Reversible Modification Of Flexural Rigidity On Dry Archaeological Leather From Wet Anaerobic Burial Sites:

An Herbal Method

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ABSTRACT

This work is based on a treatment reported in the article "Über der Weichen trockengefallener Alkohol und Formalinpräparate, Herbarblätter und von Tapagewebe" in Der Präparator from 2001 by Klaus Weichsler and co-authors. A series of experiments were performed to investigate the described effect of cherry laurel leaves and the compounds emitted therefrom upon flexural rigidity of dry archaeological leather from wet burial sites, which upon uncontrolled drying becomes rigid. To aid interpretation or to ease stress and strain on the material, it is often desirable to modify the flexural rigidity of the leather to allow for the object to be reformed. A review of current leather treatments which modify flexural rigidity: immersion, humidity chambers and infusion with humectants followed by freeze drying, indicates that some dry archaeological leathers would not withstand these treatments due to induced collapse and cross-linking of collagen fibres. Treatment with cherry laurel leaves (*Prunus laurocerasus*) has been proposed as an alternative method, but there is a general lack of literature on the treatment and no explanation of the working mechanism of the treatment. Considering the time and constrained resources, a limited number of methods were selected to first evaluate the effect of the treatment on dry archaeological leather, and then clarify the mechanism of the treatment.

An apparatus to measure the flexural rigidity of leather was designed and constructed. Results from this instrument were used to demonstrate that; a) the treatment depends upon emission of volatile compounds from the crushed leaves; and that b) benzaldehyde and water are the active compounds in the treatment. An experiment comparing the effects of a matrix of treatments: 1) chopped cherry laurel leaves in contact; 2) chopped cherry laurel leaves in non-contact; 3) benzaldehyde + distilled water; and, 4) 4-Methoxybenzaldehyde + distilled water was conducted by measuring changes in: flexural rigidity, pH, surface colour, weight, length, width, thickness and evaluate other attributes such as visual appearance, touch/texture, workability with respect to both before and immediately after treatment and also with respect to treatment reversibility through elapsed time following treatment. This experiment indicates that all treatments work in a similar way, but to different extents, and that the presence of an aldehyde + moisture is required for modification of flexural rigidity. Benzaldehyde with water was found to be the most effective treatment. The results also indicate that the treatments are reversible within an acceptable time frame with the changes in the above measured properties returning to their original values within 48 hours following treatment. Benzaldehyde with water has the added benefit of not involving the emission of HCN(hydrogen cyanide), as is the case when cherry laurel leaves are used, which is both an acute toxin and a potential hazard for the leather.

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Acknowledgement

This experimental review of how cherry laurel leaves and their compounds work on the flexural rigidity of dry archaeological leather recovered from wet burial site has been a very educating and exiting experience. To actually try to perform real scientific research has been both rewarding and challenging. This experience has enriched my understanding of biochemical processes in reaction with archaeological leather and how to plan and execute a scientific research project, both practical and theoretical.

I would like to express my gratitude to my supervisor and mentor Jacob Thomas PhD Research Assistant Professor, Department of Conservation, University of Gothenburg for giving a great support and guidance through this time. I would also like to thank Thomas Gütebier, Conservator at Medical History Museum, Gothenburg, Sweden for information about the cherry laurel leave treatment; and also Daniela Pawel, Paintings Conservator NTNU University museum Trondheim, Norway, for translating German literature for me.

Furthermore, I would like to thank my friends Paintings Conservator Lisa Edgren and Papers Conservator Liv Friis for taking your private time helping me under this time with psychological support, reading over text, giving me tips and just being the best girls ever. THANK YOU!

Irma Wennerstrand
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TABLE OF CONTENTS

1. INTRODUCTION

1.1 Background

The starting point for this study is a method of treatment for softening organic material with cherry laurel leaves. This method has been used at Übersee-museum in Bremen, Germany, Museum für Naturkunde der Hamboldt Universität zu Berlin in Berlin, Germany and Museum Heineanum in Halberstadt, Germany. These museums have contributed to the article in Der Präparator from 2001, which describes how to use cut cherry laurel leaves to soften dried out and deformed objects of animal and vegetable origin so that they can be reshaped to their original form without accumulating more damage, such as cracks or ruptures. The experiment performed by the German Museums in the article was successful within the timeframe of 24-48h. (Wechsler, 2001 pp. 24-31)

During my second year in the conservator program at bachelor level at the Department of Conservation, University of Gothenburg, I came in touch with this method described in the article through the conservator Thomas Gütebier from The Medical History Museum in Gothenburg. Thomas Gütebier had discovered and read the German article in Der Präparator and gave a lecture about the cherry laurel leave treatment in relation to the care of ethnographic objects with organic origin as part of an in-depth course at SVK (Studio Västsvensk konservering) through the University of Gothenburg in February 2014.

The article explains the use of cherry laurel leaves, which have been cut up into pieces in order to release cyanogenic glycosides that affect the flexural rigidity of dry organic materials. When the organic material is exposed to the chopped leaves in a closed environment, the organic material temporary softens and can be reshaped into a safer or more easily interpreted form. The softening effect is temporary and after ventilation of the treated organic material, it returns to its original stiffness, in the reshaped form. (Wechsler, 2001 p. 31).

Excavated wet archaeological leather when allowed to dry out under less-than ideal conditions, i.e. without humidity control, before cleaning and placement of object in relaxed interpretational manner, is often characterized by distortions (folds and creases), cracks and delaminated fragments from the grain side (see Figure 1). (Volken, 2001 p. 42).

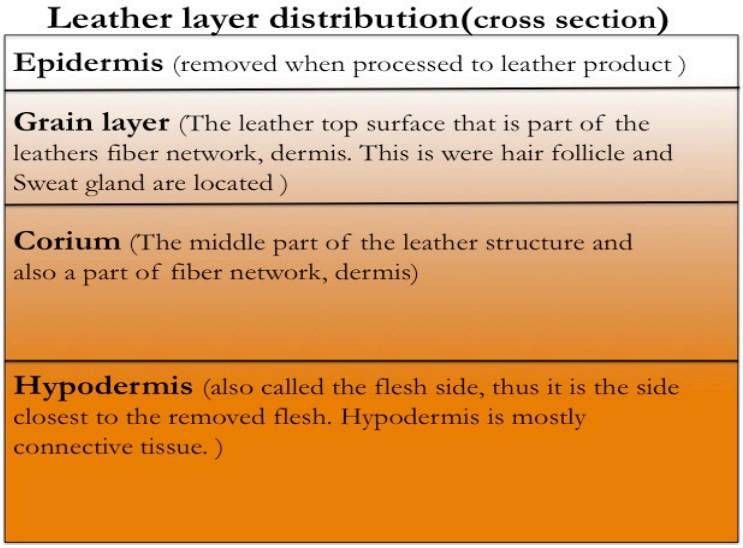


Figure 1Leather layer distribution (Larsen, 1999 p. 9)

This leather can be in such poor condition that current treatments for archaeological leather, like immersion in water with plasticizers or solvents cannot be considered as safe, since it jeopardies

collapse of leather structure (Larsen & Rhame, 1999 p.75). To interpret, study and preserve the leather a reshaping method is of interest to conservators working with dry archaeological leather, so that working marks or animal origin can be determined. The reshaping also offers a less harmful way to store the archaeological leather in museum storage facilities so that wrinkles and folds that lead to cracks and fragmentation can be prevented. The cherry laurel leaf treatment could be an option for this dry archaeological leather since it does not require immersion in water-based baths.

1.2 Problem Statement

The cherry laurel leaf treatment is not well known and it does not appear in the Scandinavian or English conservation literature. It does, however appear in the German article in *Der Präparator* (Wechsler, 2001 pp. 24-31). The lack of knowledge makes the reliability of the cherry laurel leave treatment somewhat low in terms of common conserving ethics, such as reversibility of the treatment, deterioration caused by the treatment and changes of original material so that future analyses could be restricted. The gap in the literature is, however, a part of the problem statement, and this study is a way to address that knowledge gap.

The apparently reversible effect of cut cherry laurel leaves upon organic material like animal skin or vegetative specimens implies that the working specie(s) in the cherry laurel leaves evaporate from the exposed organic material when ventilated. This statement is based only on the observed reactions of the exposed organic material in form of a ethnographical tapa textile and a historical leather hat during a lecture by Conservator Thomas Gütebier at SVK January 2014, thus the flexural rigidity changes from stiff before treatment, to less stiff under treatment, to stiff after treatment (Informant 1, 28/1-2014).

The documented effects of cherry laurel leaves upon dry archaeological leather from wet burial sites have not been found for this study. It is only the material leather, as in the leather hat treated during the lecture mentioned above that has been reviewed; though, a similar respond to the cherry laurel leave treatment could occur on dry archaeological leather as on the leather hat.

The effect of cherry laurel leaves upon dry archaeological leather from wet burial sites was not part of the case studies in the article or the lecture mentioned above, but it was proposed that the cherry laurel leave treatment could have an effect on other organic materials than the ones tested. Dry archaeological leather from wet burial sites which does not rely upon immersion in water based baths or humidity chambers with water mist, could be offered a more delicate modification of the flexural rigidity which does not jeopardise the leather structure as do other treatments.

1.3 Research Questions

1. In what way do the cherry laurel leaves affect dry archaeological leather from wet burial site, i.e transmission of active agents by surface contact or volatile species?

2. Which chemical compound(s) in cherry laurel leaves are the active agent(s) when treating flexural rigidity on dry archaeological leather from wet burial sites?

3. Could exposure on dry archaeological leather from wet burial sites to cut cherry laurel leaves or working specie(s) contained within cherry laurel leaves mechanically or chemically degrade the fibre structure, tanning agents, working marks or seams and decorations?

1.4 Aims

The purpose of this study is to investigate the effect of cherry laurel leaves upon dry archaeological leather recovered from wet anaerobic burial sites, in regards to the physical and chemical properties, i.e. flexural rigidity, colour, pH, physical measurements and other observations such as crystallisation, cracks or a soft or hard feel of the leather surface. The aim is to detect the working chemical compound in the cherry laurel leaves, and document its effects on archaeological leather. This will be obtained by observing changes under and after treatment of archaeological leather.

Dependent on the investigation outcome and interpretation of analysed data, an explanation of the working process will be done.

1.5 Objectives

By investigating cherry laurel leaves and their compounds there is a desire to demonstrate a non-destructive method for treating flexural rigidity on dry archaeological leather from wet burial sites. The intention is to generate some interest in the chemical effect of the cherry laurel leaves and their compounds on dry archaeological leather from wet burial sites in the conservation-restoration community.

1.6 Research and Knowledge base

1.6.1 Cherry laurel leave treatment on flexural rigidity of organic material

The method using cherry laurel leaves as a treatment of flexural rigidity upon organic materials like animal skins, tapa fibres and vegetative specimens is described in the German journal, Der Präparator from 2001, by Klaus Weichsler (zoologist) and Maren Rauer-Gömann (restorator) among others (Weichsler, 2001 pp. 15-31). This article is a report demonstrating that the conservators, taxidermists and zoologists in the mentioned museums in section 1.1 are using the cherry laurel leave treatment. The article is based on a series of case studies, testing the cherry laurel treatment exposure time, which is set to affect the flexural rigidity to the extent that reshaping is obtainable between 24-48h. By cutting cherry laurel leaves and placing them in a closed environment with the stiff dry organic material like a animal skin, the organic materials flexural rigidity will be affected. The organic material will go from being stiff and hard to a more flexible state that can be reshaped without breaking the fibre structure, thereby causing cracks and losing parts (Informant 1, 28/1-2014). The reshaping of the organic material can be obtained in its more flexible state under the cherry laurel treatment by filling out gaps with acid free paper or keeping parts in place with untreated cotton ribbon (Informant 1, 28/1-2014).

After treatment the organic material is ventilated, while fillings and reshaping solutions are kept in place. Shortly after the ventilation of the organic material, it returns to its previous stiff state, but retains its new shape. The cherry laurel leave treatment has mainly been preformed by the authors of the article; "Über das Weichen trockengefallener Alkohol und Formalinpräparate, Herbarblätter und von Tapagewebe" on dry and stiff animal skins (dried out wet specimens), tapa fibres and pressed plants. There is, however indications taken from the formerly mentioned article that the cherry laurel leave method could be used on dried out archaeological leather, textiles or ethnographical materials with organic origin (Weichsler, 2001 pp. 15-31). The cherry laurel leave treatment has not that I know of been tested on archaeological leather before, and the published conservation knowledge base is otherwise non-existent.

1.6.2 Current treatment of flexural rigidity on dry archaeological leather from wet burial sites

Treatment of flexural rigidity on dry archaeological leather from wet burial sites is limited, as mentioned in Section 1.1. Depending on the condition of the leather fibres, there are different ways to approach dry archaeological leather. The main goal for treating archaeological leather is to interpret the leather find. Interpretations like object identification, animal identification, original tannin methods, manufacturing marks, seams, etc. is of great interest for the historical investigation. These interpretations can answer questions like, what clothing did humans wear in specific times and places? Of what animal and animal part did they make garments of in for example 1000 BC, Scandinavia? How did they prepare leather, and what kind of tools did they use to prepare leather in for example 1000 BC, Scandinavia? There is also a desire for preserving the leather find over longer periods of time, so that future research is possible. Future research could be able to analyse these leather finds in ways that are not possible today. Therefore, a treatment of the flexural rigidity on archaeological leather is found important to those dry archaeological leather pieces that are in a very deformed state (eg. folded or formed as bundles), thus this is one of the causes of splitting, creases, laminations and embrittlement (Cronyn, 2001 pp. 269&274).

