Master's Thesis

Recognizing drying methods for waterlogged leather

A research into the possibility to distinguish the drying method carried out on waterlogged leather.

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Front cover photo: Detail of a waterlogged binding from the BZN17. Photo made by Leanne de Wit

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Abstract

English

This master's thesis will dive into the drying of waterlogged leather bookbindings. This thesis project was carried out for the Master of Arts programme in Conservation and Restoration of Cultural Heritage at the University of Amsterdam.

The drying of waterlogged leather is the most important step but also the one that involves the most risks. An appropriate drying treatment is key to ensuring a true representation of the leather object as it was found. Drying can cause significant changes in the leather. Size, feel, and change of colour and appearance are all factors that can, to a certain extent, be influenced by the drying method employed. Knowing what waterlogged leather requires and choosing the best impregnation agent and drying method is very important.

Several conservators and conservation scientists have tested different drying methods, and most of which require impregnation of the waterlogged leather due to the loss of several key compounds such as fats and tannins, caused by long term stay in the water. The impregnation agent will fill the voids left by the lost compounds and will prevent the leather from becoming stiff and brittle after drying. Two of the commonly used impregnation agents are glycerol or glycerine and polyethylene glycol (PEG). PEG has many grades but PEG 400 and 600 are most often used for waterlogged leather impregnation. In the Netherlands a slightly different treatment with glycerine and Castor oil has been used regularly in the past. After impregnation the leather must be dried and the four most common ways to dry waterlogged leather are air drying, controlled air drying, freeze-drying and vacuum freeze-drying.

It is often not clear what kind of drying treatment waterlogged leather has been subjected to due to the lack of documentation. This absence of information significantly inhibits further research possibilities. Knowing what treatment has been carried out on the waterlogged leather can help further conservation of the object. This research aims to provide some tools to examine waterlogged leather with the goal to find out if it is possible to distinguish the drying method that was performed.
In association with Batavialand, Rijksdienst voor het Cultureel Erfgoed (RCE), Provincie Noord-Holland, Restaura and Nijhoff Asser Restauratie (RNA) twelve treated waterlogged bookbindings have been examined to observe and collect their specific features after drying, in order to see if the treatment can be distinguished through sensorial research. The main reason for using sensorial techniques is to make this method more approachable for conservators who do not have access to analytical techniques.

The twelve bindings have been subjected to different impregnation and drying treatments and the results show significant differences in colour, feel and smell. However, the small amount of objects and inexperience of the author in sensorial examination prevented from drawing firm

conclusions. Examining more objects by more experienced examiners, the set-up method might aid further research into the recognition of specific drying methods. For now this thesis will show that sensorial examination can aid in the distinction between different drying methods used on waterlogged leather.

Dutch/ Nederlands

Deze masterscriptie behandelt het drogen van waterverzadigde lederen boekbanden. Het onderzoek van deze scriptie is uitgevoerd voor het programma Master of Arts in Conservation and Restoration of Cultural Heritage van de Universiteit van Amsterdam.

Het drogen van nat leer is zeer belangrijk, maar tegelijkertijd een riskante stap. Een geschikte droogbehandeling is essentieel om het lederen voorwerp in de staat zoals het gevonden werd weer te geven. Het leer moet worden gedroogd en drogen kan aanzienlijke veranderingen in het leer veroorzaken. Factoren zoals formaat, gevoel en kleurverandering kunnen tot op zekere hoogte beïnvloed worden door de uitgevoerde droogmethode. Weten wat leer vereist en daarbij de juiste droogmethode kiezen is erg belangrijk.

Variaties aan droogmethoden zijn getest door conservatoren en conservation scientists, omdat het merendeel van het waterverzadigde leer impregnatie vereiste. Doordat het leer langdurig in het water heeft gelegen is impregnatie nodig om het verlies van diverse belangrijke stoffen zoals vetten en tannines te compenseren en chemische bindingen te herstellen. Het impregneermiddel zal de holten vullen die achterblijven door de verloren verbindingen en zal voorkomen dat het leer samentrekt na het drogen en stijf en bros wordt. Twee van de meest gebruikte impregneermiddelen zijn Glycerol en Polyethyleen Glycol (PEG). PEG heeft veel gradaties, maar PEG 400 en 600 worden het meest gebruikt voor de impregnatie van waterverzadigd leer, waaronder in Nederland. Het impregneren met alleen glycerol wordt in Nederland niet vaak gedaan en voorbeelden konden niet worden gevonden. Een gerelateerde behandeling met glycerol en ricinusolie wordt vaker gebruikt in Nederland. Een boekband met deze behandeling is getest. Het leer moet na de impregnatie gedroogd worden en de vier meest voorkomende methodes zijn: drogen aan de lucht, gecontroleerde luchtdroging, vriesdrogen en vacuüm vriesdrogen.

De manier waarop het waterverzadigde leer werd gedroogd is vaak niet duidelijk af te leiden doordat er weinig informatie over te vinden zijn. Dit gebrek aan informatie zorgt voor een beperking in verdere onderzoeksmogelijkheden, want met de kennis hoe leer gedroogd is, kan latere conservering beïnvloeden. Met behulp van dit onderzoek wordt geprobeerd om hulpmiddelen te bieden met als doel droogmethoden van waterverzadigd leer te kunnen identificeren.

In samenwerking met Batavialand, Rijksdienst voor het Culturele Erfgoed (RCE), Provincie Noord- Holland, Restaura en Restauratie Nijhoff Asser (RNA) zijn twaalf behandelde waterverzadigde leren boekbanden onderzocht. Het doel was om na het drogen de specifieke kenmerken van de boekbanden te observeren en de informatie te verzamelen om te zien of de behandeling gedetermineerd kan worden door zintuiglijk onderzoek. De belangrijkste reden voor het gebruik van zintuiglijke technieken is omdat deze methode benaderbaar is voor conservatoren van grotere collecties.

De twaalf boekbanden met diverse impregneer- en droogmethoden zijn getest waaruit duidelijk verschillen in kleur, gevoel en reuk te concluderen valt. Echter belemmert het kleine aantal objecten en de onervarenheid in zintuigelijk onderzoek van de auteur, dat er duidelijke conclusies getrokken kunnen worden. De methode die dit onderzoek biedt om de droogmethode te kunnen herleiden, kan een platform bieden tot verder onderzoek door middel van het bestuderen van meer objecten door ervaren onderzoekers. Voorlopig toont deze scriptie dat zintuigelijk onderzoek behulpzaam kan zijn in het onderscheiden van de gebruikte droogmethode van waterverzadigde leren boekbanden.

1. Introduction

1.1. Why this research?

This research started with the idea of looking at the drowned leather bookbindings found in the shipwreck BZN17 near Texel in the Netherlands. The considerable amount of about 30 bindings found there is quite rare, and investigation into the provenance of the bindings was desired. However, the handling and research of wet bindings requires expertise and great caution in order to prevent damaging the bindings because the wet bindings are very fragile. Furthermore, the details of the bindings are less distinguishable due to the wet and swollen leather. To investigate the bindings and to be able to handle them more safely, the bindings need to be dried first.

Several methods can be used to dry waterlogged leather in such a way that it can closely resemble the 'acceptable representation' of an object. What an acceptable representation is, mainly depends on the aim in mind for the object which can be: preserving the object, making the object presentable for display or making it accessible for research purposes. The owner will have some influence as well and might want the object to represent the state before it drowned, like a facsimile. However, these days most custodians rather show the object as it was found in the water including the damages and therefore the history of the object. The history of books is often found in the binding and the texts that it contains. In the case of waterlogged books, the book block which contains the text, normally consists of paper and/or parchment. These two materials degrade faster in water containing conditions. Waterlogged paper can be found and salvaged up to at least 73 years, relying on the found paper remains of undelivered letters at the SS Gairsoppa.[1] However, most waterlogged books found in shipwrecks are much older and the book blocks of the books are lost, as was the case for the books found in the BZN17 shipwreck. Without the paper and parchment, a lot of information about the book is lost. The only way to get any information about the provenance of the books is through the examination of the remaining components, which often are the leather cover, wooden boards, metal furniture and in some cases rope and string. The way a book was bound can give sufficient information on the provenance as has been shown by Nicolas Pickwoad and his research into bookbindings.[2] Most research however, is focused on the tooling found on book covers. A frequently used technique to date and retrace the coat of arms and tooling is by the means of a rubbing.[3] By image search and databases for rubbings, the tooling might be traced to a specific bookbinder with these tools or to a wealthy family with their own coat of arms. This technique, however, is impossible to carry out on wet leather. Another drawback is that the wet leather is swollen with water which would affect the image perceived by the rubbing. Drying the binding is therefore necessary, but since bookbindings often consist of more materials than just leather, the drying process of the binding might entail more than one may initially think.

[1] https://www.iiconservation.org/node/7476, accessed 06-08-2018.
[2] Nicolas Pickwoad (initiator), http://www.ligatus.org.uk/lob/, assessed 06-08-2018.
[3] This technique requires a piece of paper on top of the tooling, and by lightly rubbing the pencil over the paper the image of the tooling is revealed on the paper.

Next to preserving the leather bookbinding, research is one of the main reasons the wet leather needs to be dried. This drying process can be done in many ways but needs to be part of a controlled conservation method because simply air-drying the leather may result in shrunken, brittle, stiff and dark pieces of leather. Although there are many methods for conserving waterlogged leather, most procedures, after cleaning, include an impregnation phase followed by a drying phase. There are numerous varieties of impregnation solutions and just as many drying methods recorded in literature. The most commonly used impregnation agents are polyethylene glycol (PEG) and glycerol which can be used with different additives, concentrations and solutions. The drying techniques can be divided into four groups: air drying, controlled airdrying, freeze-drying and vacuum freeze-drying.

Looking into the most common drying methods for waterlogged leather became the first step in this research in order to learn more about the found characteristics of dried leather. However, this research did not include a diagnostic element required for this thesis. So only looking at drying methods was not good enough. However, when trying to find information on drying methods used in the Netherlands, I encountered that the older conservation treatments of waterlogged archaeological bookbindings were often not recorded because it was not a common practice. The lack of documentation, however, presented the question if it was possible to figure out what drying method was used.

1.2 Problems with documentation

Only recently it is custom for conservators to give a report of what conservation treatment was executed and therefore objects treated before 1990, often do not have such reports. Usually, this report informs about the object before treatment, the method of treatment that has been carried out and the used materials, so that future conservators know what has been done to the object, to review the carried out treatment and to be able to take earlier treatments into account when re-treating the object. For waterlogged archaeological leather, this documentation is often found lacking. Giving a review of the object before treatment is complicated because the leather is wet and the colour, size and details are difficult to establish and likely to change after drying. The method of conserving and drying the waterlogged leather is often not reported and recorded details about the objects are scarce. This lack of information about the conservation method and materials is a big disadvantage for future conservation enquiries. If a re-treatment of an object is deemed necessary in the future, new materials may interact badly with the impregnation residues from the original conservation.

This lack of documentation provided for an interesting subject for this thesis and the examination of 12 dried waterlogged leather bookbindings has led to the question at the forefront of this study:

The way archaeological leather of book bindings is dried, was often not documented and this can be important for future conservation: is there a way to determine this treatment after the leather has dried?

Conservators will benefit from knowing what treatment the leather bookbinding may have received, creating the possibility to adjust their methods in order to prevent damage or unwanted chemical reactions. By means of a diagnostic experiment involving several waterlogged bookbindings that have received different treatments of impregnation and drying methods, the organoleptic senses sight, touch, smell and sound, will be used to find out if different impregnation and drying treatments can be distinguished from each other.

For this research several treated waterlogged bookbindings are required to observe the different characteristics of the treated leather. First, knowing what the requirements are for waterlogged leather to be conserved in an acceptable state need to be investigated. The next step is a literature study to get acquainted with the different methods used on waterlogged leather and the reported results of the conservation treatments, with a special focus on the reported sensorial characteristics. By means of a diagnostic experiment involving several waterlogged bookbindings that have received different conservation treatments, sensorial methods will be used to examine if it is possible to find out if different impregnation and drying treatments can be distinguished from each other. The main reason for using sensorial techniques is to make this method more approachable for conservators who do not have the access to analytical techniques. The human senses aided by the common examination tools for book conservators such as a lamp and magnifying glass will be the main tools to conduct the experiment and gather information about the leather such as animal species and information about the fibres.

Within the next chapter, the general context of this research will be described followed by a chapter about the literature found on different conservation techniques for waterlogged leather. Chapter 4 will describe the methodology for the research introducing the different methods used for examining the test objects. The next chapter will contain the information gathered from the experiment followed by the results and discussion of the tests in chapter 6. The last chapter will present the conclusions.

Sub-questions to aid the research are:

- What happens to leather that has been in seawater for a long time?
- Why is impregnation of the leather needed?
- What are the most common drying methods to conserve waterlogged leather?
- What are the main differences between the methods?
- What are the characteristics of treated leather objects?

Within this thesis the focus lies on identifying the main impregnation and drying method with the goal to lay a foundation for future research and not so much on further treatment such as surface treatments, which is outside the scope of this study.

1.3 Limitations

The author is aware that there are quite some limitations to this research. The first limitation concerns the literature review where, due to limited time and linguistic skills, only English and Dutch articles were reviewed by which other methods from other countries might have been missed. Other drawbacks were the limited access to the objects and the scarce amount and variety in treated waterlogged leather bookbindings. The author is aware that dried waterlogged leather sometimes receives a follow-up treatment which may include surface waxes and another round of impregnation. These post-treatments may affect the outcome of the experiment since the appearance, feel and smell and sound of the leather may be altered and wrong conclusions about the drying method may be drawn. Lastly, the designed survey included some tests that were not achievable for some objects since the object was reconstructed or conserved in such a way that the test could not be carried out. One example is the flexibility test for bindings that had been reconstructed to look like a book again. Therefore drawing reliable conclusions from this research must be done with caution.

1.4 Characteristics of bookbinding leather

When looking at books, people are most interested in the text of the book. However, the binding and the structure can tell a lot about the provenance of a book. Researching the provenance of a book should therefore not only focus on the text but also on the paper the text was printed on, the binding technique and the binding itself. Today there is even a running project to find out the species of leather objects and the origin of that leather by DNA samples. The experiment entails taking a micro sample of the leather by rubbing the leather lightly with an eraser taking up the sample which can then be analysed. This way the origin of the leather can be distinguished and the historical lifestock farming can be put on the map.[4] Further research into this project is necessary to find out if this method is also applicable for dried waterlogged leather.

Leather is a very versatile material which can have many different qualities. Describing a good piece of leather is therefore hard to put in words. Young animals have thinner skin than fully grown animals and depending on the prospected use of the leather a skin is chosen. Different animals have different skin qualities ranging from supple calfskin, used for bookbindings to sturdy horse butt leather used for the soles of shoes. The way the skin was processed also gives the skin certain qualities. For parchment, for instance, the animal skin follows the same first steps and only the

[4] Matthew D. Teasdale, et al. "The York Gospels: a 1000-year biological palimpsest." *Royal Society open science* 4.10 (2017): 170988. Print.

tanning process transforms the skin into leather. Considering good leather for a specific purpose all depends on the species of the animal, the tannin process and the part of the skin that is taken.

Calfskin, goat, sheep, pig and cattle can all be found regularly for book covers. Along with the skin, the tanning process of the leather is important. The tanning process gives the leather part of its strength, durability and water resistance.

The characteristics of bookbinding leather are mainly that it is often made quite thin compared to other leather objects. The paring of leather can have a significant effect on the strength of the leather. The strength of the leather can be found in the dermis layer and with paring the leather very thin the strength diminishes which causes the leather to be more prone to ripping. The fact that bookbinding leather is so thin, might also ask for a more cautious approach when it has been waterlogged and is in need of a drying method. Thin leather will dry more quickly than thick leather whereas thick leather will need a longer impregnation bath in order to let the impregnation agent permeate to the core of the leather object.

2. The context of the research

2.1 How leather was made in the past

Leather is made of animal skin and in order to become leather this skin goes through an elaborate preparation process which makes the material stable and durable. To better understand the deterioration processes of wet leather, it is important to understand how leather is made and of which components it consists.

The skin structure of an animal consists of three main layers; the epidermis layer or hair layer, the dermis layer, and hypodermis layer or flesh layer. For leather only the middle layer, the dermis layer is needed. This layer contains 98% collagen fibres and has elastic and reticular fibres. The dermis layer itself can be divided again into two layers, namely the papillary or grain region which consists of fine and loosely arranged collagen fibres, and the reticular dermis layer also called the corium. This last layer is composed of more dense tissue with more packed collagen fibres which ensures the strength of the skin. Due to processing the skin into leather the inner structure of the skin is chemically altered, an irreversible process after which the processed skin is called leather.

The protein fibres in leather are made up of amino acids; glycine, proline and hydroxyproline, and together they form triple helices also known as collagen. Through hydrogen bonds with water molecules and the amino acids the structure is stabilized.[5]

[5] Nancy Mills Reid. "Polyethylene Glycol vs Glycol. The importance of molecular structure." *AICCM Bulletin* 12.3-4 (1986): 51-61.

After the skinning of the animal, the skins would be dried and/or salted to prevent them from deteriorating. This way the skins could be easily transported to a leather tanning plant where the making of leather would start. The salts would be rinsed out, the skin is further de-fleshed and dehaired after which the skin would go into a liming bath which dehairs the skin further. A following de-liming bath stops the chemical process after which bating would be carried out. Bating was done to get rid of certain unwanted proteins and this was done with enzymes found in dog or bird faeces. After this the skin would undergo one or more tanning baths for which different materials can be used. Two main groups can be distinguished in bookbinding leather; vegetable and mineral tanning. Within the vegetable tannins two types can be distinguished namely the hydrolysable and condensed tannin type. Both of these tannins are made with organic and plant material and most commonly found in leather made in the middle ages and still is the most common, especially for books (see figure 1).

