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Evaluation of Consolidants for the Treatment of Red Rot on Vegetable Tanned Leather: The Search for a Natural Material Alternative

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Evaluation of Consolidants for the Treatment of Red Rot on Vegetable Tanned Leather:

The Search for a Natural Material Alternative

A thesis submitted in partial satisfaction

of the requirements for the degree

Master of Arts in Conservation of

Archaeological and Ethnographic Materials

by

Caitlin Carol Mahony

2014

ABSTRACT OF THE THESIS

**Evaluation of Consolidants for the Treatment of Red Rot on Vegetable Tanned Leather:
The Search for a Natural Material Alternative**

by

Caitlin Carol Mahony

Master of Arts in Conservation of Archaeological and Ethnographic Materials

University of California, Los Angeles, 2014

Professor Ellen J. Pearlstein, Chair

Inspired by an interest in finding both a natural material alternative as well as a successful

treatment approach to powdering leather surfaces on a Native American object, a comparative

study of two novel treatment materials and two established consolidants for leather with red rot

was undertaken. Natural material consolidants have been demonstrated to be preferred by tribal

members for use on materials other than leather. One of the materials tested as a potential

consolidant was neri, an aqueous mucilage most commonly extracted from the roots of the *aibika*

plant that is used in the traditional production of Japanese paper. The other material selected was

chitosan, the main derivative of the natural polymer chitin, which has recently been applied in

treatments of archaeological silk and paper. The performance of these potential materials as

leather consolidants was compared against the performance of established modified organic

consolidants, i. e. mixtures of Cellugel and Klucel G with the acrylic wax SC6000. The study

focused on evaluating each material's consolidation performance, the visual and physical

changes observed on the leather, and the chemical stability of the consolidant following heat and

light aging. Although neri proved to have excellent chemical stability, it is not recommended for

leather due to unavoidable water content and unsatisfactory working properties. Though chitosan had no adverse effects towards the appearance and feel of the leather, it is not recommended as a consolidant until further research is conducted on its chemical stability. The Klucel G with SC6000 mixture had great application properties but the wax component is questionable due to the opacity change of the aged wax. Cellugel demonstrated the most desirable properties in performance and chemical stability; therefore it was selected as the consolidant for the treatment on the Native American object. Experimental results indicate that the natural materials evaluated may be recommended as alternatives to synthetic consolidants following additional research.

The thesis of Caitlin Carol Mahony is approved.

David Scott

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2014

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1. Introduction……………………………………………………………………………………………………

       Vegetable tanning of leather has been practiced since ancient times. In the 1800s, the process became industrialized, creating a proliferation of these leathers that were used for a variety of products. There is a remarkable amount of objects in museums and libraries that are made in part of vegetable tanned leather (Thomson 1991). Due to the desirable visual and physical properties of the leather produced, vegetable tanning remains a popular technique today. Though tanning is only one step of many involved in the production of leather artifacts, if offers the most issues affecting condition and conservation (Dirksen 1997, 1). This is especially true of vegetable tanning as these tannins, especially the condensed variety, are particularly susceptible to acidic deterioration or "red rot".

       Since as early as 1842, attempts have been made to understand, prevent, and treat the red rot of leather. While there have been achievements in the understanding of the causes and reactionary mechanism behind red rot, there remains no ideal treatment solution. Preventative measures including maintaining ideal environmental conditions for these objects are known to provide some protection or delay to the leather's deterioration, while deacidification and the application of buffering salts show some promise (Larsen et al. 1997 189-198). Once active, however, intervention in the form of consolidation is the most common treatment. Within current conservation practice consolidation treatments are not so readily attempted as in the past due to an increasing consideration of ethical issues (Hansen 1998, 494). Furthermore, increasing consultation and collaboration with native communities within museums since the introduction of NAGPRA regulations, has broadened the ethical responsibility of the conservator to include non-tangible aspects of objects, especially those considered sacred. These discussions have altered the methods used for storage, display, interpretation and preservation (Sadongei 2006,

14-15, Kaminitz 2005, 96-101; Johnson et. al 2003, 216-219; Johnson et al. 2005, 203-215; Clavir 2002, 52-66; Bernstein 1992, 23-29). When considering consolidation treatments for leather with red rot on Native American objects, it is important to recognize that natural material consolidants, as opposed to synthetics, have been demonstrated to be preferred by tribal members for use on materials other materials (Ferron 2007, 48).[1]

Applying any surface treatment to leather will unavoidably affect the properties of the leather to some extent; therefore, it is accepted that a thorough understanding of a consolidant's performance and properties is required before application. This study was inspired by an interest in finding both a natural material alternative as well as a successful treatment approach to powdering leather surfaces on Native American objects. It is a comparative study of two potential natural treatment materials that would be novel materials for leather consolidation – chitosan (1-4, 2-amino-2-deoxy-β-D-glucan) and neri (82% acidic polysaccharides (polyuronides) and 17% proteins) and two well-known consolidants for red rot, Cellugel (hydroxypropyl cellulose (HPC)) and the "red rot cocktail" Klucel G with SC6000 (HPC with an acrylic wax mixture. Based on the performance and properties of each consolidant, the most appropriate consolidant will be selected for treatment of a leather Apache bag from the Southwest Autry Museum that is suffering from pervasive red rot.