Dry archaeological leather from wet burial sites can be covered with sand, silt and other materials like grass or roots that was not removed when the leather find was excavated. The sand, silt and organic residues on the archaeological leather can be covering important marks on the leather find, like grain surface, possible seams, working marks and pigments that would be easier to see and analyse if the sand and silt were removed. Silt can also cause internal abrasion of the leather when being flexed and the leather would benefit from the silts removal in that point of view (Cronyn, 2001 pp. 271&274).

Removal of sand, silts and organic residue on archaeological leather together with unfolding and reshaping of deformations on leather is easier to obtain when the leather is newly excavated and still wet. If the leather still were wet when cleansing and reshaping, the risks for braking fibre structures would decrease substantially (Cronyn, 2001 p. 271). Though circumstances like the lack of conservators, time and money result in that newly excavated archaeological leather is left without any cleaning or reshaping (Volken, 2001 p. 42).

Choice of treatment for dry archaeological leather from wet burial sites to unfold deformations and remove residues (sand, silt, grass and roots) is dependent on to what extent the leather fibres stick together. Even though the leather fibres have dried out and suffer from decay by being in a burial environment, they can still be intact. The main problem is that when wet archaeological leather dries out under uncontrolled conditions the surface tension of the retreating water front drags the decayed collagen fibres together were the fibres collapse upon one another and crosslink to each other (Cronyn, 2001 p. 271). Collagen is a protein and main component in leather together with small amounts of keratin and elastin. Collagen protein is made up of peptide chains, which consist of amino acids (Larsen & Rhame, 1999 p. 13).

Since the tanning agents and fats originally in processed leather keeping leather fibres apart could be washed out under burial, there is a risk that water is the only element keeping leather fibres apart. Uncontrolled drying would lead to water loss and heavy shrinking of the leather structure, allowing the decayed collagen fibres to connect strongly to each other and can be very difficult to reintroduce to water. The collagen fibres from the dry former wet archaeological leather though strongly connected has been shortened by decay in the burial environment and is very brittle. The risk for laminations between the leather layers (see Figure 1) cracks and brakeage in the leather structure is therefore greatly increased (Volken, 2001, pp. 37- 44).

Before any action of treatment on dry archaeological leather from wet burial sites is carried out a thorough documentation needs to take place, such as pictures, measurements, smells and other characteristics. Secondly, a decision must be made for what importance the chosen treatment have for the archaeological leather, in terms of aesthetics, research data, originality, working marks and material safety. Thirdly, can this documentation be executed without the removal of sand, silts and other residues without making a decision for cleaning or reshaping of the archaeological leather? (Volken, 2001, pp. 40-41)

Dry cleaning with soft brushes is one way to remove sand, silts and residues and can be carried out while documentation is done, but can be hardly executed on large deformities and creases on dry archaeological leather. It is under such circumstances a treatment of flexural rigidity could be discussed. If the leather could be unfolded from its deformities the sand and silt would be easier to brush off and documentation of colour, marks and seams would be easier to record. Other reasons for reshaping archaeological leather is to safely store it, so that folding and creases do not lead to cracks and breaking. (Volken, 2001, p. 40)

To treat the flexural rigidity on dry archaeological leather a control of the humidity in between the collagen fibres in the leather structure is needed, though with delicacy to not create tension to the leather structure so that the leather fibres break (Volken, 2001, p. 37). Water tends to create tension in leather, caused by its high surface energy, so that frail and decayed cell structures in the leather will collapse when water evaporates from surfaces with larger area and the retreating water front

pulls the surfaces of the fibres together. The introduction of humidity to dry archaeological leather that already suffers from collapsed fibres caused by the uncontrolled air-drying following excavation could soften the flexural rigidity of the leather, but also destruct it. This is dependent on the amount of humidity that the leather is being exposed to. Even though the leather withstand the introduction of the humidity it may not be able to keep the humidity within the leather structure, and will suffer from the water tension (capillary forces) within cells, creating fibre rupture again when the water evaporates of (Cronyn, 2001 p. 80) followed by lamination, cracking, splitting and powdering of leather surfaces. To keep humidity and effect the flexural rigidity by filling up between the leather fibres a humectant can be introduced, like oil, glycerol, sorbitol or low-molecular-weight PEGs (Poly-ethylene-glycols)(Cronyn, 2001 p. 273).

The introduction of humectants into archaeological leather is mainly carried out by humidity chambers or immersions, exposing the leather to fine mist or baths with humectant mixed with water. This is often followed by, solvent drying. The same treatment can be obtained by mixing the humectant directly with solvents. The solvents that is commonly used, is ethanol. By using a solvent that has lower surface tension then water, some of the risks with collapsed leather structure could be obtained in the drying process and also helps the humectant deposit inside the leather structure in a better way then with water. Though a rising of the water temperature is needed for good penetration and decayed archaeological leather with its low shrinkage temperature would not withstand and shrink (Volken, 2001 pp. 37-44). Archaeological leather has because of deterioration a much lower shrinkage temperature then non- archaeological leather and even small increases in temperature would make the collagen shrink (Larsen & Rhame, 1999 p. 81). Though solvents do help the humectant molecules penetrate the leather and deposit inside the leather structure, the chances are that the humectant deposit on the surface, creating a film that covers decorations, working marks and seams instead. Solvents also have a tendency to keep leather in a rigid form. Other risks apart from using water or solvent is how the humectants decay with time, Colouring, cross-linking, absorption of humidity and particles in air, fungal and other biological attacks, and parameters of these risks that will affect reversibility. (Volken, 2001 pp. 37-44)

Freeze-drying is another way to dry the immersed leather and avoid surface tension of water when drying. When freeze-drying the immersed leather you first need to freeze the wet leather taking it out of the immersion with the help of a piece of mesh under, for support (Cameron; et al. 2006, p. 246) and then putting it straight in to a freezer. When leather is frozen it can be placed in the vacuum-chamber of a freeze-dryer that offers an atmosphere nearly free from water molecules. The leather can also be frozen in a block, which is favourable when handling fragile leather pieces that would fall a part when taking them out of the water, because of water surface tension and mechanical movements in water. In the vacuum-chamber enough energy is put upon the frozen leather in the form of heat, that water molecules go directly from a solid state to a vapour state without becoming liquid. The vapour is then lead to the surrounding atmosphere and trapped on to a cold external condenser. Freeze drying can also be done without introducing the leather to a humectant and is then only filled with water when freeze-dried. Though the process of freezing increases volume in the leather and can cause structural damage, it has been beneficial in the work with reshaping and cleaning archaeological leather, though the leather would first withstand rehydration (Cronyn, 2001 p. 80).

Archaeological leather with fragile collapsed fibre structures to the extent that the above explained flexural rigidity treatments would harm more then help, light dry cleaning with soft brushes and storage free from fluctuant environment is the only alternative (Cameron; et al. 2006, p. 248)

1.7 Limitations

Limitations within this study can be acknowledged in the author's lack of reading and understanding languages other then Scandinavian and English and have affected the literature research somewhat. Though a German article was found, the understanding of this text is somewhat limited. The paintings conservator at NTNU University Museum in Trondheim, Norway, Daniella Pawel (Informant 2, 11/12-2014) helped me understand the content somewhat, but a deeper

understanding has not been possible, though the English summary of the German text has been studied closely.

The limitation in the matter of test material is chosen to be one material, archaeological leather! This decision was made to narrow down the amount of work, research, writing and analysing time that comes with testing multiple materials with different origin. The archaeological leather is devoted by Elisabeth Peacock and NTNU University museum in Trondheim, Norway, and is a leather find of a shoe from the wet anaerobic environment in Trondheim that has dried out before any action to clean or reshape the leather shoe was undertaken. Dry archaeological leather from wet anaerobic burial sites is also a material that has large variations in the terms of deterioration within one single leather piece (Larsen & Rhame, 1999 p.75). That means that every individual sample becomes unique, even though it comes from the same leather find. The result from this study are therefore only an indication of how dry archaeological leather from wet anaerobic burial sites in Trondheim, Norway respond to exposure of cherry laurel leaves and their compounds; though, the results could be transferred to other finds of similar materials.

1.8 Theoretical Framework and Ethical Issues

The theoretical framework lies within the thoughts of Muñoz Viñas, who explains the concept "science of conservation" for what it is today (Viñas M., 2011 p. 75). He explains it with the words of another man (Popper). "The very idea that science demonstrates things is not correct: scientific truths are not which are demonstrated to be true, but rather which cannot be demonstrated to be wrong" (Popper, 1992 in: Muñoz, 2011 p. 77). So the demonstrations of the experiences that are achieved in this study are the truth until demonstrations prove them to be wrong. This is what empirical science used in a inductive way implies (Popper, 1957 p.39).

To safely use, by ethical basis in todays conservation science a method of any kind to reshape a piece of leather it has to go under investigation. This is what happens in this study. This investigation will answer for if this flexural rigidity treatment ethically works or not.

To sum up one could say that this experimental study implies the use of a inductive method, on which conclusions rely on the answers from the performed experiments

2. METHODOLOGY INCLUSIVE MATERIALS

This study will mainly build upon an experimental part in three steps, where the first step will answer if cherry laurel leaves work in a volatile matter, which has been implied by the article "Über der Weichen trockengefallener Alkohol und Formalinpräparate, Herbarblätter und von Tapagewebe" in Der Präparator from 2001 by Klaus Weichsler and co-authors. By placing single leather samples in airtight polypropylene boxes together with cherry laurel leaves; either cut (cut with scissors in 0,5 cm strips) or un-cut in, contact or non-contact, and then measure the flexural rigidity in time frames of; 4h, 8h 24h and 48h of treatment, this will be obtained.

The next step in the experimental study is to figure out the working agent in the cherry laurel leaves. By looking in to the biochemistry of the cherry laurel, the next step can be planned.

The cherry laurel bush is a common hedging plant that is green all year round, and can be found in shady places where it thrives. The cherry laurel (*prunus laurocaerasus)* can be found of different sorts and sizes. Some sorts carry flowers in the spring, that in the summer turns into berries, others have bigger leaves and do not carry flowers or berries (hedges direct, cherry laurel, gathered 11/6-2015).

Cherry laurel (*Prunus laurocaerasus*) leaves produce cyanogenic glycoside compounds, primarily amygdalin, in their leaves and other tissues (Santamour, 1998 p. 1537). When the plant tissues are damaged (cell disruption), hydrogen cyanide (HCN) is liberated through a series of enzymatic reactions. This cyanogenesis is initiated by the destruction of different cells, which release the amygdalin and enzymes, mainly β-glucosidase-type enzymes respectively. Once in contact, the enzymes sequentially split glucoses from the amygdalin to form prunasin and mandelonitrile (Selmar, 2010 p. 95). Another enzyme splits mandelonitrile into benzaldehyde and HCN (see Figure 2) (Dewick, 2002 p. 455).

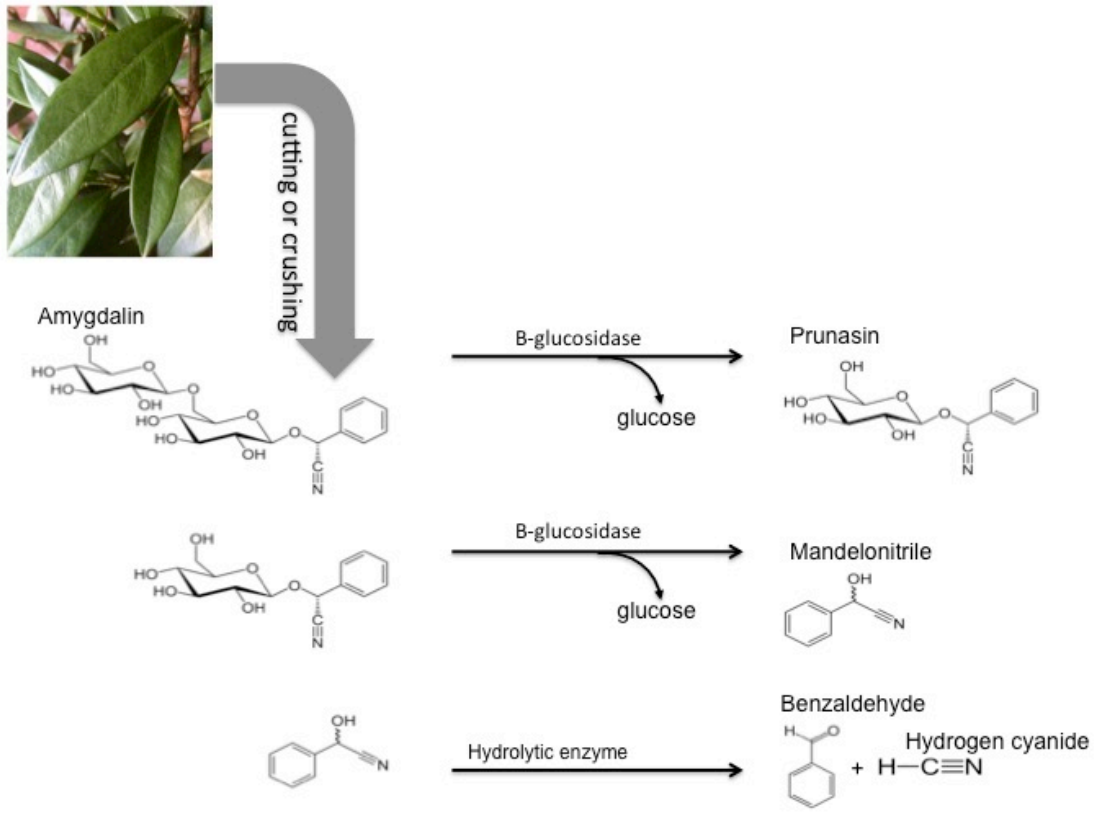


Figure 2 The Enzymatic reaction of amygdalin (Informant 3, 14/5-2015)

Considering the above reactions and their products, it is likely that mandelonitrile, benzaldehyde, HCN (hydrogen cyanide) or H_2O, or a combination of these products, are the active reagents in cherry laurel leaves.