Within the mineral tanning the most common materials are chrome salts but there are many more. Aluminium salts can also be used and although this process is permanent, it can be reversed. It is therefore not called a tanning process but rather alum tawing (see figure 1). Other types of tannin exist namely, oil tanning, aldehyde tanning and synthetic tanning. These types are less commonly found in bookbinding leathers.[6]

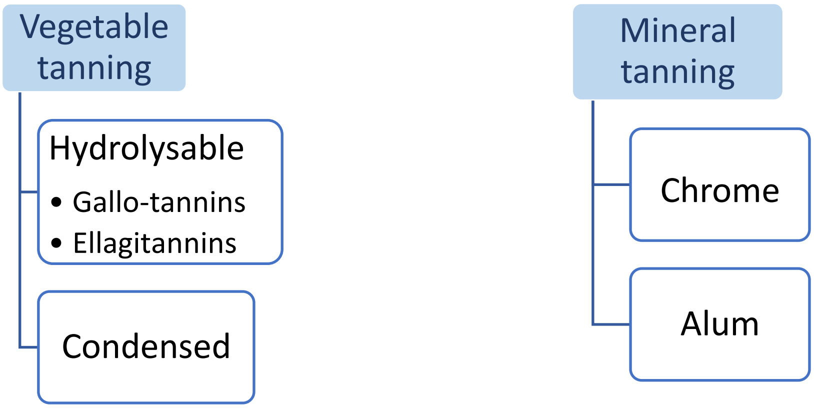

Figure 1 Diagram showing the mentioned tannin types. (figure made by author)

The main aim of tanning is making the skin more resistant to chemical and microbiological deterioration. The tannins chemically bind and fill in the empty spaces in the dermis' structure that have been caused by removing the fats, proteins and water from the skin. If these spaces would not have been filled in, the skin would dry out due to the collapse of the fibres. The tanning process causes crosslinking between the tannin and the collagen molecules and the different tannin types

[6] Roy Thomson. "The manufacture of leather." *Conservation of leather and related materials.* Eds. Marion Kite and Roy Thomson. Amsterdam: Butterworth-Heinemann, 2006. p 66-.81.

produce different types of leather.[7] The colour of the leather mainly depends on the tanning process. The tannin used partly depends on the era but at some points several methods could have been used simultaneously.

Good bookbinding leather is preferably supple and not too thick, compared to leather used for shoes and bags which has to be a lot sturdier. Common types of leather found in bookbindings are calf, goat, sheep and pig. Recognizing the species can be done by looking at the grain layer of the leather. This might prove difficult due to finishing layers but each animal type has a different hair implant. Pigskin is often easy to identify by its triangle-shaped follicle pattern. Calf or cattle does not have a significant pattern but the follicle pattern of sheep and goat form a specific line pattern. It can be tough to distinguish the type of animal. In the case of sheep and goat the follicle patterns look alike and these animals can be mixed bred as well.

Colour, follicle pattern and thickness can give information about the binding and might give clues about when the binding was made. When looking at the appearance of the leather, which is one of the key elements within this research, it is also important to look at the surface treatments like coatings, blind tooling and gold tooling. Although surface coatings can give a lot of information concerning historical bookbindings, for waterlogged bookbindings these features pose an extra challenge for identifying the conservation treatment of the leather. An impregnated and dried binding might look shiny but discerning if this was part of the original binding or caused by the impregnation agent might prove difficult. Having photos of the binding when still wet might help distinguish if the binding has undergone a surface treatment when compared to the pictures after drying. However, 'before treatment' photos were rarely made and comparing the wet binding with the dried binding is in that case not possible.

With the aim to put this research into perspective, the objects that have been part of this research and experiment will be briefly described along with the institutions the objects were part of at the moment this research has been carried out. To understand wet leather better, a waterlogged leather bookbinding still in water was examined as well to provide as a reference material for this research.

2.2 Description of a wet leather bookbinding

The first object to be described is a wet leather bookbinding that was examined by the author and her supervisor Elizabet Nijhoff Asser. This binding was given in loan to the University of Amsterdam Conservation department by Johan Opdebeeck from the RCE. This binding was kept in water and had not undergone a conservation treatment yet.

[7] Reid.: 51-61. P. 53.

The exact place where this binding was found is not clear but it was somewhere in the North Sea and it might have been a ship called the Eendracht. After it was found it was kept in a plastic container with presumably clean tap water along with some paper tissue to prevent the binding from moving around within the container. The binding was taken out of the container and placed on a metal tray for examination. When carefully examined the binding was placed on Holitex and was situated on a black and grey plastic sheet to make photos of the object.

After careful examination, it turned out that the book was made with wooden boards, presumably oak, and has messing furniture. Although previously hoped the book would still contain some paper none was found. The furniture was originally thought to be silver but it was established that this was messing. The leather cover made from calfskin is partly degraded on the tail edge. The cover has different blind tooling on the front and back cover. It seems the front cover shows a lion surrounded with a fence, and the back cover seems to depict a coat of arms. The furniture attached to the front cover was in a relatively good state opposed to the furniture on the back cover of which the bottom one is missing and the top one has some corrosion on it. The front cover furniture also holds a stylus that seems in good condition as well. The binding with its dimensions can be seen in photo 1.

Photo 1 Wet leather binding from the RCE showing the cover with measurements.
Inventory number: 2018 – NZ, Eendracht -56. Photo made by Leanne de Wit

Characteristics of the waterlogged leather were as follows: the leather was very limp and gave the appearance of falling apart with handling. The top layer of the leather had a gel-like feel to it. The front cover was in relative good condition and the wooden board was still in place, the back cover had some cracks and folds and the wooden board was missing. The leather was quite dark and the details were hard to decipher due to the very wet state of the leather. It seemed the leather was a bit swollen as well making the blind tooled patterns harder to distinguish. It is hard to describe how wet the binding was without feeling it.

2.3 The bookbindings from Batavialand

At Batavialand the author and her supervisor were welcomed and guided by Joke Nientker, a specialist in maritime materials.[8] She showed several bookbindings from the research collection of Batavialand that had been found in maritime excavations. This institution was merged out of three institutions focussing on maritime archaeological findings. The examined objects were conserved by the restoration department of the former 'Scheepsarcheologische Rijkscollectie van de Rijksdienst voor het Cultureel Erfgoed', the archaeological maritime department of the Cultural heritage agency of the Netherlands.[9]

During the visit, it became clear that, as mentioned in the introduction, the conservation reports often did not mention the drying method used on the waterlogged leather. However, Joke knew most of the treatments that have been carried out at the conservation department over the years. One of the leading leather conservators in the Netherlands was Olaf Goubitz who experimented and tested several different drying methods for waterlogged leather and who also worked for the Maritime archaeology department of the RCE.

Nientker knew that in former years the most often used procedure for waterlogged leather carried out was a PEG treatment. Next to the procedure she also explained that the treated objects are cleaned with tap water and taken apart to be able to conserve all the different materials in the best way appropriate for the materials. After drying the different components of the object, they are either stored in bags and kept together or the object will be reconstructed to represent a book again. For bindings that could not be taken apart safely, other methods were sometimes used such as Goubitz's castor oil- glycerine treatment which will be further discussed in chapter 3.2.

Next to bookbindings other objects stored in the depot were shown. Within this depot the objects are presented in glass cases and grouped by the shipwreck they were found in. Looking at some leather shoes and smelling them, the shoes could be divided into two groups depending on their smell. Knowing it was likely that one group had been conserved with a PEG treatment and the other with Goubitz' glycerine treatment, this revelation was quite useful for this research.

8 Joke Nientker is a Maritime specialist who currently works for Batavialand.
9 https://cultureelerfgoed.nl/ assessed on 04-08-2018.

During the meeting at Batavialand we got to examine about ten leather objects of which six objects were suitable for this research. The information about the bindings was provided by Joke Nientker and Arent Vos.[10] Being one of the RCE's own divers, Arent Vos gave us some information on one binding he found himself at the shipwreck BZN17, namely [MA] BZN17-6 (Object 4 in this research). The rest of the bindings of this shipwreck were, as mentioned in the introduction, found by sport divers. Several of the examined bindings turned out to have been treated with different conservation methods. The methods that were encountered will be elaborated on in chapter 3.3.

2.4 The bookbindings from BZN17

The bookbindings found at the shipwreck BZN17 near Texel were found by sport divers around 2014 except for one. Figure 2 shows a map of the part of the Netherlands indicating where the ship had sunk. These bindings have since then come into the possession of the province of North-Holland which has employed Restaura, a conservation atelier, to conserve the salvaged leather bookbindings among other objects. In February a visit to the atelier was made consisting of many professionals interested in books. Most of the bindings, still wet from the PEG solution where they were kept in, were out on display to examine. During this visit and through later contact the following information was gathered about the conservation treatment that was being carried out.

Figure 2 shows a map of the north of the Netherlands indicating where the BZN17 has sunk.(Image by Google maps)

[10] Arent Vos is a RCE specialist in Maritime archaeological shipwrecks and is currently situated at Batavialand.

There were around 30 bindings found and brought to Restaura to conserve and be prepared for display and further research. According to obtained information from Restaura, most bindings were left in water after they were found in the shipwreck and the wet bindings were wrapped in plastic foil for transportation to Restaura. Of one binding it is known that it was treated with a PEG solution before it arrived at Restaura but the drying method was unknown. This binding was quite distorted. The PEG within the binding was not removed but the binding was slightly moistened to correct the distortions.[11] The other bindings were given a PEG and freeze-dry treatment by Restaura. The exact treatment performed on these bindings will be explained in chapter 3.3.

Several of the bindings are in poor state and need further treatment to ensure safe storage, handling and display. Restaura believe further support will be needed in the form of a follow-up impregnation or the placement of an external membrane to reinforce the bindings. Before this is done however the bindings will be documented by restoration atelier Restauratie Nijhoff Asser (RNA)[12] at the request of the Provincie Noord-Holland. During a visit to RNA, the bindings were re-examined and six bindings were selected to perform the sensorial tests on. These six bindings will be further described in chapter 5 along with the results of the tests in chapter 6.

By contacting another archaeological depot, Provinciaal Archeologisch Depot Zuid-Holland' the goal was to gain information on how they had treated their waterlogged leather objects. However, focussing on saltwater objects that also had to be bookbindings greatly reduced the possible number of objects and no further information was obtained. Remarkably, the general response to my question was that the conservation method for the waterlogged bookbindings was not recorded.[13]

3. Literature review

Before discussing the literature, it is necessary to explain the methodology used in the research since the literature review will be part of this. With the help of the recorded treatments and the effects on the waterlogged leather objects reported in the reviewed literature, the characteristics of the treatment will become more clear. Investigating these characteristics will give information about the colour and feel of treated waterlogged objects and might help to link certain characteristics with a specific

[11] Elizabeth Ellen Peacock. *"Conservation of severely deteriorated wet archaeological leather recovered from the Norwegian Arctic. Preliminary results.". Conference: Proceedings of the 9th ICOM Group on Wet Organic Archaeological Materials Conference,* 7-11 June. Ed. Perr Hoffmann. Copenhagen, Denmark. Copenhagen, Denmark: International Council of Museums (ICOM). 2004. 565-577. P. 573.

[12] Restauratie Nijhoff Asser is owned by Elizabet Nijhof-Asser and Herre de Vries and is located in Amsterdam, the Netherlands. http://www.restauratie-na.nl/

[13] Email correspondence on 9-07-2018 with Mark Phlippeau, employee of the 'Provinciaal Archeologisch Depot Zuid-Holland'.

treatment. Although smell and sound are part of the sensorial test that have been carried out for this research, they have not been used as aids in the examination of the leather objects found in the literature. Taste is also excluded, in the literature as well as in this research since it might be a health hazard. Along with the information found in literature and organoleptic examination of the test objects the answer to the question if it is possible to determine a certain treatment for waterlogged leather should become clearer. Furthermore, to conduct this literature review an annotated bibliography was made that can be found in Appendix I.

Diving into the literature about the conservation of waterlogged leather it was surprising to find so many different methods for impregnating and drying waterlogged leather. The older literature seems to focus more on the impregnation method than the drying method. It is often even the case that there is no distinction made between freeze-drying and vacuum freeze-drying, making it harder to compare the literature. Also, the scope of the found articles deal with how well different conservation treatment have worked, in other words, if a certain conservation treatment was successful. Within this research the focus lies on the appearance of the leather rather than the successfulness of the treatment. However, the outcome of a treatment and the characteristics that are described in the literature can benefit this research. This chapter, therefore, explores the different impregnation methods and drying methods. To understand why waterlogged leather does need special treatment, it is important to look at what happens when leather is waterlogged first.

Not surprising is that none of the found literature specifically focuses on waterlogged bookbindings, presumably because it is quite rare to find these. It is therefore not known if the leather bookbindings found, received a different kind of treatment than other leather objects apart from verbal communication such as with Joke Nientker. Some conservators do mention the need for special conservation methods for composite leather artefacts.[14] Despite the fact that there is hardly any literature about waterlogged bookbindings, for the main impregnation and drying treatments, the literature for waterlogged leather can be used to aid this practice.

3.1 Conserving waterlogged leather

As mentioned briefly in the introduction, conserving waterlogged leather roughly consists of three steps: cleaning, impregnation and drying. The drying of the leather is the most important step since the drying phase of the treatment of waterlogged leather is the one that gives the leather object its final appearance and shape.[15] However, without an impregnation agent and without supervision the

[14] V. Jenssen. "8 - Conservation of wet organic artefacts excluding wood." *Conservation of Marine Archaeological Objects.* Ed. Colin Pearson. Oxford: Butterworth-Heinemann, 1987. 122-163. P. 136.
[15] Angela Karsten and Karla Graham. *Angela Karsten and Karla Graham, Study on the Stability of Leather Treated with Polyethylene Glycol. In Leather drying trial, a comparative study to evaluate different treatment and drying techniques for wet, archaeological leather. Archaeological conservation report.* 70 Vol. Fort Cumberland, Portsmouth: English heritage, 2011. Print. P.11.

leather may dry out, shrink and the object may be lost. The following paragraph explains the reactions within the waterlogged leather and the need for stabilization by impregnation and drying.

3.1.1 Waterlogged leather reactions

Waterlogged leather needs a different treatment compared to historical leather. Where historical leather often receives surface conservation treatments, waterlogged leather needs an internal stabilizer. Due to longtime water exposure, several sources state that the water-soluble components within the leather, such as tannins and degradation products of oils and fats may leak out of the leather, creating voids. Next to biological and microbiological degradation of the leather, chemical reactions are induced by the sea water. This leaves the leather vulnerable to water-catalysed hydrolysis, a process where the presence of water causes the hydrogen bonding between the collagen and water molecules to meet its limit. The salts present in seawater can also interact with components in the leather and materials surrounding the leather and induce further deterioration.[16]

Although water has some bad effects on the leather it also ensures the survival of the leather. The deterioration of leather is mainly caused by oxidation and hydrolysis reactions. Buried in sand, clay and seawater, these reactions are held off due to the lack of oxygen.

The voids of the dissolving components of the leather are taken in by water. As stated by Florian in her article 'The mechanisms of deterioration in leather' [17], leather contains two types of water; free water and molecular bound water. Briefly stated, free water reacts with its surroundings and bound water is attached to the collagen structure by molecular bonding. The bound water has effect on the physical and chemical properties and by removing this water, the polymers will bond to themselves, causing shrinkage and stiffness of the leather. Leather therefore needs about 20% water to keep its stability.[18] Florian mentions that freeze-drying can remove this bound water and it is therefore that freeze-drying is questioned by several conservators.[19] Here again, the distinction between freeze-drying and vacuum freeze-drying is not made.

The most important factor in conserving waterlogged leather is drying, it can cause major problems, such as shrinkage, drying out and becoming brittle. To prevent this from happening substitutes for the lost compounds and water can be introduced into the leather. Two of the most often used impregnation agents for waterlogged leather are Polyethylene Glycol (PEG) and glycerol. The article

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[16] Peacock. 565-577. 572-573. And Jenssen. 122-163. 128-129 and Reid. : 51-61. P.55-57.
[17] Mary-Lou Florian. "The mechanisms of deterioration in leather." *Conservation of Leather and Related Materials.* Eds. Marion Kite and Roy Thomson. New York, United States: Routledge, 2011. 36-57. Print. P.41.
[18] Reid. : 51-61. and Florian. 36-57.
[19] Olaf Goubitz. *"What is Wrong with Freeze-drying? In Leather drying trial, a comparative study to evaluate different treatment and drying techniques for wet, archaeological leather. Archaeological conservation report.". Research report series n. 70-2011. English heritage.* 5-8 April 1995. Eds. P. B. Hallebeek and J. A. Mosk. Amsterdam: ICOM-CC Working Group on Leather and Related Materials. 2014. 36-38. Print. And Karsten and Graham.

of Nancy Mills Reid 'Polyethylene glycol vs glycol. The importance of molecular structure' focuses on the molecular structure of these two impregnation agents. In her article she mentions different properties of glycerol and three grades of polyethylene glycol based on molecular weight. According to Reid, the length of the molecular chain, when deciding on a conservation agent, should be considered. The longer the molecular chain the longer it takes for it to penetrate the object. If the impregnation agent has not penetrated the object enough the leather could still shrink where the substitute was missing. For the more tighter packed fibre structure of leather, impregnation agents with lower molecular weight are more fitting. Another important factor to consider for the impregnation agents is the capacity to bind to the leather object by hydrogen bonding. According to Reid, the choice of impregnation agent should be made with the object and the degree of degradation in mind.[20]

Both PEG and glycerol are frequently tested and reported on in literature. Both are soluble in water and seem to do a good job of strengthening the leather structure. However, both agents are susceptible to fungal growth which is often prevented by adding an anti-mould product. The following sub-chapters will give more information on these two important impregnation agents and the reported characteristics.