2. Leather and Vegetable Tanning………………………………………………………..

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[1] For more information on the topic of conservation collaborations with native communities see Sadongei 2006, 14-15, Kaminitz 2005, 96-101; Johnson et. Al 2003, 216-219; Johnson et al. 2005, 203-215; Clavir 2002, 52-66; Bernstein 1992, 23-29

The use of animal skins for shelters, clothing, utilitarian objects, and decoration is one of the oldest human activities exhibited universally through cultures. Because untreated skins are subject to rotting, there was a need for processing them into stronger more flexible material that would be protected against the natural decaying process. Tanning is the chemical process that developed to convert skin into leather, which exhibits those desired properties. The history of leather production is believed to extend as far back as the Paleolithic era where some form of the process was likely to exist to produce leather containers (McGrovern et al 2009, 7361). In many ancient cultures, the tanning processes became popularized and standardized. Both the Romans and Egyptian civilizations were notable for the quality of the leather they produced as are many American Indian groups, which were prolific in their leather production. Throughout history tanning processes have been continually developed to eventually reach the industrialized methods of leather manufacturing in modern times (Stetler 1994, 1). In the past, as well as today, leather has been most commonly produced through vegetable, mineral (either chrome or alum), or oil tannage (semi-tannage). Regardless of which tanning process was applied to the leather, the skin of the animal is first prepared in a similar fashion.

The skin of animals is made up of three layers, the epidermis (outer layer), the dermis or corium (middle layer), and the flesh (bottom layer). To prepare for tanning, the epidermis, which includes the hair follicles, as well as the sebaceous and sweat glands, and the flesh, which includes the fat, are typically removed from the skin. The dermis that is composed of a three dimensional network of collagen is what remains and is processed into leather. Collagen is characterized by high levels of the amino acids: lycine, proline, and hydroxyproline. It is a natural polymer that consists of long chains made up of units of amino acids linked covalently through peptide bonds, forming long helical peptide chains (Horie 1990, 115, Haines 1991, 5). It

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is the unique chemical and structural properties of the collagen fibers that allow raw skin to become leather (Dirksen 1997, 1). The collagen molecules of the dermis allow for this transformation by serving as a binding matrix for all tannins often through ionic, hydrogen and van der Waals bonds (Florian 2007, 88).

Vegetable Tanning

Though it is not thought to be the earliest tanning technique, vegetable tanning of some form is thought to be an ancient practice, with possible origins in the Mediterranean region (Falcão and Araújo 2011, 149). In this tanning technique, skins are placed in baths containing water extracts derived from various plants sources; the most common sources being oak, oak bark, chestnut, and other deciduous and leguminous trees (Falcão and Araújo 2011, 149-150). Vegetable tannins are generally phenolic compounds that are water-soluble, weakly acidic and easily oxidized under alkaline conditions (Florian 1985, 1). While soaking in the solution, bonds form between the tannin and the collagen through hydrogen bonding and cross-linking. This step not only increases the chemical and hydrothermal stability of collagen but separates the fibers to give leather its softness (Florian 2007, 88). This particular tanning process is slow and can take up to two years to produce (Dirksen 1997, 1-4). But the end result is a tough, durable and workable piece of leather, often with an emphasized grain pattern.

The vegetative material used as the source of the tannin is particularly important and can greatly affect the ageing characteristics. While initially contributing to a stabilizing effect on the animal hide, certain vegetable tannins may also deteriorate and hence contribute to leather deterioration over time (Florian 2007, 88). Based on their chemical structure, tannins are either

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hydrolysable or condensed, though the plant source itself may contain both varieties.[2] Of the two

types, the condensed is greatly susceptible to red rot deterioration. Condensed tannins are

flavonoid compounds, formed by the polymerization of the colorless phenolic flavonoids. These

tannins occur in primitive vascular plants known as 'proanthrocyanidins'. Some sources of

condensed tannins are the quebracho, mangrove, mimosa, Burma cutch, and Gambier (Bickley

from Haines 1991, 16). It is important to know that although the popular tannins, oak and

chestnut are predominately hydrolysable, they contain significant amounts of condensed tannins.