To determine the active reagent, one or two of the above mentioned products (chemicals) will be placed in; non-contact (in pyrex glass vessels, 0,020L) with single archaeological leather samples in polypropylene boxes with airtight-casketed lids (1,2L)(see Figures 3 and 4), for different time periods. For better evaporation rate a cotton cloth can be placed in the glass-vessels, serving as a wick, if needed. Exposure of chemical compounds on the archaeological leather will occur in vapour phase via the evaporation of the liquids within the vessels and wicks.

The exposure time periods will be determined under the on-going experiment, starting with taking the first measurements of flexural rigidity after 48h of exposure treatment.

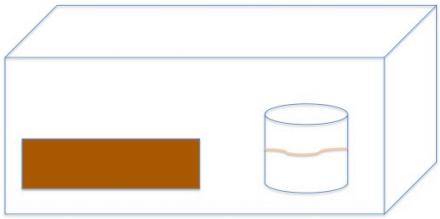


Figure 3 Polypropylene box with a leather sample in non-contact with one glass vessel filled with a single chemical.

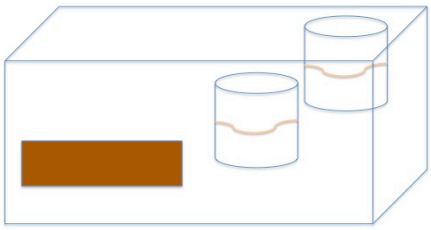


Figure 4 Polypropylene box with a leather sample in non-contact with two glass vessels with a single chemical in each vessel.

The aim of Experiment 3 is to investigate the original method with cherry laurel leaves, and compare it with the active reagent(s). There is also a desire to determine how the treatment works. This will be obtained by placing leather samples in polypropylene boxes as mentioned above, 3 samples in each box) in non-contact together with the active chemical compound(s), or, cut cherry laurel leaves in contact and non-contact. Measurements of pH, surface colour, weight, length, width and thickness; pre- and post treatment in time-frames determined after the results in Experiment 2 will then follow.

The hypothesis is that the aldehyde, benzaldehyde, from the enzymatic chain reaction explained above, could work as the active compound. This statement is based on the knowledge that aldehydes have been used as tanning agent throughout the history, via smoke tanning. By exposing rawhide to smoke made from plants that with the help of fire, extract and transport the aldehydes from the plant to rawhide, which then cross-links with collagen fibres preventing shrinkage on drying and hydrolysis (Cronyn, 1990 p. 265). According to the literature, benzaldehyde binds to cellular macromolecules, particular free amino groups of protein, forming Schiff´s bases (Miyakawa, 1979 pp., 1026-1027). Leather, which mainly consists of collagen, and is a polymer built of amino acids (Cronyn, 1990 p. 263), should bond with an aldehyde (in this case benzaldehyde) when being exposed to the volatile species released from cut cherry laurel leaves.

Benzaldehyde, which is the simplest representative of the aromatic aldehydes and derives mainly from the cyanogenic glycoside amygdalin via the enzymatic hydrolysis of mandelonitrile, can also be

prepared synthetically. Benzaldehyde is used primarily in the manufacture of dyes, cinnamic acid, perfumes and flavouring agents (William, Encyclopaedia Brittanica, Gathered 6/5-2015). Benzaldehyde oxidizes to benzoic acid when coming in contact with air (Bishop J. 1990 p. 12).

Benzaldehyde has a benzylic structure that could increase its stearic hindrence[1] and stabilise bonds formed through resonance structure[2], so that the benzaldehyde can react with an amino acid to form an imine, or Shiff´s base. This reaction is explained in figure 5 and detailed in Figures 6-8; however, most aldehydes should be able to react with amines to form imines. Aromatic aldehydes should produce resonance stabilised imine structures and would reduce cross-linking to further reactions between collagen fibres as happens with the smoke tanning mentioned above. This would allow a greater reversibility of the treatment via reformation of the aromatic aldehyde and amine via hydrolysis, as in Figure 8. (Informant 3, Gathered 19/5-2015).

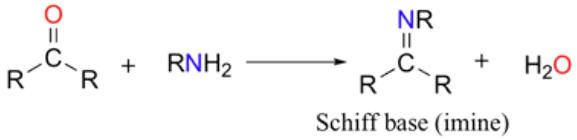


Figure 5 Shiff´s base (Informant 3, 12/3-2015)

Step 1 in the reaction. The electrophilic carbonyl carbon of the aldehyde undergoes nucleophilic attack by the nitrogen of an amine (see Figure 6) (Chemwiki, Shiff´s base 12/3-2015)

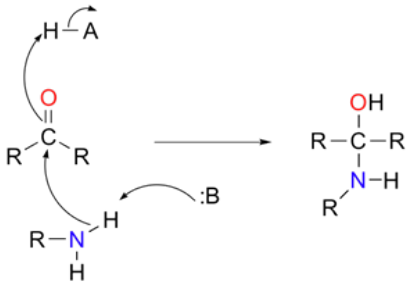


Figure 6 Step 1. Nucleophilic action (Informant 3, 12/3-2015)

Step 2 in the reaction: under acidic conditions, like with the amino acid, the amine is deprotonated and a carbon nitrogen double bond is formed. The carbonyl oxygen is protonated a second time and departs as water. Consequently, Schiff´s base formation is a condensation reaction of an aldehyde with an amine (see Figure 7). (Chemwiki, Shiff´s base 12/3-2015)

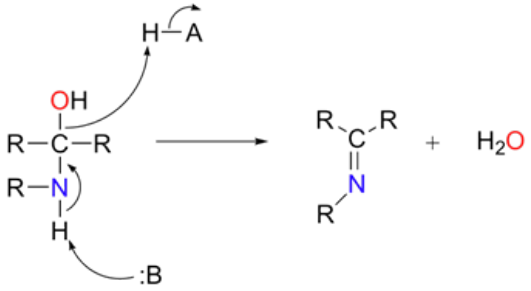


Figure 7 Step 2. Condensation action (Informant 3, 12/3-2015)

Step 3 in the reaction: an imine can be converted back to a carbonyl and amine through a hydrolysis reaction (see Figure 8). (Chemwiki, Shiff´s base 12/3-2015)

[1] Stearic hindrence = stopping of a chemical reaction which might be caused by a molecule's structure (Your dictionary, stearic hinderence, gathered 21/5-2015).

[2] Resonance structure = Resonance structures are used when one Lewis structure for a single molecule cannot fully describe the bonding that takes place between neighboring atoms relative to the empirical data for the actual bond lengths between those atoms. Lewis structures is a way of showing covalent bonds in many molecules of a representative element(Chemwiki, reconance structure, gathered 21/5-2015).

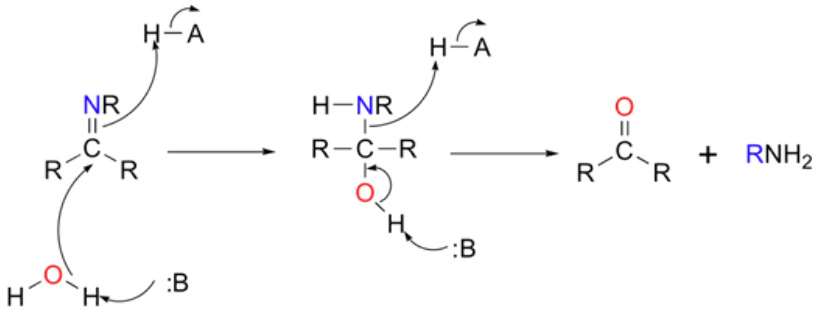


Figure 8 Step 3. Conversion back by hydrolysis reaction (Informant 3, 12/3-2015)

If benzaldehyde were the active reagent there would be interesting to compare benzaldehyde with another aldehyde, for example 4-methoxybenzaldehyde. By doing so, there can be a better understanding of the impact on deterioration, reversibility of flexural rigidity treatment, and changes of the original material (dry archaeological leather).

2.1 Leather

Archaeological leather from an anaerobic burial environment of the medieval cultural levels in Trondheim, Norway was used in this study. Because it has survived the wet environment, the leather is presumably vegetable tanned, as leather of other tanning processes do not survive in wet archaeological burial environments. This is an accepted knowledge in the archaeological conservation community (Botfeldt, 2007 p. 25).

2.2 Chemicals And Other Material Used For This Study

The cherry laurel leaves used in this study derives from the cherry laurel bush "Otto Luyken"(*Prunus laurocaerasus 'Otto Luyken),* that was bought on Blomsterlandet in Sisjön Gothenburg in Mars 2015. "Otto Luyken" was purchased so that access of cherry laurel leaves would not be a problem under the experiments.

The cherry laurel leaves was used intact or cut into approximately 0,5 cm thick pieces with scissors, placed in contact or non-contact in pyrex glass vessels (0,20L) with the leather samples. The amount of leaves was set in relation to the weight of the leather samples used in every experiment. One leather sample weighs approximately 2g, the double amount in weight; 4 g leaves will be used for every sample. By personal experience, the active agent(s) in the leaves reduces after 24 - 48h (dependent on the condition of the leaves), and must be replaced by new leaves. This is also a phenomenon that the conservator Tomas Gütebier has observed (Informant 1, 28/1-2014).

Polypropylene boxes with airtight-casketed lids (1,2 L) purchased at Ö&B Nordstan Gothenburg were selected to be the container under the treatment of the leather samples with cherry laurel leaves or other compounds and mixtures derived from the cherry laurel leaves. As needed one or two glass vessels was to hold different liquid compounds and were placed in each box. Muslin (cotton cloth) wicks were placed in each vessel to increase area for evaporation of the liquids.

None of the chemical compounds used in the study will be in direct contact with the archaeological leather. Exposure of chemical compounds on leather only occurred in vapour phase via the evaporation of the liquids from the vessels and wicks described earlier in this section.

Distilled water (H2O) was obtained from the tap in the laboratory in the department of conservation at the University of Gothenburg.

Mandelonitrile (C_8H_7NO) in a 80% solution was purchased from Alfa Aesar, A Johnson Matthey Company. Mandelonitrile is a yellowish liquid with an odour of almonds and has a melting point of -10°C and a boiling point of 168-170°C (Alfa Aesar, Gathered 6/5-2015).

Benzaldehyde (C_6H_5CHO) in a 98% solution was purchased from VWR Prolab Chemicals. Benzaldehyde is a colourless liquid with an odour of almond oil. It has a melting point of −26 °C (−14.8 °F) and a boiling point of 179 °C. It is only slightly soluble in water and is completely soluble in ethanol and diethyl ether (William H. B., Encyclopaedia Britannica, Gathered 6/5 -2015).

A 10 % solution of HCl was prepared from concentrated HCl using distilled water from the tap in the laboratory. HCl is used in this study to simulate the effect of HCN which is one of the final products of the step-wise enzymatic hydrolyses of amygdalin emitted from plants of *Prunus amygdalus* var. *amara*; Rosaceae and other *Prunus* species (Dewick, M. P., 2002 p. 455). Because of HCN´s toxicity HCl is used to simulate the HCN (Informant 3, gathered 18/2-2015). HCN (hydrogen cyanide) is a toxic chemical and is a colourless or pale blue liquid below 25.6°C and a colourless gas above 25.6°C. Hydrogen cyanide is a monomer and has an odour of bitter almond smelled in the concentration range of 1-5 ppm (Centres for Disease Control and Prevention, Hydrogen cyanide, Gathered 6/5-2015). Hydrogen cyanide penetrates the human skin causing cyanide type poisoning if levels are over 50 ppm exposed under 30 min. Only butyl or Teflon can protect the skin from absorbing these toxicants and prevent poisoning (INEOS USA LLC, HCN 2006 p. 2).

4-methoxybenzaldehyde ($C_8H_8O_2$) in a 98% solution was purchased from Merck Schuchardt and it is a substituted aromatic aldehyde used in the experimental treatment to compare the effect of benzaldehyde. 4-methoxybenzaldehyde is a colourless to pale yellow liquid with a melting point of 0-2°C and a boiling point of 247-249°C (Alfa Aesar, product specification, Gathered 6/5-2015). 4-methoxybenzaldehyde also known as 4-Anisaldehyde occurs naturally in the fennel and anise plants and is used in various products as soaps, detergents, cosmetic creams, perfumes, artificial food flavouring (anise, caramel, chocolate, strawberry, vanilla), insect attractant for pest control, antihistamines and electroplating (Toxipedia, p-Anisaldehyde, Gathered 6/5-2015).