3.1.2 PEG

Although there are many different methods recorded to conserve waterlogged leather the one that seems to be used most often involves impregnation with polyethylene glycol (PEG). PEG is a polyether compound with many possible grades depending on molecular weights. PEG is often said to be first used as a conserving agent for a waterlogged wooden ship, the Vasa. This ship had sunk before the coast of Stockholm.[21] After finetuning this chemical compound for conservation treatment, it came also in use for other organic objects such as leather. The article 'The conservation of archaeological leather' by Cameron, Spriggs and Will report that PEG treatments for leather were first tested at the British Museum, although with bad results.[22]

PEG comes in many possible molecular weights, ranging from 100 to in the millions. As a conservation agent for organic materials, up to 4000 can be suitable and next to a hydrogen bonding agent the higher molecular weights can also be used as a bulking agent. The use of PEG as an impregnation agent for leather has been tested many times, using different molecular weights. The higher grades have been discarded quite quickly because this is often a warm treatment and it has the

[20] Reid. : 51-61. , Emma Hocker, Gunnar Almkvist, and Malin Sahlstedt. "The Vasa experience with polyethylene glycol: A conservator's perspective." *Journal of Cultural Heritage* 13.3 (2012): S175-82. Print.p. 59.

[21] Emma Hocker, Gunnar Almkvist, and Malin Sahlstedt. "The Vasa experience with polyethylene glycol: A conservator's perspective." *Journal of Cultural Heritage* 13.3 (2012): S175-82. Print. P.156.

[22] E. Cameron. "The conservation of archaeological leather." *Conservation of Leather and Related Materials.* Eds. Marion Kite and Roy Thomson. New York, United States of America: Routledge, 2011. 244-263. Print. P. 248

tendency to became hard after drying. This is because the higher grades of PEG come in solid form whereas the lower PEG grades are in liquid form. Most articles agree that the best molecular weights of PEG for leather are 400 and 600.

Although the result of PEG impregnation also relies on the drying method, Wouters (1986) and Goubitz (1995) both record a dark object as a result. PEG is also said to corrode certain metals and therefore might be damaging to metal furniture found on bookbindings. This is something to keep in mind when looking at the bookbindings. At Restaura the metal furniture of the bookbindings were coated in a purple coloured silicone rubber to prevent the PEG from coming in contact with the metal. According to Cameron, the increase in molecular weight results in a decrease of polarity of the PEG concluding that the lower PEG grades have a higher hygroscopicity. A high hygroscopicity expresses itself in a moist feeling because water molecules from the air are attracted to the PEG molecules.[23] PEG has been recorded as having a corrosion reaction with objects containing iron. For composite objects like leather bookbinding precautions should be taken to prevent the metal from corrosion caused by PEG.[24]

3.1.3 Glycerol

Glycerol or glycerine, $C_3H_8O_3$, is used for many purposes such as the food industry, medical industry and personal hygiene. The compound has a sweet smell and taste and a high hygroscopicity.
The article of Sully and Suenson-Taylor, 'a condition survey of glycerol treated freeze-dried leather in long term storage' from 1996, informs the reader about glycerol treated waterlogged leather from the Museum of London (MOL). Although the main focus of this article lies on the implementation of the CARS condition survey, the article gave useful information on performed conservation treatment.

What Sully and Taylor rightly point out is that the chosen treatment should also depend on the final goal of the treatment being either stability of the object as it is now, or restore the object to what it would likely have looked like before it was found. The objects surveyed were found in fresh water, which may show different characteristics from objects found at sea salvages.[25] The treatment carried out at the MOL have been revisited in 2013 and the results of the treatment seem to have been successful since no significant changes were noted.[26]

Glycerol as a waterlogged leather impregnation agent is used quite often judging from the literature, and for quite a good reason. Glycerol works as a kind of anti-freeze, cryo-protected, and

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[23] Hocker, Almkvist, and Sahlstedt. : S175-82. P. 176
[24] Jenssen. 122-163. P. 133
[25] Dean Sully and Kirsten Suenson-Taylor. "A condition survey of glycerol treated freeze-dried leather in long-term storage." *Studies in Conservation* 41.-1 (1996): 177-81. Print.177
[26] Amanda Watts, Liz Goodman, and Jill Barnard. *"Forty Years of Glycerol Treatment Revisited". Proceedings of the 12th ICOM-CC Group on Wet Organic Archaeological Materials (WOAM) Conference Istanbul 2013,* Eds. Tara Grant and Clifford Cook. Istanbul, Turkey. Canada: International Council of Museums- Committee for Conservation (ICOM-CC), Working Group on Wet Organic Archaeological Materials. 2016. 1-334. Print.

therefore works quite well with freeze-drying. It also works as a stabilizer and humectant which means it regulates the moisture content within the leathers collagen structure and through hydrogen bonding binds water molecules to the collagen structure. Glycerol is therefore a hygroscopic substance and leather treated with it, may be perceived as slightly moist.[27] The method for glycerol treatment is comparable with the PEG treatment method using immersion to let the agent penetrate the leather object. Sadly, the impregnation method with a mainly glycerol base is not often carried out in the Netherlands and test objects with this impregnation method could therefore not be included in this research.

3.1.4 Trials comparing impregnations and drying methods.

From 1980 onwards, the question about how to conserve waterlogged leather became more important. One of the first articles about testing different impregnation methods followed by different methods of freeze-drying for waterlogged leather was that of Jan Wouters, from 1986.[28] Although outdated, he converses some important information about different treatments that were carried out during his time. The article has a quite strong chemical viewpoint but he explains some phenomena quite well, such as the process of vacuum freeze-drying, also called lyophilization. Briefly, the steps to vacuum freeze-drying are as follows: first, the object is quickly frozen, then the object is put under a high vacuum and lastly, the temperature is increased slowly to dry the object. The trials he carried out compared to more recent tests are quite elaborate and seem in some ways more complicated than necessary compared to more recent studies. However, he explains the procedure sufficiently and elaborates in great detail about how the treatment was carried out. One detail he fails to mention though is why he pre-treated the leather objects with EDTA, something that seems quite important. According to Angela Karsten and Karla Graham the use of an EDTA pre-treatment is regularly done but most literature often fail to converse why. In the article 'the leather drying trial', Karsten and Graham mention their research into the reasons for, and the effects of EDTA as a pre-treatment for waterlogged leather. Their conclusion is that pre-treatment with EDTA apparently lightens up the colour of the treated leather, gives the leather more flexibility and helps against corrosion of metal fittings on the object when followed by an impregnation.[29]

The leather drying trial reflected on by Karsten and Graham was carried out in 2009-2010 and is therefore more recent then Wouters trials. It focuses on the most used impregnation agents PEG and Glycerol and compares four different drying techniques; air drying, controlled air drying, freeze-

[27] Sully and Suenson-Taylor. : 177-81. P. 180.
[28] Jan Wouters. *"A comparative investigation of methods for the consolidation of wet archaeological leather. Application of freezedrying on polyethylene glycol impregnated leather.". Symposium on ethnographic and water-logged leather,* 9-11 June 1986. Ed. P. B. Hallebeek. Amsterdam, Netherlands. Amsterdam, Netherlands: CL Publication; International Council of Museums (ICOM). 1986. 61-69. Print.
[29] Karsten and Graham. P. 8.

drying and vacuum freeze-drying. To test the hypothesis of the use of EDTA, this component was also added to the testing. The parameters of the test were measured and compared by looking at shrinkage, flexibility and appearance. As an extra, they also placed time and cost into the perspective. An overview of the recipes used in this trial and recipes found in other literature can be found in Appendix II.

The results concerning the flexibility of the leather objects showed that the samples that were not impregnated and the samples with PEG had decreased in flexibility. Although measuring the flexibility with the CARS method did have the drawback of being very subjective since the evaluator decided whether the leather is appropriately flexible. The leather drying trial also used to CARS overall condition score where the highest decrease of condition was found for items that were vacuum freeze-dried. It was concluded that the results on account of appearance were overall quite the same. Only pieces pre-treated with EDTA seemed to have a slightly different colour, a slightly red-brown hue, from the rest of the objects although it is not certain if the original colour of the object was already different. The change of colour is something that was predicted with the incorporation of EDTA although instead of a red hue it was thought the colour would become lighter. The objects that had been vacuum freeze-dried were initially perceived more dry and brittle when compared to the other objects although after time the appearance changed to resemble the other samples.
From this leather drying trial, the main conclusion that was drawn about the impregnation phase is that:

> *"Although 20% Glycerol impregnation resulted in slightly less shrinkage compared to 20% PEG, glycerol is more hygroscopic than PEG, which is an important consideration for future storage or display. As can be expected, the 'No Impregnation' samples resulted in rather high shrinkage values and for that reason, an impregnation should always be carried out."*[30]

The conclusion for the drying phase is that all the methods, except for controlled air drying, worked quite well and showed good results.

In the article 'Conservation of wet organic artefacts excluding wood' by V. Jenssen the same four drying methods are mentioned as in the 'the leather drying trial'. The author states that controlled air-drying and vacuum freeze-drying quickly remove water which causes the leather fibres to rapidly contract resulting in shrinkage and hardening of the object.[31] Although the article is quite dated, the

[30] Angela Karsten and Karla Graham. *Angela Karsten and Karla Graham, Study on the Stability of Leather Treated with Polyethylene Glycol. In Leather drying trial, a comparative study to evaluate different treatment and drying techniques for wet, archaeological leather. Archaeological conservation report.* 70 Vol. Fort Cumberland, Portsmouth: English heritage, 2011. Print. P. 34.
[31] Jenssen. 122-163. P. 129.

author describes the different methods of impregnation with PEG and glycerol and combining them with the drying methods air-drying and freeze-drying.

3.2 Two methods used in the Netherlands

Already mentioned, one of the leading conservators of archaeological leather in the Netherlands was Olaf Goubitz. He has carried out many conservation projects including treatments for waterlogged leather. Because leather was something often badly understood within archaeology, Goubitz mentions in his article 'What's wrong with freeze-drying', that because of this leather was also badly conserved.[32]

One of the conservation treatments for waterlogged leather he invented and recorded in the same article, was carried out as followed: first, the leather was cleaned and left to air dry to about 80% humidity followed by impregnation with PEG 600 (60%) and water for about 36 hours. The way he measured the humidity was by feel and 'experience'. Another of Goubitz methods was a treatment with castor-oil. This treatment also included cleaning and air-drying but instead of PEG 600 a mixture of castor oil (35%), glycerine (15%) and tertiary butyl alcohol (50%) was used. Goubitz used this particular treatment when it was necessary to glue the leather pieces since the PEG-treated leather did not take glue well. Another reason for choosing this treatment might have been the fact that this treatment, compared to PEG does not react badly with metal elements. The drying of the objects was mostly done on cheap paper because, according to Goubitz, 'using expensive blotting paper for this is a waste of money'.[33]

According to Marquita Volken, who reassessed leather objects treated with these methods after several years, the leather was still in stable condition, supple and pliable although the PEG-treated leather was slightly lighter in colour.[34] Goubitz mentions that PEG 600 is often used in the Netherlands and that this has partly to do with the atmospheric humidity in the Netherlands. PEG 400 would, according to Goubitz "perspire".[35]

3.3 Encountered recipes

Within the literature review several recipes or methods for treating waterlogged leather are mentioned. The several objects that are part of this research have been treated with different methods as well. In this section the different treatments of the examined objects will be explained. In Appendix

[32] Olaf Goubitz. "The Conservation of Archaeological Leather." *Stepping through Time, Archaeological Footwear from Prehistoric Times until 1800.* Zwolle, The Netherlands: Foundation for Promoting Archaeology (Stichting Promotie Archeologie), 2001. 127-130. Print.
[33] Goubitz. 36-38. 37.
[34] Marquita Volken, Practical approaches in the treatment of archaeological leather. In: n.e., *Leather wet and dry:* current treatments in the conservation of waterlogged and desiccated archaeological leather, ed. Barbara Wills ArcheType, 2001) 93-37.37-40.
[35] Goubitz. 127-130.

I, two tables shows the different impregnation methods and drying methods found in literature. The treatment recipes of the leather drying trial have been described here as well along with the recipes of the treatments carried out on the sample objects.

Karsten and Grahams' Leather drying trial:
The samples pre-treated with EDTA were immersed in 5% Na_2EDTA for two hours and rinsed. The impregnation solutions were 20% PEG400 and 20% glycerol and the object was immersed in the solution for three days. How vacuum freeze-drying works has already been explained. The drying method air-drying involves literally that, drying the object to the air. Controlled air-drying was obtained with the aid of saturated salt solutions and freeze-drying the objects was done in a domestic freezer.

BZN17 bookbindings:
The wet bindings were carefully cleaned with demineralised water and Acticide, a solution to prevent mould growth. After cleaning, the bindings were put in a 20% PEG 600 solution with 80% demineralised water at a temperature of 21-25°C. The normal procedure at Restaura is to leave the leather objects in PEG for four to six months, however, due to several causes the drying phase was postponed leaving the leather objects in PEG for 18 months, however no ill effect of the prolonged treatment was detected. With this process the bindings were also desalted. To ensure safe handling and storage within the basins, the bindings were put on cotton rags on top of each other. The basins were checked every month to ensure the stability of the 20% PEG solution and to check for moult. Freeze-drying was used as a drying method for all these bindings. To prevent curling up during the drying process the bindings were prepared separately into a package containing 3 layers of hardboard, the binding was lain open and flat on the board with rope supports in the ribs on the spine. On top of the front and back cover was put another layer of board leaving the spine open. This package was then secured with elastic bands to prevent distortion while drying the leather. The bindings have first been frozen quickly at a temperature of -40°C followed by vacuum freeze-drying at -28 °C. The process carried out included the leather bindings and wooden objects and each day the temperature was raised with 1 degree. The whole process has taken 54 days to complete. The vacuum freeze-drying machine used was custom-made for Restaura.

The reported results after vacuum freeze-drying was significant in the colour change, the change in flexibility and rigidness. Compared to the dark colour of the wet leather before treatment, the bindings now seem to have a more distinct hue that can be associated with leather. The flexibility of the leather is slightly less than before but is said to be positive regarding to the object. Right after drying the bindings might seem quite dry but this is expected to change due to the hygroscopicity of the PEG.

After the drying phase, a few bindings have received a coating of PVAc. This after treatment is meant to stabilize the binding further and to make the binding more resilient to climate change.

Batavialand bookbindings:
The examined bindings at Batavialand have received different treatments including:
A treatment where the object was first rinsed with tap water, then left to air-dry till about 80% humidity and followed by a bath of PEG 600 and water at 50/50% (v/v) for a duration of at least 48 hours. The impregnated objects were then left to air-dry.

Another method used was a warm PEG method often used for wooden objects. This includes a warm PEG 3000 bath.

Lastly, the Goubitz method mentioned above was also used. The objects were first 'cleaned' with white spirits to get rid of the remaining water within the object. The object was then immersed in a bath of containing castor oil (35%), glycerine (15%) and tertiary-butyl alcohol (50%).

4. Methodology

4.1 Method of the research

Important to mention is that most of the literature, understandably, discusses the results of the waterlogged treated leather and not so much the specific characteristics of colour, feel and smell. Within this research the focus lies on the recognition of the most commonly used conservation treatments for waterlogged leather.

To be able to conduct the experiment a methodology had to be composed. To make the experiment repeatable and usable for conservators, the use of analytical techniques was excluded. Analytical techniques often require samples which may be quite invasive and, although the research of Gabriele Zink represented in the article 'Shrinkofobia', focused on conservation outcome, it showed that sensorial examination can tell a lot about the piece of leather. In her research, the help of analytical techniques could not find much more information than was already found during sensorial examination by leather experts.[36] Without analytical techniques, the examination will be simpler and cheaper.

To be as thorough as possible during the examination of the test objects, sensorial examination was carried out. With the aid of portable magnifiers, a LED light and a bone folder the objects were

[36] Gabriele Maria Zink. *"Shrinkophobia - the conservator's natural fear of shrinking leather". Proceedings of the 12th ICOM-CC Workinhg Group on Wet Organic Archaeological Materials Conference,* 2013. Eds. Tara Grant and Clifford Cook. Istanbul. Canada: International Council of Museums (ICOM), Committee for Conservation, Working Group on Wet Archaeological Materials. 2016. 327-334. Print.

examined. Because there are several treatments for of waterlogged leather and several methods to conduct the treatments, it was a challenge to find out what the performed treatment exactly entailed by just sensorial examination. To aid the investigation it is necessary to search for clues on what treatments have been performed over the years at the institution where the object was treated. With this information examining the objects may guide you to the performed treatment carried out on that specific object. Because sensorial examination is very subjective it can be helpful to compare the bindings with each other. This method is however only possible when working on a small scale. Examining many objects would have to be done by several people making this kind of examination more complicated. Providing a well-designed survey along with clearly defined definitions would be key when large-scale examination is required.

