

A comparative study on surface treatments in conservation of dry leather

With focus on silicone oil



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Image on cover is the bag from which one of the type samples were cut. Photo: Lena Ludwick 2012

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ABSTRACT

In the museums, private collections and historical houses, there is a wealth of leather artifacts, in various need of conservation. The treatment options, however, are few, and all with their drawbacks. This thesis aims to evaluate silicone oil as a surface treatment for dry leather, in comparison to two other treatments, Klucel G and British Museum leather dressing (BML). The study shows that the silicone oil treatment yields satisfactory results, and the literature and previous studies have indicated superior long term characteristics. Klucel G gave less than satisfactory results, but has better long term characteristics than the BML, though the BML also had satisfactory direct results.

The chemical composition, tanning and deterioration of leather are also described. The properties and chemical composition of the silicone oil treatment are reviewed and discussed. The treatment consists of three components: the silicone oil, a cross-linker and a catalyst. They create an internal scaffolding in the cell wall, stabilizing the cellular structure.

The biggest drawback of the silicone oil treatment is that it is non-reversible, and that has to be factored in to any decision made to conserve an object. The ethical implications are discussed, and the decision whether or not to use the silicone oil treatment should be done on a case-to-case basis, weighing in all factors

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1. INTRODUCTION

1.1 Background

Since the earliest days of man, skin and leather materials have been used to clothe, protect and shield from the elements. Before the technology of spinning and weaving could produce textiles in larger formats, skin and leather was the only material available in large sheets. It is an infinitely versatile material, and the ability to preserve skin has been vital to the survival of early man. This ability to preserve skin, and tan it to make leather, has a very long history and it has evolved to a long complicated process, and is indeed still evolving today. Now, we know most of the chemical and physical mechanisms that turn skin into leather and we know why it happens. But once, leather making was considered mystical, almost as a dark art. (Covington, 2006, pg. 34)

Leather has been used consistently throughout all of history, and preserved objects made of the material can provide a great deal of information of our past. As it has been used by more or less all societies and all social classes and groups, it gives us a unique insight and grounds for comparison within and in between cultures. By analyzing the objects themselves we can get information about the former owner and the culture he or she lived in. It can be very specific; the wearer of the leather shoe was a child who walked on his toes, or general; this specific society had plenty of sheep, but few goats, and an advanced tanning process.

1.2 Aims

There are limited options for those seeking to conserve dry leather, and all with their own drawbacks. This thesis aims to evaluate and compare some of them and to possibly introduce a fairly unused method to the conservators repertoire. It will hopefully aid in the choice of method when confronted with a leather object that needs a consolidant or a surface treatment.

1.3 Objectives

There are, to date, several different methods of conserving dry and desiccated leather with surface treatments. The objective of this study is to test three methods including silicone oil as a surface treatment for leather, which will be the focal point of this thesis. The results of these tests will be evaluated, compared and discussed, with consideration to aspects such as the leathers physical properties, aesthetics, longevity, availability and ethics.

1.4 Scope and limitations

This study is limited to examining and evaluating the methods and results of three different methods of surface treatments and consolidants, with focus on one type of silicone oil, which can be used as both. Of the other methods, one was what can be considered a surface treatment or a finish and one was a consolidant. The tests were conducted on historical leather, not archaeological, and three different artifacts were used. It was done in a laboratory environment on test pieces of non-painted surfaces. No impregnation of the material was done, i.e. all methods were surface-applied.

2. THE MATERIAL LEATHER

Leather is by definition a skin material of a vertebrate animal gone through a process of tanning to resist the natural process of decay. It is a sheet material made of the dermis layer of a skin with sizes ranging from a few square centimeters to over seven square meters, depending on the animal used. Unlike rawhide, which is the common name for untreated skin, leather maintains its flexibility and is opaque after drying. (Thompson, 2006a, pg. 1)

2.1 Structure and chemical composition

The skin is built up by layers – on mammalian animals the epidermis and dermis. The epidermis is the very outermost layer consistent of mostly dead and cornified cells. Here, the cells are arranged in rows and layers, rather than in fibers as in the rest of the skin. The epidermis is removed chemically in the process of making leather, along with the hairs.

The dermis layer is composed of the grain and the corium. The grain layer contains the hair, sweat and sebaceous glands and blood vessels. The fibers in the grain layer are increasingly fine towards the surface. They are mainly composed of the proteins connective tissue fibers and elastin. (Larsen et al., 2009, pg. 7)

The corium is the layer closest to the flesh, and it is the thickest. It is composed almost exclusively of connective tissue fibers, mostly collagen fibers. The fibers in the corium interweave in a three-dimensional network, with angles from 0-90° from the body outwards. The skin, and therefore also the leather, is naturally more elastic across the body and more tensile lengthwise. Below the corium is the flesh, hypodermis. Any remnants of the flesh on the corium after the animal is skinned are removed when making leather. (Larsen et al., 2009, pg. 9)

The skin is composed of proteins, widely common in nature in various shapes with differing physical and chemical properties. The main protein in skin is collagen, which also is a main component in bone, cartilage and teeth. Also commonly occurring in skin are the proteins keratin and elastin, though in the process of making leather it is sought to remove as much of any other protein than collagen as possible. (Larsen et al., 2009, pg. 10) Therefore, leather is composed almost solely of collagen.

Collagen is a fibrous protein, formed by the linking of amino-acids. There are about twenty amino-acids occurring in nature that together in different formations form all proteins. Amino-acids are molecules that contain a carboxyl group (-COOH), an amino group (NH₂) and a hydrogen atom (-H), as well as a side chain (-R) formed around a central carbon atom. (Larsen et al., 2009, pg. 10) This is the base of all amino-acids, the different side chains are what makes them different from each other, and gives them unique properties. Side chains can be as simple as a single hydrogen atom, which makes the amino-acid glycine, or they can be a bigger complex group. A side group can either be non-polar, which consists of only carbon and hydrogen atoms and is chemically inert or polar which contain oxygen and is chemically reactive. (Haines, 2006, pg. 4-5)

The amino-acids are linked together with covalent peptide bonds between a carboxyl group and an amino group. A link of two amino acids is called a dipeptide, three is a tripeptide and so on, until they are simply called polypeptides (Larsen et al., 2009, pg. 11)

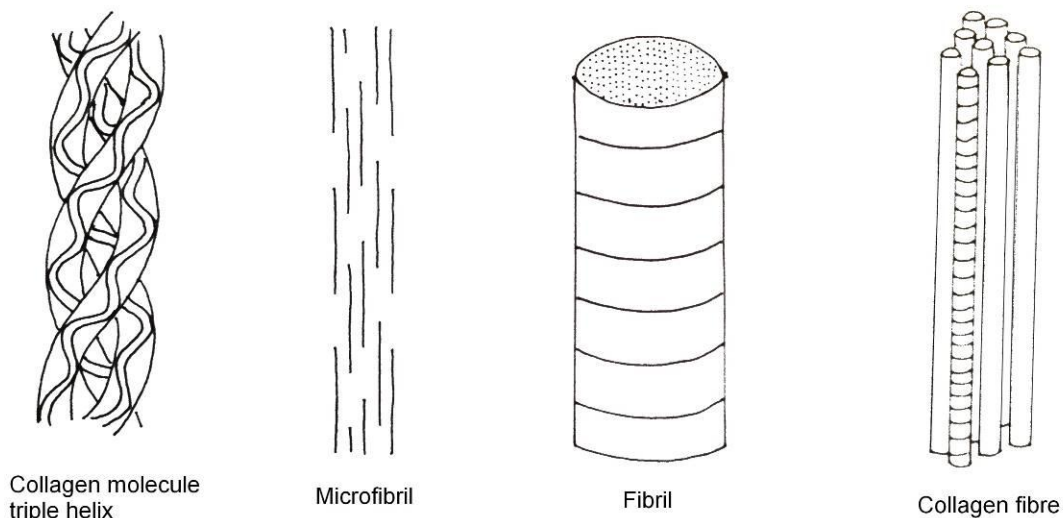


Figure 1. Collagen structure build, from molecule to fiber

The collagen molecule is a triple helix, made up of three left-handed coils that twist around each other to make a right-handed coil, see figure. 1. The coils are chains of amino-acids, with a high proportion of glycine (30%). Many segments in the chains of amino-acids in collagen consist of a reoccurring pattern of a tripeptide of glycine and two other amino-acids, the first of which is often proline or hydroxyproline. These have side chains that are ring structures, which are the cause of the twisting that make the coils. (Haines, 2006, pg. 5)

2.2 The process of making skin into leather

The raw skin is in itself a poor material for clothing, shelter, upholstery or any other of the many uses of finished leather. Untreated, the skin is subject to rapid bacterial deterioration. Also, the un-tanned skin will become stiff and un-flexible, making it unsuitable for many uses.