2.3 Flexural Rigidity Apparatus

As the modification of the flexural rigidity of the archaeological leather is the key evaluation parameter of the treatment it was of great importance to construct an instrument for its measurement. By looking into an instrument that has been used for measuring flexibility on textiles and is a part of the British standard BS 3356:1990 the flexural rigidity apparatus was build (Booth, 1968 p. 284) (see Figure 9)

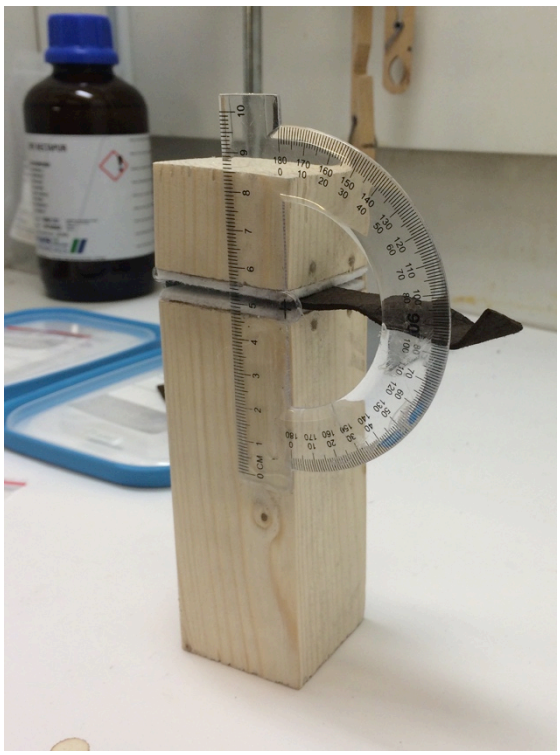


Figure 9 Flexural rigidity apparatus

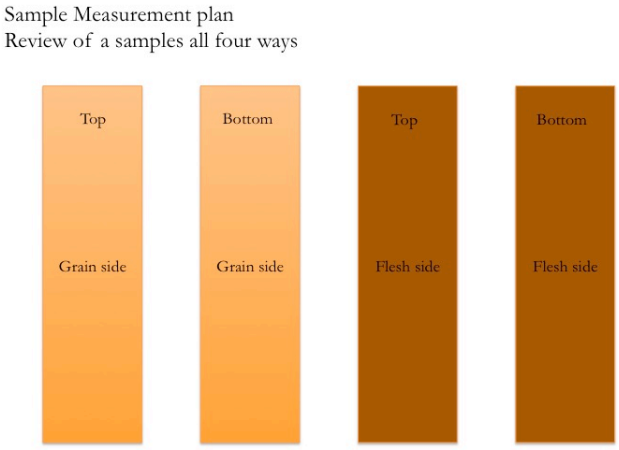


Figure 10 A leather samples all four ways

The flexural rigidity apparatus measures the hang of the leather sample from one point in angle to another in degrees from where the nearest edge on the leather sample lies towards the protractor and crossing the protractor at its outer point. The sample is placed exactly 1 cm from the front edge toward a marked line in between the blocks of the apparatus, so that all samples have the exact same position under all the measurements and can be reproducible. Because of uneven leather samples dependable result is obtained by measuring the samples all orientations. The mean value is then calculated and used as data in the experiments (see Figure 10).

The sample size depends on the chosen measuring device and is limited by the total amount of available test material (archaeological leather). The pH-tests are invasive and destructive, and each test require 20 mg of material and are performed three times, 1x pre- and 2x post-treatment. The initial leather samples cut from the find will therefore need to have a sufficient size so that they can be measured in the flexural rigidity apparatus even after several pH-tests. With that in mind, the size of the samples will be approximately rectangular in shape (7x2 cm) and weigh ca. 2 g. Samples were cut by a scalpel using a template with the correct measurements (7x2cm). The dimensions (width, length and thickness of every individual sample were measured by a calliper, and each sample was weighed at each stage of the treatment.

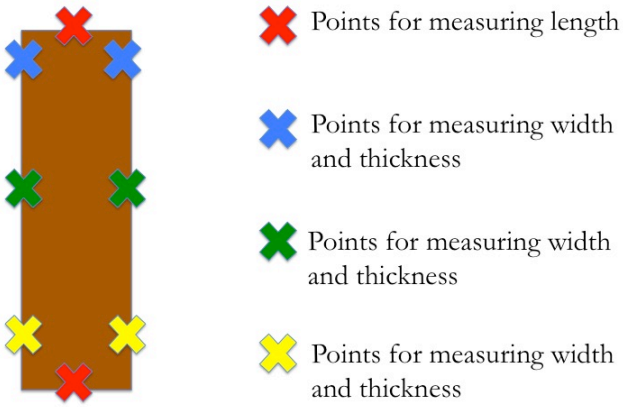


Figure 11 Points for measuring

Figure 11 presents a diagram of the points for each measurement. Each sample was traced onto a sheet of paper with the measurement points marked on this template to ensure reproducibility of the measurement points. Length is measured from centre point to centre point of the short edges of each sample. In the same way the width was reproducibly measured near each end and in the middle of each sample. The thickness of the samples was measured at six points corresponding with the points for the measurement of width. The mean width (from three measurements per sample per occasion) and mean thickness (from six measurements per sample per occasion) were calculated. The weight of the samples was measured with an analytical balance scale with an accuracy of 0.001g.

2.4 pH Measurement

Measurements of pH-levels of archaeological leather can indicate condition and deterioration degree. It can even, to some extent reveal the cause of deterioration. A normal pH for vegetable tanned leather is 3,5-5,2 pH (Stambolov, 1969 p. 36). For archaeological leather there are however a lot of parameters that affects the pH. The parameters that could influence are the character of soil and placement in burial environment. The contact with water, iron, oxygen, sulphuric dioxide and nitrogen oxides are possible parameters that could have effect on archaeological leather, in the terms of pH. The different environments can make the leather undergo different degrading cycles. For example: pH 3 and 6-7 makes the leather undergo acid hydrolysis, and a pH over 7 makes the leather undergo alkaline hydrolysis (Botfeldt, 2007 p. 25). The recommended range for pH on archaeological leather is between 4-6 pH, where neither bacterial or fungal growth are supported (Peacock, 1984 p. 2)

Testing the pH of archaeological leather is invasive and requires a minimum sample size of 20 mg. This follows the instructions of Larsen and Rhame (1999 p. 125). In this study, the leather samples were taken with punch pliers, and thereafter soaked in 1ml of distilled water for approximately 24h. The 1 ml leather extractant is then measured with the pH-meter, Metrohm 120 V | 827 pH lab

digital pH-meter calibrated with a 2-point calibration of pH 4 and 7 standard solutions. If the measured pH is under pH 4 or over pH 10, the differential should be measured. This can be achieved by diluting the extraction with 10 ml of distilled water. The dilution is measured in the same way as the extraction, and thereafter the differential can be calculated with simple algebra (see Figure 12). The differential number from the calculation express how strong the acid/base is, and cannot exceed the value of 1.0. For acidic leather under pH 4 a differential value of 0.7-1.0 would mean that a strong acid is present (Larsen & Rhame, 1999 p. 125).

Differential = pH diluted - pH extraction

Figure 12 Differential calculation in pH (Larsen, 1999 p. 125)

2.5 Colour Measurement

A Konica Minolta FD-5 spectrodensitometer was used for measuring the colour of the archaeological leather surfaces, and from these measurements calculate pre- and post- treatment colour differences. To determine specific colour the CIE L*a*b* colour space was used. This colour space was defined by CIE (Commission Internationale de l'Eclairage) in 1976. In this colour space L* indicates the lightness, and a* and b* the chromaticity coordinates. This colour space can be represented as a 3-dimensional Cartesian coordinate system where L*, a* and b* relate to the three axes. Values for L* ranges from 0 (black) to 100 (white), and both positive and negative values are possible for a* and b*. Positive a* is the red direction; negative a* is the green direction; positive b* is the yellow direction; and negative b* is the blue direction. The origin of the coordinate system is achromatic. The difference between two points in this system can be calculated on each axis: ΔL*, Δa* and Δb* and these values may be positive or negative:

- ΔL* (L* sample minus L* standard) = difference in lightness and darkness (+ = lighter, - = darker)
- Δa* (a* sample minus a* standard) = difference in red and green (+ = redder, - = greener)
- Δb* (b* sample minus b* standard) = difference in yellow and blue (+ = yellower, - = bluer)

The total difference, CIE ΔE, between two points in the colour space can be calculated in several ways, but the result is always positive.
The simplest colour difference formula is the CIE ΔE_{76}^{ab} which calculates the sum of the root mean squares of the ΔL*, Δa* and Δb* of the points: $\Delta E_{76}^{ab} = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$ (Konica minolta, Gathered 6/4 - 2015). This is the original calculation formula from when the colour space was defined by CIE in 1976. Through time, this calculation has been updated and other terms to correct for inhomogeneity in the colour space were introduced. To achieve a more dependable result an Excel macro was used to calculate colour differences according to the CIE ΔE 2000, $CIE\ \Delta E_{00}^*$, (See Figure 13). The tolerance for changes or noticeable differences of colour is smaller for darker colours then brighter, but the acceptable change is still in the ranges up to 1.0 in the ΔE units (Mokrzycki, Tatol, 2012 p. 6). For archaeological material larger changes have been accepted in the ΔE units (Informant 4, gathered 3/6-2015)

For better understanding of the changes in the different dimensions of the colour, the L*, a* and b* units can be compared. Tolerance of changes in the L*, a* and b* units should not exceed 0.57 in modern material (Mokrzycki, Tatol, 2012 p. 6). For archaeological material a larger change in the individual L*, a* and b* units is acceptable (Informant 4, gathered 3/6-2015).

$$\Delta E_{00}^* = \sqrt{\left(\frac{\Delta L'}{k_L S_L}\right)^2 + \left(\frac{\Delta C'}{k_C S_C}\right)^2 + \left(\frac{\Delta H'}{k_H S_H}\right)^2 + R_T \frac{\Delta C'}{k_C S_C}\frac{\Delta H'}{k_H S_H}}$$

Figure 13 Delta E 2000, Calculation of surface colour (Guarav et al. 2004 p. 22)

During repeated colour measurements it is critical that the orientation of the spectrodensitometer is the same every time, creating reproducible data. The leather sample also needs to be in the same

direction every time. Reproducibility of both the orientation of the instrument and the leather is of importance because of the nature of the surface of the leather (grain, smoothness/roughness, follicle patterns etc.) and how it reflects light. Leather has an uneven surface, and though the same point is being measured it can show different results if the measured point has been turned, for example 30° (Informant 3, 18/2-2015).

The colour measurement of the leather samples was taken at one specific point right below the hole that was taken with punch pliers for the pH-test. The same point was measured once at each subsequent time point. Since the sample is rectangular the spectrodensitometer was placed from the short edge and in toward the specific point of measurement.

3. EXPERIMENTAL REVIEW

In this chapter the experiments will be reviewed one by one explaining the aim for the individual experiment, for what materials being used, methods for using those materials, results and discussion about the outcome.

3.1 Experiment 1: Volatile or not?

3.1.1 Aim

The aim of this experiment was to determine the manner of action of the cherry laurel leaves upon the archaeological leather. That is, whether or not the leaves need to be in contact with the material to work. This can be inferred whether volatile species are the active reagents. A simple comparative test was developed where the effectiveness of the treatments (e.g. contact vs. non-contact) was evaluated using flexural rigidity as the metric.

3.1.2 Materials and methods

Three samples of archaeological leather were placed in three identical plastic boxes with airtight lids (one sample per box). Each sample was measured using the flexural rigidity apparatus, as described above in Section 2.3 before placement in the box (see Figure 2). At the same time length, width and thickness were also measured. Three experimental configurations were used (see Figure 14). Four grams of leaves (intact or cut) were placed in each box either in contact or not in contact with the leather sample. After 24h of exposure, each box was refilled with four grams of leaves, so that the active reagents in the leaves would not decrease.

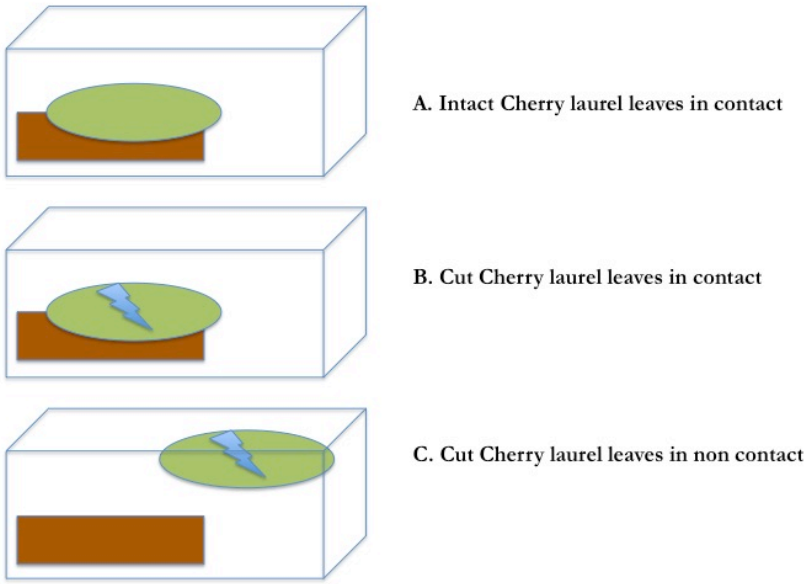


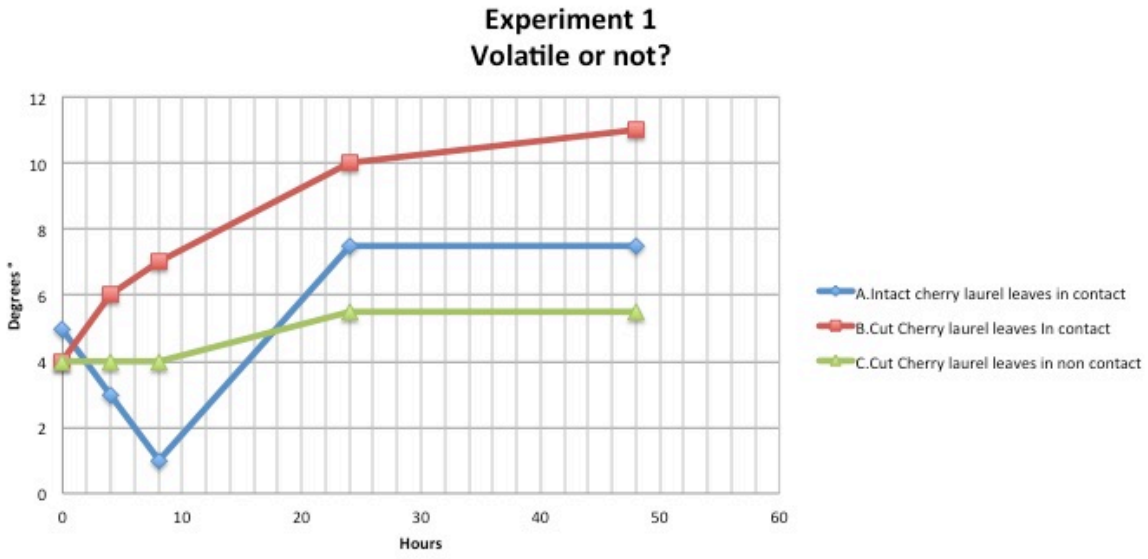
Figure 14 Sample and leaf placement in Experiment 1

Flexural rigidity measurements were regularly taken during treatment after 4, 8, 24, and 48 h of exposure.