     Historically, as leather production became more industrialized, other tanning techniques

fell out of favor and vegetable tanning along with mineral tanning became the preferred methods

of manufacture (Stetler 1994, 1). Thomson (1991) projects that a majority of leather objects

found within museums are vegetable tanned (12). While today about 80% of leather is produced

through mineral tanning, when compared to vegetable tanned leather, these leathers retain a

significant amount of water and do not easily hold their shape (Kite and Thomson 2006, 53).

Hence, vegetable tanned leathers are still highly valued for use in upholstery, bookbinding,

saddlery, and footwear.

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[2] There are specific microchemical tests to identify whether leather has been vegetable tanned and whether the tannin used in condensed or hydrolysable. The two best-known spot tests applied to vegetable-tanned leather are the ferric test (indicating vegetable tannins) and the vanillin test (indicating condensed tannins) (Poulsen 2002, 792).
Spot tests become less significant if deterioration of the involved tannin is increased. It can therefore be very difficult to identify the tannin type in heavily deteriorated vegetable-tanned leather. The ferric and the vanillin tests would react less willingly and the results become less significant. Deterioration products would most likely interfere with the rhodanine test, as gallic acid react and yield a positive reaction (Poulsen 2002, 796).

3. Red Rot and Treatments for Red Rot …………………………………………………………………….

Red rot is the name for the distinct acidic deterioration of the collagen fibers in vegetable tanned leather due to the hydrolysis of condensed tannins (Florian 2007). When compared to the oxidative breakdown of vegetable tanned leather, this acidic deterioration is faster and more aggressive. Red rot is evidenced by several condition issues. The deteriorating leather exhibits continual powdering, reduced strength, and lowered hydrothermal stability. The acidity of the leather increases, often resulting in surface readings within the range of 3.0- 4.0 pH, and the leather becomes increasingly redder in color. This change in color and a general misunderstanding early on of the causes of the process is where it gets the name red rot. The red is actually coming from the formation of red colored phlobaphenes and anthocyadins due to the hydrolyzation of condensed tannins (Florian 1985, 2; Florian 1983, 38).

The condensed tannin of the vegetable tanned leather is hydrolyzed through the presence of acids. There are a lot of acids in leather either due to fabrication or use; however, it is believed that the main source of the acidity for red rot is the hydronium ions formed through the absorption of sulfur dioxide from air pollution (Kite and Thomson 2006, 53). According to Kite (2006) **"tannins in leather act as sinks for sulfur dioxide and ….under the same conditions, condensed tannins will absorb twice as much sulfur dioxide as compared with hydrolysable tannins"** (Kite 2006, 40). The process begins as sulfur dioxide transforms into sulfur trioxide through exposure to sunlight. The sulfur trioxide is then absorbed into the leather where it is hydrolyzed by water. The sulfuric acid is then dissolved through the presence of moisture into active hydronium ions (Kite 2006, 38-40). The hydronium ions break the links between the amino acids in the collagen chain, causing it to break and causing the leather to powder and loose strength.

Though the deterioration is caused by the presence of acids, the deterioration mechanism is greatly influenced by the environment surrounding the leather, specifically the relative humidity, temperature, light, and atmospheric gases. The condition and past processing of the leather object also plays a role (Kite 2006, 38). In fact, **t**he first signs of this chemical decay appear as cracks in the leather surface especially in areas that have been worn from use. Then through its progression, the decay becomes more pervasive and spreads to adjacent areas and further into the collagen fibers leading to an eventual disintegration of the leather into a reddish-brown powder (Dirksen 1987, 2).

It is believed that vegetable tanned leather made between1850 to 1900 is particularly susceptible to red rot in part due to the removal of what are called non-tans while manufacturing leather during this time period (van Soest 1990, 662; Dirksen 1997, 1). Non-tans are protective enzymes usually found in animals skins. When the animal is alive, non-tans help to protect the animals' skin from environmental influences as well as to increase durability. When compared to leather objects made from non-industrialized production, the stability of the industrialized leather during this time is much less because of the removal of non-tans. According to Haines (1991) before 1850 organic acids were used during the hair removal process. As these acids are not as active as mineral acids, they did not removal all of the non-tans. After 1850, however, liquid sulfuric acid, a more active mineral acid, was used and it removed all the non-tans and increased the acidic conditions of the leather. While the application of sulfuric acid produced a more uniform finish and accelerated the tanning process, it also created a leather product that would prove to be exceptionally unstable overtime (Dirksen 1997, 1).