To understand the leather, which is chemically altered from its raw form, one must have at least a basic understanding of the leather making process. The differences in methods and materials give very varied end results, which in turn can have an impact on the choice of conservation method.

2.2.1 Pre tanning treatments

The preparation of leather has evolved over the millennia, but the main processes all work towards similar results. There are several steps in preparing leather, and they can be done in quite a few different ways.

If treatment of the skin doesn't start immediately after skinning it of the animal, it will quickly become ruined. To prevent ruining, the skin can be cured while waiting by drying, salting or freezing. (Larsen et al., 2009, pg. 22)

For a clean leather, and to make it possible for the tannins to penetrate the skin, the residue flesh layer has to be removed. This is done mechanically, by scraping, and is often done several times during the whole process.

To make leather, as opposed to skins, the hair needs to be removed. This is mainly done with the help of chemicals, although mechanically removing the hairs by scraping also has been done historically. Removing the hair chemically could be done by using acids, ashes, urine, scalding or acid swelling. Today, the most common method of removing hair in the leather industry is by liming. This method was first mentioned in the 9th century, in the Lucca manuscript, and has been the predominant method ever since. (Larsen et al., 2009, pg. 25-26) It is a process of several baths of calcium hydroxide followed by rinsing and acid baths to remove excess lime and stabilize the pH, although today ammonium salts are more commonly used. Liming is an alkaline process that swells the fibers and loosens the hairs.

2.2.2 Tanning

Tanning has several purposes and is the main process in the making of leather. The finished leather should be resistant to rotting when wet, strong and flexible when dry, and should retain those properties even after being wet then dried. The different tannins have different ways to reach the goal of finished leather. Following is a very basic introduction to common tanning processes and tannins.

Mineral tanning

Mineral tannins are based on for example aluminum, iron, chrome, zirconium, and/or titanium.

Potash alum, (potassiumaluminumsulfate, $KAl(SO_4)_2 \cdot 12H_2O$) is the oldest of the mineral tannins and was used 4000 years ago by the Egyptians. By itself, it does not create proper leather, because it loses its properties after being wet, although when combined with for example vegetable tannins it can meet the criteria for true leather. A special form of potash alum tanning called tawing was a very popular method from the 14th century due to the white leather it gave. The method lessened in popularity in the 17th century due to the development of bleaching leather white instead. (Larsen et al., 2009, pg. 33-34)

Chrome tanning is another type of mineral tanning, using chromium (III) salts. Invented in the 18th century, a widely usable method was not patented until 1884 by American August Schultz. Simply put, the tannins create a cross linking between the collagen molecules. This can only be done between pH 2-4 necessitating another process to lower the pH of the skins, as it is around pH 8 after the pre tanning processes. The process is done by adding acid to a solution of salt, normally NaCl.

Chrome tanned leathers are very stable when in contact with water, and generally have a shrinkage temperature of over 100°C. A typical characteristic of chrome tanning is the grayish blue color the leather becomes. (Larsen et al., 2009, pg. 36-37)

Vegetable tanning

In nature, most plants and plant material contain polyphenols which can act as tannins. When used, they are called vegetable tannins. Finds made in Egypt and analyzed showed vegetable tannins to be used 1500 B.C.

All vegetable tannins have certain characteristics in common; they are amorphous in their molecular structure, they are slightly acidic, they can bind to albumin, gelatin and various alkaloids, and in an aqueous solution they have a colloidal nature. (Larsen et al., 2009, pg. 38-39)

Vegetable tannins can be categorized into two main types: hydrolysable tannins and condensed tannins.

The hydrolysable, or pyrogallol, tannins are sugar derivatives, based on polyphenolbenzoacids and hydrolyze in reaction with mineral acids and enzymes, forming esters with glucose molecules. (Larsen et al., 2009, pg. 40) New vegetable tanned leather

typically has a shrinkage temperature of 75-80 °C, but due to the presence of trihydroxy groups that allows complexation with metal ions, semi-metal tanning, the shrinkage temperature can be as high as 120° C.

The shrinkage temperature gives an indication of the collagen stability in the leather, the higher the temperature, the more are the stable bonds in the collagen structure. (Larsen et al., 2009, pg. 103)

As well as forming through hydrolysis, they are also susceptible to breaking down by hydrolysis, resulting in “bloom” in the leather; etherified acids being deposited in the fiber structure.

Hydrolysable tannins can be subcategorized into gallotannins or ellagitannins. (Covington, 2006, pg. 23)

The gallotannins, for example Chinese gallotannin, sumac, mango or tara, form gallic acid and glucose through hydrolysis.

The ellagitannins, for example myrabolan, chestnut, oak and divi divi, form ellagic acid and glucose through hydrolysis. Ellagitannins, unlike gallotannins, precipitates in an aqueous solution when left standing. (Larsen et al., 2009, pg. 40)

Condensed, or catechol, tannins, for example mimosa, quebracho, spruce, birch or willow, are the most commonly used vegetable tannins during the last 100 years, even if some have been used for much longer.

The condensed tannins are based on flavanoid rings that are heterogeneous groups commonly found in nature, of which the condensed tannins are made of the subgroup flavanols. (Larsen et al., 2009, pg. 42)

Condensed tanning creates leather that reddens by light exposure due to the molecule's ring structures ability to crosslink through oxidation. Typical shrinkage temperature for new leather tanned with condensed tannins is 80-85°C, which is higher than hydrolysable tannins, but without the ability to form semi-metal tanning. (Covington, 2006, pg. 26)

Syntans/Synthetic tanning

The first synthetic tannin was patented in Germany 1911, from a need for a substitute to vegetable tannins which there was a shortage of in several countries during World War I. Now, it is often used as a pre-tanning for vegetable tanning. It can also be used to bleach chrome or vegetable tanned leather.

Tanning is achieved through condensation of phenol or acids with formalin, which forms a resin with a viscosity much like thick syrup at the most commonly used molecular weight, 300-400 g/mol (Larsen et al., 2009, pg. 45)

Aldehyde tanning

The primary types of aldehyde tanning are with formaldehyde and glutaraldehyde.

Formaldehyde mainly works through a condensation reaction between the formaldehyde and the ε-amino group in lysines' and hydrolysines' side chains. It is most often used in combination with other types of tanning.

Glutaraldehyde cross links with the protein fiber due to its bifunctional nature, and is also capable of condensing into bigger cyclical compounds.

Tanning by hanging skins in smoke to preserve them is one of the oldest ways known to make leather. It has been used continuously from ancient to modern days by some cultures, sometimes in combination with other tanning methods. Smoke contains several reactive compounds that willingly bind to protein. They include aldehydes, ketones, and free radicals. (Larsen et al., 2009, pg. 47)

Fat tanning

Fat tanning is done with substances rich in lipids, such as animal fat, brains, bone marrow, butter or egg yolks. It is, along with smoke tanning, one of the oldest ways of tanning leather, and is still used in some cultures.