Organoleptic or sensorial examination is the first step when dealing with an object. There are several disciplines where the senses are used to examine objects, humans or food. For cultural heritage the senses are also the first step in determining the condition of an object. Most of the senses can be used to determine the condition/state of a treated waterlogged object as well. However, defining the terms and conditions is challenging due to subjectivity. The articles of Vildan Sülar & Ayşe Okur, 'Sensory evaluation methods for tactile properties of fabrics'[37] and Susanna Harris's 'Sensible Dress: the Sight, Sound, Smell and Touch of Late Ertebølle Mesolithic Cloth Types'[38] focus on sensory examination of textiles and fabrics but do define useful condition terms for this thesis experiment. Both articles point out that there are different methods for sensory examination and that defining the definitions is the key for this kind of research. According to Sülar two methods can be used for sensorial evaluations: Using the chosen terms and rating the object according to them, and secondly, compare the test objects with each other.[39] For this experiment the second method was used as a guide along with a descriptive method by writing down what is perceived during the examination. Because the tested object were not all examined in the same place not all objects could be compared with each other. A descriptive account of the object is given for each object and 'ratings' of different qualities of the bindings were given by comparing the object to each other and recorded in the 'tables' found in sections 5.2.1. and 5.2.2.

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[37] Vildan Sülar and Ayşe Okur. "Sensory evaluation methods for tactile properties of fabrics." *Journal of Sensory Studies* 22.1 (2007): 1-16. Print.
[38] Susanna Harris. "Sensible Dress: the Sight, Sound, Smell and Touch of Late Ertebølle Mesolithic Cloth Types." 24.1 (2014): 37-56. Print.
[39] Vildan Sülar and Ayşe Okur. "Sensory evaluation methods for tactile properties of fabrics." *Journal of Sensory Studies* 22.1 (2007). p.7.

4.2 Sensorial examination – tactile, visual, smell and sound

As a human, we have five senses to perceive the world around us: touch, vision, smell, sound and taste. Although taste is a sense that can be used in some cases in conservation, for this experiment it is ill-advised since there are chemicals involved which can cause health hazards.

Sound is a sense that is often used as an examination skill in for instance paper and textile identification although it is difficult to define the conditions and therefore a challenge to use within this experiment. However, using the rating skills defined in Sülar & Okur's article an appropriate method was found by only recording two opposites.[40] By categorizing the perceived sound within two groups: low sound and high sound. A comparison of the sounds that were produced lifting the binding and tapping it with a bone folder on different places, either a high or low sound was recorded. A low sound will correspond to a more limp, moist binding and a high sound can indicate a dry inflexible leather. The sound produced depends on wavelengths and it is established that short wavelengths produce a high sound.

Tactile and visual senses can be distinguished as the most important within this experiment. The feel of the treated object can give quite some information if one relies on evidence found in literature. Vildan Sülar & Ayşe Okur propose the following terms to describe tactile experience: "softness," "stiffness," "roughness," "tightness," "fullness" and "pliable".[41] These definitions will also be used in this experiment along with "moist" and "dry". A moist feel indicates a high hygroscopicity while a dry feel might indicate a dry and stiff leather. Stiffness and pliability of an object can be perceived by means of bending it slightly. The experience of roughness and smoothness can be defined by registering the resistance of the leather while rubbing it lightly. The number of indentations and ridges determine the rough or smooth feeling of the leather. Within the proposed experiment the tactile experience can be expected to reflect on the combination of impregnation and drying method. For thigtness and fullness other terms were used, namely cohesivity and friability. These two terms are introduced with the CARS rating scale and better fit the purpose of this experiment.

With visual senses colour can be perceived which might give clues on the treatment used on the leather. Although it must be kept in mind that with waterlogged leather, the colour of the leather object before it drowned is not known. It is therefore difficult to establish the original colour of the leather and hence tough to determine if the treated leather has changed/ darkened due to the conservation treatment, the long stay in the water or if it might be that the leather was already quite dark before the book drowned. Colour, abrasion, smoothness, dullness and shine can all be perceived

[40] Vildan Sülar and Ayşe Okur. "Sensory evaluation methods for tactile properties of fabrics." *Journal of Sensory Studies* 22.1 (2007).
[41] Vildan Sülar and Ayşe Okur. "Sensory evaluation methods for tactile properties of fabrics." *Journal of Sensory Studies* 22.1 (2007). P.4.

by visual examination. A high shine can indicate a high dose of impregnation agent, but it can also mean that the binding had a surface coating before it drowned. With the aid of a small magnifying glass (60x magnification, used for currency) and LED light the surface of the objects was examined. Within the proposed experiment sight can be expected to reflect on the combination of impregnation and drying method.

The last of the five senses is smell and although one might not necessarily think to smell the treated object, it may give some clues on the kind of conservation treatment that is carried out. Although PEG is noted in most safety data sheets as odourless, the shoes at Batavialand seemed to give out a distinctive smell. The smell could be described as a sharp sour smell. Within several disciplines odour evaluation is used and specific characteristics of smell have been defined to find a way to define smell as objectively as possible. These specific characteristics can be found on the odour descriptors wheel, mentioned in “"Odor Basics", Understanding and Using Odor Testing." by Charles M. McGinley and Michael A. McGinley.[42] For this experiment, only two categories have been used, namely sour and sweet. The way the objects were smelled was by holding the object about 10 cm from the nose. The smell of the objects might have been caused by additives used to prevent mould growth but smell will be tested within this experiment because it might prove a good way to separate the samples in treatment groups. It would in this case probably reflect only on the impregnation method and not the drying method.

4.3 CARS

As mentioned above, sensorial examination will be the main tool for this research. Along with the basic sensorial tests, the CARS condition score method will also be incorporated into the research. CARS stands for Criterion Anchored Rating System and the main principle is that surveyed object will be rated on three factors. Together the rates will form the overall condition score which can be used to compare the conditions of the surveyed objects. The condition score was composed by Dean Sully and Kirsten Suenson-Taylor. The survey focuses on three criteria for leather namely; cohesivity, friability and flexibility. These three criteria are rated separately with a low number resembling a bad condition and a high number for a good condition. The overall score given for a specific object represents the condition with a minimum of 3, very bad condition and a maximum score of 10 pointing to a good condition. For each criterion, a definition provides the surveyor with the information needed to grade the object. The outline of the survey can be seen in figure 3.

[42] Charles M. McGinley and Michael A. McGinley. *""Odor Basics " , Understanding and Using Odor Testing.

".* The 22nd Annual Hawaii Water Environment Association Conference Honolulu, Hawaii: 6-7 June 2000. Print.

Cohesivity	1	2	3	4
Consider the leather on a macro scale and the integrity of the object as a whole. Look at vulnerable areas liable to loss. Bear in mind the nature and shape of the object.	Many fragments readily detached during handling.	Several fragments readily detached during handling.	Minor areas of vulnerable fragments	Leather intact no vulnerable fragments.

Friability	1	2	3	4
Diagnose primarily on the grain surface only. However some account should be taken of exposed edges. Where grain surface is no longer present, define condition of the remaining fibre surface.	Fibres easily detached during handling, resulting in total loss of surface.	Greater part of surface and exposed edges liable to loss.	A few areas of grain surface liable to loss of fibres.	Grain surface intact no loss of fibres.

Flexibility	1	2
Flexibility must be appropriate to the object. If flexible, not so weak as to be damaging to the object. If inflexible not so brittle as to allow damage to occur during handling.	Unacceptable - weak or stiff and brittle.	Flexible

Figure 3 showing the different definitions and their rating according to the CARS rating system. This table was copied from the article of Sully and Suenson-Taylor (1996).

This system for determining the condition of waterlogged leather is quite often used according to the reviewed literature. The CARS system was invented specifically for assessing large quantities of leather objects and this survey can be used on treated and untreated leather. Using the survey in this manner can give a better picture of the results of the treated leather. Although this system is more focused on the overall condition of the leather, the main principle for looking at the cohesivity, friability and flexibility is quite important when looking at treated leather. The way the fibres are arranged, might tell something about the treatment that was carried out. The cohesivity and the flexibility of the treated object might give clues on the drying method employed.

So, although the condition score will not have a leading part in this experiment, it is always useful to look at the condition of the object and within this research it is suspected to give some useful extra information next to the sensorial examination.

4.4 Expected results

Within the literature about waterlogged leather treatments, the aim lies on the conservation treatment and whether the treatment was successful or what treatments are considered to give the most desirable results. From the information found in the literature, expected results can be outlined for the ability to compare them with the actual results gathered in the research of this thesis.

From the information obtained from the different institutions, the used treatment for the examined bookbindings was known beforehand. For the BZN17 bindings treated by Restaura it is known that they used PEG 600 as an impregnation agent followed by vacuum freeze-drying. Within this experiment the aim is, therefore, to note the characteristics of the bindings with the goal to get an idea of the features of this specific drying method.

For the bindings examined at Batavialand it was less clear what impregnation and drying method were carried out. Joke Nientker knew two common practices but finding out the actual treatment took some searching in the reports. The bindings were initially examined without knowing the carried out drying method. After the main examination, the reports were reviewed revealing most, but not all conservation methods used. In the end the objects viewed could be categorized in three groups. For these bindings the characteristics were noted down as well.

The expected results would be to find common features among the bindings that have been treated in the same manner. If this is the case, these common features can be used as a guideline when looking at a waterlogged binding without knowing the drying treatment. If the characteristics do not match it can be concluded that a drying treatment for waterlogged leather cannot be distinguished through this kind of sensorial examination but the research might benefit further research into this subject.

4.5 Step by step outline of the experiment

To make clear how the experiment was carried out the following steps were taken to compose a thorough account of the examined object:

General description:

1. Inventory number
2. Place found
3. Known history of the object
4. Conservation method used
5. Take the measurements of the object
6. Thickness of the leather
7. Determine the species of the animal
8. Describe the binding
9. Describe the furniture (where applicable)
10. Describe the tooling (where applicable)

Sensorial examination:

11. Vision – Describe the colour of the binding
12. Vision – Describe deterioration characteristics: cracks, folds, missing pieces
13. Vision – describe the look of the leather: shine, dull, abraded
14. Vision – Describe corrosion (where applicable)
15. Smell – Describe the smell

16. Tactile – Describe the feel of the object: moist or dry to the touch
17. Tactile – Describe the suppleness of the object: easy or hard to bend
18. Tactile – Does the leather feel rough or smooth to the touch
19. Sound – When tapping the leather, does it produce a high sound or low sound?

CARS examination:

20. Friability – consider the leather and its integrity as a whole: how vulnerable does the leather look?
21. Cohesivity – Look at the grain layer of the object: how is the condition of the leather fibres?
22. Flexibility – is the flexibility of the leather appropriate to the object?

For the CARS examination the condition score as explained above, in figure 3, will be applied.

5. The experiment

Within this chapter, the conditions in which the experiment was carried out and the characteristics of the bindings will be recorded. For each of the 12 objects one photo has been included. More detailed photos of some of the specific features found on a binding, can be found in Appendix III. The noted details will be processed and put in excel sheet to give a clear representation of the found results. The information from the records of Batavialand was limited and therefore some information will not be included.

5.1 Conditions during the experiment

The conditions in which the bindings were examined and stored are as follows:

Batavialand – The objects at Batavialand are kept in special glass cases along with other objects found in the same shipwreck. There is therefore a possibility of off-gas from other objects but the glass cases are ventilated. The climate in the storage room is kept cool and there is a form of air control although no measurements of the temperature and relative humidity have been carried out yet. This is something that is in the process of being introduced. The objects were examined in the storage room so no climatizing was needed. Worth noting though are the conditions of the old storage area in the old building. The building was shaped in the form of the body of a ship laying up-side-down. In 2007-2008 research was done by the Technical University of Eindhoven (TU/E) into the climate of the room and this showed that the conditions of the room were not ideal to house the archaeological objects. Improvements were made but the stored objects have been subjected to the less than optimal climate for several years.

Restaura – The climate conditions at Restaura are monitored and most of the time the bookbindings were at Restaura they were kept in the PEG. After drying the bindings were kept in plastic bags with holes and stored into cardboard boxes. Quite soon after drying the bindings were moved to RNA for examination.

RNA – The climate conditions at RNA are monitored at 18-20° C and a relative humidity of 55%. Due to the very hot weather during the day of examination the temperature was around 26°C with a relative humidity of 55-60%. The bindings were left to climatize and were then examined using the methods explained in chapter 4.

5.2Characteristics of the examined objects

Within the following paragraph the details of each of the examined objects are recorded. The information given in points 1 to 4 was provided by the contact persons of the institutions the bindings were treated. Points 5 to 10 give more information on the binding while points 11 to 22 are part of the sensorial tests and the CARS rating tests.

5.2.1. Leather bindings from the RCE

Object 1:

Photo 2 Batavialand binding, [MA] SO1 32058. Photo from their record.

1	Inventory number	[MA] SO1 32058
2	Place found	Shipwreck Scheurrak SO1
3	Known history	The ship had sunken in 1593 according the record.
4	Conservation method	Cleaned with tap water, air-dried till 80% humidity, impregnated with PEG 600 and finial air-dried
5	Measurements	14 x 20 cm
6	Thickness of piece	1 mm
7	Animal species	Calf
8	Description	The binding consists of a leather cover, metal clasps and wooden boards. All the different components have been conserved separately. The turn-ins are still recognizable. One corner of the leather is loose. There are also three leather fragments presumed to be leather straps. The loose corner was not ripped off but it is a corner that was attached to the rest of the leather by either the leather maker or bookbinder because the piece of leather was not big enough for the

		book cover. Evidence for this is the un-tooled edge of the corner where the leather overlapped. This book is presumed to be a bible.
9	Furniture	The clasps are made of messing and consist of two hinges and three nails.
10	Tooling	Decorated with clearly visible blind-tooling depicting men, women, geometric figures and the repeating words SPES, FORT, FIDES.
11	Colour	Brown of colour.
12	Deterioration	The leather has some deterioration at the right side.
13	Appearance	The leather probably had a surface coating when it was in use due to the smooth appearance of the surface but the shine has mostly gone.
14	Corrosion/abrasion	There are some abraded parts where the grain layer is visible.
15	Smell	Sour, unpleasant smell.
16	Feel- moist of dry	Little bit moist and sticky to the touch.
17	Suppleness	The leather is quite supple.
18	Rough or smooth feel	Smooth to the touch.
19	Sound	Low sound
20	Friability	[3] Some parts look a bit fragile, but the binding is mostly in good order.
21	Cohesivity	[3] Just a few areas of grain surface visible and the fibres do not easily come loose.
22	Flexibility	[2] The leather has a very nice flexibility.

Object 2

Photo 3 Batavialand binding, Z1954- X1122 / 2391. Photo from their record.

1	Inventory number	Z1954- X1122 / 2391
2	Place found	Shipwreck E165NOP near Nagelen.
3	Known history	The ship probably sunk at the end of the 18th century/start 19th century.
4	Conservation method	Not known.
5	Measurements	5 x 11 x 15 cm.
6	Thickness of piece	Not possible to measure due to the reconstruction made in book format.
7	Animal species	Calf.
8	Description	This binding has been reconstructed to look like a book again. New board have been inserted to strengthen the leather cover along with new cords to fill out the spine ribs and to attach the boards. The bookblock core is made of cardboard. (see appendix III) The book has some nice blind tooling and used to have fastenings of which only the messing catch plates are still attached to the leather and part of the leather straps are still attached by decorated nails. (See appendix III).
9	Furniture	Decorated messing furniture in good condition.
10	Tooling	The blind tooling has pomegranates in the corners and a stamp of a shepherd in the middle.
11	Colour	The leather is of brown colour.

12	Deterioration	The leather is slightly abraded and has some tears. Specially the spine leather has some cracks and white crystalline-like residue is visible in the cracks of the spine.
13	Appearance	The leather probably had some surface coating but most of the shine is gone.
14	Corrosion/abrasion	The furniture seems in good state with no corrosion material of the metal on the leather. The leather has some white residue especially on the spine. It does seem to be a fat that can be found in the cracks on the spine. Might be a surface treatment.
15	Smell	No apparent smell.
16	Feel- moist of dry	Dry to the touch but with a light smooth but sticky touch.
17	Suppleness	Not tested since the leather was fitted with new boards and attached to a cardboard core to represent a book.
18	Rough or smooth feel	Smooth feel except for the abraded areas. The spine has a lot of cracks which you could feel.
19	Sound	Not tested since the leather was fitted with new boards and attached to a cardboard core to represent a book.
20	Friability	[4] The leather was in relatively good condition with only a slight risk for the loss of material.
21	Cohesivity	[4] The fibres were partly visible at the joint but seemed well packed together.
22	Flexibility	Not tested since the leather was attached to a cardboard core to represent a book.

Object 3

Photo 4 Batavialand Binding, [MA] BZN3 -20. Photo taken from their record.

1	Inventory number	[MA] BZN3 -20
2	Place found	Burgzand Noord 3.
3	Known history	The ship has probably sunk around the middle of the 17^{th} century.
4	Conservation method	Cleaned with white spirit, impregnated with castor oil, glycerine and tertiary-butyl alcohol. After which the binding was air-dried.
5	Measurements	16 x 11 x 6 cm.
6	Thickness of piece	No measurable due to the reconstruction in book format.
7	Animal species	Calf
8	Description	This binding is surprisingly light in colour and the leather binding is reconstructed to represent a book again. The covers are attached to a very light weight block of wood. The book has clasps that can still be open and closed. Some transparent glue residues where the leather was glued to the wood.
9	Furniture	The furniture is made from messing and consist of clasps and catch-plates that are decorated.
10	Tooling	The tooling appears dark against the light colour of the leather. The tooling is mostly in blocks and stripes with geometric forms.
11	Colour	Light yellow-brown.
12	Deterioration	In relatively good condition.
13	Appearance	The leather has a light shine.
14	Corrosion/abrasion	'Concretie' has formed around the fastenings.
15	Smell	Bit of an oily smell. More sweet then sour.
16	Feel- moist of dry	Dry to the touch but not bad and less dry than object 1 and 2.

