



Waterlogged Leather: Preservation and Conservation Techniques

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Abstract:

The preservation and conservation of waterlogged leather pose distinct challenges owing to its high vulnerability to degradation. A successful treatment approach generally necessitates a regulated drying procedure, which often begins with immersing the leather in a polymer solution aimed at stabilizing its structural integrity. Subsequently, a bath containing glycerin and ethanol may be administered to ensure the material retains its flexibility and to avert any shrinkage throughout the drying phase. Additionally, methods such as ultrasonic cleaning can be employed to eliminate contaminants while safeguarding the leather from potential harm. Ultimately, the selection of an appropriate technique is contingent upon the leather's specific condition and the intended objectives for its preservation.

Keywords: Heritage, Leather, Waterlogged, Conservation, Preservation

I. INTRODUCTION

Waterlogged leather typically arises in environments that limit microbial proliferation, which allows organic matter to endure longer than it would in areas abundant in oxygen. This state of preservation can yield significant insights into historical techniques, everyday existence, and cultural practices. Nevertheless, the shift from a moist to a dry environment presents notable hazards, such as shrinkage, fissuring, and a decrease in suppleness.

The formation of waterlogged leather is primarily the result of a transformation occurring under anaerobic conditions. The degree of this transformation is largely contingent upon the specific environmental factors, pH levels, and the types of microorganisms present. In this leather, the collagen fiber bundles and other proteinaceous fibers undergo conversion to a more or less pronounced glutinous state.

Upon drying, the ability of these fiber bundles to slide over one another is compromised, resulting in a material that is hard and brittle. Furthermore, it is likely that the original density of the weave, the degree to which bundles have separated into individual fibers, and the specific treatment the leather has previously undergone will influence the rate at which degradation occurs.

1- Methods Of Conservation Wet Leathery

1-1 Preliminary Cleaning

It is important to keep leather objects clean, as accumulation from dust and dirt absorbs and locks in moisture from the air. Often it is enough to vacuum with a brush, especially if done on a regular basis so the dust does not have a chance to solidify, making it hard to remove. There is an abundance of tools for dry cleaning, and they should be used in the order of mild to harsh. Examples of these tools are smoke sponges, wishab erasers, groomstick and different brushes.

Wet cleaning should be done with the utmost care, avoiding it if at all possible. However, if water is to be used, it should be applied lightly to the dirt, being careful not to wet the leather. Adding non-ionic detergent to the water can help dissolve dirt, making sure to remove residues with clean moistened swab. Different solvents can be used, alone or in aqueous solution, to quicken the evaporation and help dissolve the dirt, taking great care as solvents can also dissolve oils and tannins in the leather.ⁱ

The conservation of wet leather, especially within archaeological settings. Necessitates the application of specialized methods aimed at maintaining the material's structural integrity and extending its lifespan. Below are several fundamental approaches employed in the conservation of wet leather:

Leather may require a variety of mechanical cleaning technique, depending on the condition of the leather and the particular cleaning probleme.soft brushes, water jets, ultrasonic cleaners and a cavitron, an ultrasonic dental tool, may be required.ⁱⁱ

When it comes to the preservation of leather, opting for a treatment that minimally impacts the material is generally advisable. Like all porous substances, it is essential to eliminate the majority of soluble salts that may resurface. The methodology to achieve this mirrors the processes utilized for the conservation of bone and ceramics.

Prior to any conservation efforts concerning archaeological leather, a washing step is imperative to eliminate any entrenched dirt. Initial attempts should involve rinsing with water alone. If this approach proves ineffective, alternative cleaning methods should be considered. The condition of the leather and the specific cleaning challenge may necessitate various mechanical cleaning techniques. Tools such as soft brushes, water jets, ultrasonic cleaners, and a Cavitron—a dental ultrasonic instrument—might be required. In instances where chemical cleaning is warranted to address stubborn dirt, a diluted non-ionic detergent solution (approximately 1%) or sodium hexametaphosphate can be employed. Should Calgon, a commercial water softener, be used, it is crucial to

ensure that the pH remains between 3 and 5, as the addition of other substances may compromise the safety of the treatment on leather. Thorough rinsing post-washing is essential. It is important to avoid any chemicals that could damage the collagen fibers, which are the primary structural component of leather.ⁱⁱⁱ

For the safe storage of waterlogged leather or similar organic materials, a solution can be prepared by combining 90% of a stock solution made up of equal parts water and ethanol, to which 10% glycerin and 2 to 3 drops of formaldehyde are added. A 50% ethanol and water mixture serves effectively as a storage medium for various materials.