Lipids can be categorized into oils, fat, and waxes after their melting temperature, or by chemical composition; oils and waxes are composed of glycerin and higher fatty acids.

2.3 Deterioration of leather

Deterioration of leather is a chemical process in which there are a great number of contributing factors. All these factors, in combination with the complexity of the leather and tanning chemistry, combine to give very complex and diverse deterioration mechanisms. The environment in which leather is stored greatly influences the deterioration, and factors like moisture (water), heat, light, pollution, oxygen and heavy metals get absorbed into the leather and causes harmful results. For vegetable tanned leather the main causes can however generally be categorized into hydrolysis and oxidation, in which all factors stated above can be an influence. The deterioration occurs in the leather itself, in the amino acids and peptides of the collagen, and in the chemicals used in tanning and treatment. (Florian, 2006, pg. 37)

2.3.1 Hydrolysis

Of the two main causes for deterioration in vegetable tanned leather, hydrolysis is generally considered the more aggressive. It is often the primary cause of deterioration for leather in polluted environments. (Larsen et al., 2009, pg. 62) Hydrolysis occurring in an acid environment, acid hydrolysis, is the most common form, but hydrolysis in other forms can also occur in basic or neutral environment. (Florian, 2006, pg. 38)

Acid hydrolysis occurring in an environment polluted with sulphur dioxide is caused by the tannins in the leather absorbing the sulphur dioxide and transforming it into sulphuric acid, which in turn the moisture in the leather dissolves into positive hydronium ions (H_3O^+). These ions break the bonds between amino acids in the collagen causing deterioration of the leather. The process is basically the same for any acid coming in contact with leather, creating and releasing hydronium ions (Florian, 2006, pg. 38) that lower the pH to below stable conditions for the peptide chains in the collagen. It is especially leather tanned with condensed vegetable tannins that are susceptible to hydrolytic deterioration, due to their ability to absorb greater amounts of sulphur dioxide, up to 6% of its weight. (Larsen et al., 2009, pg. 62) The discovery of this fact in a scientific study done 1905 resulted in the recommendation that all leather for bookbinding should be tanned with hydrolysable tannins. (Skans, 1999, pg. 161)

As a result of the deterioration by high levels of pollution of for example sulphur dioxide, a phenomenon called red rot will often appear. The leather will crumble into a powder, reddish brown in color. (Skans, 1999, pg. 160)

2.3.2 Oxidation

Oxidation is one side of a redox reaction, the other being reduction. Oxidation is when a substance (commonly but not exclusively oxygen) transfers an electron to another substance, leaving one positively and one negatively charged. (Florian, 2006, pg. 38)

While hydrolysis is considered the more aggressive of the two causes for deterioration in vegetable tanned leather, oxidation can be caused by several different factors, such as oxygen, light, heat or high energy free radicals.

Free radicals, which are involved in most oxidative reactions (Florian, 2006, pg. 38), are formed by the breaking of covalent bonds in proteins, tannins or fatty acids by heat, radiation or reactive compounds. The free radicals are highly reactive molecules with a

free, unbound electron, for example $CL\cdot$ or $O_2\cdot$, that in forming breaks the bonds in the peptide chains in collagen thus causing deterioration. (Larsen et al., 2009, pg. 62)

2.3.3 Results of deterioration

The chemical deterioration of vegetable tanned leather results in a gradual disintegration of the fiber network thus weakening its structural integrity. Basically, it can become brittle and stiff, distorting or ruining its shape. The structural integrity can be ruined to a point where flaking and loss of material can occur. Also, deteriorated leather will have a lowered shrinkage temperature, which determines at what temperature wet or moistened leather will irreversibly shrivel up and shrink to a about third of its original size. (Thompson, 2006b, pg. 60) In extremely deteriorated leather, the shrinkage temperature can in some cases be almost as low as room temperature, risking devastating shrinkage and distortion if introduced to an excess of moisture.

A common sign of deterioration in environments with high levels of pollution of for example sulphur dioxide can be the onset of red rot, which results in the crumbling of the leather into an orange-red powder. (Skans, 1999, pg. 160-161)

3. CONSERVATION OF HISTORICAL LEATHER

The methods of conserving historical leather are limited, and often the only possible for leather in need of conservation is preventive measures. This may be because of the objects fragility or uniqueness, or the conservation facilities budget, time or staffing issues. Although controlling the environment can go a very long way in preserving a deteriorating object, a perfect climate and environment can be hard to achieve, especially if the object is to go on display, or even be used. In certain cases, active measures have to be taken in order to prevent an object to ruin and be lost forever.

The circumstances of the object for which conservation is needed must be taken in to account when choosing method and level of treatment. An object in museum storage has very different needs than one in a historic house being used occasionally. (Angus et al., 2006, pg.113)

As this paper is focused on surface treatments and consolidants, this chapter will present the methods and materials commonly used. To give a full picture it will also briefly show some methods of cleaning and preventive measures.

3.1 Preventive conservation and cleaning

A lot can be done for an object with only simple measures. When treatments of different kinds have been deemed unnecessary, too risky, or by some reason or another impossible, simply taking good care of the object can go a very long way.

3.1.1 Storage recommendations

As stated earlier, vegetable tanned leather is very susceptible to deterioration by pollution with sulphur dioxide. Therefore, the concentration of sulphur dioxide in the air should not be over 0.06 ppb (parts per billion). To accomplish this, an air purifier is necessary.

The temperature should be constant and not fluctuating, keeping below 18°C to slow down oxidation. The relative humidity (RH) also needs to be constant, staying between 50-55%, as fluctuations causes stress in the material. RH above 60% increases the risk for microorganisms, and for very degraded leather with a low shrinkage temperature it also risks spontaneous shrinkage. (Skans, 1999, pg. 162). If the RH is too low, the leather can dry out and become stiff and brittle and prone to cracking. (Angus et al., 2006, pg.115)

Ideally, leather should be kept in the dark, away from radiation that can trigger oxidation. Any radiation with a wavelength between 100-1000 nm, which includes UV, visible light and infra red, should be avoided. Objects should be kept supported with custom-shaped supports so as to not lose their shape.(Skans, 1999, pg. 162)

3.1.2 Cleaning

It is important to keep leather objects clean, as accumulation from dust and dirt absorbs and locks in moisture from the air. Often it is enough to vacuum with a brush, especially if done on a regular basis so the dust does not have a chance to solidify, making it hard to remove. There is an abundance of tools for dry cleaning, and they should be used in the order of mild to harsh. Examples of these tools are smoke sponges, wishab erasers, groomstick and different brushes.(Kite et al., 2006, pg. 124)

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

aqueous solution, to quicken the evaporation and help dissolve the dirt, taking great care as solvents can also dissolve oils and tannins in the leather. (Kite et al., 2006, pg.125)

3.2 Consolidation

When leather deteriorates, it can become brittle or powdery, risking material loss. A badly deteriorated leather can also be very difficult to clean or mend, risking even further damage if attempted. In these cases, consolidation of the material might be considered. (Kite et al., 2006, pg. 128)

There are several different consolidants and methods available for leather. Although care must be taken as many of the products originally were produced for the leather industry, thus not always being suitable for conservation, many have been further developed and have been used with satisfying results. (Brewer, 2006, pg. 33)

Aspects to consider when choosing a consolidant for leather conservation are the needs of the object and the characteristics and properties of the consolidant. Desired properties include continuous flexibility, chemical and physical stability, non-tacky, and reversibility. (Brewer, 2006, pg. 33)

Following is a short presentation of some in the literature commonly mentioned consolidants.

