a second 100% ETOH the same is done replacing the ETOH with acetone in increments until 100% acetone is achieved. The length of time in these successive baths is based on the size and condition of the artifact (small and very porous requiring less time that the very large and dense artifact). Once the artifact has gone into 100% solvent baths the duration of the bath can be shortened slightly. We have the artifacts go through two baths of 100% ETOH before beginning the ETOH/Acetone baths to ensure that as much water as possible has been removed from the wood. It is necessary that every organic artifact is in clean 100% acetone prior to immersion in the silicone oil solution. The artifact must be dripping wet with acetone as it is put into the silicone oil solution. It is important to note that acetone is the highway or mechanism that brings the treatment solution into the cellular structure of the material.

Now we come to the tools and technologies available to the archaeological conservator. The most recently developed tool is the Silicone Oil Treatment. This treatment was developed through the CRL and the Archeological Preservation Research Lab (APRL) at Texas A&M University in conjunction with the research based at Dow Corning Corporation in Midland, MI. This treatment uses Dow Corning's 6o+ years of organo-polymer chemistry research as its basis for development. The results of this research has led to numerous patents of the resulting conservation technologies. This innovative technology uses specific polymers which speed up the process, allow for significantly less shrinkage and warping and keep the artifact stable for a significantly longer period (a minimum of 3-4 times longer) than many traditionally-utilized conservation treatments. This technology also imparts more strength to most artifacts, enables future researchers to handle the artifact directly, and the artifact can be stored in less-than-ideal museum conditions. This innovative technology involves many chemicals that are less toxic to humans and the environment and can be recycled for longer lab use. This treatment technology will enable many archaeological materials from third-world nations to be preserved, displayed, stored and enjoyed for less cost over the long-term. This treatment strategy allows the conservator to stabilize and often strengthen a wide variety of materials, and many composite artifacts before disassembly to ensure that the fragile and often very friable components of an artifact can be stabilized and saved in situ thus maintaining its shape and size. Often these degraded, fragile organic components end up being sacrificed in order to retain the more robust components or to conserve the metal components in a treatment that can be detrimental to the fragile organic components.

The artifacts that elicit the most interest and often information are composites. They are comprised of differing materials (e.g. metals and organics). These can range from the relatively simple to the very complex. They may be a single type, or piece of metal and a single type or piece of an organic component like a wood handled iron bladed trade knife or they can compose of multiple metals (brass, iron and silver) and multiple pieces of wood or leather or rope or even textile (longarms, navigational instruments, blocks and tackle, leather shoes, clothing with embellishments and buttons). The conservator must not only understand what these components are but how they were put together and how the various conservation technologies conserve the disparate materials and most importantly, how they will interact from this basis we determine which technology should be applied to the artifact as a whole for optimal results, can the artifact be disassembled prior to any technology is applied. Or in what order the treatments should be performed, and when the various treatments have been completed - can the artifact be re-assembled. This weighing of the various conservation options in the conservators tool box is done for each individual artifact. Although there may be multiple artifacts of the same type, they will be in varying states of degradation/preservation and may not all require the same intensity of conservation.

We have been working with this technology for over 14 years in the CRL and have stabilized numerous types of materials and thousands of artifacts. This includes 650,000 glass beads, dozens of glass bottles, sand glasses, numerous instrument lenses, hundreds of feet of rope (sisal and hemp), hundreds of bones, numerous carved bone and ivory artifacts, dozens of glass mirrors, portions of multiple wooden boxes, crates, barrels, hundreds of wood handles knives and tools, leather shoes and pouches, wood buttons (some with thread still attached), small pieces of silk damask, ribbon, felt, woven and knitted wool, cotton canvas, parts of two baskets, hair, fur, cork, bark, dozens of ship's rigging pieces, wood combs, paper, wood navigational instruments, hundreds of seeds and thousands of insects parts.