17	Suppleness	Around the corners it feels quite supple but difficult to discern due to the reconstruction of the binding.
18	Rough or smooth feel	Nice smooth feel.
19	Sound	Not possible to test due to the reconstruction into a book format.
20	Friability	[4] Very good condition.
21	Cohesivity	[4] Very good condition.
22	Flexibility	[2] It seems the leather is approximately flexible although hard to discern.

Object 4

Photo 5 Batavialand binding, [MA] BZN17-6. Photo made by Leanne de Wit.

1	Inventory number	[MA] BZN17-6
2	Place found	Burgzand Noord 17, near Texel.
3	Known history	Ship probably sunk in the 17th century. At least after 1641 indicated by dendrochronology. The binding found at the same shipwreck as many other book bindings from the BZN17. This book was probably found in another spot though. This binding was found by Arent Vos.
4	Conservation method	Cleaned with tap water, air-dried till 80% humidity, impregnated with PEG 600 and finial air-dried.

5	Measurements	11,8 x 7,0 x 3,0 cm.
6	Thickness of piece	1 to 2 mm.
7	Animal species	Calf
8	Description	Binding is in good condition, no furniture and no boards found. Blind tooled binding. According to the records, this book was possibly a small bible.
9	Furniture	-
10	Tooling	Blind tooling on the covers and spine with geometric figures, lines and flowers. Some residue of gold tooling (see appendix III)
11	Colour	Brown of colour and quite equally coloured.
12	Deterioration	The binding is in good condition with very little signs of deterioration.
13	Appearance	The leather is smooth with a bit of shine.
14	Corrosion/abrasion	There are some abraded areas on the binding.
15	Smell	No apparent smell.
16	Feel- moist of dry	The binding feels quite moist to the touch.
17	Suppleness	The binding is appropriately supple.
18	Rough or smooth feel	Nice smooth feeling except at the abraded spots.
19	Sound	The sound is low.
20	Friability	[4] Very good condition, no loose parts.
21	Cohesivity	[4] The leather is in good condition
22	Flexibility	[2] Nice flexibility, appropriate to the object.

Object 5

Photo 6 Batavialand Binding, [MA] BZN8-344A. Photo taken from their record.

1	Inventory number	[MA] BZN8-344A
2	Place found	Shipwreck Burgzand Noord 8
3	Known history	The shipwreck has probably sunk around the third quarter of the 17^{th} century.
4	Conservation method	The leather was cleaned with tap water, air-dried till 80% humidity, impregnated with PEG 600 and finial air-dried. The wooden board have received a warm PEG 3000 treatment.
5	Measurements	13 x 7,5 x 4 x 7,5 cm.
6	Thickness of piece	1 mm.
7	Animal species	Calf
8	Description	This binding has floral elements in blind tooling. The book used to have wooden boards made of birch of which only one small corner is left attracted to the leather. The rest of the boards are in several big and small pieces and are kept separately. There are 2 notches for straps detectable in the leather.
9	Furniture	-
10	Tooling	Nice floral decorated stamp in blind tooling.
11	Colour	Brown with a yellow undertone.
12	Deterioration	Deterioration at the top edge and a tear along the spine.
13	Appearance	Dull appearance.
14	Corrosion/abrasion	Quite abraded at some spots.

15	Smell	No apparent smell.
16	Feel- moist of dry	Dry to the touch.
17	Suppleness	Stiff when bending.
18	Rough or smooth feel	Bit of a rough feel.
19	Sound	High sound.
20	Friability	[2] Some fragments. Seems quite fragile though
21	Cohesivity	[2] Relatively large exposed areas especially on the back where the leather is blackened.
22	Flexibility	[1] Stiff and not appropriately flexible.

Object 6

Photo 7 Batavialand binding, [MA] BZN8-266. Photo taken from their record.

1	Inventory number	[MA] BZN8-266
2	Place found	Burgzand Noord 8.
3	Known history	Ship had probably sunk in the third quarter of the 17th century. According to the records, this binding was recoded as a leather binding but after conservation treatment most of the leather had disappeared.
4	Conservation method	A warm PEG 3000 treatment, often used for wood.
5	Measurements	~ 7,7 x 4,7 x 2,6 cm of the wooden boards.
6	Thickness of piece	Less than 1 mm of leather on the boards.
7	Animal species	Not confirmed.
8	Description	This 'binding' used to have a leather cover, of which pieces are still attached to the wooden boards.

9	Furniture	The furniture includes clasps and a stylus. It seems the furniture is wrongly re-attached to the binding since the board would not be correctly mirrored when put into a binding again. This can be seen by the shape of the boards.
10	Tooling	-
11	Colour	Brown.
12	Deterioration	Most of the leather is gone.
13	Appearance	Very dull.
14	Corrosion/abrasion	Most of the leather is gone and the grain layer is gone as well.
15	Smell	Sour sharp smell.
16	Feel- moist of dry	The leather feels very dry to the touch.
17	Suppleness	Not possible to measure.
18	Rough or smooth feel	Very rough to touch.
19	Sound	Not possible to test.
20	Friability	[1] Not much of the leather is left.
21	Cohesivity	[1] Very hard, dry and short fibres.
22	Flexibility	Not possible to test.

5.2.2. Leather bindings from BZN17, in possession of Provincie Noord-Holland.

Object 7

Photo 8 BZN17 binding, PDC222. Photo provided by Restaura.

1	Inventory number	PDC222
2	Place found	Burgzand (BZN17) shipwreck near Texel .
3	Known history	Binding found by sport diver around 2014 and later came in the possession of the Province of Noord-Holland. The binding is part of a large collection of binding found. Ship probably sunk in the 17th century. At least after 1641, indicated by dendrochronology according the preliminary research.
4	Conservation method	Cleaned with demineralised water, impregnated with PEG 600 and vacuum freeze-dried.
5	Measurements	16,2 + 9 + 16,5 x 26 cm.
6	Thickness of piece	1 to 2 mm.
7	Animal species	Goat/sheep.
8	Description	Wooden boards, metal furniture 2 clasps and 2 (broken leather straps but the fastening of the straps are still in place. The binding is elaborately blind tooled with the same pattern front and back. The spine was also tooled. Looking at the ribs it can be determined

		that the book had double sewing supports most of the spine leather is deteriorated. The leather is quite distorted and laminated at several places. Part of the cord is still visible within the boards along with the pegs to hold the cords. Presumably 4 spine ribs by looking at the blind tooling.
9	Furniture	The furniture has quite some erosion on it with different colours: green, red/orange and whitish and black. There is still some purple residue on one. There seems to be some leakage of corrosion material around the furniture.
10	Tooling	The binding is elaborately blind tooled with the same pattern front and back. The spine was also tooled.
11	Colour	The colour is relatively light yellowish-brown with darker tooling. Not an equal colour brown. It seems the tooling included a smooth surface but is now abraded.
12	Deterioration	Many missing pieces on spine and front cover. Leather seems burned in some places and is severely abraded. Although the leather of the straps is soft, very supple, but easily loosing fibres.
13	Appearance	The leather is abraded and most of it is quite dull.
14	Corrosion/abrasion	De-lamination and missing pieces and cracks.
15	Smell	Sour sharp smell.
16	Feel- moist of dry	Dry to the touch.
17	Suppleness	Spine leather relatively supple but brittle. The rest not possible to test due to the attachment to the boards.
18	Rough or smooth feel	Considering the thickness of the leather, the leather has an appropriate suppleness.
19	Sound	High sound.
20	Friability	[2] Very vulnerable at the abraded places and where missing pieces are.
21	Cohesivity	[3] Again where the layer is exposed through loss of material.
22	Flexibility	[2] Appropriate flexibility, athough not as supple as new leather.

Object 8

Photo 9 BZN17 Binding, PDC54.Photo provided by Restaura.

1	Inventory number	PDC54
2	Place found	Burgzand (BZN17) shipwreck near Texel.
3	Known history	Binding found by sport diver around 2014 and later came in the possession of the Province of Noord-Holland. The binding is part of a large collection of binding found. Ship probably sunk in the 17^{th} century. At least after 1641 indicated by Dendrochronology according the preliminary research.
4	Conservation method	Cleaned with demineralised water, impregnated with PEG 600 and vacuum freeze-dried.
5	Measurements	18+8+18 x 25 cm.
6	Thickness of piece	1 mm.
7	Animal species	Calf
8	Description	No boards. Leather is even and in quite good condition. Five spine ribs can be discerned, no furniture no indication of straps. Fold-inns all there except on head of the spine. Indication of packed sewing on the inside. Spine leather inside seems dry, dark and has upper cracks.

9	Furniture	-
10	Tooling	Blind tooling in lines and letters 'T' and 'G' and gold tooling in lines and coat of arms on front and back cover. Seem the same. Gold tooling on the spine and on the ribs.
11	Colour	The colour is a yellowish brown. Quite even except for slightly abraded places where it is lighter.
12	Deterioration	Along the spine quite some folds. Some holes and a piece of tail spine missing. The front and back cover have some slight fold indications.
13	Appearance	There is a nice shine to the leather. You can still see strokes of a surface coating.
14	Corrosion/abrasion	Some gold is gone but not much. Back cover has some cracks on a fold.
15	Smell	Bit sharp sour smell.
16	Feel- moist of dry	Dry to the touch.
17	Suppleness	Slightly hard to bent. But still relatively supple.
18	Rough or smooth feel	The leather outside feels quite smooth. Inside (flesh side) rough to the touch and bit hard. Not soft such as new leather.
19	Sound	High sound.
20	Friability	[4] Very few pieces.
21	Cohesivity	[4] Very few loose fibres, quite compact.
22	Flexibility	[2] Appropriate flex. Although not as supple as new leather.

Object 9

Photo 10 BZN17 Binding, PDC219A. Photo provided by Restaura.

1	Inventory number	PDC219A
2	Place found	Burgzand (BZN17) shipwreck near Texel.
3	Known history	Binding found by sport diver around 2014 and later came in the possession of the Province of Noord-Holland. The binding is part of a large collection of binding found. Ship probably sunk in the 17th century. At least after 1641 indicated by Dendrochronology according the preliminary research.
4	Conservation method	Cleaned with demineralised water, impregnated with PEG 600 and vacuum freeze-dried.
5	Measurements	12.3 x 18,5 cm.
6	Thickness of piece	1 mm.
7	Animal species	Calf
8	Description	Small binding, no boards, no furniture, four ribs. Tooling on the spine ribs suggest double cords. All fold-ins present. Blind tooling that is slightly faded. Tooling slightly darker. Traces of red along the (former) edge on the inside.
9	Furniture	-

10	Tooling	Elaborate tooling on covers and spine look the same on both covers.
11	Colour	The colour is a light yellowish-brown with darker tooling. Not an equal colour brown.
12	Deterioration	Slightly abraded but in fairly good condition. No missing pieces.
13	Appearance	Most of it is quite dull with very dull at the abraded places.
14	Corrosion/abrasion	Abraded at some places.
15	Smell	Sharp sour smell.
16	Feel- moist of dry	Dry to the touch.
17	Suppleness	Can bend but not supple.
18	Rough or smooth feel	Quite smooth surface.
19	Sound	High sound.
20	Friability	[4] One solid piece.
21	Cohesivity	[3] Very few were abraded a bit.
22	Flexibility	[2] Appropriate flex. Although not as supple as new leather.

Object 10

Photo 11 BZN17 Binding, PDC219. Photo provided by Restaura.

1	Inventory number	PDC219
2	Place found	Burgzand (BZN17) shipwreck near Texel.
3	Known history	Binding found by sport diver around 2014 and later came in the possession of the Province of Noord-Holland. The binding is part of a large collection of binding found. Ship probably sunk in the 17th century. At least after 1641 indicated by dendrochronology according the preliminary research.
4	Conservation method	Cleaned with demineralised water, impregnated with PEG 600 and vacuum freeze-dried.
5	Measurements	13 x19,7 cm.
6	Thickness of piece	< 1 mm.
7	Animal species	Calf
8	Description	Wooden boards cord and pegs still visible on the back cover. Front cover board piece missing. Spine leather quite supple. Head edge leather is quite abraded at the turn-ins. Looking at the 3 spine ribs it can be determined that the book had double sewing supports due to indentation in the leather. One large tear along the joint of the front board originating for the top edge.

9	Furniture	Metal furniture 2 clasps (one missing) and 2 catch plates.
10	Tooling	The binding is elaborately blind tooled with on the front board heads, floral pattern and two 'C''s. Back cover with the leather straps and clasps also heads and floral pattern (roll) but instead of 'C''s Fleur de Lis and small flowers next to it, of which only one is still gold. One 'C' and 2 fleurs do show signs of gold tooling. The spine was also tooled with lines.
11	Colour	The colour is dark brown (chocolate) with darker tooling. Not an equal colour brown. Abraded parts look greyish brown. Seems the tooling included a smooth surface but is now abraded.
12	Deterioration	Large tear. Corners open. One hole on the spine looks like woodworm. Abraded places specially along the edges.
13	Appearance	Bit of shine but no high shine.
14	Corrosion/abrasion	Big nails to hold leather straps have a whitish corrosion.
15	Smell	Sharp sour smell.
16	Feel- moist of dry	Dry to the touch.
17	Suppleness	Thin leather, easy to bend.
18	Rough or smooth feel	Smooth to the touch.
19	Sound	Low sound, specially compared to the rest
20	Friability	[3] One piece but the tear makes it vulnerable.
21	Cohesivity	[3] Where the layer is exposed through the tear the fibres are quite loose. Although still quite long.
22	Flexibility	[2] Appropriate flexible.

Object 11

Photo 12 BZN17 Binding, PDC224A. Photo provided by Restaura.

1	Inventory number	PDC224A
2	Place found	Burgzand (BZN17) shipwreck near Texel.
3	Known history	Binding found by sport diver around 2014 and later came in the possession of the Province of Noord-Holland. The binding is part of a large collection of binding found. Ship probably sunk in the 17^{th} century. At least after 1641 indicated by Dendrochronology according the preliminary research.
4	Conservation method	Cleaned with demineralised water, impregnated with PEG 600 and vacuum freeze-dried.
5	Measurements	21,5+ 7,5+21 x 34 cm.
6	Thickness of piece	1 mm.
7	Animal species	Sheep/goat
8	Description	No boards, four ribs (double). One turn-in spine missing. Bit abraded and folds, tears and de-lamination apparent. Cracks along tooling lines. Important: de-lamination on several places of the binding. Part of the top layer is loose from the layer underneath with air in between.
9	Furniture	Holes for ribbons to tie the binding close.

10	Tooling	Blind tooling with coat of arms in gold and fleur de lis in the corners. Also, some flowers in gold on the spine.
11	Colour	Brown with a reddish hue undertone. Not equal in colour. Seems the tooling included a smooth surface. Can see the brush strokes.
12	Deterioration	The binding is in bad condition but does not show very severe signs of deterioration. A bit of the leather is deteriorated at the top edge. Many folds and several cracks visible. De-lamination determined and gold missing. Some abrasions look greyish.
13	Appearance	The leather has some grey dull stains. The red/brown areas have a significant shine to them.
14	Corrosion/abrasion	The leather is abraded at some places and the grain layer is visible.
15	Smell	Sour smell.
16	Feel- moist of dry	Dry to the touch.
17	Suppleness	Not very supple.
18	Rough or smooth feel	Smooth to the touch.
19	Sound	High sound.
20	Friability	[3] Some pieces look like they can break off easily. Especially the abraded parts.
21	Cohesivity	[3] Where the layer is exposed through loss of material. Short fibres but packed and black.
22	Flexibility	[2] Good enough for it purpose.

Object 12

Photo 13 BZN17 Binding, PDC273. Photo made by Leanne de Wit.

1	Inventory number	PDC273
2	Place found	Burgzand (BZN17) shipwreck near Texel.
3	Known history	Binding found by sport diver around 2014 and later came in the possession of the Province of Noord-Holland. The binding is part of a large collection of binding found. Ship probably sunk in the 17th century. At least after 1641 indicated by Dendrochronology according the preliminary research.
4	Conservation method	Cleaned with demineralised water, impregnated with PEG 600 and vacuum freeze-dried. After drying the leather received a coating of PVAc.
5	Measurements	21 x 32,5 - front or back cover plus part of spine.
6	Thickness of piece	1 mm.
7	Animal species	Calf
8	Description	Only one cover and piece of spine. Dried to represent a book with the spine leather bend down in a 90-degree angle. The binding has holes where ribbons would have been.

9	Furniture	-
10	Tooling	Blind tooling with lines, gold tooling in the coners, fleur de Lis and coat of arms in the middle. Also, flowers in gold on the spine.
11	Colour	The colour is very dark brown almost black. Equal in colour over the whole piece. Seems the tooling included a smooth surface coating. Can see the brush strokes.
12	Deterioration	Part of the cover and spine leather missing. Cracks and folds and a tear in the front cover.
13	Appearance	High shine. Looks almost like plastic.
14	Corrosion/abrasion	Does not look abraded.
15	Smell	Not a very distinctive smell. Bit of a sweet oily smell. Definitely different from the others.
16	Feel- moist of dry	Bit moist and oily.
17	Suppleness	Very hard.
18	Rough or smooth feel	Very smooth.
19	Sound	High sound.
20	Friability	[3] Some pieces look like they can break off easily.
21	Cohesivity	[3] Where the layer is exposed through loss of material. Short fibres.
22	Flexibility	[1] No, very hard.