Klucel G (Hydroxypropylcellulose) is a non-ionic cellulose ether that can be solved and used in ethanol. It is commonly used in conservation of leather book bindings, generally with satisfactory results. (Cains, 2006, pg. 226)

Although it does not penetrate deeply into the leather it holds together powdery and flaky surfaces, (Kite et al., 2006, pg. 128) and is often used in the treatment of red rot. Its disadvantages include breaking down when coming in contact with sulphuric acid and becoming quite rigid with time, cracking if put under stress. (Ruzicka et al., 2006, pg. 230-231)

Pliantex is a flexible acrylic resin, commonly mentioned in leather conservation literature. It is more effective in the treatment of fragile powdery leather than flaking. (Sturge, 2000) Despite frequent mentions however, it has not been commercially available since 2004. (Kite et al., 2006, pg. 128)

Paraloid B67 and B72 are acrylics used not only in leather conservation, but are used widely in many different material categories. They are hard resins, with the disadvantage of risking to stiffen the leather if applied to liberally, but they do not make the surface tacky. (Sturge, 2000) Paraloid is most commonly used as a protective final coating, and is sometimes used to consolidate painted surfaces of leather. (Kite et al., 2006, pg. 128)

SC6000 is an acrylic wax blend with consolidating properties most commonly used as a surface treatment. (Kite et al., 2006, pg. 128) It also somewhat protects the leather from acidic pollutants that causes hydrolytic deterioration. Among its drawbacks are discolorations than can occur when not properly applied, (Brewer, 2006, pg. 34) and the strong film SC6000 gives can split the grain layer from the corium if applied to the former. Combined with Klucel G, these effects are tempered and the mixture has been called “red-rot cocktail” (Ruzicka et al., 2006, pg. 232)

3.3 Dressings

Dressings, or finishes, are usually oil or wax based and surface applied with the intent to restore flexibility, protect from deterioration and enhance appearance. For a long time, dressings used to be the standard treatment used in conservation of leather. This has

proved to be the cause of many problems, as there are a myriad of drawbacks with dressings as a conservation method.

Since the base components are fatty substances, overuse can cause oxidization and stiffening, discoloration and staining, a tacky surface that attracts dust and dirt, encouraging of micro organism-growth, and hampering of future conservation efforts. Overapplying can also result in the depositing of spew on the surface, a white substance of free fatty acids, sometimes looking like mold. As well as oils and waxes, dressings often include some type of solvent. These bring with them potential problems of their own, such as dissolving of original surface treatments, adhesives or paint and wetting, swelling and deforming. (Kite et al., 2006, pg. 128)

Despite these drawbacks, dressings are still commonly used,(Sturge et al., 2006, pg. 268, 273, 274, 278 & 286), mainly due to aesthetic reasons, giving the object a finished look.(Angus et al., 2006, pg. 115)

Two of the dressings most often mentioned in literature are briefly presented below.

Pliantine (British Museum Leather Dressing, BML) consists of lanolin, beeswax, cedar wood oil and diethyl ether or hexane. The beeswax is sometimes omitted, as its purpose is to act as a polish, (Hamilton, 1999, pg. 29) although it also prevents air pollutants to enter the leather.(Brewer, 2006, pg. 33) The cedar wood oil acts as a fungicide, preventing micro biological growth.

On the downside, it can considerably darken the leather, and overapplying leaves the surface tacky. The beeswax also closes off the pores of the leather, hindering not only air pollutants from absorbing, but also disturbs the moisture balance, risking drying. (Brewer, 2006, pg. 33)

When used considerably and sparingly, it can yield satisfactory results. (Kite et al., 2006, pg. 129)

Microcrystalline wax, such as Renaissance wax polish, is used as a surface protectant and an aesthetic finish. It gives the leather “a pleasant sheen” (Kite et al., 2006, pg. 129) and also has a certain cleaning ability, due to its content of white spirits.(Kite et al., 2006, pg.125)

4. SILICONE OIL IN CONSERVATION

Silicone oil is a collective term for any polymerized siloxanes with organic side chains of a certain viscosity.

They are widely used in different forms in the industry, often as lubricants or hydraulic fluids. While this might not sound much like a potential material for conservation, it can be synthesized in many variations with a wide range of characteristics.

Here in this thesis, silicone oil will be used as a simplified term for hydroxyl-ended functional polymers used in conservation, as it is used in the day-to-day workings in the labs that work with the material.

4.1 Silicone oil chemistry

Silicone is the collective term for polysiloxanes, and they are built up by linking oxygen between silica atoms, making a Si-O-Si chain. Basic silicone has the formula $[R_2SiO]_n$ with R being an organic side chain such as methyl or ethyl. (Nationalencyklopedin, 2012, silikon)

Silicone is formed by polymerization; chlorosilanes or tetraethoxysilane hydrolyze when obtaining silanol (SiOH) and forms polysiloxanes through poly-condensation catalysis, see figure 2. (Tejedor, 2010, pg. 37)

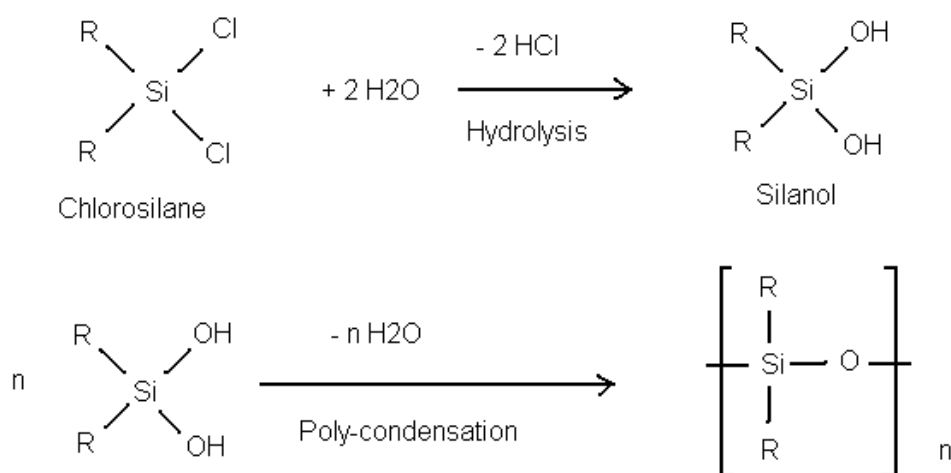


Figure 2. The polymerization of silicone. After (Tejedor 2010, pg. 37)

The polymers can be varied practically endlessly by varying the initial monomer, thereby changing their properties. Silicone is normally classified into oils, resins or elastomers according to their viscosity, which is determined by their molecular weight.

The silicone oil treatment discussed in this thesis is comprised of three components; a passivation polymer, a crosslinker and a catalyst.

The passivation polymer is in this case silanol terminated polydimethyl siloxane. It comes in different molecular weights, i.e. different viscosities measured in centistoke. The

crosslinker is usually methyltrimethoxysilane, $(\text{CH}_3\text{O})_3\text{SiCH}_3$, (MTMS) a hydrolysable, multifunctional alkoxy silane monomer that forms a silane triol and methanol, which in turn condenses with other silanol monomers or available hydroxyl groups to form siloxane resins. (Smith, 2001)

The most commonly used catalyst, though there are several options, is a dibutyl tin diacetate compound (DBTDA). It is a tin based catalyst with the chemical formulation $\text{C}_{12}\text{H}_{24}\text{O}_4\text{Sn}$ that has a working life of approximately 24 hours. (Smith, 2003, pg. 11)

What happens when these three components are combined is a cross-linking with each other and with the cellular walls of the object treated creating scaffolding for the cell, but leaving the rest of the cell empty of bulking agents. To put it simply, the crosslinker in the combination links with the carbanols (-COH) in the cell structure, with the silicone oil polymers and with itself, creating a three-dimensional network inside each cell. When a catalyst is introduced a three step polymerization begins that will fix the network in place.

1. The catalyst, the DBTDA, will spontaneously hydrolyze when in contact with the ambient water vapor in the air, causing a cleavage of an acetal group which is replaced by a hydroxyl group (-OH), resulting in dibutyl tin acetate hydroxide.
2. In a reaction with the crosslinker MTMS the hydroxyl group is replaced with trimethoxysilane.
3. Finally, from the compound created by the reaction between the crosslinker and the dibutyl tin acetate hydroxide, a trimethoxy silane group is replaced with an alcohol functional group in the silanol terminated polydimethyl siloxane, i.e. the silicone oil.