3.1.3 Results

All samples show a response to the exposure to cherry laurel leaves. After 48 h of treatment, an increased flexibility was observed for all experimental configurations (see Figure 15). In the same chart, you can see that closer contact (B.) between cherry laurel leaves and archaeological leather will increase the mean flexural rigidity. Though it must be noted that while all samples were taken from the same object there is great variability in their pre-treatment condition, which is discussed in detail

in section 1.2.



Exp1 Volatile or not?					
Flexural rigidity (mean value in °)	Before treatment	After 4h of treatment	After 8h of treatment	After 24h of treatment	After 48h of treatment
Hours	0	4	8	24	48
A.Intact cherry laurel leaves in contact	5	3	1	7,5	7,5
B.Cut Cherry laurel leaves In contact	4	6	7	10	11
C.Cut Cherry laurel leaves in non contact	4	4	4	5,5	5,5

Figure 15 Experiment 1: Volatile or not?

3.1.4 Discussion

The first conclusion is that the active agents are released by damaged leaves and picking a leaf from the plant results in some damage, and finer cutting should lead to greater release of the active agent(s), by increasing the surface area from which the agents are emitted.

Additionally, the experimental results demonstrate that treatment with cherry laurel leaves does not require contact between the leaves and the material to be effective. This indicates that one or more volatile species are the active agents. However, the best results were obtained in the box where the archaeological leather was in direct contact with the cut leaves, and the effectiveness could therefore be dependent on the concentration of the active reagents at the surface of the leather. If the reagents were produced by cut cherry laurel leaves, there should be a local decay in concentration of the volatile agents, and therefore, dependent on distance from these concentrations. With time, diffusion should result in an even distribution of the reagents. Exposing the samples in the non-contact configuration for longer time periods should result in similar effect on flexural rigidity. Heating, which increases the rate of diffusion, might also increase the rate of action of the non-contact method.

The results of this experiment are significant because contact between the cut leaves and the leather could result in the transfer of plant sap to the leather find, which would have unknown effect on the degradation of the leather and possibly contamination for future studies. Therefor a non-contact treatment is desirable because it reduces the risk for contaminating the find.

3.2 Experiment 2: If Volatile. What Is Volatile? Determination Of Active Specie(s) In Cherry Laurel Leaves On Archaeological Leather?

3.2.1 Aim

The aim of this experiment is to determine the active volatile specie(s) in the cherry laurel leaves. By testing the chemical compounds derived from the enzymatic chain reaction that occurs when cherry laurel leaves are being cut (see section 2) this will be obtained. This will lead to additional questions:

- If the active agent(s) is determined, in what way does it work?
- Does using chemically derived agents require shorter exposure time or longer exposure time?
- How does the treatment system respond to heating?

3.2.2 Materials and methods

Ten samples of archaeological leather were placed in 10 identical polypropylene boxes with airtight lids (one sample per box). Each sample was measured using the flexural rigidity apparatus, as described above in Section 2.3 before placement in the box. This procedure is exactly the same as in Experiment 1. To the glass vessel(s) in each box, 10 ml of each substance described in Section 2.2 were added. Combinations of species were achieved by adding additional glass vessels, with their own individual substance, placed in the same polypropylene box making sure no contact with the archaeological leather sample occurred. To increase evaporation of species, a piece of muslin acting as a wick was placed into the substance. Sample A-D did not have a wick.

Sample A-D were used to determine if a single volatile agent is as effective as cut cherry laurel leaves. For samples A-D, single agents were used without a wick, and leather samples were exposed to the single agents for 48h. Flexural rigidity was measured before exposure and after exposure of 48h; thus that was the optimum exposure time in Experiment 1. Figure 16 describes samples A-D.

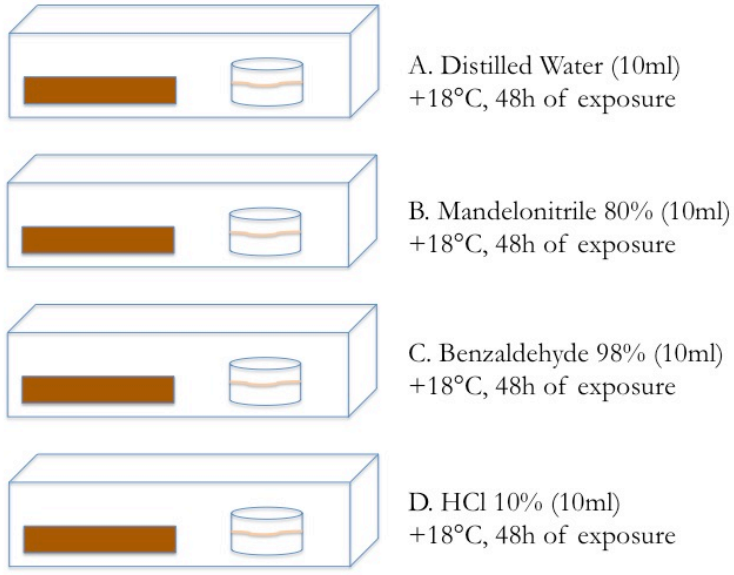


Figure 16 Exp. 2 Sample A-D

Samples E-J build upon the results of samples A-D and attempt to answer some additional questions regarding heating and required treatment time. The combined effect of two agents was evaluated in samples E-H to determine which, if any, two agents in combinations was as effective as the cherry laurel leaves. Exposure time for sample E-H with two combined agents was set to be 72h at first. Timeframe for sample E was then elongated and measured again after 96 and 120h to detect loss in effect. Flexural rigidity was measured for sample F-H before treatment and after 72h of treatment. Flexural rigidity was measured for sample E before treatment and after 72, 96, 120h of treatment.

Sample I build upon the answers in sample E and is set to answer for the effects of treatment on flexural rigidity under the timeframe of 4, 8, 24, 48, 72h to compensate for the information gap in the early timeframes in term of the flexural rigidity in sample E. Sample J measures the flexural rigidity after treatment of 4 and 48h under gentle heating to 38°C ±2°C. If the leather could withstand the heat itself (see shrinkage temperature in Section 1.6.2), it was proposed that the timeframe under heating could be decreased. With that in mind, I wanted to see how the treatment under heat affected the leather despite the risk of shrinkage.

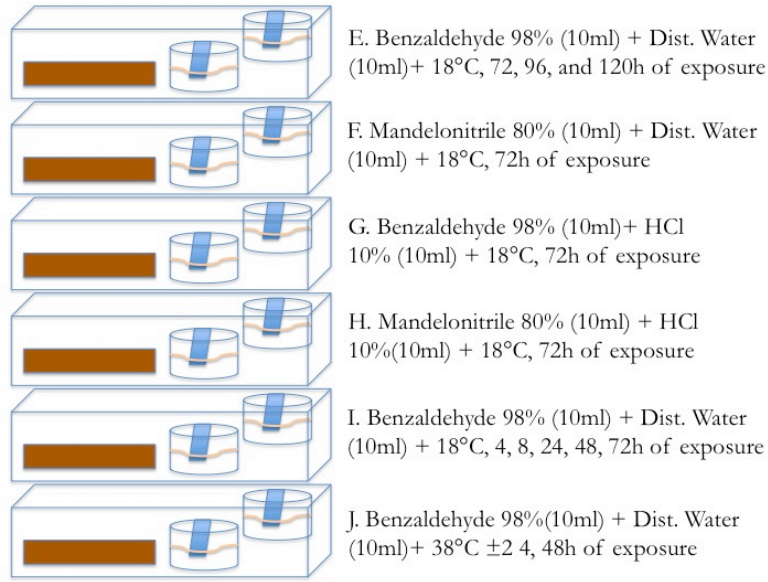


Figure 17 Exp.2 Sample E-J

3.2.3 Results

After 48 h of exposure, samples A-D showed only a vague response to treatment for all agents (see Figure 18). Exposure to water vapour resulted in a slight increase in flexibility, while exposure to mandelonitrile resulted in an even less increase in flexibility. Exposure of benzaldehyde and HCl both resulted in a decrease in flexibility. See Figure 18 for a summary of the results. This indicates that in non-contact treatment with cherry laurel leaves it is either the water liberated from the cut plant tissue that is softening the leather (water as a plasticiser), or that it is a mixture of two or more volatile agents that together act to soften archaeological leather during such a treatment.

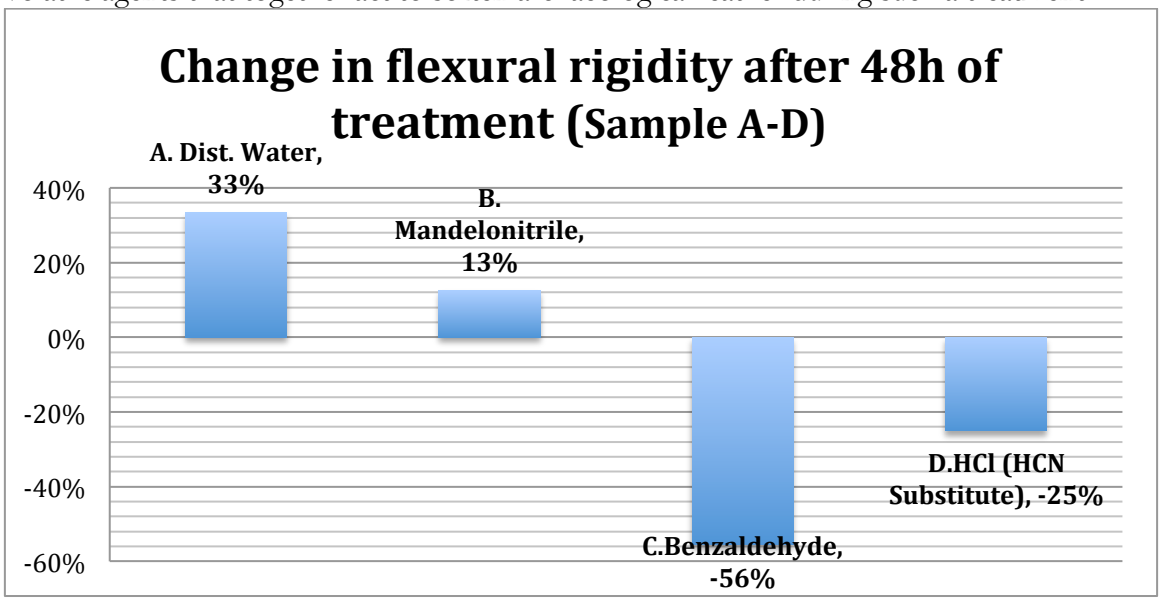


Figure 18 Flexural rigidity of samples A-D

This leads to the tests E-H, which evaluated the combined effect of pairs of agents. Figure 19 presents the results from these pairings. After 72 h of treatment, benzaldehyde with water results in

a fourfold increase in flexibility, while the other agent pairings had little effect or a negative effect on the leather samples. Note that with cut cherry laurel leaves only a 2.5 fold increase in flexibility was observed after 48 h of treatment (see Experiment 1 Figure 15 above). This indicates that benzaldehyde and water together are the active agents.

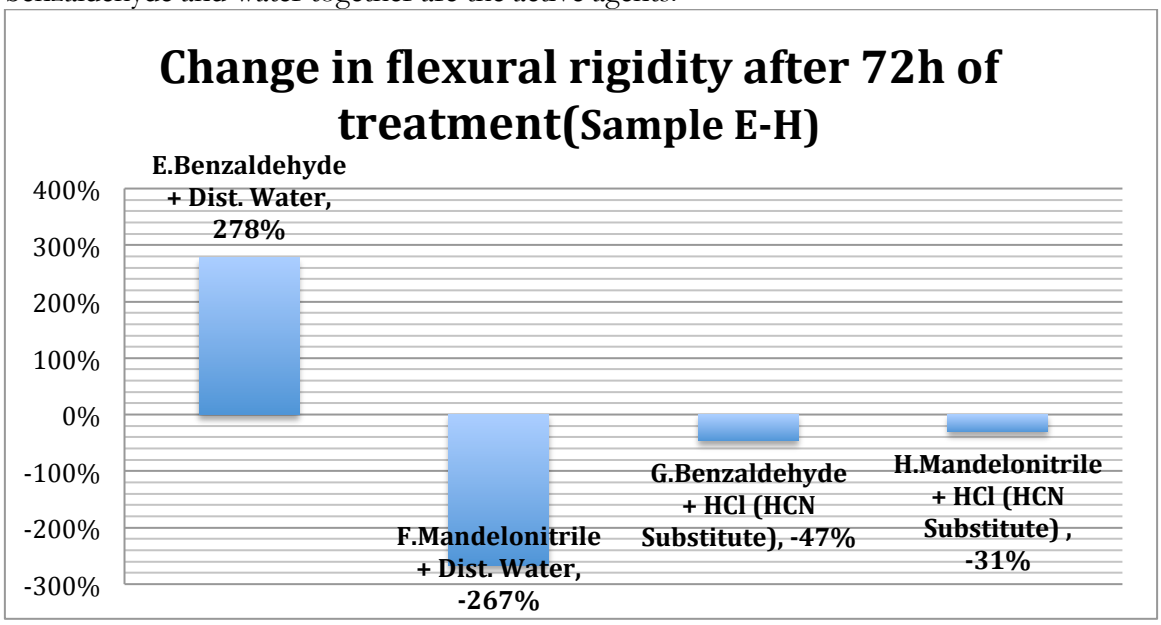


Figure 19 Flexural rigidity of sample E-H

Sample I repeated the benzaldehyde + water experiment but with shorter timeframes. Benzaldehyde + water in room temperature (approximately 18°C) has effect after 8 h of exposure. After 72 h the flexural rigidity has desired reshaping abilities. The dip seen in the flexibility at 48 h is due to the wick falling into the water bath sometime between the 24 h and 48 h of measurements, which reduced the rate of evaporation of water in the sample treatment chamber.