The silicone oil treatment is primarily comprised of a solution of a silicone oil and a crosslinking agent that is catalyzed after application. The silicone oil can be of a single molecular weight or a combination of multiple molecular weights. The differing molecular weights achieve differing properties of flexibility, brittleness, strength, aesthetic appearance, or surface texture. The crosslinking agent is a silane in a solvent – Methyltrimethoxysilane (MTMS). This crosslinker helps bind the polymer chains to the cells in the material on a molecular level. The minimum proportion of the crosslinker chemically necessary is 3-8% by volume. When combined with the silicone oil to create a solution that provides the most consistent results on the majority of artifacts is approximately 20%. For most artifacts the silicone oil/crosslinker solution we use is 66% lower (SFD1) and 34% higher (SFD5) molecular weight silicone oils (80%) plus the MTMS. This solution is by volume. After immersion or topical application of the silicone oil solution the artifact/material is exposed to a catalyst - dibutyltin diacetate (DBTDA) which completes the stabilization process by locking the polymer chains in place to ensure the long-term stability of the material and the treatment polymers. It is important that each time the silicone oil/crosslinker mixture is used, the solution is tested to ensure that it will polymerize at the end of the treatment. Testing requires a very small sample of the silicone oil/crosslinker solution (less than a soup spoon of solution), add a few (3-4) drops of catalyst and stir. Within a few minutes this mixture should begin to thicken and then set up (polymerize). Remember to make sure that the silicone oil solution is covered/sealed when you mix up the sample because it takes very, very little (10s of parts per million) of the catalyst vapor to start the polymerization process. Once ascertained that the solution is viable then the artifact is immersed in the treatment solution.

At this point time is your ally. The artifact can sit in the solution indefinitely or as is convenient to the conservator. We determined that almost all of the wood and leather artifacts were conserved under ambient pressure and temperature. During the height of the conservation process of organic materials we processed a large quantity of artifacts and large objects. We carried out the entire treatment at ambient pressure and ambient temperature as part of a six week schedule- this was as a matter of convenience to have all dehydration baths and the silicone oil bath in the same rotation. It was a way of controlling location and movement of artifacts through the process. However, depending on the type of material (glass, paper, and textiles) and the individual artifact, it is even possible to put the solution with the artifact in a vacuum to slightly speed up the process of acetone/silicone exchange. For these specific types of materials that could physically withstand undergoing a vacuum they were placed in the silicone oil/crosslinker solution at ambient pressure for hours to days and then placed inside a vacuum chamber and left under a low vacuum for a week to three weeks depending on the condition of the material and size of the artifact. It was observed that glass responded very well to the technique.

After the length of time in the silicone mixture is determined to be appropriate for the artifacts being treated they were removed from the silicone oil/crosslinker solution and allowed to drip dry. Because the solution is reusable we have the artifacts drain/drip the excess oil back into the bath or into a reservoir that can be poured back into the silicone oil/crosslinker solution container. Depending on the condition of the artifact as much as possible surface cleaning of sediments, grime and grit was done prior to exposing the artifact to the catalyst to polymerize the bonded silicone oil in the artifact. If the surface of the artifact was still too fragile to mechanically remove excess dirt or encrustation, we used cloth or paper to blot away any excess silicone and then exposed the artifact to the catalyst to strengthen the material prior to mechanical cleaning.

We preferred to expose the artifact to the catalyst as a vapor. We dribbled approximately 10-15cc of DBTDA in an aluminum sample dish or on to crumpled paper towel and put the artifact and the catalyst in a resealable plastic bag or closed plastic container. On some artifacts whose surface is very smooth or robust we did topically apply the catalyst to speed up the catalyzing. It is important to make sure that you do not allow the catalyst to pool or remain on the surface of the artifact because you will get a very hard white area where the silicone has polymerized into a hard lump/area that can be unsightly and difficult to remove. Because the catalyst has a limited working life (24 hours), once a day for up to a week we changed the catalyst. We then allow the artifact to off gas before we do any more mechanical cleaning to remove any remaining dirt, sediment, foreign material and encrustation. As occasion required we immerse artifacts, after polymerization, in hydrochloric acid (10-12% HCl) in order to soften and remove residual encrustation. This is done very judiciously under observation to ensure that the artifact is not harmed by the process. These artifacts are then rinsed in deionized water to remove the HCl, and allowed to air dry with no adverse effects to the artifact. The concretion is mechanically removed. If the artifact is comprised of multiple materials and components it ias disassembled and/or reassembled in order to accommodate the treatments necessary for the disparate materials, as determined by the conservation treatment strategy for that particular artifact. Once the last cleaning was done the artifact was completed.

For those composite artifacts that are too fragile to be disassembled prior to the silicone oil treatment and needed to have the metal components treated separately we took them apart after the silicone oil treatment. We find that the majority of artifacts are easier to disassemble after treatment. We then conserve the metallic components of the artifact and the reassemble. We also find that there is minimal movement of wood through the silicone oil process allowing reassembly for the majority of artifacts. This is true if the material did not undergo any uncontrolled dehydration during excavation or treatment.

One must always add a caveat during a report on the conservation of artifacts especially organics from waterlogged sites. In spite of the conservators best efforts some artifacts do not survive the conservation process. This is why we must document the artifact prior to conservation, if possible during the process and definitely post conservation.