The finished results are a polydimethyl siloxane, a methyltrimethoxysilane, and a dibutyltin acetate hydroxide. (White, 2008, pg. 17-18)

To sum it up, the finished object treated with a silicone oil treatment will have an internal scaffolding without filling up the voids in the cell. The materials are resistant to moisture and UV-light, making the treated object in practicality immune to most environments, even those usually harmful to the object. In fact, humidity and UV-light helps the polymerization process, further stabilizing the material as time goes on. (Dewolf, 2010, pg. 3) The expected half-life for artifacts treated with a silicone oil treatment is approximately 250 years, at which time either a recatalyzing or totally retreating the object can be done. (Smith, 1999, pg. 162)

4.2 Background in conservation

The term silicone was coined in the late 19th century by the British chemist Frederic Kipping to include the products formed by alkyl and arylsilanol through intermolecular water cleavage (Nationalencyklopedin, 2012, Frederic Stanley Kipping)

The first suggestion for using a silicone compound, however, came even before the term silicone was invented. 1861, A.W von Hoffman recommended using "silicic ether" (today known as a form of tetraethoxysilane) for the conservation of limestone on the London Houses of Parliament. (Tejedor, 2010, pg. 40)

Silicone, in the form of silane in different compositions, has long been used in the conservation of stone with two main effects: consolidation of a friable surface and resistance to water. (Horie, 2010, pg. 277)

Siloxane compounds have for a number of years been suggested for various treatments for different material categories, often glass. It has been used as an oil, a rubber, a resin and an adhesive with varying results. It is also often used for making detailed moulds. (Horie, 2010, pg. 280-281)

Silicone is often used as an adhesive to glass, as the main component is silica, making them highly compatible. Important to always remember though, is that a silicone compound is a non-reversible material, making it an unsuitable treatment in some instances. (Tejedor, 2010, pg. 42)

As seen, the use of silicone compounds in inorganic conservation has quite a long history. The use of the silicone for organic materials is somewhat newer.

In the 1960s some of the first experiments with organo-silicone polymers (polymethylphenylsiloxane, polymethylsiloxane, polyphenylsiloxane, polyaminhydrosilane and polycyclosilan) were conducted on archaeological wood by Natela Yashvili. A mixture of polymer and catalyst was brushed on the objects, put under vacuum and polymerized at 55-60°C. Yashvili reported excellent results after the procedures, and accelerated aging tests were done with satisfying results. (Tejedor, 2010, pg. 47)

After Yashvili's experiments, others followed, such as Henry T. Irwin and Gary Wessen in 1976 with other types of organo-silicones.

In 1977 German anatomist Gunter von Hagens patented a method of conserving biological specimens called plastination. The procedure aims to remove the body fluids from the specimen and replacing it with silicone polymer compounds, giving a finished product that does not differ much from a totally fresh sample. (Hagens, 1977) The original purpose of the plastination technique was for anatomical studies, creating durable specimens that retained all characteristics, but the technique has shown to be very versatile and is used in several fields of study. (Tejedor, 2010, pg.42)

Von Hagens has, since the first patent, further developed the plastination technique, but the basic procedure remains much the same. It is done in four main steps: fixation, dehydration and defatting, forced impregnation and curing. The dehydration and defatting is done in solvents, typically acetone, first in -25°C and then at room temperature. The forced impregnation is the replacement of the solvents with a polymer mixture and this is done in -25°C under vacuum. This is because the polymer mixture is a combination of silicone polymer and a catalyst that, when mixed, begin to cure immediately. If kept in -25°C, the mixture remains fluid for long enough time for the specimen to be sufficiently penetrated. The curing is done by vaporizing a crosslinker in a closed environment with the specimen. (Tejedor, 2010, pg. 44-45)

The result of von Hagens plastination technique can be seen in the long running international travelling exhibition *Body Worlds*.

In the mid 1990s the Archaeological Preservation Research Laboratory (APRL), directed by Dr. C. Wayne Smith, was founded as a branch out of the Conservation Research Laboratory (CRL) at the Texas A&M University.

APRLs focus is research and development of new conservation and preservation processes for organic artifacts with organo-silicone chemistry, polymers and their application techniques. The work done in cooperation with the Dow Corning Corporation in Midland, Michigan resulted in 6 patents over the years, the first in 1998 for methods of conserving waterlogged material with silicone oil. (Klosowski and Smith, 1998)

The founding of APRL was shortly after the discovery of the shipwreck *La Belle* in Matagorda Bay, Texas, in 1995 by the Texas Historical Commission. The ship, sunk in 1686, was filled with cargo which along with the ship itself, the rigging, and the crews' personal belongings, encompasses over a million individual artifacts in a fairly good state of preservation. The CRL were contracted by the Texas Historical Commission to conserve the entire ship and all its contents. The sheer scale of the conservation, with the vast number of diverse organic artifacts in their good state of preservation, made it necessary to use a more efficient method of conservation that yielded stable results on a deadline. It also created an opportunity for large scale testing and case study of the use of organo-silicones and polymers in conservation for the first time.

The work of conserving *La Belle* and its artifacts is still ongoing, as is the research at APRL.

4.3 Silicone oil – practical applications

4.3.1 The chemicals

There are a great many different silicone oils, crosslinkers and catalysts on the market to choose from when facing a conservation project, and it is possible to completely customize the treatment after the object being considered.

The silicone oils are mainly silanol terminated polydimethyl siloxane polymers, and which one used is chosen mainly depending on the viscosity needed, and at APRL a range of a low viscosity of 2000 centistoke to high viscosity of 19500 centistoke are used. (Smith, 1999, pg. 160) Commonly used at CRL is a mixture of two silicone oils with different molecular weight and therefore viscosity (internally called SFD-1 and SFD-5). One is a low viscosity polymer and the other is slightly thicker. This allows for use of a wide range of mixtures with different viscosities that can accommodate the different needs of the material being conserved. Wood and bone, for example, require a less viscous mixture, while textile and leather can tolerate more viscosity. (Dewolf, 2010, pg. 3)

The crosslinker that is considered the best general purpose crosslinker is methyltrimethoxysilane, MTMS. In Dr. Smith's publications, it is called CR-20 which consists of 97% methyltrimethoxysilane, 2% methyl alcohol and 1% dimethyldimethoxysilane. (Smith, 1999, pg. 160) (Smith, 2001, pg. 614)

There are several catalysts to choose from, but the most widely used is dibutyl tin diacitate, DBTDA, and can be applied topically or, more commonly, vaporized in an air-tight environment.

4.3.2 The conservation processes

The treatment process is slightly different depending on what material needs to be conserved and whether or not it is water-logged. The method of treating with silicone oils was originally developed for water-logged materials but can easily be adapted to dry or desiccated material.

The instructions here based are those developed and used at the CRL, written down in an internal instruction manual by Dr. Helen Dewolf, head conservator at CRL.