It is critical to recognize that leaving stains on leather is sometimes preferable to the potential damage incurred from attempts to remove them. Some metal stains are indeed stable. For addressing stains, particularly those caused by iron, a solution of 3-5% ammonium citrate or ethylene-diamine-tetraacetic acid (disodium EDTA) can be utilized. Commercially available forms of EDTA include Titriplex III and Disodium Deterate. The leather should be soaked for 2 to 3 hours while being closely monitored. Following this, it should be rinsed in running water or standing tap water until all chemical residues have been washed away.^{iv}

To ascertain the complete removal of chemicals, the pH of the water bath containing the leather should be tested. It is important to bear in mind that the chemicals employed to clean rust and mineral deposits (such as oxalic acid and EDTA) may further hydrolyze the collagen fibers that constitute the leather, along with potentially stripping away tanning agents, colorants, painted decorations, and other diagnostic features inherent to the leather object. The preservation of diagnostic attributes is paramount and should never be compromised. Caution is warranted when applying any of these chemicals to leather.

For the treatment of waterlogged leather, methods such as freeze drying and solvent dehydration are often preferred frequently without the addition of any lubricants. Notably, significant success has been recorded in the conservation of bog bodies through freeze drying, utilizing 15% PEG 400 as a lubricant to mitigate shrinkage of both skin and bone during the drying process.

The drying characteristics of any leather piece are influenced by multiple factors including its condition at the time of deposition, the burial environment, the species, health, and sex of the individual—whether human or animal—the location of the skin on the body, the method of manufacture or tanning employed, and the historical context of the leather object itself.

1-2 PEG Treatments For Waterlogged Leather

Numerous techniques have been documented for the preservation of waterlogged leather, yet the method most frequently employed involves the use of polyethylene glycol (PEG) for impregnation. PEG, a polyether compound, exists in various grades that are determined by differing molecular weights. Historical accounts suggest that its initial application as a conservation agent was for the preservation of the waterlogged wooden ship known as the Vasa, which sank off the coast of Stockholm. Following the optimization of this chemical compound for conservation purposes, its application extended to other organic materials, including leather. In their article "The Conservation of Archaeological Leather," Cameron, Spriggs, and Will note that initial experiments with PEG treatments on leather were conducted at the British Museum, albeit yielding unsatisfactory results.^v

Dry leather can be saturated with water or alcohol and treated with PEG 1450, PEG 540 blend, PEG 600 or PEG 400. In the past, leather was treated in PEG which was heated to a temperature of 40-50o C.

Presently, most leather treatments are carried out at room temperature because heat in any form is generally detrimental to leather.

The PEG treatment consists of immersing leather in a dilute solution of PEG, i.e., 10%, and increasing the consolidant concentration in 10% increments as the leather absorbs the PEG. A final concentration of 30% is adequate. Keep the artifact immersed for several days until the leather is flexible. Once pliable, remove from the PEG and clean off excess PEG with toluene or water. Allow treated leather to dry slowly under controlled conditions.

As mentioned above there are several types of PEG and each has its own characteristics. PEG 540 Blend (equal parts of PEG 1450 and 300) is slightly hygroscopic and becomes moist at high humidity; for this reason the surface of the leather is sometimes sealed with a hard wax, i.e., a mixture of 100 gm. micro

wax and 25 gm. polyethylene wax. PEG 3250 is very hard and is not very hygroscopic. Its main disadvantage (in some cases an advantage) is that the treated leather is rigid. When using PEG 3250, form the treated specimen to its final shape while the wax is still warm and then allow the artifact to cool. PEG 1450 seems to give consistently good results. The various PEG treatments are more commonly used for the conservation of dry leather. 15% PEG 400 is commonly used as a pretreatment when the leather is to be freeze dried.^{vi}

1-3 Glycerol(Glycerin) Treatment

Glycerol (1,2,3,propanetriol) is a relatively small molecule with two primary and one secondary hydroxyl groups. The size of the glycerol molecule, it has a molecular weight of 76-92, compared to 380-420 for PEG 400, may be a contributory factor to its success in the treatment of waterlogged leather. Multiple hydrogen bonding between the three hydroxyl groups of the glycerol molecule and polar areas of the collagen triple helix, stabilises the leather fibre structure, enabling water to be safely removed. The molecular structure of glycerol, that is the position of polar groups and chain length, may facilitate the stabilising effect.^{vii}