Obsolete Treatments for Red Rot

There is an extended history of treatments for this condition as it is a pervasive

conservation issue for historic leather objects. Past treatments for consolidating leather have been

addressed in numerous publications (Kite and Thomson 2006, Anderson et al. 2003, Haines

2002, Abdel-Maksoud et al. 2000, Larsen 1997, Waterer 1972a, Waterer 1972b). The treatments

include both preventative treatments, and stabilization treatments applied once red rot has

developed. Various materials have been applied to the surfaces of leather in the form of buffering

salts, gases, waxes and lubricants, and consolidants. [3] The focus in this section is to highlight

treatments that are mostly obsolete in modern practice due to negative outcomes.

In terms of prevention, conservators have applied several materials to the surface of the

leather to stabilize the pH or provide an environmental barrier against pollutants that may

catalyze deterioration. For example, buffering salts, namely potassium lactate and citrate, have

been applied to offer protection to the leather against acidic deterioration. However, according to

Larsen et al. (1997), there is an immediate stiffening and discoloration of the leather when the

buffer salts are applied and there is also a problem with blooming of lactic acid crystals overtime

(197). In terms of deacidification, ammonia fumes have been used to neutralize the acidity of the

leather, yet the treatment only proved to have only a temporary effect (Larsen et al. 1997, 197).

In the past, lubricants and dressings with wax additives were often liberally applied to

leather surfaces not only to improve the appearance, flexibility, and strength of the leather but to

provide protection to the surfaces from exposure to the pollution. This list included lanolin and

neatsfoot oil as well as beeswax (Brewer 2004). One of the most common wax mixtures used for

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[3] A consolidant is considered a soluble resin that that penetrates the surface to solidify a weak structure whereas a
dressing is often a substance that coats the surface to provide a protective barrier and address aesthetic concerns
(Kite and Thomson 115). Leather dressings can also be considered lubricants which are oil-based substances.

leather was Pliantine also known as the British Museum Leather Dressing. This mixture was a thick brown liquid containing beeswax, lanolin, and a small amount of cedar wood oil. Originally the solvent was hexane, yet this was eventually replaced with 1, 1, 1-trichloroethane (Haines 2002, 3). Critiques specifically of Pliantine include unavoidable darkening of the surface and creation of a surface stickiness, which acted as a dust trap. Waterer (1972a) attempted to use a modified form of the British Museum Leather Dressing as a consolidant for leather, and found that while it initially seemed to offer some promise of longer life, the lanolin did not provide a sufficiently positive support for any length of time (126). Additionally, the solvent 1, 1, 1-trichloroethane has proven to be damaging both to humans and the environment. It was discovered that the solvent can affect the central nervous system of humans and it has a negative effect on the ozone layer of the atmosphere. Unsurprisingly, its use is being phased out (Doherty 2000). In the effect on objects, the main issue with these materials is the tendency of oils and fats to cause surface spew, oxidation and stiffening of the leather, as well as discoloration and staining (Kite and Thomson 2006, 128; Raphael 1993). The wax additives in the dressing such as British Museum Leather Dressing not only changed the surface appearance, but because of their nature often impeded further treatment to the surface. Any fatty acids present added the risk of corroding any metal elements on objects, while any sulfated oils used in other dressings would lower the hydrothermal stability of the leather (Werner et al. 2012, 3; Larsen et al. 1997, 198).

As with today, many consolidants were used in the past to stabilize the powdery surface of leather. These materials are no longer popular either due to their negative effects or lack of availability. Perhaps one of the most popular consolidants used throughout the twentieth century and no longer in use today was Pliantex, a flexible polyacrylic resin based on ethyl acrylate. Pliantex was supplied as a 30% solution in ethyl acetate and was diluted with the solvent 1, 1, 1-

trichloroethane in the proportions of 1:2 or 1:3 parts resin to solvent. Yet, it could also be diluted in esters, ketones, and aromatic hydrocarbons and could be brushed or injected into the affected areas of the degraded area (Waterer 1972b, 36). Apparently, it produced a very soft flexible film after the evaporation of the solvent. It did not swell in water and aging of the material did not produce crosslinking. However, Pliantex often created unwanted surface tack. Wills (2001) used Pliantex for archaeological leather with reasonable success as she found it offered improvements to strength and flexibility, but reported that this was countered with color change and stiffening (Wills 2001, 61). Eventually, as with the Pliantine, Pliantex was taken off the market, because the 1, 1, 1-trichloroethane component was no longer produced. Due to regulations that developed worldwide in the 1990s, this solvent as well as other chlorinated solvents were banned as they were considered responsible for depleting the stratospheric ozone (Doherty 2000, 92).