Mixing the silicone oil

The silicone oil crosslinker solution has to contain at least 3% crosslinker (by weight) to properly polymerize when catalyzed. It is possible however to have as much as 50% crosslinker in the solution, but the higher the crosslinker proportion the more stiff and even brittle the finished product can be. A lower crosslinker proportion, gives more flexibility, but can darken the surface, and can give a "wet" appearance. The silicone oil and crosslinker solution can be re-used several times, but it is very important to test the polymerization of the solution before each use, to make sure there is enough crosslinker and that neither chemical is contaminated. This is done by taking a small sample of the silicone/crosslinker solution and adding a few drops of the catalyst and stirring. The mixture, if still viable, should polymerize in a few minutes, thickening and finally hardening to a rubbery consistency. This has to be done very carefully on a separate worktable; keeping the catalyst and all equipment separate from the rest of the silicone oil/crosslinker solution since very little of the catalyst vapor can start the polymerization process. If either the catalyst or the silicone oil/crosslinker solution hardens on its own, they have been contaminated and have to be discarded. (Dewolf, 2010, pg. 1-3)

Water-logged materials

For water-logged materials the key is dehydration, as silicone and water do not mix. This is carried out by progressive solvent dehydration, done in 25% increments of first ethanol/water then ethanol/acetone, see table 1 below

Table 1. Solvent dehydration process

Bath	Water/H₂O	Ethanol/C₂H₆O	Acetone/(CH₃)₂CO
1	75%	25%	
2	50%	50%	
3	25%	75%	
4		100%	
5		100%	
6		75%	25%
7		50%	50%
8		25%	75%
9			100%
10			100%

This is to make sure all water is gone from the objects. The length of time in each bath is dependent on the material, size and condition of the artifacts. The objects are then transferred directly into the silicone oil solution, and are not allowed to dry.

At this stage, the process becomes the same for all objects being conserved by immersion.(Dewolf, 2010, pg. 1)

Immersion treatment

When immersing an object in the silicone oil/crosslinker solution, it is often necessary to weigh it down, as they have a tendency to float. This can be done with a plastic or aluminum mesh with weights. The objects can be kept in the solution practically indefinitely, allowing the conservator to take them out for cleaning and catalyzing at their convenience. At CRL the objects are kept in the solution for 6 weeks as part of a rotating schedule, and that is often more than enough as smaller objects require shorter time. To speed up the process, the solution with the object is sometimes put in a gradual and slight vacuum. This works well for stable material categories such as glass, but is not recommended for most woods as they have a great tendency to warp and sometimes collapse if not done very carefully.

When the object is ready to be removed from the silicone oil/crosslinker solution, it is recommended to let the excess oil drip back into the container as the solution can be used again. It can then be left to drain on paper towels until cleaning.

Removal of excess oil left after draining can be cleaned in MTMS, either in a bath or mechanically. If the object is too fragile to be cleaned mechanically, catalyzation can be performed before the cleaning as the object will become more stable. Work with MTMS is recommended to be done with gloves and under a fume hood or near an exhaust. Care must be taken not to leave the container with MTMS open, as it oxidizes and loses its cross-linking ability.(Dewolf, 2010, pg. 2)

Catalyzation

Catalyzation is done, as stated earlier, with dibutyl tin diacetate, DBTDA. The preferred method is by vaporization in a closed environment. 10-15 ml DBTDA is put into a small aluminum testing dish or soaked into a crumpled paper towel and put into a resealable plastic bag or a sealable plastic container together with the object or objects. The catalyst has to be exchanged every 24 hours as it has a limited working life. Large objects require daily changing for about two weeks, smaller objects need less time.

For optimum coverage of the vapors, the objects can be placed on accordion folded metal mesh, so that as much of the object as possible is exposed to the vapors.

Catalyst can also be topically applied and immediately wiped off, making sure there is no excess left as this can result in very hard white areas of polymerized silicone that can be difficult to remove.

If further cleaning is required, it can be done mechanically after catalyzation. If cracks have occurred, or if an object needs mending, the glue to use is cyanoacrylate glue, as most

other types do not adhere well to silicone treated surfaces. Otherwise the object is basically finished. (Dewolf, 2010, pg. 2)

Topical application

The process of topically applying silicone oil is simple and fast. The same mixture of silicone oil and crosslinker used for immersion treating waterlogged objects can be used for topical application. The object being treated can be cleaned before commencing, but it is not necessary, especially if the surface is fragile. The application of the silicone oil/crosslinker solution does have a certain cleaning effect, and the object can easily be further cleaned after completed treatment.

The simplest way of applying, which is also the most gentle, is by rolling a cotton swab dipped in the solution onto the surface, then following with a clean swab to remove the excess. This can be done more than once on a surface for a deeper penetration. To ensure that there is no excess in the material before catalyzing, it can be carefully wrapped in absorbent paper towels and left to rest, until no more oil comes out.

The object is then catalyzed in the same way as described above.

5. EXPERIMENT: COMPARATIVE STUDY

This experiment compares a commonly used consolidant and a commonly used leather dressing with silicone oil on dry leather.

Leather was acquired and in order to be as scientifically precise as possible, some preliminary investigations were done. These will be presented in chapter 5.1, along with the choice of methods. The experiment itself was constructed to be as simple and representative of reality as possible on small samples, and will be described in chapter 5.2.

5.1 Materials and methods

The materials and methods in this study were both chosen to represent common situations in the conservation of leather, although consideration to availability and time had to be taken.

5.1.1 Presentation of test materials

For this study three types of leather were acquired, one from a shoulder bag acquired in a second hand shop in Sweden and the two other of different thicknesses from a saddlery in Texas, USA.

To simplify, the types of leather will be called 1, 2 and 3.

Leather type 1 comes from a leather shoulder bag bought at the second hand shop Myrorna¹ in Gothenburg (see figure 3). It is the thinnest of the samples, 1,5mm thick. It ranges in color from a light medium orange-brown to a medium brown color depending on the wear of the bag. All the sample pieces have a slight bend in them, after a fold in the original objects shape. It is in fairly good condition, with a smooth and a slight glossy surface, though with scratches on the grain surface

Leather type 2 is the thinner piece of leather acquired at Don Gonzales saddlery², ranging in thickness from 4-4.5mm (see figure 4). It varies in color from a rusty orange color to a dark brown. It is a well used and worn strap, quite stiff with evidence of red rot and mold. The piece is also fairly dirty and full of cracks, which gets worse when handled and bent. The leather was stated to be cow by the saddle maker.

Leather type 3 is the thicker strap of leather acquired at Don Gonzales saddlery, approximately 7mm thick (see figure 5). It is a dark brown on the grain side and ranges from a rusty orange to a dark brown on the flesh side. It is fairly dirty and in places covered with white residue, probably a saddle soap or a leather dressing. It is more flexible than the type 1 leather, taking its thickness into consideration, and it does not crack in the surface when bent. Also stated to be cow by the saddle maker.

¹ Myrorna, Järntorgsgatan 10, 413 01 Göteborg, Sweden

² Don Gonzales Saddlery, 3701 Highway 21 W Bryan, TX 77803, USA.



Figure 3. The leather type 1 bag. Photo: Lena Ludwick 2012



Figure 4. The leather type 2 strap. Photo: Lena Ludwick 2012



Figure 5. The leather type 3 strap. Photo: Lena Ludwick 2012

5.1.2 Methods

The methods of conservation chosen for this study are Klucel G as a consolidant, Pliantine (BML) as a dressing and Silicone oil as the focus comparative. Both Klucel G and Pliantine were chosen because they are widely used and readily available, and they both have properties that are desirable in other methods, such as silicone oil.

The Klucel G was a 10% solution in 98% ethanol.

The pliantine was mixed for this study by the following recipe:

200g anhydrous lanolin

30ml cedarwood oil

350 ml diethyl ether

The beeswax used in some recipes was omitted, as its primary function is polishing, and was deemed unnecessary.

The silicone oil chosen was a mix of SFD-1 and SFD-5, the low and medium viscosity polymers, in the proportions of approximately 2/3 SFD-1 and 1/3 SFD-5 by volume. This is the basic general purpose mixture used at CRL, and positive results have been previously observed in a similar project by the author.

It was mixed with methyltrimethoxysilane, MTMS, but as the mixture had been previously used at CRL, MTMS had been added several times, making it impossible to exactly determine the proportions. It was estimated to be about 20% MTMS by weight, and had a viscosity similar to thick heavy cream.

5.2 Experimental study

The study was conducted at two locations, the department of conservation at the University of Gothenburg and at the conservation research lab at Texas A&M University. This was necessary partly due to the problems acquiring the right materials, the silicone oil, in Sweden in time.