6. The results and discussion

The information gathered from the different objects have been submitted into an excel sheet. Table 1 shows the collected data from this sheet. The first six objects were the objects from Batavialand and objects seven to twelve are the bindings from the BZN17.

Table 1. Collected data from sensorial tests and CARS tests.

	senses															CARS				
	sight							smell		feeling				sound						
object	dark colour	light colour	abraded	rough	smoot	shine	dull	sweet	sour	smooth	rought	wet	dry	high	low	friability	cohisivity	flexibility	score	comments
1	x		x	x		x			x	x		x			x	3	3	2	8	
2	x		x			x				x		x				4	4	x	8	
3		x			x	x		x		x			x			4	4	2	10	smell is bit oily
4	x				x		x			x		x			x	4	4	2	10	
5	x		x	x			x				x		x		x	2	2	1	5	
6	x		x	x			x		x		x		x			1	1	x	2	
7		x	x				x		x		x		x	x		2	3	2	7	
8	x				x	x			x	x			x	x		4	4	2	10	
9	x				x		x		x	x			x	x		4	3	2	9	
10	x		x			x			x	x			x		x	3	3	2	8	
11	x		x			x			x	x			x	x		3	3	2	8	
12	x				x	x		x		x		x		x		3	3	1	7	smell is bit oily

By studying the table three bindings seem to fall out of place. Binding number 3 is light in colour, smooth and has a shine. What stands out the most is the combination of the sweet (and oily smell) and the dry surface of the binding. While examining the binding at Batavialand, this binding immediately stood apart from the rest. After checking the conservation report it became apparent that this particular binding had not perceived a PEG 600 impregnation treatment but a 'Goubitz' impregnation treatment involving glycerine, castor oil and tertiary butyl alcohol. Judging by the sensorial tests and the CARS test it can be concluded that this method has worked significantly good for this particular binding.

Another binding that stands out judging by the CARS condition score is binding number six. This object only nearly qualifies as a leather binding. By checking the documentation for this binding it became apparent that the binding was classified as a leather binding before treatment was carried out. After treatment however, most leather was gone only leaving a few traces of leather. The documentation of the conservation reported that the object was treated with a the warm PEG3000 solution normally used on wood. It can be presumed that this treatment had a negative effect on the leather.

The last binding that seems different form the other bindings in its group, the BZN17 bindings, is sample number 12. The sweet and oily scent combined with the wet feel of the leather indicated a difference from the rest of the BZN17 bindings. Further information was obtained by looking at the cardboard storage box during the visit to RNA. Binding 12, with the inventory number PDC273, had received an 'after treatment', namely and PVAC coating. Photo 14 shows the information on the cardboard box.

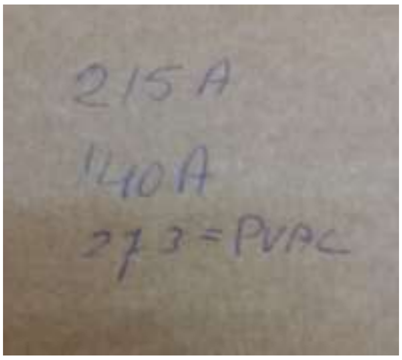

Photo 14. Photo showing information found on a storage box. Made by Leanne de Wit.

Looking at the characteristics for the sense of sight, no specific conclusions can be drawn. The bindings after treatment do show some similarities but due to the lack of information about how the binding looked before treatment, it cannot be discerned if for instance the dark colour of the binding is due to the impregnation method or if it is the original colour of the binding.
The smell of the bindings however do seem to indicate a relation. The sharp sour smell recorded might give an indication to PEG treated objects. Especially the BZN17 bindings all had the same kind of smell. For some of the bindings at Batavialand a sour smell was also observed. To get stronger evidence for the relation between PEG and the sour smell, more bindings need to be tested and it should be established when the bindings were treated.

The column indicating 'wet to the touch' and 'dry to the touch', it seems that except for the strange binding number 12, all the bindings feel dry. By comparing the literature about freeze-drying and the results found in table 1, it might be concluded that freeze-drying does give the leather a dryer feel. Excluding the two bindings with different treatment from Batavialand only one binding from that group is perceived as dry. This exception might be caused be the relatively bad state of the leather earning only 5 points at the CARS rating scale.

For the sound tests of the bindings, no solid conclusions can be drawn. Most bindings of the BZN17 collection were rated with a high sound indicating a stiff leather. From the objects of Batavialand only three bindings could be tested for sound because three of the bindings were reconstructed preventing a comparable sound test. The bindings that were tested for sound though, were rated with a low sound. This result may give the indication that the freeze-dried bindings of Restaura produce a higher sound compared to the air-dried bindings of Batavialand, excluding object 10, which received and 'after-treatment'. Including the literature, the bindings that were air-dried might contain more water than the freeze-dried bindings resulting in a different sound. Although it might be a likely conclusion, not enough data is collected to support this theory.

The CARS rating scale was useful in the sense that it gives a better view of the condition of the leather. It also shows that whether a binding is freeze-dried or air-dried, both objects can still receive 10 points indicating a good condition of these bindings.

Because of the lack of tested objects, drawn conclusions should be seen as preliminary conclusions. The testing of more objects is needed to be able to really use this technique for determining the performed drying treatment on waterlogged leather.

It would have been very helpful for this experiment to be able to do some blind testing where the treatment is not known beforehand. By means of the gathered information from the examined bindings the aim would be to see if it could be established if it was possible to distinguish the carried out drying treatment. However, the possible test objects were limited even as the possible conservation methods encountered. In that way the main experiment of this thesis has failed. However, providing a way to examine the leather and being able to distinguish certain features can still be useful for further research.

7. Conclusion

By looking into the specifics of waterlogged leather it could be discerned that wet leather needs an impregnation agent to stabilize the leather proceeding the drying phase. Without an impregnation agent the leather fibres would contract due to interlinking of the hydrogen bonds. According to the studied literature, the most common impregnation agents for leather are PEG 400, PEG 600 and glycerol. In the Netherlands however, glycerol treatment is scarce and instead a method of glycerine and castor oil is used. The most frequently used drying methods in the Netherlands are vacuum freeze-drying and air-drying.

The scope of the experiment was too limited to find out if it is possible to determine the drying treatment carried out on waterlogged leather, however some indications can be made that point to a certain treatment. By comparison of literature and testing, a cautious assumption can be made indicating that a dry feel combined with a high sound might be associated with the vacuum-freeze-drying method. However, normal freeze-drying has not been tested.

Hopefully other conservators can use the set-up of this experiment to try and determine the conservation treatment of waterlogged leather. The author is aware that based upon the relatively small set up of this experiment, drawing conclusion may be difficult. In this case I hope to give conservators the tools to experiment themselves. And along with research they might find the answers themselves. Setting up a database would also be a solution in the lack of information on conservation treatments of waterlogged leather. Furthermore, documenting the exact treatments carried out on waterlogged leather is needed to better understand the subject.

This research also showed that objects with combined materials such as bookbinding, need extra attention and there are several ways to treat these objects. Either take the whole binding apart

and treat every material separately resulting in objects that are presumably good preserved. When taking the ethic viewpoint, the binding should be considered as a whole and treating the composite object should be done as well as possible considering all the different elements.
Lastly, the use of a 'after-treatment' can clearly change the leather in a significant way. More research should be done into this direction to ensure the usefulness of this treatment.

7.1 Further research

To support this research, more bindings should be tested and compared. Making a database would probably help along with a sample book where different impregnation treatments and drying treatments can be compared. The scope of this research was too small to test more objects but by testing more objects the examiner becomes more acquainted with the different materials, methods and their characteristics.

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Appendix I – Annotated bibliography

Conservation of Severely deteriorated Wet Archaeological leather recovered from the Norwegian Arctic. Preliminary results. (2004)

Elizabet E. Peacock

About the preliminary results obtained in developing a method to stabilise the deteriorated wet leather found on Svalbard.

Asked question: "when is the condition of wet archaeological leather such that the conservation intervention must focus on stabilisation rather than conservation?

The leather was not left in water but open to the elements.

Mostly found shoes and leather offcuts.

"water-soluble tannins, oils and fats have a tendency to leach out of leather leaving the water-saturated collagen fibres susceptible to denaturation by water-catalysed hydrolysis." (569)

"salts can bring about physical breakdown of the collagen network upon drying out of the leather. Salt solutions increase the swelling effect of water saturation, and salts may become very concentrated during subsequent freezing." (570)

"it can be difficult to assess the chemical condition of wet archaeological leather while wet." (570)

Cleaning of the leather pieces was done with tap water. This also reduced the soluble salt content. No cleaning was done using running tap water because of the fragility of the leather.

"Since the mid-1980s the leather has been pre-treated by immersion in dilute concentrations of PEG 400 together with glycerol (propane-1,2,3,-triol) followed by vacuum freeze-drying/ b oth glycerol and PEG 400 are widely used to stabilise wet Archaeological leather. The use of both of these in combination is not common. Glycerol is a relatively small molecule with a molecular weight of 76-92: whereas, PEG 400 has a molecular weight of 380-420. The approach of using both in combination is not unlike the two step PEG method developed for the conservation of wet archaeological wood in with wood is pre-treated with PEG of two different molecular weights." (572-573)

Treatment at Trondheim: investigated: "items where pre-treated for five days with 7,5% PEG 400 combined with 7.5% glycerol (both v/v in water). The solution was not agitated during the course of the pre-treatment, and larger items were raised of the bottom of the pre-treatment container. Prior to pre-cooling, the leather was rinsed with tap water briefly to remove surface PEG and glycerol. After

pre-cool at -25C freeze-drying carried out in a cooled chamber at -20C under vacuum was successful for the better preserved leather. It did not stabilise the degraded leather; in fact, the results were similar to trial samples that had no pre-treatment and were air-dried. Variations were made in the concentration of the aqueous PEG-glycerol solutions, and the time of immersion in pre-treatment solutions with no better effect. Treated leather was dry, shrunken stiff and curled up or brittle. It was delaminated and individual pieces cracked and broke up during handling. Edges and exposed interior areas where the grain surface was no longer present shed fibres (leather dust). For the hobnail shoe soles, pre-treatment solutions based on glycerol only were investigated with similar results." (573)
Carried out treatment for the Kapp Wijk leather: "

Leather wet and Dry. Current treatments in the conservation of waterlogged and desiccated Archaeological leather. (2001)

Edited by Barbara Wills

Whitin:

A method of assessing the condition and treatment of waterlogged leather: a summary of work at the museum of London.

By Kirsten Suenson-Taylor

Museum of London used glycerol (propane 1,2,3-triol) followed by freeze-drying.
In 1994 evaluation of the treatments. Objectives: effects of treatments, examination of current treatment, effects of various methods of pre-treatment storage, study of the mechanisms of stabilisation, and, examination of effect of freeze-drying on leather.
Suendon-Tylor has introduced an assessment sheet for waterlogged leather treatment.

Practical approaches in the treatment of Archaeological leather.

By Marquita Volken

According to Volken, non-vegetable tanned leather will not survive wet burial.
Method used by Olaf Goubitz: first clean, than airdry till aprox 80% humidity (determined by visual and feel) then solution of 60% PEG 600, 40% water. Left in the solution for about 36 hours. This treatment was carried out 30 years ago and object still seem in good condition. Drawback is that it does not take glue easily. Slightly lighter in colour after few years.
In case of glue-need, treatment with castor oil was carried out. Same method but instead of PEG, a solution of sulfonated castor oil 35%, glycerine 15% and tertiary-butyl alcohol 50% was used.

Both methods seem to have good result and are cheap. Leather remained supple, pliable and stable. (p37-40)

A condition survey of glycerol treated freeze-dried leather in long-term storage. (1996)

By Dean Sully and Kirsten Suenson-Taylor

The designed survey was designed to evaluate archaeological leather treated by glycerol impregnation and freeze-drying done at the Museum of Londen (MoL) from 1982 and later.

"One criticism of the freeze-drying treatment has. Been that, in the case of weak and friable artifacts, it cannot impart sufficient strength. In addition the long-term stability of the treated objects has been questioned [3]. The selection of any technique for the treatment of waterlogged leather can be seen as a compromise between two contrasting schools of thought. One maintains that the object should be returned to a near facsimile of its pre-burial condition; the other argues that stability should be achieved." (p.177)

Cohesivity	1	2	3	4
Consider the leather on a macro scale and the integrity of the object as a whole. Look at vulnerable areas liable to loss. Bear in mind the nature and shape of the object.	Many fragments readily detached during handling.	Several fragments readily detached during handling.	Minor areas of vulnerable fragments	Leather intact no vulnerable fragments.

Friability	1	2	3	4
Diagnose primarily on the grain surface only. However some account should be taken of exposed edges. Where grain surface is no longer present, define condition of the remaining fibre surface.	Fibres easily detached during handling, resulting in total loss of surface.	Greater part of surface and exposed edges liable to loss.	A few areas of grain surface liable to loss of fibres.	Grain surface intact no loss of fibres.

Flexibility	1	2
Flexibility must be appropriate to the object. If flexible, not so weak as to be damaging to the object. If inflexible not so brittle as to allow damage to occur during handling.	Unacceptable - weak or stiff and brittle.	Flexible

"The aim of the survey was to evaluate the success of past treatments and monitor long-term stability. To do this the standard survey form was modified to include a criterion-anchored rating scale comprising three 'condition score' criteria specific to leather: cohesivity, friability· and flexibility. Each object was scored (1-4) for cohesivity and friability; flexibility was defined as unacceptable or acceptable (1-2). The parameters were defined before the survey commenced, and subsequently refined (Fig. 1). Even though the use of such a scoring system is subjective, every attempt was made to limit surveyor bias. This was done by using a large sample population, adhering closely to the condition definitions and maintaining a consistent surveying protocol. The use of clear definitions, rather than a sliding scale for each point on the criterion-anchored rating scale [CARS], reduces differences in interpretation and therefore increases the reliability of the data." (p.178)

"The scores for each condition criterion were added to give an overall condition score, a maximum of 10 representing material in very good condition and a minimum of 3 representing material in very poor condition. In this system, cohesivity and friability were given greater weight than flexibility, which accounts for a less significant proportion of the overall score. Any artefact receiving a score below 6 was considered to be in an unacceptable condition." (p.178)

"Glycerol functions in a number of ways, as a cryoprotector, a humectant and a stabilizer. As a cryoprotector it acts as an antifreeze and reduces osmotic pressure during cooling. Optimum protective action occurs at 30%, but glycerol will protect over a wide range of concentrations. Glycerol acts as a humectant by regulating the effect of moisture content changes on bound water within the collagen structure. Stabilization is achieved by multiple hydrogen-bonding with the charged areas on the collagen molecule, replacing tightly bound water molecules on the surface of the triple helix. The structure of the glycerol molecule itself may also enhance stability by enabling water structures with appreciable lifetimes to be built up around the collagen molecule. This in turn promotes the viability of the glycerol bond with collagen." (p.180)

Leather Drying Trial. A comparative study to evaluate different treatment and drying techniques for wet, archaeological leather. Archaeological conservation report. (2011)

By Angela Karsten and Karla Graham

A report constructed by the English heritage and the "aim of the study was to evaluate different treatment and drying techniques for wet archaeological leather; using parameters such as shrinkage, flexibility, appearance, time and costs."

"The aim of remedial conservation1 is to remove all the water so that the leather is stable in ambient environmental conditions2 to facilitate further study and to enable deposition at an appropriate repository. The remedial conservation must replace the water (which is supporting the leather) with an inert substance which will support and bulk out the degraded structure, and allow it to retain its flexibility." (p. 2)

The impregnation treatments that were evaluated are: polyethylene glycol (PEG) and glycerol with a concentration of 20% for three days.

The drying methods evaluated were air-drying, controlled air-drying (salts), freeze-drying and vacuum freeze-drying.

The Sully and Suenson-taylors condition score method (cohesivity, flexibility and friability) was used to evaluate the different treatments, along with shrinkage, appearance, time, effort and equipment needed.

The leather samples were all photographed, a detailed drawing was made and dimensions taken. The change in the flexibility of the leather was recorded by suspending it partly over an edge and using a protractor to record the change of the angle. (p. 5)

Although often not stated why and how in literature, EDTA is sometimes used as a pre-treatment before the impregnation treatment. Informal discussion between conservators revealed the following reasons: "the lighten up the colour, to produce a more natural looking artefact, to produce a more flexible artefact, when contamination with metal corrosion products has taken place from nearby objects or metal fittings of the same object". (p.8)

"The mineral content of wet archaeological leather is sometimes considered to be a problem, which can result in iron staining and brittleness. Sequestering agents are used to reduce the mineral content, which is also thought to prevent future problems in the oxidation of iron compounds especially during storage." (p.8,9)

"No data seems to be available to quantify the mineral content and the threshold above which it is likely to cause problems in the future due to oxidation activity or hydrolysis." (p.9)

Drying methods mentioned:

- Air drying: The leather is simply allowed to dry at ambient conditions. This process can be slowed down by covering the leather with a piece of plastic.
- Controlled air drying: Specialist equipment or saturated salt solutions can be used to manipulate and control the environment around the leather to achieve a very controlled and slow drying environment. The relative humidity is incrementally reduced down to approx 55% RH, at which the leather is considered dry.
- Solvent drying: Here, the leather is placed in successive solvent-water mixtures with increasing amounts of solvents. The water in the leather is replaced with a liquid of lower surface tension. Once the leather has been immersed in 100% solvent the leather is slowly air dried.
- Non-vacuum freeze drying: This drying method relies on the process of sublimation: frozen water within the leather is transformed from the solid ice state directly to the gas state. Without going through the liquid water state eliminates surface tension. This can be carried out in a domestic chest freezer.
- Vacuum freeze drying: The same principle as for freeze drying applies, but the method is carried out in a vacuum freeze drying chamber. The vacuum speeds the process up by directing the sublimed water to the condenser, where it collects once again as ice.