Another less popular consolidant used was soluble nylon (N-methyoxymethyl nylon) (Kite and Thomson 2006, 124). The material was first recommended in 1958 as a consolidant for artifacts with powdery surfaces that required soaking to remove soluble salts. The use of soluble nylon is no longer recommended as several negative properties were exhibited. According to Sease (1981), soluble nylon exerts strong contractile forces that can cause severe deformation of treated objects (108). It was also difficult to achieve deep penetration and became insoluble upon ageing.

Current Treatments for Red Rot

Current treatments for red rot include both preventive and interventive methods; however in working with leather objects, contemporary conservation approaches are moving towards

preventative when possible. As the deterioration of leather is often catalyzed by fluctuations in humidity and temperature levels and through exposure to light, dust, microorganisms, and atmospheric pollution, the first steps towards preventing red rot from occurring involve maintaining proper storage. For example, the Canadian Conservation Institute recommends humidity levels in the range of 45% - 55% for leather objects and temperatures between 18 C° to 20C°. They also recommend limited exposure to sunlight or direct light, and storage in the dark.

Due to the varying nature and condition of leathers and leather artifacts as well as treatment parameters and material availability, there are currently numerous types of consolidants used for red rot, each with their own set of advantages and disadvantages. Perhaps the most ubiquitous consolidants are those made from hydroxypropylcellulose (HPC), mainly Klucel G, due to its particular molecular weight and solubility in non-aqueous solvents. Two HPC consolidants are used for this study and therefore will be discussed more extensively in a later section. Other leather consolidants found in conservation literature are Acryloid F-10 (butyl methacrylate) (Abdel-Maksoud and Panagiaris 2000), cellulose acetate(Abdel-Maksoud and Panagiaris 2000), Tylose MH 300 P (methyl hydroxyl ethyl cellulose) (Abdel-Maksoud and Panagiaris 2000), Mowilith DMC2 (vinyl acetate) (Abdel-Maksoud and Panagiaris 2000; Cruickshank 2001), parchment glue (Abdel-Maksoud and Panagiaris 2000), BEVA 371 (Morgan 1984), Paraloid B-72 (Morris and Seifert 1978, Kite and Thomson 2006, 128), Paraloid B-67 (ethyl acrylate/methyl methacrylate Kite and Thomson 2006, 128), Lascaux wax resin adhesives (443-95), and gelatin (Kite and Thomson 2006, 233). According to Cruickshank (2001), Mowital B30H with 2.5% ethanol or 10% v/v solution of Super Epoxy resin diluted with acetone has been used to consolidate desiccated archaeological leather onsite. It was found that the Mowital did not provide adequate strength and the epoxy gave strength but an unacceptably

shiny finish (68-69). Cruickshank did not comment on the reversibility or retreatment of the Super Epoxy resin. According to Wills (2001) Paraloid B-72 and Mowital B30H poly vinyl butyral are used on red rotted leather but neither improves the flexibility of the leather. Paraloid B72 with added Paraloid G10 (lower Tg) gives more flexibility but gives the possibility of tackiness and migration. Wills (2001) also states that polyurethanes such as Lankrothane 1304/Quasilan EL 1263, both moisture-cured two-part polyurethanes, are used for powdering archaeological leather but there are several undesirable aspects related to its use. First, polyurethanes are irreversible and may not allow retreatment. Additionally, the catalyst (isocyanate) is toxic and there are severe restrictions on its use. The use of polyvinyl acetate emulsions such as Vinamul 3252 has been documented, though their water content, increasing acidity, instability and discoloration with age may disqualify their use (Wills 2001).

4. Experimental Parameters ………………………………………………………………………

This study aims to evaluate four consolidants for leather suffering from red rot deterioration. Four consolidants have been selected, chitosan, neri, Cellugel, and Klucel G with SC6000 wax. They will be evaluated based on their ability to demonstrate ideal characteristic desired for consolidants as well as to meet the conservation standards set for materials used for long term treatments. These consolidants are also being evaluated for their suitability for the consolidation treatment required for a leather Apache bag that is currently deteriorating.

Conservators evaluate all conservation materials for their ability to remain chemically and physically stable over a long period of time, chemically inert with the material being treated, soluble in appropriate solvents, and retreatable. Therefore, each consolidant was aged in accelerated heat and light conditions to project the ability of these materials to exhibit these factors overtime. Their stability was monitored using Fourier Transfer Infrared Spectroscopy

(FTIR), color measurements with a spectrodensitometer, and solubility changes. These methods provided information on their chemical stability, solubility shifts, and color changes.