Sample J evaluated the effect of gentle heating to increase the rate of evaporation and diffusion of the gas phase agents during treatment to decrease the required treatment time. Increasing the temperature to 38°C ±2°C did not increase the working rate of the flexural rigidity treatment with benzaldehyde and water, it rather decreased it. The archaeological leather did not withstand the increased temperature, and already after 4h of treatment the leather became stiff and hard.

Another phenomenon noted when using benzaldehyde + water is the formation of white crystals. These were noted as appearing on the water wick and elsewhere in the polypropylene box after 72 h of treatment. The crystals were not noted on the leather sample until 96 h of treatment. The conditions were repeated without leather present in the box and the white crystals were again noted after ca. 72 h of treatment. Looking in to the chemistry these crystals are likely benzoic acid, which readily forms from oxidising benzaldehyde in the presence of water (mhhe.com, oxidation of aldehydes to acids, Gathered 11/5-2015).

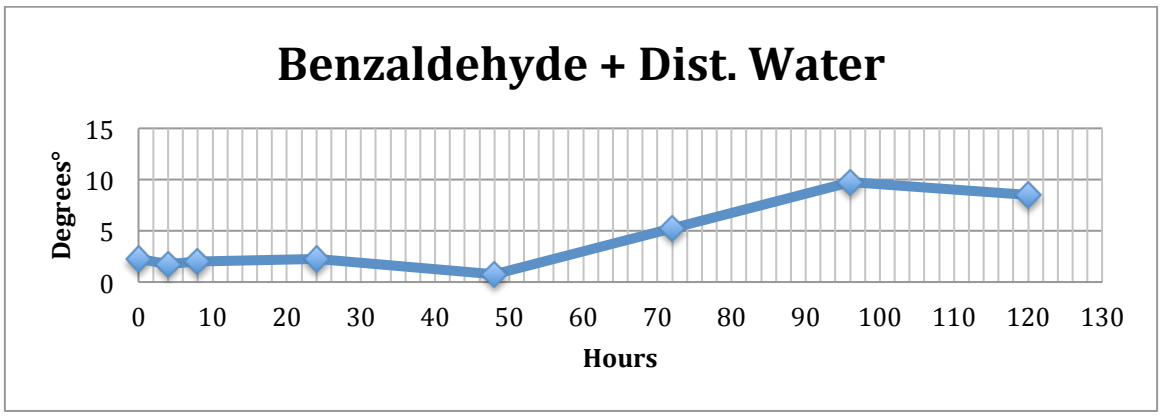


Figure 20 Flexural rigidity of benzaldehyde + dist. water. Sample E and I

3.2.4 Discussion

The results demonstrate that benzaldehyde and water are the active agents, and that they work without contact in room temperature (approximately 18°C). Because water has a slight effect on leathers flexural rigidity and benzaldehyde has no effect on leathers flexural rigidity (experiment 2, samples A-D), it seems that water is needed to first swell the leather structure so that benzaldehyde can get access and react with the collagen fibres in the leather. Heating is not an option to improve the working agents, thus adding heat during treatment did not decrease the timeframe for the working agents and instead made the leather samples lose flexibility, becoming stiff and hard already after 4h of treatment. This was an expected result, as archaeological leather is sensitive towards heat because of its low shrinkage temperature, as mentioned in Section 3.2.2.

The dip seen in the flexibility at 48 h caused by the wick falling into the water bath sometime between the 24 h and the 48 h of measurements reduced the rate of evaporation of water in the sample treatment chamber. Therefore it could be possible that 48 h, rather than 72 h, of treatment are required to achieve the minimum change in flexural rigidity for reshaping. It also indicates that both agents are required for the treatment to work, and that change in their concentrations, at least of the water, results in reduced effectiveness of the treatment. Thus care should be taken to fasten the wicks to the sides of the vessels with a wooden clip, during treatment.

Another point of view, seeing that benzaldehyde and water have a better effect on flexural rigidity than cut cherry laurel leaves when comparing results from Experiment 1and 2, it also offers a safer working environment for both human and sample. Cherry laurel leaves do produce HCN, and exposure to humans is toxic and could have negative effects on leather. Benzaldehyde and water offers a safer treatment, though further investigations need to be carried out, in the terms of how the crystals (benzoic acid) would effect the leather.

For a better understanding of the mechanism under the treatment of leather with benzaldehyde and water, other features then the flexural rigidity need to be investigated, as mentioned in Section 2: like pH, surface colour and measurements before and after treatment of the leather samples width, thickness, length and weight. There is also the question, if another aldehyde could work in the same way as benzaldehyde.

3.3 Experiment 3: The Effects Of Cherry Laurel Leaves And Their Compounds

3.3.1 Aim

The effects of treating archaeological leather with cherry laurel leaves are investigated here. The former tests have brought information of the working species in cherry laurel leaves (benzaldehyde + water). As predicted, benzaldehyde was a part of the process.

Benzaldehyde was not able to react with the leather by itself and it seems from the results in Experiment 2, that benzaldehyde needs water to transport itself into the archaeological leather. The aim of this experiment is to investigate the original method with cherry laurel leaves, and compare it with the aldehyde + water treatment and furthermore having it compared with one more aldehyde (4-methoxybenzaldehyde).

3.3.2 Materials and methods

Four polypropylene boxes with airtight lids were prepared with three leather samples in each box (see Figure 21). Before placement in boxes, samples were measured in weight, length, width, thickness, pH, surface colour and flexural rigidity (see Section 2.3-2.5). Every sample is marked with a coloured cotton thread, to not confuse them with each other under the experiment. 12g of cut cherry laurel leaves was placed in contact with the leather samples in Box 1 and refilled after 48h with additional 12g of cut cherry laurel leaves. In Box 2, 12g of cut cherry laurel leaves were placed in non-contact and supplemented with an additional 12g of cut cherry laurel leaves after 48h. In Box 3 two glass vessels were placed with a cotton wick in each vessel to increase evaporation surface. One vessel was filled with 10 ml of distilled water and the other with 10 ml of benzaldehyde 98%. In Box 4 two glass vessels was placed with a cotton wick in each box, just as in Box 3. One vessel was

filled with 10 ml of distilled water and the other vessel was filled with 10 ml of 4-methoxybenzaldehyde 98%.

Time frame for measuring varied from one measurement to another. Since loosing contact between sample and effective species while being measured, leads to a reduction of treatment effect. Time consuming measurements were therefore reduced to fewer occasions then the non-time consuming measurements.

Flexural rigidity and surface colour, which can be measured in a non time-consuming way, were measured before treatment, after 24h, 48 h, 72 h of treatment and 24 h, 1 week, 3 weeks after treatment.

Weight, length, width and thickness are measured before treatment, right after 72 h of treatment and 24h, 1 week, 3 weeks after treatment.

The pH was measured on fewer occasions, as it is a time consuming and an invasive measurement. 20mg of the leather sample will be removed with every measurement. This will effect other measurements such as weight and flexural rigidity to a larger extent with further measurements.

The timeframe for measurement of pH is set to be before treatment where a leather sample was taken before measurement of weight, length, width, thickness and flexural rigidity to not interfere with the first measurements.

After 72 h of treatment where a leather sample was taken for the pH-test after measurements of weight, length, width, thickness and flexural rigidity to be measured under the same conditions as previous measurement before treatment.

3 weeks after treatment where a leather sample was taken for the pH-test, after measurements of weight, length, width, thickness and flexural rigidity. This is set to have minimum interference with the measurements, though some interference; manly on flexural rigidity is inevitable from the 20mg taken after 72 h of treatment.

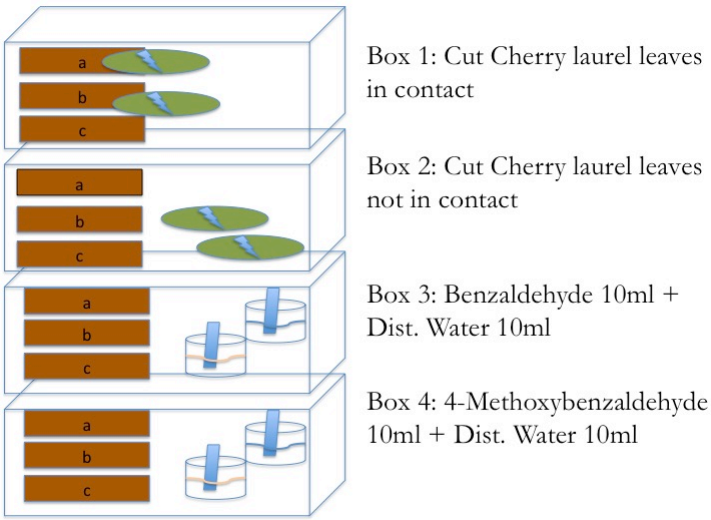


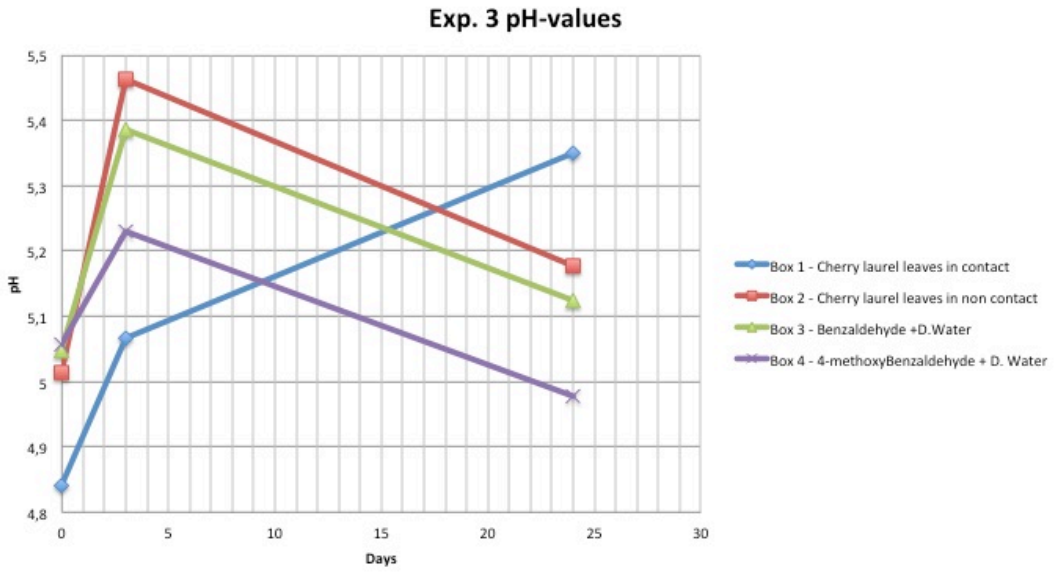
Figure 21 Exp. 3 Sample placements

3.3.3 Results

The results from Experiment 3, which is presented as mean values, shows that cut cherry laurel leaves in contact, cut cherry laurel leaves in non-contact, benzaldehyde +distilled water and 4-Methoxybenzaldehyde + distilled water work in similar ways. All samples followed the same pattern; change from original state before treatment to a obvious change in every parameter: flexural rigidity, pH, weight, width, thickness, length and surface colour after exposure of 24h-72h treatment. Nearly

all samples reverted back to their original state after 24h of post-treatment. After 3 weeks post-treatment the leather samples do not show any measurable change from previous measurement at 24h post-treatment, except for one or two cases.

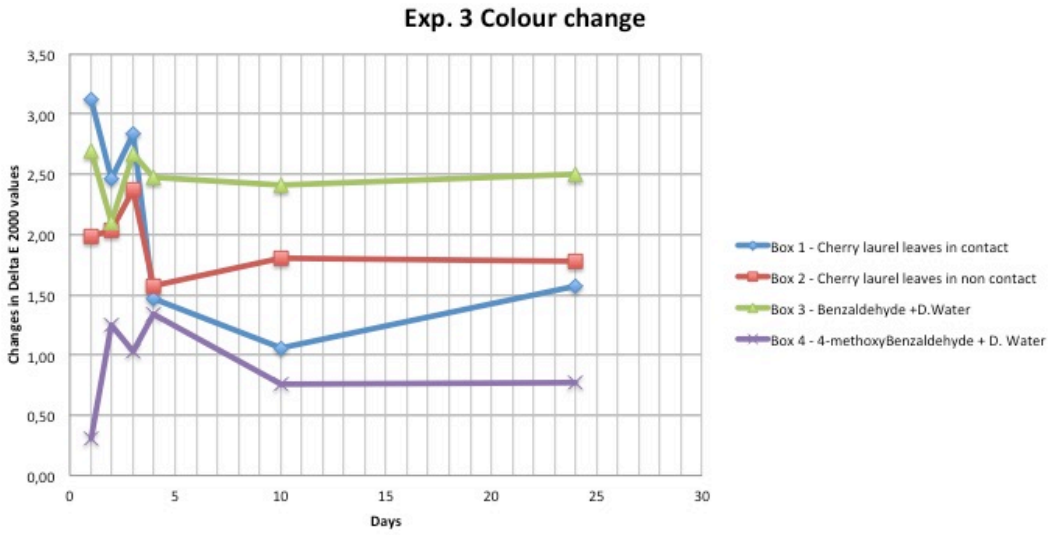
The pH levels changes in all the samples regardless exposure treatment and ranges from 4.8 - 5.5pH following exposure of 72h. 3 weeks post-treatment the samples return back toward the original pH ±0.2 pH, except for Box 1 where the pH do not return to its original pH, but instead increases the values from 4.8pH to 5.35pH (see Figure 22).



pH (mean valiue in pH)	Before treatment	72h of treatment	3w Post-treatment
Days	0	3	24
Box 1 - Cherry laurel leaves in contact	4,84	5,07	5,35
Box 2 - Cherry laurel leaves in non contact	5,01	5,46	5,18
Box 3 - Benzaldehyde +D.Water	5,05	5,39	5,12
Box 4 - 4-methoxyBenzaldehyde + D. Water	5,06	5,23	4,98

Figure 22 pH values of samples pre- and post-treatment

The general trend in surface colour change (expressed in ΔE units comparing pre-treatment values to each treatment period) are not greater than 1 for all the samples except for the samples in box 1(cut cherry laurel leaves in contact) where the changed units was over 1 under and after exposure. Looking closer at the individual L*,a* and b* units this is not a trend for all of the samples, but a trend for one sample(sample 1C). It seams like sample 1C reacts with the exposure of cut cherry laurel leaves in contact in the L* coordinate toward a lighter surface colour. Both samples 1A and 1C have a intense reaction to the exposure of cut cherry laurel leaves in contact after 48h, but then returns back to their original units post-treatment, except 1C in the L* coordinate (see Figure 23).