"The drying of waterlogged material even after impregnation is the most crucial part during the treatment of waterlogged organic materials. The final shape and appearance of the artefact is determined during this stage." (p. 11)

"Leather, which chiefly consists of collagen, mainly survives due to waterlogging. During burial the collagen protein swells in water. The structural integrity of the collagen chain is lost, when hydronium ions (H3O+) in the water break bonds within the collagen chain. The final result is that protein turns into a gelatine colloidal solution (Florian 2006). This means that leather can be found in a structurally weakened state of preservation, and contains varying amounts of water. During treatment the free water within the leather is removed. This results in some shrinkage. The behaviour of leather during conservation with regards to shrinkage is also influenced by the animal species, where on the animal the leather came from, tanning method and treatment during use, burial environment, length of burial and finally the conservation treatment itself." (p.13,14)

"It becomes evident that all samples that received the 5% EDTA treatment only resulted in the highest shrinkage values, regardless of the drying method. This is not surprising, as it is widely accepted that EDTA removes minerals (and possibly other material) from the leather. In doing so, it opens up the fibre network, which results in leather that can contract more. This effect however seems to be counteracted by the subsequent addition of either PEG or Glycerol. So even if certain minerals are removed by EDTA, the addition of a bulking agent fills the fibre network and prevents the leather from increased shrinkage." (p. 14)

No impregnation showed the most shrinkage but the method of only using the pre-treatment of EDTA. The test result show the least shrinkage with the glycerol method. EDTA + glycerol, PEG, EDTA+ PEG follow respectively. (p.16)

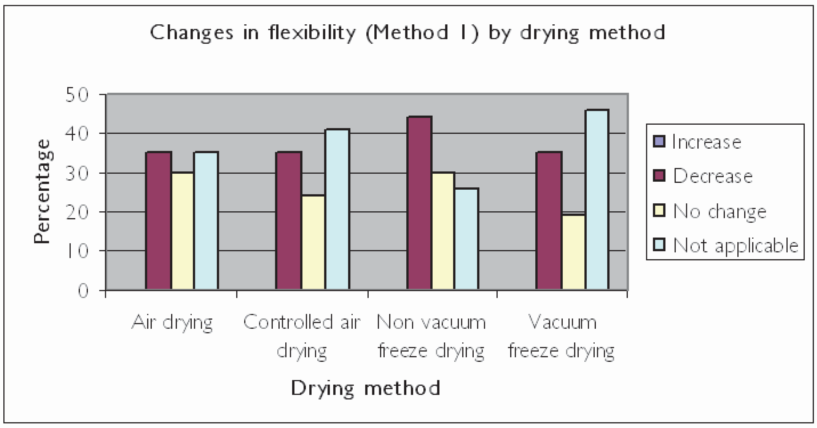
In general the results of the study for shrinkage showed that air-drying gave the best results. Vacuum freeze-drying and non-vacuum freeze-drying showed almost the same results with vacuum freeze-drying having slightly better results. Controlled air-drying showed significant more shrinkage compared to the other drying methods. (p.16)

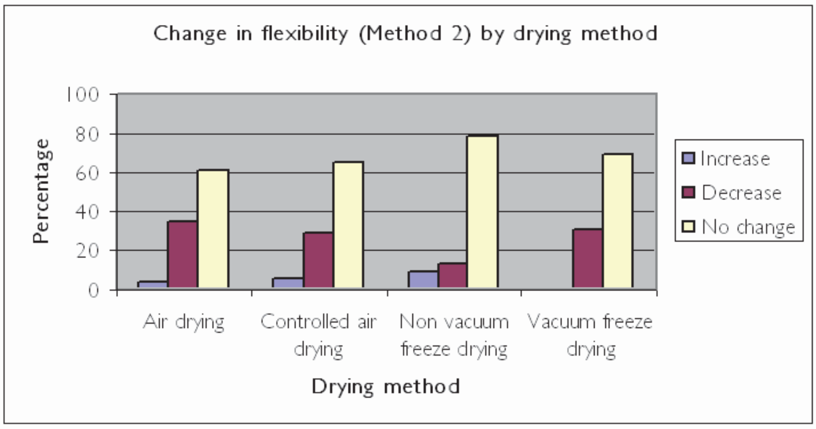
The discussion that followed the evaluation of the shrinkage mainly was about the fact that evaluating and comparing remains difficult since 'leather does already come with a number of variables which all influence the shrinkage during treatment.' Another problem noted is the shrinkage in 3 dimensions. (p.17)

The evaluation of the flexibility was tested in two ways; standalone flexibility, using suspension over an edge and measure the change of movement. The second way was with the condition score system of noting acceptable flexibility or unacceptable weak or stiff. For method 1 a changed flexibility of 32% was noted. For method 2, 38% of the samples changed in flexibility (both increased and decreased flexibility). (p.17)

The different impregnation methods showed different results considering the different recording methods. According to the recorded results for method 2 most samples showed no change in flexibility except for 'no impregnation where the majority of the samples showed a decrease in flexibility. Samples treated with EDTA+glycerol, glycerol and only EDTA respectively showed the most increase in flexibility but these treatments also included samples with a decrease in flexibility. Both PEG and PEG+EDTA treated samples included a considerable amount of samples with a decrease in flexibility.

For recording method 1, quite a lot of samples turned out to be not applicable for this recording method. No samples showed a increase in flexibility and quite a considerable amount of samples showed no change in flexibility at al. PEG and no impregnation respectively showed the most decrease in flexibility whereas glycerol + EDTA and PEG + EDTA share the 3th place where decrease in flexibility is concerned. Of the samples impregnated with just glycerol about 35% showed a decrease in flexibility and samples only treated with EDTA about half of this. (p.18)
The drying method evaluation showed the following:





On the discussion about flexibility the article mentions that both recording methods have their drawback since method 1 'tried to overcome the subjective nature of method 2'. Another drawback was the size and nature of the leather samples. This last one proved to be a great disadvantage for measuring flexibility with method 2 and showed (by the standard deviation) that the method is not replicable.

Polyethylene glycol vs glycol. The importance of molecular structure. (1986)

By Nancy Mills Reid

Both glycerol and polyethylene glycol are relatively cheap, non-toxic, compatible with water and capable of hydrogen bonding interactions. They have similar properties and therefor looking at molecular weight might influence the choice for treating waterlogged leather.

"hydrogen bonding is defined as the association of an electronegative atom such as oxygen, with a hydrogen atom which is chemically bonded to another electronegative atom and therefore has a partial positive charge. Water is most dense at 4ºC and expands on freezing due to the formation of the more ordered and quite open structure. In liquid water each molecule has about 4.5 nearest neighbours as compared to 4.0 in the ice structure. Above 4ºC the density de-creases again due to increased kinetic motion." (p.51)

"leather consists basically of a three-dimensional network of protein fibres. Single protein strands made up from the amio acids glycine, proline and hydroxyproline are associated together to form the triple helices of the structural protein known as collagen. These collagen strands are also associated to form fibrils and the fibrils in turn form the leather fibres." (p.52)

"The collagen structure is stabilized by the presence of hydrogen bonds both between the constituent amino acids and between these and water molecules." (p.53)

"The main aim of the various processes unknown collectively as tanning is to make the animal skin resistant to microbiological and chemical degradation. Metal tanning processes achieve this by increasing the cross-linking between collagen fibres. Conversely, vegetable tannins lower the extent of this cross-linking (hydrogen bonding) by competing for the same sites and appear to work simply by rendering the leather more hydrophobic." (p.53)

"Seasoned wood and tanned leather may contain 10 to 20% water. In both cases this relatively small amount of water is essential in maintaining the stability of the polymeric organic material." (p.53)

The article gives many solvents that do and do not mix well with glycerol. It also gives several properties of glycerol and also of the polyethylene glycol (table 1&2).

"During immersion in seawater, organic materials undergo not only biological and microbiological attack but also the chemical processes of hydrolysis (reaction with water). Hydrolysis will eventually result in a situation where the hydrogen bonding requirements of degraded organic material/polymers are satisfied by the presence of many water molecules. If these water molecules are removed, the polymers contract in an attempt to satisfy their hydrogen bonding needs." (p. 55&57)

"It is desirable in the conservation of all waterlogged organic materials […], to satisfy the hydrogen bonding requirements by the substitution of other molecules for water during dehydration." (p.57)

Dehydration is an important process in the consolidation of waterlogged material. To achieve this the common processes are air-drying, freeze-drying and solvent displacement. Reid seems to prefer freeze-drying. She mentions that that glycerol is good because of the small molecular size and capacity for hydrogen bonding. It works well in replacing water in the degraded organic material. Down site of glycerol is the change of bacterial growth and its relatively high hygroscopicity. Another concern is the possibility of evaporation of the glycerol after treatment although this has not been established at any significant rate (yet). (p. 58)

For PEG the bacterial problem is less then glycerol and even reducing the higher the molecular weight/seize. The higher the PEG the slower it can move into the material. If the PEG has not penetrated enough shrinkage may occur due to internal hydrogen bonding when drying.

Reid states that choosing the impregnation agent and its concentration should depend on 'the extent of degradation of the item(s) to be treated but also on what the actual mode of stabilization is considered to be.' (p.59)

"the action of polyethylene glycol as an impregnation agent is considered to be either as a hydrogen bonding substitute for water or as a bulking agent. Glycerol and the lower molecular weight PEGs are considered to act only as water-substitutes. In leather and rope conservation the impregnate may also act as lubricants, allowing fibres to slide over one another rather than bind." (p.59)

"A further advantage of using aqueous glycerol and polyethylene glycol impregnation methods lies in their behaviour under freeze-drying conditions." (p.60)
"polyethylene glycol 400, for example, forms two phases of ice and wax from dilute (10%) solution with a significant reduction in the expansion of the water on freezing. The PEG remains as a porous microcrystalline was while water is removed by sublimation. Glycerol acts in a similar fashion by forming a matric of small crystals." (p.60)

Reid concludes that hydrogen bonding might be the most important requirement for an impregnation treatment and that both glycerol and PEGs under 600 are in these cases the most appropriate. 'The relatively high hygroscopicity of these impregnates will be lessened by the existence of hydrogen bonding interactions with the particular organic material in treatment.'

A comparative investigation of methods for the consolidation of wet archaeological leather. Application of freeze-drying to polyethylene glycol impregnated leather. (1986)

By Jan Wouters

Old article about the conservation of waterlogged leather. Within this article different methods of consolidating waterlogged leather with polymers is examined.

"Vegetable tannins were amply used in fact for the fabrication of leather; they are partly water soluble and are not all tightly bound to the collagen fibers of the hide. The leaching out of vegetable tannins from the leather leaves the dermal fiber network with less protection against biological and chemical attack. Factors such as oxygen, iron slats, and other soil contents may enhance and/or complement this detannization, so that even the protein fibers may be attacked. When such leather is unburied and left to dry at room temperature, it will shrink and harden and, possibly, break." (p. 61)

"Most conservation treatments for waterlogged leather can be divided into four main groups:
- the use of polyethylene glycols up to a molecular weight of 1500; the impregnation is eventually followed by lyophilization (freeze drying) and finishing techniques
- other synthetic polymers, mixed with plasticizers and/or small hygroscopic molecules, e.g., glycerine, peg 400.
- application of a fatliquor or a dressing, after thorough cleaning.
- replacement of water by a less polar solvent." (p. 61)

"Freeze-drying (the transition of ice to water vapor) is a physically much less disruptive process than boiling (transition of liquid water to water vapor). Moreover, an object can keep its intended shape in a frozen condition during the elimination of the ice. However, freeze-drying requires a rigorous control of physical parameters, such as the temperature of the object and the cold trap, as well as the pressure in the lyophilization chamber. The resistance of materials to low temperatures and to strains due to the difference in specific volume of liquid and solid water should also be considered carefully." (p.62)

The samples were first manually cleaned of dirt and then pre-treated with EDTA (2%) for 24 hours followed by washing of the leather with running tap water for 8 to 16 hours.

The monomers used were 3-aminopropyltriethoxysilane (Ta) and glycidoxypropyltrimethoxysilane (Tg) combined with peg 400 as a plasticizer. To avoid polymerization during impregnation the leather was 'soaked in de-natured ethanol for 72 hours. After 35 days, polymerization was initiated by the addition of water.'

"the total duration of all impregnations was 46 days. Afterwards, each sample was cut in two pieces: (a) and (b). The(a) pieces were packed airtight in plastic bags, frozen at -30°C for 1 hour, removed from the plastic and lyophilized. The dimensions were checked after conditioning at 55% relative humidity and 21°C for two days. The (b) pieces were not lyophilized, but conditioned in a similar way. 'they were checked for suppleness and, later on, dried in a vacuum dessicator over silicagel and NaOH to establish the moisture content." (p. 62-63)

"Impregnations with p/glycerin and with Peg 400 gave the best results. The higher hygroscopicity of glycerin caused a higher moisture content and, hence, a more or less humid
touch. Except in cases where the leather was completely hardened, lyophilization improved its suppleness." (p.63)

The author explains how freeze-drying works and the chemical and physical aspects of Polyethylene glycols.

"Suppleness and visual aspect were very good for all treated samples. Impregnations with 50%PEG of any grade tended to make the leather darker and stiffer, expect for PEG400, where no difference was noticed. The untreated samples were hard, almost non-pliable, but lighter in colour. Impregnation with 50% PEG caused the samples to feel moist to the touch under the atmospheric conditions described above. Shrinkage was minimized by both higher PEG concentrations and lower prefreezing temperatures. In 50% PEG400, it did not seem necessary to prefreeze the sample at all." (p. 67)

From impregnation experiments using PEG 400 at different concentrations, followed by various prefreezing conditions, it may be stated that:

1. Prefreezing is not necessary with 50% PEG400, because a shrinkage of less than 2% is obtained.
2. For very critical applications or very deteriorated leather, prefreezing at -80°e of 50% PEG400 impregnated leather might be the method of choice; the only drawback of high PEG concentrations is the slightly moist touch at 55% RH and 21°c.
3. Impregnation with 35% PEG400, followed by prefreezing at -80°e represents the best compromise: good visual aspect, dry touch, and limited shrinkage (about 1%).
4. 20% PEG400 is too low a concentration to prevent considerable shrinkage (5-7%) in all circumstances.

What is wrong with Freeze-drying (1995)

By Olaf Goubitz

This is an article about preformed tests to establish the best method for treating waterlogged leather done by Olaf Goubitz.

In this article, Goubitz explains that the methods he used for conserving leather have more been established by trial, error and experience rather than science.

He mentions that he does use freeze-drying on wood but does not like to freeze-dry leather. Although he kept up with new developments around freeze-drying leather, he still felt is was dangerous for leather. While many investigated, one thing became clear, even with freeze-drying, leather needed a lubricant. PEG 400 seemed to be the best impregnation solvent in combination with freeze-drying and Goubitz comments that he thinks PEG 400 is too hygroscopic. Apparently, leather treated with PEG 400 sweats and when too diluted, gives no body to the leather which causes the leather to dry out. Goubitz considers PEG 400 therefor unsuitable as a pre-treatment. PEG 400 used as a post-treatment makes the leather really wet again.

Goubitz considers freeze-drying as a waste of money, time and energy since there are easier and cheaper alternatives.

Goubitz uses a method of gentle cleaning, slight air drying until about 80% of water has left the leather followed by a PEG 600 bath (PEG 600 60%/ 40% water) for about 36 hours after which the object is let to air dry again.

The way of cleaning is something that Goubitz does by experience just as the knowledge of when the leather has dried enough. Using your own senses are the most important tools in this. After cleaning and drying "the leather is closest to its original form so this is the time to measure, draw, and record all important information." (p. 3)

Coming out of the bath, the leather is quite dark. Over time some of the PEG evaporates lightening the colour of the leather. Goubitz advocates that bleaching the leather would not be healthy for the leather and can't assure that the leather becomes the colour it originally was.
Due to experience Goubitz knows that some leathers need a re-treatment after a while.
Depending on the leather and the treatment, shrinkage can vary but is always present and therefor registering the details before the final drying is important.

This leather treatment takes about three days compared to a method with freeze-drying which takes about 10 or more days.

One other leather treatment Goubitz performs is with Castor oil (35%), glycerol (15%) and Tertiary butylalcohol (50%) and dehydrated first with methylated spirit. This treatment gives a lighter leather, can be glued and can be used with metals in contrary to PEG which can have a bad effect on metal and does not take glue well.

Lastly, Goubitz mentioned that the type of leather may effect the outcome of the treatment.

Stepping through time (2001)

By Olaf Goubitz

The chapter 'the conservation of Archaeological leather is of importance in this book. According to the author, archaeological leather was badly treated in the past. From the '80' onward better methods were used but these have not much changes since. The author mentions that conserving the leather is necessary to prevent drying out and becoming brittle. Because of this it is necessary to preserve the leather to prevent drying. The best way is to keep the leather submerged in water in a dark and cool place. Very important is to prevent fungal growth. Another method of preserving, according to the author would be freezing it. "the leather will rarely be damaged by the formation of ice crystals". "prior to the conservation, a thorough cleaning of the find is very important, because this makes visible the structure of the leather, its texture, quality and grain, and any technical features such as stitch-holes."