For leather consolidants, a variety of properties may be desired. Haines from the Leather Conservation Centre (2002), for example, states that a leather coating should be continuous and flexible, firm not tacky, bring minimal change in color, texture, and dimensions, and should retard the exchange of moisture between the leather and the external environment, thus slowing the rate of deterioration (Haines 2002, 1). She also includes in the evaluation the ease of application and the effects on surface appearance. Noting the more practical requirements of a treatment material on a museum object, Feller (1978) emphasizes the importance of the application in an appropriate solvent for the material and application of that solvent at an appropriate temperature, so as to not damage the object (3).

Based on this review as well as the needs of the Apache bag, the consolidants will be evaluated based on their ease of application, consolidating performance, as well as their alteration of the visual and haptic properties of leather samples. This will be done qualitatively as well as with color measurements using a spectrodensitometer. For this analysis, 24 leather samples were sourced from a pair of leather children's moccasins that were donated for this study by the Eiteljorg Museum of American Indians and Western Art in Indianapolis. These moccasins were in poor condition due to severe red rot deterioration throughout. A condition report of the moccasins can be found in Appendix A. An additional six leather samples were collected from a leather bookbinding suffering from red rot deterioration that was donated by the University of California at Los Angeles, Library Preservation Laboratory.

5. Consolidants…………………………………………………………………………

Table 1: Consolidants used

Consolidant	Concentration	Solvent	Appearance
Chitosan	0.5 % (w/v)	Deionized water/ ethanol (1:1)	Clear, slightly yellow, 5.5 pH when applied
Chitosan	0.5 % (w/v)	isopropanol	clear, slightly yellow
Neri	0.1 % (w/v)	Deionized water/ ethanol (1:1)	Clear, colorless
Cellugel	unknown	isopropanol	Clear colorless
Klucel G with SC600	2%, 1:1 ratio	isopropanol	Somewhat opaque, yellowish

5.1 Chitosan

Chitosan is the main derivative of the natural polymer chitin obtained through the hydrolysis
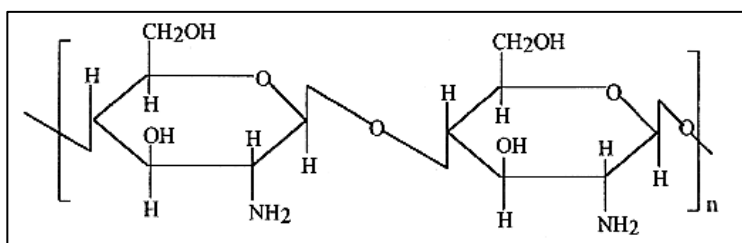
1. Chemical structure of chitosan (from Kumar 2000, 2).

of acetamide groups of chitin or deacetylation through treatment with concentrated alkaline solutions. When the degree of deacetylation (DD) of chitin is greater than 50 %, it is considered chitosan (Alves and Mano 2008, 402). However, the DD varies significantly within the chitosan that can affect its properties; therefore, it is important to know the quality of chitosan being used for application.

Chitosan (1-4, 2-amino-2-deoxy-β-D-glucan) is a linear polysaccharide composed of glucosamine and N-acetyl glucosamine units linked by β (1-4) glycosidic bonds (Alves and Mano 2008, 401). In its structure, it is essentially cellulose with 2-hydroxyl groups replaced by a primary amino function (Del Pilar Ponce-Himenez et al. 20002, 243). Chitosan is insoluble in water, yet, unlike chitin, the presence of free amine groups along its chain allow for it to dissolve in diluted aqueous acidic solutions due to the formation of positively charged ammonium ions. It is important to note that some literature claims the maximum pH needed to solubilize chitosan is

between 5.7 and 5.8 and states that above this range, the chitosan easily precipitates out of solution. [4]

Next to cellulose, chitin is the second most abundant natural polymer, occurring as a principal component of many living forms, including fungi, insects, and crustaceans. There has been a growing interest in chitosan in various fields due to chitin's natural abundance, biodegradability, low toxicity and various physical forms and properties (Abdel-Maksoud et al. 2009, 70; Del Pilar Ponce-jimenez 2002, 244). Chitosan's biocompatibility and biodegradability into non-toxic, non-immugenic and non-carcinogenic products creates prospective applications in fields such as biomedicine, waste water treatment, functional membranes, and flocculation (Alves and Mano 2008, 402). Its film-forming capacity has been the object of many studies for industrial evaluation because the films demonstrate high mechanical strength, resistance to stress, good elasticity, and high permeability for vapor and gases (Matteini et al. 2010).

Chitosan's beneficial properties also have created interest within conservation. Del Pilar Ponce-Jimenez et al. (2002) considered the application of chitosan for sizing and protection on historic papers, because it of its antifungal and antibacterial properties. They found that the application of chitosan salts immediately reinforced the wet and dry strength of the paper. When compared with cellulose ethers they believe chitosan performed better and had superior impregnation at the same concentration (2%) than the cellulose ethers.