5.2.1 Preliminary investigations

The leather was tested to determine how it was tanned, and the leather type 1 was visually examined to attempt to determine animal of origin.

The determination of tannins used was done micro-chemically in two steps.

First, a test with ferrous sulphate was done to determine whether the leather was vegetable tanned. The phenols in vegetable tannins are reactive when in contact with iron salts and change color intensely. (Larsen et al., 2009, pg. 113)

Two small samples of each type of leather were taken with a scalpel and placed on opposite ends of a slide; a drop of distilled water was dripped on each and covered with cover slips. By the edge of one of the cover slips a drop of 2 % ferrous sulphate³ was placed with a Pasteur pipette and was pulled in to replace the water in the sample with the help of filter paper absorbing the water on the other side. Any changes in color were noted. This procedure was done twice with each type of leather.

The second test is to determine what type of vegetable tannins was used, hydrolysable or condensed. This can be done with a vanillin test, as condensed tannins give a bright red color in a solution with vanillin. (Larsen et al., 2009, pg. 114)

³ 2% iron (III) sulphate in distilled water

Similarly to the previous test, small samples of the leather were taken and placed on either side of a slide. A drop of concentrated hydrochloric acid⁴ was put on one of the samples and a drop of vanillin reagent⁵ on the other sample, then covering both with cover slips. A drop of hydrochloric acid placed on the side of the sample was pulled in under the cover slip with filter paper from the other side. Any changes in color were recorded.

To determine what type of animal the leather was made from, the samples were optically examined under a working microscope in x20 magnification and compared with images from “Læder, pergament og skind” by René Larsen and Dorte Vestergaard Poulsen. (Larsen et al., 2009, pg. 82-91)

5.2.2 Execution of experiment

The leather acquired was documented by photography before it was cut up into rectangular sample pieces. The sample pieces were kept in marked polyethylene zip lock bags between treatments to separate them and prevent confusion.

One sample of each leather type was treated with Klucel G and Pliantine, respectively. Two samples of each type were treated with silicone oil; one single coated one double coated. Lastly, one set of samples were left untreated as references. No samples were cleaned prior to treatment.

The procedure for application on the samples went as follows:

Klucel G was solved in 98% ethanol to a 10% solution. The solution was applied with a 10mm wide synthetic brush. Surplus solution was removed with cotton wool in a worked circular motion as per the recommendations by Anthony Cains in “Conservation of leather and related materials”(Cains, 2006, pg.227)

The pliantine (BML) was applied sparingly with a cotton cloth, working the dressing well in circular motions on the surface. It was left to rest for a day, and then worked again with a clean cloth.

The silicone oil was first tested to still be viable by adding a few drops of catalyst into a sample of silicone oil/crosslinker solution in an aluminum test tray. The treatment was then executed by rolling cotton swabs dipped in silicone oil and MTMS across the surface, then removing the excess with the same motion with a clean swab, working a small area at a time. On one set of samples this was done once, on the second set it was done twice for a double coating. The samples were then catalyzed in a large polyethylene zip lock bag placed on accordion folded metal mesh to allow full circulation of the catalyst vapors. The catalyization was done twice, for 24 hours per time.

5.2.3 Analysis

Each sample was optically examined and its feel was evaluated. Samples were also measured and pH tested.

Visual examination with plain sight was done to detect any changes in color or sheen, or any notable distortion. The samples were also examined under a stereo microscope, on the grain side and in a cross section.

The samples surface feels were compared by simply feeling them, noting any tackiness or smoothness.

⁴ 37% HCl

⁵ 2 grams vanillin (4-Hydroxy-3-methoxybenzaldehyde, C₈H₈O₃) dissolved in 96% to a total of 50ml.

pH testing was conducted by cutting up 0.2g of each sample and placing them in individual test tubes filled with 10ml distilled water in each. The test tubes were stoppered, shaken and left for 24 hours. pH testing was done directly in the test tubes with a pH meter⁶ calibrated in standard buffer solutions with pH 4,0 and 7,0 between each measurement.

⁶ Orion, model SA720

6. RESULTS

6.1 Results of the preliminary investigations

Ferrous sulphate test

All three types of leather showed a dark bluish coloration when tested with ferrous sulphate, indicating that they all were vegetable tanned.

Vanillin test

The type 2 and type 3 leathers both showed a bright red color when tested with vanillin, indicating that they were both tanned with condensed vegetable tannins.

Testing of the type 1 leather was inconclusive, the samples becoming only slightly red, almost a little towards orange, one sample a little more red than the other. The changes in coloration were enough for not wanting to rule out condensed tannins altogether, but not enough to positively identify them as condensed.

Animal identification

When compared with pictures, the type 2 and type 3 leather proved to indeed be bovine, probably cow.

The type 1 leather was also determined to be cow.

6.2 Results of the comparative study

6.2.1 *Silicone oil treatment*

When first applying the silicone oil, a distinctive darkening could be observed, especially on the flesh side of the leather samples. After finishing the treatment, the color of the type 1 leather had returned to a shade indistinguishable from the original and from the control samples.

Any color changes in the type 2 leather samples, both the single and double coated, were harder to distinguish as they varied greatly in color to begin with, and were in places covered in mold and red rot. The treatment removed the mold that was optically visible, and also the red rot, leaving no orange-red residue when handled. Besides that, no great changes in color were observed.

The type 3 samples darkened considerably after the treatment due to the cleaning effects of the treatment removing the white residue and the dirt. When compared to a control sample from a part of the strap that was in very good condition (i.e. no white residue and quite clean) the coloration is very similar.

Not observed in any of the treated samples was a drastic change in the sheen. The type 1 sample retained its slightly glossy surface, and no difference could be optically observed between the treated sample and the control.

The single coated type 2 sample did obtain a very slight sheen on the grain side, while the more red rotted double coated sample did not.

The type 3 samples, although cleaner, have retained a mainly matte surface, with only a tiny bit of sheen, similar to the clean control sample.

No discernible difference was observed between the treated samples and the controls when viewed in a stereo microscope.

The feel of the grain surfaces on the treated samples was a bit more slippery than the control. Especially on the type 1 sample, there was a little bit less friction when rubbed. On the type 2 and type 3 leather, this effect was only just discernible. No tacky feel of the surface could be felt on any of the samples.

The samples all retained their flexibility, no additional stiffness was observed. On the type 1 leather the bend in the sample kept its shape, not flattening out. The type 2 sample was even a bit more flexible than its control counterparts, and the surface did not crack more when bent, though the original cracks were left unchanged. The type 3 sample retained the flexibility that it had before the treatment. (See figure 6).



Figure 6. Silicone oil: control samples and post treatment. Samples to the left are control samples. Top: type 1, middle: type 2, bottom: type 3. Photo: Lena Ludwick 2012

6.2.2 Klucel G treatment

As with the silicone oil treatment, when applying the Klucel G the leather samples darkened drastically. When drying, the darkening went down a bit, but not all the way down to the original shade on all the samples. This can clearly be seen on the flesh side on sample 1, which was not fully treated, and on the cross section of sample 2 and sample 3 which have lighter sections not treated. The treatment cleaned off the visible dirt of both the type 2 and the type 3 samples, and also the white treatment off the type 3. No orange-red substance came off the type 2 leather that had red rot when rubbed.

In terms of sheen, the type 1 sample lost a bit of its gloss after treatment, giving it a duller surface appearance. On the type 2 and type 3 samples, no great difference in sheen was observed.

When studied under a stereo microscope, white substance can be discerned in the recesses of the grain side on the treated samples. It can be seen, more or less clearly, on all samples, but on the type 3 sample a white substance could also be seen on the control sample, making it hard to differentiate between the Klucel G and the previous treatments on that sample.

The surfaces of the treated samples have a more slippery feel to them than the control, the control samples having more friction when rubbed. This is especially clear in the type 1 sample. There is no tacky feel to any of the treated samples.