The chapter continues on the best way to clean the leather from dirt and rust stains and the author mentions that the colour of the leather at that stage is to be accepted and not to bleach it.

"the aim of conservation is to immediately replace the groundwater or rinsing water that has permeated the leather by an impregnating agent that fills up the empty leather cells and keeps the fibres supple without the leather having to dry first. For this, products are used that will act with the water that is still contained within the leather. Glycerin is such a chemical, but it has the disadvantage of encouraging fungal growth. Polyethylene glycol (Peg) produces roughly the same effect as glycerine, without attracting fungi and with longer effectiveness."

The author mentioned the method of freeze-drying but explains that much expertise is needed to do this right and that it is difficult to get the leather "neither too dry or too moist'. Goubitz mentions that PEG 600 is often used in the Netherlands and that this has partly to do with the atmospheric humidity in the Netherlands. PEG 400 would, according to Goubitz "perspire". "For restorable objects, conservation with oil is better, because glues will not hold on Peg-impregnated surfaces." Goubitz mentions that, like with every conservation treatments, testing the treatments should be done. Recording the size and al the parts is important as well.

Goubitz mentions a quick way to preserve the excavated leather by slowly air dry it. This way the leather can still be treated later by emerging it in water again.

Goubitz mentioned that for a treatment with oil, the leather should be dehydrated first because oil and water do not mix. Alcohol can be used to get rid of the water.

"When conserving leather, including that of any third party, it is very important to keep a record of what was used to treat the leather, and in the case of restoration to note what material were used and in which areas. If an artefact is later cared for by others, they will need to know how it was treated and when, where and by whom. […] Future conservation can then take earlier treatments into account.

Lastly, Goubitz gives some leather conservation advice on how to do it and what materials to use.

Shrinkophobia. The conservator's natural fear of shrinking leather (2013)

By Gabriele Maria Zink

This article provides an overview of the author's experience in archaeological leather conservation conserving the shrinkage, colour and flexibility. "the paper shows the limitations of using shrinkage, colour and flexibility to judge the conservation outcome." (p.327)

In the introduction the author mentions that treatments differ depending on the main articles in a certain language. The following table was made to determine the success of a leather treatment:

Table 1. Three characteristics to determine the success of leather treatments.

	Characteristic	Technique	Aim
1	Shrinkage	Sketching	Minimum shrinkage
2	Color	Visual inspection	Lighter
3	Flexibility	Manual inspection	Softer, natural handle

Shrinkage is always part of the conservation also because of the nature of the material leather. To explain this she mentions the structure, build-up and making of leather. Depending on the animal, and part of the animal the leather is made from, shrinkage differs. "the three layers differ in their properties in that they determine the war and tear and presumably also the shrinkage. The loose interface between reticular and papillary layer may result in the so-called 'looseness'. […] If such objecs are dried after conservation, the two layers shrink differently: the reticular layer shrinks while the dense and less mobile hyaline layer prevents shrinkage of the papillary layer." (p. 328)

"if we understand shrinkage as an external result of an internal cause we could start asking: what happens to fibre bundles and fibrils while drying? How close can fibrils of different leathers engage without being harmed while drying even if some fragments look like shrinkage occurred externally?" (p.328)
"as long as the applied conservation method prevents internal shrinkage, should the result not be classified as 'satisfying'? (p.329)

"generally, polysaccharides […] are not suitable for leather. […] Perhaps we should focus on size and distribution between the fibres to learn more about those mechanisms? How small does our conservation substance have to be? Moreover, how it is to be applied and how it is to be dried, needs to be understood in order to realize perfect separation and lubrication throughout the leather. Conservation should not only ask the chemical question 'what to apply?' but also the physical question 'how to apply?'" (p.329)

The author, Zink, explains that the characteristics of colour and flexibility are interlinked from the tanning process on. The use of the tannin has a direct effect on the colour and the flexibility of the leather. "Vegetable tannins are complex phenolic substances that blacken if iron is present – which is very likely in an archaeological context. The possible processes of re-tanning causes leather to darken and get stiffer. (p.329)

In Germany EDTA has been used as a chelating agent to remove iron. However, using this wrong can cause new problems.

At the Schloss Gottorf demineralised water and airbrush are used to clean of excess dirt. Careful handling is key because fragile leather and other import remains may easily get lost or destroyed.

"After cleaning, excess water is removed by blotting, the leather is bulked with 35% v/v PEG 600 for two to a maximum of eight days depending on the size and complexity of the object." (p.330)

Before freeze-drying, the leather is divided into two groups depending on size and thickness. If necessary objects are reshaped. To make sure cooling and freezing are homogenous the objects are placed in boxes with holes and spacers. If possible, the flesh-side of the leather is exposed. This side has a more open structure and improves the evaporation of the water. One should strive to only loose the bulk of the water to prevent the leather from drying out. "the freeze-drying is now stopped when the amount of ice accumulating in the condenser slows down and the pressure n the chamber remains almost constant for the first two minutes." After removing the leather from the chamber the boxes are wrapped with plastic to acclimatise the leather. Reshaping after freeze-drying can be done by using saturated salt solutions and can take weeks. Flat strips of polyethylene can be used to keep pieces into place. Assembling part is not done by resewing but by using 3 layers of Japanese paper and non water based glue. (p331& 332)

A second method that is used is Polyethylene glycol 600 followed by airdrying. The author mentions his work with Olaf Goubitz and his dislike for freeze-drying. However, the autor mentions that: "these papers have to be understood in their historical context due to different freeze-drying times employed in those days.

"Goubitz decided on PEG 600 (60% v/v/ for 36 hours) followed by slow airdrying. PEG 600 is solid at room-temperature so no migration of liquid to the surface occurs. It does not attract mould as glycerol or PEG 400 do when used in high concentrations."

In 2001, Volken re-published Goubitz technique with good results. Minimal to no shrinkage was recorded, various shades of brown were visible and the feel of the leather was natural and not humid or tacky. (p.332)

Schloss Gottorf also used PEG 600 in low concentrations during the 60s and reviewing treated leater showed that the leather was still in good condition.

Goubitz older method with PEG 600 100% was less successful and was 'cleaned' and retreated with PEG 600 at 30%. After impregnation of two days the objects were freeze-dryed and the result was significantly better than taken the characteristics mentioned in table 1. Therefore: "PEG 600 seems to five longtime stable results while staying re-treatable." (p.332)

Last advice given by the author when freeze-drying is not an option is to use the Goubitz PEG 60% method and slow air-drying since it gives better results than solvent-drying. "this technique is easy, fast and produces leather which fulfils all three characteristic listed in table 1." (p.333)

Assessing the physical condition of waterlogged archaeological leather (2010)

By Ekaterini Malea

"the aim of the present study was to determine the condition of waterlogged archaeological leather by a series of simple visual and physical examinations testing the flexibility, strength and coherency of the fibres, and then correlate these assessments with the condition of leather as determined by various chemical a physical analyses." (p.571)

"The degree of leather preservation at the point of excavation can vary from flexible, with a strong physical structure, to a non-cohesive fibrous mass, which lacks physical integrity. Factors such as type of burial environment and the original nature of the leather will strongly influence its condition, with biodeterioration and chemical hydrolysis influencing its decay." (p.571)

"Treatment of waterlogged archaeological leather must be intrusive in order to provide an easy-to-handle and visually acceptable object. In the past, empirical analysis of leather condition has often produced successful treatment results." (p. 571)

"By using statistics the researcher has sound methodological tools that enable him to make accurate conclusions on the underlying process that generates the data itself." (p. 572)

For historical leather many examining techniques are possible and many different analytical techniques have been carried out to find out information about compounds in the leather and it's state of deterioration. As mentioned before, for archaeological leather the possibility of testing is limited. Researching if using basic test to establish the state of the archaeological leather would give enough or as much information as expensive and elaborate analytical techniques.

"the samples (15) were classified into three categories of preservation (C1- good condition, C2 – intermediate state of preservation and C3- poor condition), using subjective physical test although it has been reported by other scientists (young 1990) that sometimes neither the physical appearance not the feel give any indication of the extent of deterioration.[…] Terminology and methodology used here, was based on scientific research reports of ENVIRONMENT leather project."

Simple physical tests were performed to test flexibility, strength and coherence of the fibres (Larsen and Vest 1995) in order to classify the samples:

- Flexibility of the samples was tested empirically by trying to bend/fold the leather.
- Tear strength was empirically tested by holding the leather, tearing it by hand then subjectively assessing the ease of doing this according to the following categories: easy, difficult, extremely difficult.
- Coherency was tested by scraping the grain with a fingernail and its removal was classified according to the following categories: easy, difficult, and extremely difficult.
- Coherency of the fibres was determined by cutting a fragment of the leather into small pieces with a scalpel, and then classifying it into one of the following categories: poor coherence, intermediate coherence, good coherence.

After the physical test chemical and physical analysis was done including pH testing, determination of the hydrothermal stability (Ts) and amino acids analysis. Samples were also examined by SEM-ADAX technology. With the gained information a statistical analysis of the data was made. The author mentions that 'the small number of samples and the large number of variables presented significant problems for statistical analysis.'

"some leather experts who advocate that it is not possible to identify specific deterioration of the leather from changes in the microscopic appearance (Haines 1998)."

"No correlation was found between pH values and shrinkage temperatures (Ts) and/or classification into the three different state of preservation: C1, C2 and C3." (p. 579)

"No one correlation was evident between the different states of preservation (C1, C2 and C3) and the shrinkage temperatures, although it is known that the shrinkage temperature is a valuable indicator of the extent of deterioration (Larsen et al. 1993)." (p. 579)

"there is a decrease of the basic amino acids and an increase of the acidic ones. This altering in the amino acid distribution normally happens during oxidative breakdown. In the present study these values are not related to the visual/physical or SEM classification." (p 580)

"In general, this study has revealed the problems associated with the analysis of waterlogged archaeological leather and has shown that empirically categorizing leather condition is unpredictable and highly subjective. It has also shown that the use of more complex analytical procedures can reveal more information about the condition of waterlogged archaeological leather but they do not provide a clear ranking of its degree of deterioration and its overall condition. […] simple physical tests will continue to aid conservators in their selection of conservation procedures, even though they are not reproducible." (p. 587-588)

Note: very little samples, mentions samples from Greece although there is just one. Very invasive testing of the leather.

Forty years of Glycerol Treatment Revisited (2013)

By Amanda Watts, Liz Goodman and Jill Barnard

"At the 11th WOAM conference in 2010, discussion about the long term effects of pre-treating waterlogged leather with glycerol instead of polyethylene glycol (PEG) revealed views both for and against its use." (p.3)

Within this article the glycerol treated waterlogged leather from the MOL is revisited. The article of Suenson-Taylor and Sully (1996) mentioned the treatment that is performed at the Museum of London and this article reviews the collected data (using CARS score) and re-examines the treated objects for any flaws in the performed treatment – glycerol impregnation followed by freeze-drying. "It has been theorised that the hygroscopic qualities of glycerol may actually benefit the leather by retaining water above the critical 9% level below which leather suffers irreversible micro fibril cross-linkage (Hallebeek 1994)." (p.3)

Her work (Amanda Wallace, 1997) concluded that glycerol pre-treatment appeared to increase the size of the interstices between the fibre bundles." (p.3)

The next step in the investigation is to compare the data from the 94-96 survey to the data from the 2011 survey.

"Preliminary observations made during the survey indicated that the leather was not suffering any treatment-related failures. This is not to say that all of the leather was in good condition, but rather that none of the objects exhibited humidification, inflexibility, blooms, crystallisation or any other indication that the plasticiser (glycerol) had become mobile or failed at any point. Initial visual/handling observations suggested that the leather remained stable in storage, although some deterioration was seen in composite objects." (p. 5)

"The 2011 data is slightly less clustered around the mean than the PTS 94-96 data, though there is no significant difference in the distribution of the two sets. This indicates that the data is not artificially distributed near the mean, and that surveyor bias was, therefore, not a significant issue." (p.6)

"During the 2011 survey, the objects appeared to be stable. The team did not come across any of the expected problems of humidification, weeping, crystallisation or embrittlement that are associated with treatment failure of leather plasticisers." (p.7)

"While the data supports the idea that the objects are stable overall, it is difficult to make a judgement on how significantly any of these above-mentioned variables affect the stability of archaeological leather treated with glycerol. The data identified that overall condition stability varied from site to site, which indicates that the burial environment may play an important role in the condition of objects after treatment." (p.10)

"The CARS method of condition assessment has also proved a powerful tool in this attempt to quantify object condition for statistical analysis. By grouping condition levels into ordinal categories, numbers can be assigned to these categories producing a score for each object. These scores can be ranked and compared from one data set to another to understand the overall condition of the sample and, most importantly, measure the change between one data set and the second. This continuity of assessment methods was the key to this review of glycerol as a treatment for archaeological leather." (p.10)

"There are concerns regarding composite objects, specifically Roman hobnail shoes. As with all composites, preferential storage is biased towards the organic element. Further investigation using corrosion inhibitors needs to be considered." (p.11)

” The CARS assessment system developed at the MOL was used for the statistical applications. This system is suitable for recording and analysing condition information, though the limitations of its results must be taken into consideration. The numerical scores are integers that represent non-interval data, which can be misleading if one takes the scores at face value as measurements of condition, as they merely represent discreet categories of condition; the number simply lends itself to statistical comparison more readily than verbal scores such as fair, good, poor etc.

The second limitation, as with any type of condition survey, is the human factor of surveyor bias.” (p. 11)

The author does mention that the leather samples were all found in river water. Salt water may have a different effect.

Appendix II – Recorded treatment recipes

Table 2 Impregnation methods for waterlogged leather found in literature. NS = Not stated.

	Method												
	PEG			PEG + EDTA			Glycerol		Glycerol + EDTA			Glycerol +Castor oil+ tertiarybutylalcohol	
source		duration	concentration		duration	concentration	duration	concentration		concentration	duration	duration	concentration
Leather drying trial (2001)	400 PEG	3 days	20%										
				400 + Na_2EDTA	3days - 2 hours	20% PEG - 5% EDTA							
							3 days	20%					
									Na_2EDTA	20% Glycerol- 5% EDTA	3days - 2 hours		
A condition survey of glycerol treated freeze-dried leather in long-term storage (1996)							NS	15-25 % glycerol					
Polyethylene glycol vs glycol. The importance of molecular structure. (1986)	20-600 PEG	NS											
Conservation of Severely deteriorated Wer Archaeological leather (2004)	400 PEG	5 days	7,5% (v/v in water)				5 days	7,5 % (v/v in water)					
A comparative investigation of methods for the consolidation of wet archaeological leather (1986)				400 PEG	EDTA 24 hours	20-50% PEG - 2% EDTA							
What is wrong with Freeze-drying (1995)	600 PEG	36 hours	60% PEG, 40 % water										
													35% caster oil, 15% glycerol, 50% tertiary butylalcohol
Shrinkophobia. The conservator's natural fear of shrinking leather (2013)	600 PEG	2-8 days	35% (v/v in water)										

Table 3 Drying methods for waterlogged leather recorded from literature. NS = Not stated

	Method							
	Air-drying		controled air-drying		Freeze-drying		vacuum freeze-drying	
source		duration		duration		duration		duration
Leather drying trial (2001)			Barium chloride – 90% RH, Potassium iodide – 70% RH, Magnesium nitrate – 55% RH	second slowest				
	Air-drying	second fastest						
							vacuum freeze-drying	fastest
					freeze-dy in domestic freezer.	slowest		
A condition survey of glycerol treated freeze-dried leather in long-term storage (1996)					freeze-drying?	NS	freeze-drying?	NS
Conservation of Severely deteriorated Wet Archaeological leather (2004)							vacuum freeze-drying	NS
A comparative investigation of methods for the consolidation of wet archaeological leather (1986)							vacuum freeze-drying	NS
What is wrong with Freeze-drying (1995)	air-drying	3 days						
Shrinkophobia. The conservator's natural fear of shrinking leather (2013)					freeze-drying?		freeze-drying?	

Appendix III – Photo documentation

Photo documentation of the examined bindings with more details. The photo's are taken by the author unless stated otherwise.

Object 1,

Photo 15, [MA] SO1 32058. Close-up of the loose corner.

Photo 16, [MA] SO1 32058. Close-up of an abraded part.

Object 2

Photo 17, Z1954-X1122 / 2391. Photo of the front cover of the binding.

Photo 18, Z1954-X1122 / 2391. Close-up of the white corrosion on the spine.

Object 3

Photo 19 [MA] BZN3 -20. Photo of the spine and front cover.

Photo 20, [MA] BZN3 -20. close-up photo of the clasps.

Object 4

Photo 21.[MA] BZN17 - 6. Close-up of an abraded area.

Photo 22. [MA] BZN17 – 6. Close-up of a blind-tooled corner.

Object 5

Photo 23.[MA] BZN8 – 344A. Close-up of a floral stamp.

Photo 24. [MA] BZN8 – 344A. Inside of the binding. Very deteriorated appearance.

Object 6

No additional photo's.

Object 7

Photo 25 PDC222. Detail of the one of the catch plates showing corrosion of the metal and some purple residue of the silicon rubber.

Photo 26 PDC222. Detail of the metal plate that held the leather strap. Part of the leather strap is stil visible along with the corrosion of the metal.

Photo 27 PDC222. Detail of a corner furnished with metal.

Object 8

Photo 28 PDC 54. Detail of the binding showing the brush strokes in the top coating.

Object 9

Photo 29 PDC 219A. Detail of the corner showing cracking of the top layer.

Object 10

No additional photo's available.

Object 11

Photo 30 PDC 224A. Detail of the cracks and delamination on the spine.

Object 12

No additional photo's available.