Abdel-Maksoud and Saad (2009) also evaluated the efficacy of cellulose acetate and chitosan at different concentrations for the preservation of historical papers. Their chitosan had

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[4] Some authors claim to work with chitosan at pH of 5 then after application raising the pH to 10 to deposit the polymer on the fibers out of solution (Del Pilar Ponce-Jimenez et al. 2002, 244). Others simple state that below a pH of 6 is enough to keep chitosan solubilized (Conti et al. 2011, 8).

an 85% DD and they tested 0.5, 1, 1.5, and 2% (w/v) solutions of chitosan in water applied through impregnation. Overall, they found that the 0.5 and 1 % were more satisfactory compared to the 1.5 and 2%. They found that the chitosan had a tendency to yellow with accelerated aging, and while it increased the crystallinity of the paper before aging it decreased the crystallinity after heat aging.

Chitosan's consolidating properties have also found use beyond paper conservation. Conti et al. (2011) applied chitosan as a consolidant for archaeological silk textiles. As silk is a polar substrate they believed the amino and hydroxyl groups of the chitosan would interact with the silk to generate strong durable hydrogen bonds. Their consolidation treatment using a chitosan solution on a silk archaeological textile was through immersion and the use of an ultrasonic bath. They observed no change in color and good optical transparency. They found that even in reduced concentration of consolidant (0.3%) stable bonds were formed between the polysaccharide and the protein resulting in increased integrity of the textile. Ultrasonic application improved penetration. Chitosan creates a bridge between the fibers thus stabilizing the structure and rendering it more flexible (16). Overall, they concluded that the treatment met their criteria for compatibility, durability, and retreatability. An examination of this treatment, done by Kata (2013) at the 2013 Association of North American Graduate Programs in Conservation Conference (ANAGPIC) did not find the same suitability of the chitosan for silk. While she concluded that sufficient bridges were formed to strengthen the silk, the application distorted the shape of the material.
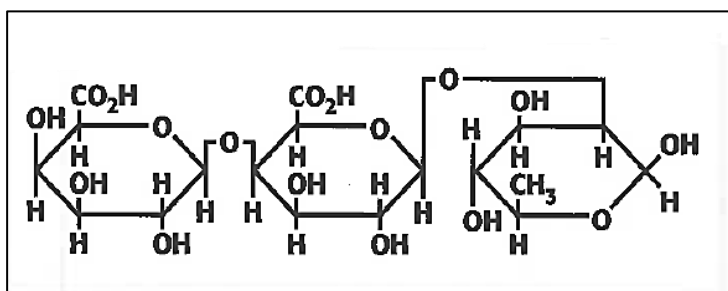
Preparation of Chitosan

A low molecular weight chitosan was purchased from Sigma Aldrich for this analysis. It has a reported 75% degree of deacetylation (DD), meaning that 25% of the material remains in

the chitin form. Two distinct chitosan solutions were created for the purposes of this evaluation. Both of the solutions were 0.5 % (w/v) concentrations; however, one is in a mixture of deionized water and ethanol, and one is in pure isopropanol. Both solutions came from the batch solution made in the following steps. First, the chitosan was weighed and added to deionized water to create a 1 % (w/v) solution. To reach the low pH required for chitosan to be soluble in water, 2 M acetic acid was added drop wise to the solution until a pH of 5 was obtained. Then, the solution was left on a stir-plate overnight until the chitosan dissolved. During this time, the pH of the solution was monitored using Beckman ϕ340 pH/Temp Meter. The pH repeatedly rose above the desired pH and more acetic acid was needed to keep the solution below pH of 5. Once the chitosan was solubilized in the deionized water, a portion of this solution was used to create a solution of 0.5 % chitosan in deionized water and ethanol (1:1) solvent mixture in order to reduce the amount of water in the solution as it can have adverse effects to leather. During the experiment it became clear that all water would need to be avoided for application onto the damaged leather. Therefore, a 0.5 % chitosan in isopropanol was created by taking some of the original 1% stock solution in water, drying it out (thus removing the water), and then, resolubilizing it in isopropanol.

5.2. Neri

Neri is an aqueous mucilage most commonly extracted from the roots of the aibika plant (genus and species: *Abelmoschus manibot medicus*; Japanese:

2. Chemical structure of the main component of Neri, rhamnogalacturonan-di-galacturonic acid (from Lorenz et al 2010, 10).

Tororoaoi) that is used in the traditional production of Japanese paper. In paper making literature, it is also referred to as *nori*. It is also extracted from tororo –aoi (*Hibiscus Manihot*, L.) and nori –utugi (*Hydrangea paniculata*, Sieb) (Zyugaku 1942, 46). The mucilage consists of 82% of acid polysaccharides (polyuronides) and approximately 17% of proteins. The polysaccharide part of the mucilage consists of L-rhamnose, D-galacturonic acid and D-glucuronic acid.