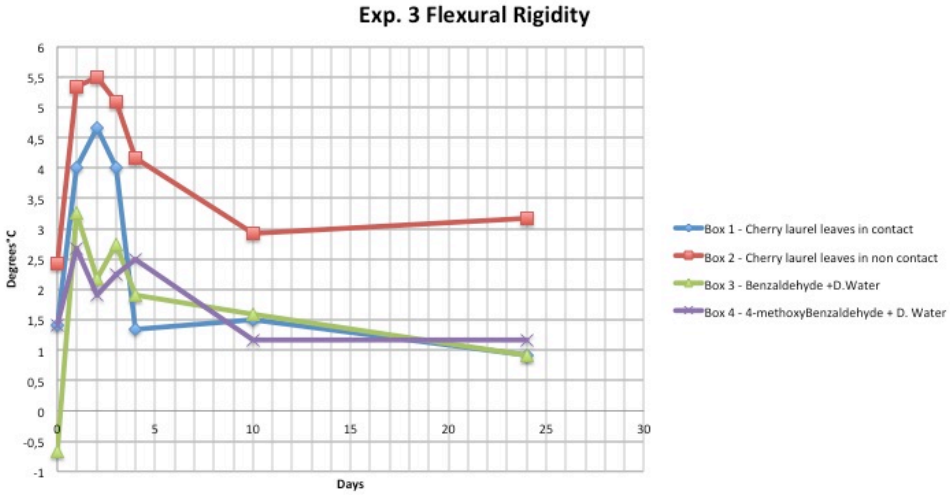


Delta E 2000 Values (mean value)	24h of treatment	48h of treatment	72h of treatment	24h Post-treatment	1w Post-treatment	3w Post-treatmentt
Days	1	2	3	4	10	24
Box 1 - Cherry laurel leaves in contact	3,12	2,46	2,84	1,47	1,06	1,57
Box 2 - Cherry laurel leaves in non contact	1,99	2,04	2,38	1,57	1,80	1,78
Box 3 - Benzaldehyde +D.Water	2,69	2,10	2,67	2,47	2,41	2,50
Box 4 - 4-methoxyBenzaldehyde + D. Water	0,31	1,25	1,03	1,34	0,76	0,77

Figure 23 Average colour changes of samples pre-and post-treatment

The flexural rigidity of both cut cherry laurel leaves in contact and in non-contact reacts by changes of approximately 3° at most after 48h of exposure and then returned towards the original flexural rigidity ±0.5°. The change of flexural rigidity of benzaldehyde+ distilled water was approximately 4° at most after 24h of exposure and then returned towards the original flexural rigidity ±1.75. The change of flexural rigidity for 4-Methoxybenzaldehyde though noticeable it is negligible.

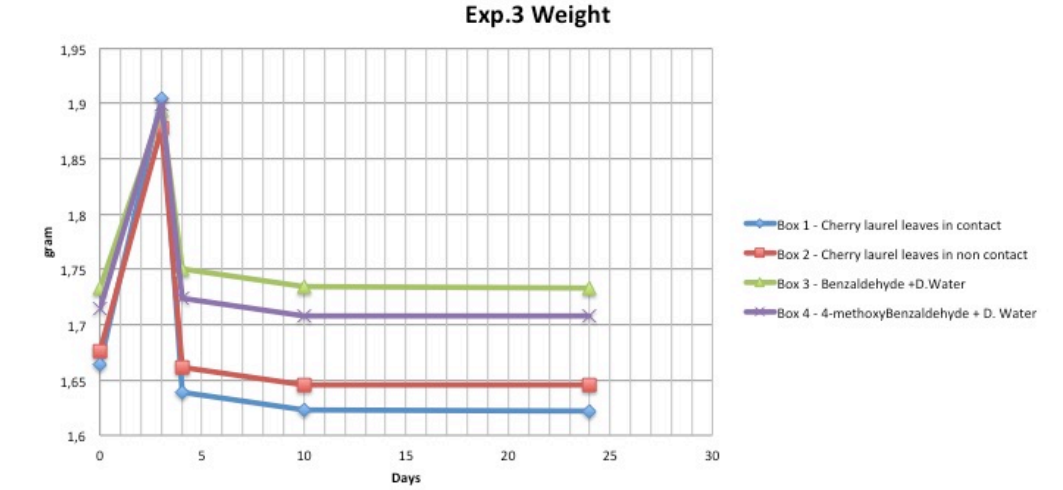
The dip in the benzaldehyde + water flexural rigidity data indicates that it would show more effect from the exposure if the wick in the glass vessel with 10ml distilled water had not fallen into the water and decreased the evaporation rate of the water. See Figure 24.



Flexural rigidity (mean value in degrees °)	Before treatment	24h of treatment	48h of treatment	72h of treatment	24h Post-treatment	1w Post-treatment	3w Post-treatment
Days	0	1	2	3	4	10	24
Box 1 - Cherry laurel leaves in contact	1,42	4,00	4,67	4,00	1,33	1,50	0,92
Box 2 - Cherry laurel leaves in non contact	2,42	5,33	5,50	5,08	4,17	2,92	3,17
Box 3 - Benzaldehyde +D.Water	-0,67	3,25	2,17	2,75	1,92	1,58	0,92
Box 4 - 4-							

Figure 24 Flexural rigidity of samples pre-and post-treatment

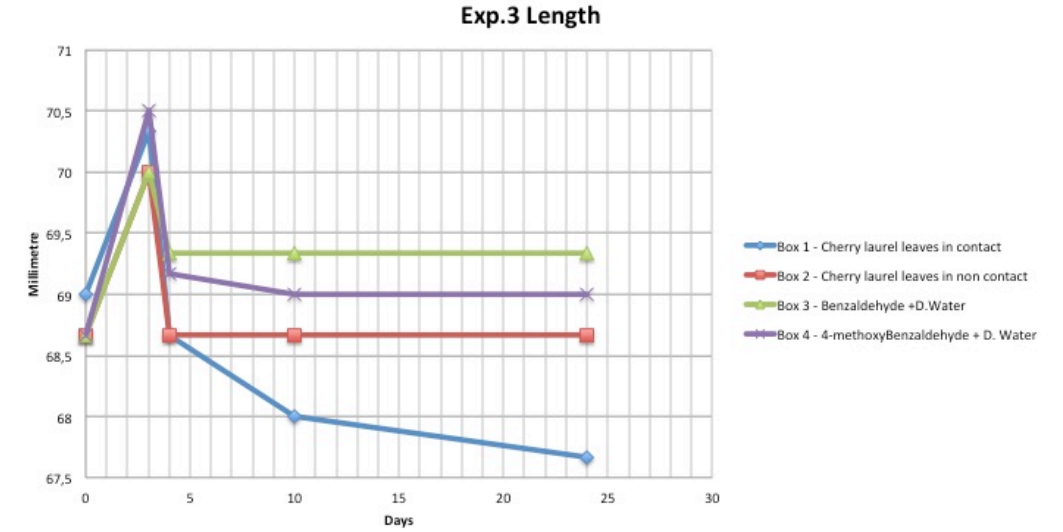
The changes in weight were for all samples regardless exposure or treatment in the range of +0.2 g after 72h of exposure. 24h after post-treatment the weight returned towards their original values -0.05g, which is the approximate weight that has been taken from the samples to the pH-test. See Figure 25.



Weight (mean value in gram)	Before treatment	72h of treatment	24h Post-treatment	1w Post-treatment	3w Post-treatment
Days	0	3	4	10	24
Box 1 - Cherry laurel leaves in contact	1,66	1,91	1,64	1,62	1,62
Box 2 - Cherry laurel leaves in non contact	1,68	1,88	1,66	1,65	1,65
Box 3 - Benzaldehyde +D.Water	1,73	1,89	1,75	1,73	1,73
Box 4 - 4-methoxyBenzaldehyde + D. Water	1,71	1,90	1,72	1,71	1,71

Figure 25 Weight of samples pre-and post-treatment

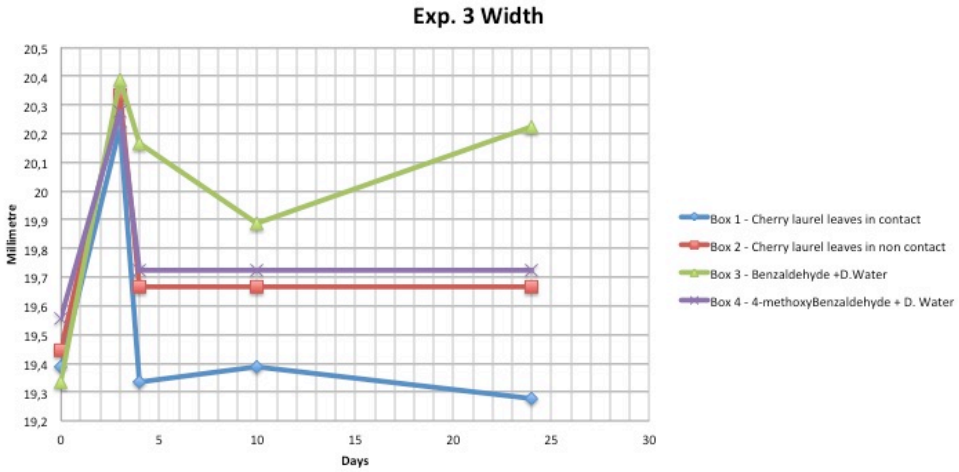
Changes in length were for all the samples regardless exposure or treatment in the range of 1.5 - 2.0 mm at 72h of exposure. 24h post-treatment the length returned towards its original state within ±0.75mm, except the samples in box 1 especially sample 1c where the length was shorter than the original length by more than 1mm even after 3 weeks of post-treatment (see Figure 26).



Length (mean value in mm)	Before treatment	72h of treatment	24h Post-treatment	1w Post-treatment	3w Post-treatment
Days	0	3	4	10	24
Box 1 - Cherry laurel leaves in contact	69,00	70,33	68,67	68,00	67,67
Box 2 - Cherry laurel leaves in non contact	68,67	70,00	68,67	68,67	68,67
Box 3 - Benzaldehyde +D.Water	68,67	70,00	69,33	69,33	69,33
Box 4 - 4-methoxyBenzaldehyde + D. Water	68,67	70,50	69,17	69,00	69,00

Figure 26 Length of samples pre- and post-treatment

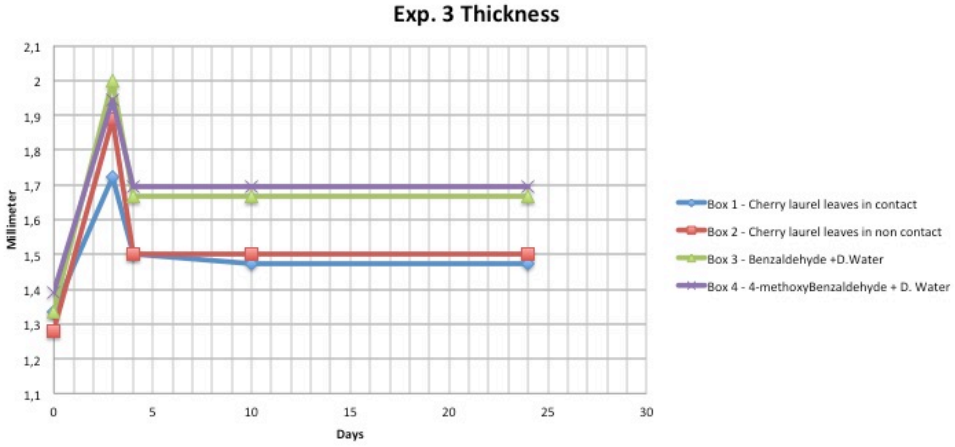
Changes in width were for all samples regardless exposure or treatment in the range of 1mm following 72h of exposure. 24h after post-treatment, the width have returned towards its original state ±0.3mm, except the samples in box 3 and especially sample 3b where the width after three weeks of post-treatment still was 0.9 mm from its original value (see Figure 27) .