Waterlogged leather recovered from excavations is conserved by placing it in a solution of 30% glycerol, 70% Alcohol (ethanol) for 2 weeks. The leather is then dried by 3 baths of acetone, 3 hours long each. Glycerol is not miscible in acetone and is thus not removed in the acetone baths. Good results can be achieved using a glycerol treatment by using 10-40% glycerol mixed in 90- 60% alcohol or water. Avoid using concentrated glycerol. While the solutions in alcohol can remove tanning agents, alcohol speeds up the process. In alcohol solutions, the leather has more overall strength during treatment. In other words, the alcohol allows the leather to support itself better than does a water solution, because the alcohol keeps the leather fibers stiff. removed by air drying and sometimes with the use of vacuum.^{viii}

1-4 Treatment of Brittle and/or Desiccated Leather

Brittle and desiccated leather is restored by adding lubricants, with the addition of glycerol and alcohol, which act as hygroscopic agents called humicants. The Smithsonian method is used to treat and soften the leather, which is^{ix} :

59% glycerin (glycerol) and 39% water

1% formaldehyde or 1% Dowicide 1

OR

25% glycerin and 75% alcohol.

Submerge the artifact in the solution until the leather reaches a state of pliability. The use of an alcohol solution complicates the assessment of leather pliability, as the alcohol tends to render the leather rigid. This treatment may extend over several weeks. While it effectively restores flexibility, it is important to note that glycerin is hygroscopic and may foster mold proliferation. Despite this drawback, the treatment has seen considerable successful application historically.

Although this method fell out of favor temporarily, recent years have seen a resurgence of interest in it, as noted by Jenssen (in Pearson, 1987). As is true for all organic conservation techniques, caution is advised when applying this treatment.

For instance, waterlogged leather excavated by The Museum of London is preserved by immersing it in a mixture of 30% glycerol and 70% ethanol for a duration of two weeks. Following this, the leather undergoes drying through three successive baths of acetone, each lasting three hours. It is crucial to remember that glycerol is not soluble in acetone. Basic success can be achieved with a glycerol treatment by utilizing a mix of 10-40% glycerol combined with 90-60% alcohol or water, while concentrated glycerol should be avoided. Although alcohol solutions can eliminate tanning agents, they also expedite the treatment process. In alcohol mixtures, the leather maintains greater overall strength throughout the treatment, enabling it to better support itself compared to a water solution.

This treatment has also been utilized for other materials such as basketry, matting, and sandals to enhance pliability, although it has frequently led to unfavorable outcomes. It is essential to keep in mind that there is no necessity to render an object flexible if it was not inherently pliable. The glycerin treatment can be effectively paired with PEG. To re-treat items previously conserved with glycerol, such as basketry, it is imperative to remove the glycerol through a series of alcohol baths.^x

2- Dehydration Using Organic Solvents

The wet leather can be immersed in a series of baths that include organic solvents such as water, isopropanol, ethanol, methanol, methyl ethyl ketone (MEK), and acetone. This sequence may consist of varying concentrations of H₂O and isopropanol, followed by baths of 100% isopropanol, then 100% ethanol or methanol, subsequently transitioning to 100% methyl ethyl ketone, and culminating with 100% acetone and finally 100% ether.^{xi}

Water can be replaced by a less polar solvent, using a sequence of solvents of decreasing polarity. The glutinous collagen fibres are so desiccated, thus rendering their surface less sticky, before they approach each other again as a result of capillary forces occurring between them on evaporation of the solvent.

At the National Museum of Copenhagen (private communication) acetone is used to replace water. A detailed description of the process is not yet available.

The method used in the laboratory of the Swiss National Museum is as follows : 1. Thorough cleaning from soil deposits, among which clay particles are the most resistant. Removal of dark iron tannates by immersion for instance *in* a solution of disodium ethylene-diaminetetraacetate ; the objects are surrounded by wire gauze and treated for 30 minutes with ultrasound, then carefully rinsed with pure water.

2. The objects are immersed in acetone and this is repeated several times. Methylethylketone is sometimes preferred in view of its lower volatility.