All three samples are much stiffer than before treatment and compared to the controls. The type 1 sample flattened out, losing the shape of the bend, and is not quite as pliable as the control. The type 2 sample feels hard when tapped and pressed on, and while not very flexible to begin with, became almost completely stiff. The same was observed on the type 3 leather, it being very hard and stiff. (See figure 7)



Figure 7. Klucel G: Control samples and post treatment.
Samples to the left are control samples. Top: type 1, middle:
type 2, bottom: type 3. Photo: Lena Ludwick 2012

6.2.3 British museum leather dressing treatment

The treatment darkened all three samples slightly, most apparently the type 2 sample, and least apparently the type 1 sample. The type 2 sample was cleaned of dirt and orange-red powdery red rot substance, and obtained a quite uniform surface. It did not remove the previous treatments on the type 3 sample, in which a lot of dirt was ingrained. It was quite difficult to remove all excess treatment from the uneven, pitted surface.

Samples type 1 and 3 did not obtain any noticeable sheen not present in the controls, while the type 2 sample has a bit of a glossier look to it.

When examined in a stereo microscope, no residue of the treatment could be seen in the type 1 or type 2 samples, but some type of residue was seen in the type 3 sample. This could, however, be from earlier treatments, as the control samples have similar white residue in the recesses of the surface.

The type 1 sample has a very similar surface feel to the control, almost no discernible difference could be felt. The type 2 sample surface obtained a slightly smoother feel, and the type 3 sample feels a very little bit tacky.

No change in stiffness or shape was observed in any of the samples.



Figure 8. British Museum Leather Dressing: Control samples and post treatment. Samples to the left are control samples. Top: type 1, middle: type 2, bottom: type 3. Photo: Lena Ludwick 2012

6.2.4 Results of the pH testing

The results of the pH testing before and after treatment can be seen in table 2 below.

Table 2 Results of the pH testing

Sample type	Control	Klucel G	Silicone oil	BML
Type 1	pH 4.44	pH 4.23	pH 4.04	pH 4.27
Type 2	pH 3.61	pH 3.40	pH 4.06	pH 3.94
Type 3	pH 4.34	pH 4.23	pH 4.44	pH 4.48

The measurements seem to indicate that the type of leather is more significant to the pH than the treatment methods, but the results are so diverse that it is difficult to determine positively. Seen is that the type 2 sample treated with silicone oil has a slightly higher pH than the other type 2 samples, here indicating that the treatment has given a less acidic leather, which in turn is less prone to degradation, but the margins are too small to be conclusive. Also, silicone oil treated type 1 sample has the lowest pH of that type, contradicting the indication that the treatment lessens the acidity.

When preparing the samples for the pH measurements, it was observed that all the samples treated with Klucel G drew up water very quickly and sank to the bottom of the test tubes almost instantly, while the other samples and the controls had to be vigorously shaken for the sample pieces to wet properly. This could indicate that leather treated with Klucel G will wet easily and draw up water into the object.

7. CONCLUSION AND DISCUSSION

The comparative study in this thesis is very small-scale, making it difficult to positively determine any results. The results that have been obtained, however, in combination with the literature studies indicate that the silicone oil method of conserving leather gives superior long term results than the other methods examined. The technique is versatile, simple and gives the conservator a great deal of control throughout the process. The application methods are far gentler than the rubbing and wiping needed for a dressing application. As for the results, the silicone oil treatment yields a texturally correct, flexible finished product that can withstand handling and a non perfect environment. On the negative side, the chemicals needed are difficult to define and have several different brand names, making it hard to determine exactly what one is looking for. These factors can make obtaining the chemicals very difficult, as one has to find the brand name the distributor is currently using as well as finding the correct distributor in your country.

One of the biggest concerns many conservators have with the treatment is that it is totally non reversible, and though testing has been done for about 25 years, it is still precarious to try to say what will happen with the material in a longer period of time.

In considering which treatment to use on an object in conservation, regards of standing conservation ethics should always be taken. Deciding on a treatment is often a see-saw between doing too much and doing too little, risking ruining an object either by letting it degrade or by over-treating it. In this thesis, the burning subject for many conservators is reversibility, as the treatment method in focus is not in the least reversible.

ICOM (International Council of Museums) has published a Code of Ethics that is generally accepted as a general guiding set of rules for the museum world. On the subject of conservation it says:

“The museum should carefully monitor the condition of collections to determine when an object or specimen may require conservation-restoration work and the services of a qualified conservator-restorer. The principal goal should be the stabilisation of the object or specimen. All conservation procedures should be documented and as reversible as possible, and all alterations should be clearly distinguishable from the original object or specimen.” (ICOM, 2006, §2.24)

As ICOM states, any conservation should be as reversible as possible, but the goal is to stabilize the object. That can be interpreted as the stabilization supersedes the notion of reversibility in a situation when having both is not possible. In a museum environment the two can be mutually exclusive. Sometimes in order to save an object from total ruin, a technique must be used that is not totally reversible. It can then be argued that it is more important for the object to be retreatable. (Caple, 2000, pg. 64)

The ICOM code of ethics is specifically written for museums, not taking private collections, historical houses and objects in use into consideration. Although still applicable for such objects, the commissioners of conservation often have other goals in mind than just stabilization; reversibility and alterations being distinguishable from the original might not be as high on the priority list as for museum objects.

As the idea of true reversibility in conservation has started to be viewed as impractical and outdated, new terms have sprung up in its place, as the earlier mentioned retreatability, and minimum intervention. Minimum intervention is the idea that no more be done than to ensure the future safety of the object. This immediately raises more questions; for how long a future? In what environmental conditions and with what kind of handling? (Caple, 2000, pg. 65) Minimum intervention can mean very different things for objects in different situations.

When considering a conservation method, whichever it may be, all these aspects have to be taken into consideration for every object. There is no universal “perfect method” that will work for every situation. As conservators, we must sometimes be open to try new techniques and materials- how else will the profession move forward?

As for the silicone oil as a treatment for dry leather, there are situations when it is the most suitable treatment available. From the experiment, the literature study, and the discussion, the author of this thesis concludes that it can very well be used in cases where the leather is still in use and handled, such as in furniture upholstery and book covers, or when an object has to be kept in a far from ideal environmental conditions, such as in historical houses. There is also the scenario of when an object is so degraded that it has only one chance of treatment or it will be lost.

8. SUMMARY

Skin materials have been used by mankind for millennia, throughout history by all social classes. It is very much present in our museums and collections, and it is a fairly sensitive material that degrades easily in the wrong environment and with the wrong treatment.

Leather is a skin material that has been tanned, and it consists of layers mainly of the proteins collagen and elastin. The proteins, consisting of collagen molecules in a triple helix, are bunched in fibers.

Leather deterioration can be put into two main categories, hydrolysis and oxidation, resulting in cracking, crumbling or flaying leather that can be brittle and very fragile. Hydrolysis can lead to red rot, which turns the leather into an orange-red dust.

Treatment of degraded leather can be done several ways, including consolidating and dressing the surface.

In the direct results of the treatments, the silicone oil and the British Museum Leather dressing (BML) both gave similar and satisfactory results, while the Klucel G treatment yielded a hard and stiff leather. In the long run, Klucel G is often preferred over BML despite hardened leather as BML is a dressing based on fatty substances and can have several long term disadvantages, such as stiffening, micro-organism growth, and tackiness that attracts dust and dirt. The silicone oil does not yield any of those issues, but is not reversible, meaning a treatment cannot be undone and the chemicals can never be removed from the cellular structure of the leather. Despite extensive testing, it is impossible to with complete certainty say what will happen in the far future. This is however true of any material used in conservation, and the notion of reversibility is not an absolute truth. It can be argued that the silicone oil treatment can be considered a minimum intervention, in cases where the objects are handled and used or where they are on the verge of ruin. In those scenarios using a treatment like silicone oil may be the least that can be done to ensure the objects future.

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