Width (mean value in mm)	Before treatment	72h of treatment	24h Post-treatment	1w Post-treatment	3w Post-treatment
Days	0	3	4	10	24
Box 1 - Cherry laurel leaves in contact	19,39	20,22	19,33	19,39	19,28
Box 2 - Cherry laurel leaves in non contact	19,44	20,33	19,67	19,67	19,67
Box 3 - Benzaldehyde +D.Water	19,33	20,39	20,17	19,89	20,22
Box 4 - 4-methoxyBenzaldehyde + D. Water	19,56	20,28	19,72	19,72	19,72

Figure 27 Width of samples pre- and post-treatment

Changes in thickness were for all samples despite exposure or treatment in the range of 0.4-0.7mm at 72h of exposure. 24h post-treatment the thickness returned towards its original state ±0.3mm for the aldehydes (Boxes 3 and 4) and ± 0.2mm for the cut cherry laurel leaves. There was a general trend that all treatments result in a 0.15-0.20 % thicker leather, even after 3 weeks post-treatment (see Figure 28).



Thickness (mean value in mm)	Before treatment	72h of treatment	24h Post-treatment	1w Post-treatment	3w Post-treatment
Days	0	3	4	10	24
Box 1 - Cherry laurel leaves in contact	1,33	1,72	1,50	1,47	1,47
Box 2 - Cherry laurel leaves in non contact	1,28	1,89	1,50	1,50	1,50
Box 3 - Benzaldehyde +D.Water	1,33	2,00	1,67	1,67	1,67
Box 4 - 4-methoxyBenzaldehyde + D. Water	1,39	1,94	1,69	1,69	1,69

Figure 28 Thickness of samples pre- and post-treatment and following 3 weeks of post-treatment

3.3.4 Discussion

Generally, the results of the samples in Experiment 3 demonstrate a change in pH, surface colour, weight, length, width and thickness as well as flexural rigidity during treatment, which then returned to near the original values approximately 24 h post-treatment. All samples regardless treatments trend in the same way, indicating that the mechanism of action is the same in all cases.

The results show that cut cherry laurel leaves in non-contact can influence dry archaeological leather in a volatile manner with the best sufficient timeframe for reshaping action in approximately 48h, in which results show softening action at 24h and a loss in efficiency after 72h. The active species in cherry laurel leaves is proven to be benzaldehyde in the presence of water, which has the sufficient timeframe for reshaping action in 48h were result show softening action at 24h and a loss in efficiency after 92h. During 72h of treatment with benzaldehyde and water, the formations of crystals appeared on leather surface. Although small crystals were noticed during treatment, it is first after 72h of treatment that they appeared on the leather sample. These crystals are likely benzoic acid resulting from oxidation of benzaldehyde in the presence of water vapour (McGraw-Hill Higher Education, oxidation of aldehydes to acids, Gathered 11/5 -2015). Though a more thorough investigation should take place since microcrystals, not seen by the naked eye, could occur on the leather surface in an earlier state.

The results from Experiment 3 indicate that all the treatments are influencing the flexural rigidity of the archaeological leather samples under treatment between 24-72h, and that the affects of treatments of the flexural rigidity is reversible with 24h of post-treatment. The treatment of benzaldehyde +distilled water is the most effective, though it does result in some residual dimensional changes that can be possible indicators of reversal behaviour from the original shrinkage that occurred during uncontrolled drying of the samples after excavation. The treatment using 4-methoxybenzaldehyde+water demonstrated that other aldehydes are effective, but that the presence of a methoxy group in the para position decreases the effectiveness of the treatment. This might be caused by the increased stearic hindrance limiting access of the aldehyde to the amine centres on collagen (Informant 3, Gathered 19/5-2015).

The pH data show that all treatments changed in pH levels during treatment and then returned towards the original pH, except for the treatment with cut cherry laurel leaves in contact, that did not returned to its original pH values. Even though pH levels in samples exposed to cut cherry laurel leaves in contact did not return back towards original values, none of the samples where out of the zone where the pH is unacceptable for archaeological leather, that is 4-6 pH (safe zone)(Peacock, 1984 p. 2).

The surface colour change for the samples in Boxes 2, 3 and 4 all has acceptable colour changes within the limits of the ΔE unit of 1. In Box 1 a change over 1 ΔE unit is recorded and could be signs of a reaction within one sample. As mentioned before in this study individual leather samples can vary within the same leather piece and this sample may have a constitution that reacted with cut cherry laurel leaves in contact which caused a colour change. It seems that sample 1c differ in the L* coordinate and this affected the mean value of ΔE. This indicates that it is this specific sample 1c that react to the treatment of cut cherry laurel leaves in contact and not all archaeological leather samples in Box 1. Though larger changes than $1\Delta E$ is acceptable for archaeological material (see Section 2.5), it is of interest for the investigation to account for this specific change, thus it points out that archaeological leather do respond in unpredictable ways even though samples is taken from the same object.

The changes in weight, length, width and thickness all returned towards their original state after 24h post treatment. This shows that the treatment is reversible. It also shows that expanding and shrinking of the leather structure occurs. Expanding and shrinking of the leather structure can cause stresses that lead to decay if the fluctuates is large and frequent, as mentioned before in section 1.6.2. From looking and feeling the leather samples after treatment there where not any reasons to believe that any of the treatments had led to additional damages, such as cracks, splits or laminations. The

mechanical damage such as torn edges caused on the leather samples are a result from the measuring methods and cannot be considered as damage caused by the specific treatments.

4. DISCUSSION AND CONCLUSIONS

Three experiments were designed to answer the following experimental questions:

1. In what way do the cherry laurel leaves affect dry archaeological leather from wet burial site, i.e transmission of active agents by surface contact or volatile species?

2. Which chemical compound(s) in cherry laurel leaves is the active agent when treating flexural rigidity on dry archaeological leather from wet burial site?

3. Could exposure on dry archaeological leather from wet burial sites to cut cherry laurel leaves or working specie(s) contained within cherry laurel leaves mechanically or chemically degrade the fibre structure, tanning agents, working marks or seams and decorations?

To be able to explain the results of each successive experiment it was necessary to conduct further literature research to give a scientific grounding to the results and guidance for execution to further experiments.

From the experimental results and the literature research it is possible to conclude that contact between cut leaves and archaeological leather is not necessary, and that cherry laurel leaves work on dry archaeological leather in a volatile manner; Experiment 1. When the cut leaves secrete sap containing the cyanogenic glycoside amygdalin, they also release enzymes, which catalyse the hydrolytic chain reaction to successively liberate prunasin, mandelonitrile, benzaldehyde, hydrogen cyanide and water, see Figure 2. Benzaldehyde in collaboration with water is the active species on the archaeological leather. It can be inferred that light swelling caused by the water gives benzaldehyde access into the leather structure where it can react with amino sites on collagen to form a Schiff base (Experiment 2). The optimal timeframe of exposure treatment with benzaldehyde + distilled water (as well as the other treatments) was determined to be 48 h because modification of the flexural rigidity had reached a limit where reshaping of the samples could take action, and where the time limit relating to the formation of benzoic acid crystals had not yet been reached (Experiment 3). Though, the benzoic acid crystals should be investigated closer, as mentioned in Section 3.3.4.

The surface area for water evaporation has a big influence on the treatment with benzaldehyde; this can be concluded from the fact that the effect of treatment was greatly decreased when evaporation surface became smaller due to the wick dropping into the distilled water (Experiments 2 and 3). The wicks should always be secured to the edge of the vessel with a wooden clip to ensure that they do not fall during treatment. One prospect that was not explored was how increased surface area for evaporation might reduce the treatment time. The results seem to indicate that the initial presence of water decides rate and limits of the action on the leather.

The results indicated that benzaldehyde works as an aldehyde-tanning agent on leather through the reaction to form a Schiff's base (see Section 2) led to testing of another aromatic aldehyde (4-methoxybenzaldehyde) to demonstrate whether it is in fact aldehydes in general and not just benzaldehyde that are one of the active agents. This treatment could be optimised by testing additional aldehydes, both aromatic and aliphatic, to determine the fasting acting agent while still retaining the reversibility of the treatment.

From looking and feeling the leather samples after treatment there where not a reason to believe that any of the treatments had led to additional cracks, breaks or laminations. The mechanical damage such as tarnished edges on the leather samples are a result from the measuring methods and cannot be considered as damage caused by the specific treatments. However, internal structural damages cannot be excluded when considering the relatively rapid dimensional changes that the leather underwent during all treatments. Another point to consider is the long-term effect of the treatments on the leather samples. However, because the leather responds so negatively to even

gentle heating (Experiment 2), artificial thermal aging might not reveal real change; and so a real-time ageing experiment is advisable, but this was outside the time frame of this study.

Looking into health and safety issues for the conservator in the matter of treatment choice, cherry laurel leaves do produce hydrogen cyanide when being cut and regular plastic gloves made of vinyl or latex are not sufficient because HCN can penetrate these polymers and enter the skin resulting in cyanide type poisoning if the levels are over 50 ppm exposed under 30 min. Only butyl or Teflon gloves are sufficient to prevent HCN from crossing the glove-skin barrier (INEOS USA LLC, HCN 2006 p. 2). Also of concern is the volatility of HCN at room temperature. While HCN does have a characteristic odour of bitter almonds, which can be detected (smelled) in limits of 5 ppm (INEOS USA LLC, HCN 2006 p. 3), and lethal limits are below 50 ppm as mentioned above, the odour is masked by mandelonitrile and benzaldehyde which both smell of almonds. These health issues are something to consider when using the cherry laurel leave treatment. Benzaldehyde with water provides a more effective and a less hazardous treatment for the conservator. There would however be beneficial to investigate the levels of HCN in cut cherry laurel leaves closer, since the method are being used. There have been recorded levels of HCN in cherry laurel leaves of 3100 μg/g under a investigation in "*Phytochemistry"* vol. 47 (Santamour, 1998, p. 1538.). But it seems that the HCN levels can vary from different time periods of the year, which makes it hard to guarantee that these levels always are 3100 μ/g (Santamour, 1998, p. 1538).

5. SUMMARY

On the basis of the article "Über das Weichen trockengefallener Alkohol und Formalinpräparate, Herbarblätter und von Tapagewebe" in *Der Präparator* from 2001 by Klaus Weichsler and co-authors, a series of experiments were undertaken to investigate the cherry laurel leaf flexural rigidity treatment upon dry archaeological leather from a wet burial site. This type of a material presents great difficulties if modification of the flexural rigidity is desired for interpretational reasons or to ease physically damaging positions of the leather. The first hurdle to overcome was the general lack of literature sources regarding this treatment. As an alternative and as a means to highlight the need for a new treatment such as cherry laurel leaves, a review of the current optional treatments to modify the flexural rigidity of leather, such as immersions and humidity chambers, infusion of humectants followed by freeze drying, is presented. However, certain dry archaeological leathers, because of internal damages caused by a number of reasons, but mostly due to uncontrolled drying leading to collapse and cross-links of collagen fibres, cannot withstand these currently accepted treatments.

To analyse the effect of the cherry laurel leave and treatment upon dry archaeological leather several metrics (flexural rigidity, pH, colour change, dimensional change, weight change, and working property change) were selected with consideration of the information they could generate as well as available resources: time, money and knowledge. Efforts were taken to ensure that the same size of samples and agents were used and that airtight treatment chambers ensured that volatile species were not lost to the atmosphere during treatment. In addition to the cherry laurel leave treatment, alternative treatments based on the chemistry of the cherry laurel leaves treatment where examined, but instead using pure reagents exposing and evaluating in the same manner.

A flexural rigidity testing apparatus was constructed and played a substantial part in Experiment 1 where it demonstrated that cut cherry laurel leaves work in a volatile manner, and in Experiment 2 where it demonstrated that benzaldehyde with water is the active agent. In Experiment 3, four treatments: cut cherry laurel leave in contact, cut cherry laurel leaves in non-contact, benzaldehyde + distilled water, and 4-Methoxybenzaldehyde + distilled water were compared by evaluating their effects on the flexural rigidity, pH, surface colour, weight, length, width, thickness and other parameters such as touching, feeling and visual appearance. The results from Experiment 3 show that all treatments work in a similar manner, and that benzaldehyde with water was found to be the most effective treatment. They also indicate that the presence of an aldehyde + moisture is the criteria proven to work on modifying the flexural rigidity. The changes in measured parameters before, immediately after, and following post-treatment shows that the treatments have the desired effect of modifying flexural rigidity to allow for reshaping within acceptable timeframes (48 h), and that the parameters return close to their original values within 24 h following post-treatment. Thus, by the chosen measured parameters, this method can be considered to be reversible.

Signs of additional deterioration, cracks and breaks were not observed except for when treating the archaeological leather for times longer than 72 h with benzaldehyde + water in which crystals, presumably benzoic acid, appear on the leather surface.

When considering the health and safety of the conservator performing the treatment, cherry laurel leaves produce hydrogen cyanide via an enzymatic chain reaction. Hydrogen cyanide can penetrate most commonly used laboratory gloves, only butyl or Teflon gloves are sufficient barrier. A dose of 50 ppm under 30 min in air or by transport through the glove-skin barrier is sufficient to cause acute cyanide type poisoning. Benzaldehyde with water present, are a more effective and safer treatment without exposing the conservator or the object to the risks of hydrogen cyanide.

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Informant 2: Daniella Pawel, Paintings Conservator, NTNU Vitenskapsmuseet, Trondheim, Norway, Conversation 11/12-2014

Informant 3: Jacob Thomas, PhD. Gothenburg University, Department of Conservation. Mail correspondence, gathered 12/3 -2015 and 14/5-2015. Conversation, gathered 18/2-2015. Comment in thesis via mail Gathered 19/5-2015.

Informant 4: Elisabeth Ellen Peacock, Professor. Gothenburg University, Department of Conservation. Examination, Gathered 3/6-2015.

List of Figures

All the figures without references are created by the author.

Experimental Data

To get access too more specific data from the experiments, contact the author.