3. The leather is soaked for some minutes in carbon tetrachloride containing a fungicide, e. g. tributyltin oxide or tributyltin naphthenate and then allowed to dry between sheets of blotting paper and glasse-plates. In most cases a light-coloured leather of good flexibility was obtained. The sole leather was less flexible than the top leather, as might be expected from its original function.^{xii}

3- Treatment Of Wet or Waterlogged Leather

Leather is an organic material that is affected by the marine environment, and a complex change occurs in its internal structure.^{xiii} Water is used with the leather artifacts, which were found submerged in water, as the treatment process for such artifacts begins with washing in neutral, non-ionic water.^{xiv}

3-1 PEG Treatment

To treat desiccated leather, utilize PEG 400, 540 Blend, 600, 1450, and 3350, following the previously outlined procedure. It is advisable to initiate the process with a dilute

solution of PEG, ranging from 1% to 10%, and progressively elevate the concentration by either evaporating the solvent or incrementally adding PEG until achieving a concentration between 30% and 100%. This method facilitates the evaporation of water as PEG is introduced in equal proportions to replace it.

While aqueous PEG solutions operate at a slower pace, they are more economical compared to solvent-based solutions, which, despite their higher cost, offer a more rapid treatment and yield leather that is lighter and exhibits more consistent shrinkage. Preferences among conservators vary; some advocate for alcohol treatments, whereas others contend that such treatments induce greater shrinkage in leather compared to aqueous alternatives.^{xv}

All PEG treatments can be effective on their own. However, their efficacy is significantly improved when concluded with a freeze-drying process, mirroring the steps applied in wood treatment. The optimal results are typically achieved using a commercial freeze-drying vacuum chamber, though satisfactory outcomes have also been reported with domestic chest freezers. The former method generally requires about a week to complete, while the latter may extend to several weeks. Monitoring the progress can be accomplished through regular weighing of the object to track moisture loss as the leather undergoes desiccation.

3-2 Bavon Treatment

Bavon asak-apb is a commercial leather dressing, based on polyhydric alcohol ester-hydrocarbon copolymer and mineral oil^{xvi}.

1. Wash leather in a 1% solution of Lissapol; never use commercial detergents on leather as they may extract tanning materials. Use castile soap, soft soap or saddle soap.

2. To remove iron stains place leather in 3-10% Disodium EDTA (pH 4) or ammonium citrate (pH5) for a maximum of an hour; shorter if possible. Tap water can be used. The H₂O may yellow from the EDTA dissolving iron tannate. Note: EDTA has been reported to damage fibers of leather, but is relatively safe if used selectively and cautiously. A 3-5% ammonium citrate (pH 5) can also be used and, in fact, is recommended over Disodium EDTA by the Canadian Conservation Institute. This step is necessary only if iron stains are present.^{xvii}

3- If deemed necessary, immerse the material in a 2% hydrochloric acid solution for a duration of up to one hour to facilitate the dissolution of any calcareous deposits.

Conduct a thorough rinsing under running water for thirty minutes to achieve a pH level between 3 and 6, or to match the pH of the rinsing water.

Proceed with dehydration using acetone, employing two or more baths; for instance, utilize four consecutive baths, each lasting one hour.

Allow the material to air dry until it attains a texture reminiscent of leather, subsequently placing it between absorbent tissue and glass for a drying period of twenty-four hours.

With the aid of a brush, apply Bavon Leather dressing, ensuring to flex and manipulate the leather throughout the application process.^{xviii}

Bavon Leather Dressing

1 liter of stabilized 1:1:1 trichloroethane

1 gram Dowicide 1

50 grams anhydrous lanolin

20 grams Bavon ASAK-ABP.

3-3 Treatment Freeze Drying

A freeze-drying process for leather developed by Rosenquist⁸ makes use of polyethylene glycol 400, but does not mention surface treatment or consolidation. At the MSMRCC, a modified freeze-drying treatment uses PEG 1500.⁹ The process includes the following steps in sequence: impregnation, drying and surface treatment, followed by consolidation, support, and reconstruction when necessary.^{xix}

Conclusion

In conclusion, the preservation of submerged leather artifacts necessitates a multifaceted approach that encompasses thorough evaluation, desalination processes, the strategic use of humectants, and the maintenance of a regulated storage environment. These techniques are essential for safeguarding the historical and cultural value of these distinctive items, thereby ensuring their availability for future scholarly inquiry and public appreciation.

Researcher Hamilton advocates for the employment of solvent-based drying methods, subsequently complemented by the application of a leather dressing. He asserts that air drying from a wet condition is ineffective, as the contractile forces generated by the evaporating water tend to consolidate the protein fibers, resulting in the leather becoming rigid and diminished in size. Alternatively, some practitioners favor freeze-drying, particularly when it is preceded by a treatment involving PEG 400. The primary expenses associated with these processes stem from the use of organic solvents required for drying, as well as the investment in freeze-drying equipment. These two methods represent the most prevalent approaches within the field, and both yield satisfactory outcomes.

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