Neri has had a long extensive use in traditional Japanese paper making. In their process, neri is added to the paper pulp along with water to form a suspension that is then scooped into the mold and shaken into place. The addition of neri allows for a suspension of the fibers and an entanglement that achieves a homogenous distribution of the fibers on the paper making screen. It also prevents freshly made paper sheets from sticking together (Lorenze et al. 2012, 10). There is a limited amount of Japanese literature on neri that is currently available in English. Lorenz et al. (2012) however did an extensive review of neri, its properties, and potential applications. According to Lorenz et al. neri has usual properties that can be advantageous for many applications. For example, while neri does not have any adhesive properties, it does have a dispersive effect due to the content of water-soluble polysaccharides such as galaturoni acid in the Neri root (2012, 10). These polymers help it form a gel-like network when in the presence of water. It is important to note that neri cannot be heated as there will significant loss of the colloidal properties by heating due to irreversible disruption of the network structure caused by oxidation.

As of yet, neri has not been applied as a material for conservation treatment. Without adhesive qualities, it is questionable whether it could be applied as a consolidant, however, Lorenz et al. states "In the treatment of damaged leather Neri could be tested as an impregnation

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agent. It might enclose the fibers of the leather and form a stabilizing but flexible film" (Lorenz et al. 2012, 15). Therefore, it was included in this examination.

Preparation of Neri

Neri was purchased in white powder form from Hiromi Paper Inc. The preparation instructions provided on the packaging were for creating a solution of neri for a paper pulp separator. It was decided that the proportions given would be used to create the batch solution, and then they would be adjusted to create a solution with desired working properties and viscosity. The instructions called for a ratio of 1 tablespoon of neri to 1 gallon of water. By estimating the amount of grams in a tablespoon and calculating the amount of liters in a gallon, the solution was estimated at 0.4 % (w/v). The proportions were measured of each component and the mixture and placed on a stir-plate for several hours until the powder went into solution. Once completed, the solution appeared clear and colloidal. At this concentration, it was very thick and uneasy to handle due stringiness. In an effort to lessen the amount of water and improve the qualities for application, ethanol was added in approximately equal proportion to the solution resulting in approximately a 0.2% concentration of neri in water and ethanol.

5.3. Cellugel

Cellugel and Klucel G are both hydroxypropyl cellulose (HPC), a derivative of cellulose achieved through alkalization and etherification of cellulose under heterogeneous conditions (Varshney and Naithani 2011, 55). HPC is classified as a cellulose ether as it is a water-soluble polymer with a cellulose backbone and ether containing substituents.

As cellulose is the most abundant renewable and biodegradable polymer, the applications for cellulose derivatives are diverse and expansive. Cellulose
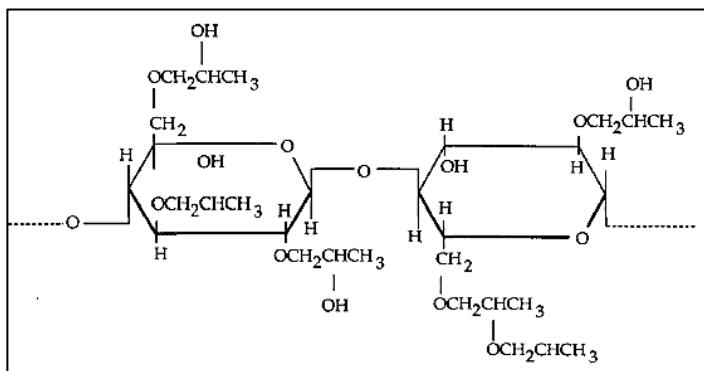
3. Chemical structure of hydroxypropylcellulose (structure of Cellugel and Klucel G) (from Feller 1990, 16).

ethers, in particular, have the ability to impart viscosity to aqueous solutions through the formation of a complex rheological system composed of higher-level structures (Varshney and Naithani 2011, 57). HPC and other cellulose ethers have been used in food, cosmetics, pharmaceuticals, coatings, adhesives, moldings, paper, paint removers, encapsulations, inks as well as other film-forming or thickening applications (Feller 1990, 97; Varshney and Naithani 2011, www.talasonline.com). HPC has also had extensive use in the field of conservation (Shashoua and Rugheimer 1998, Feller and Wilt 1990). Initially, HPC was mostly used in paper conservation; however, it began to gain popularity in the 1990s as a consolidant and adhesive for other materials (Shashoua and Rugheimer 1998, 159). In 1990, Feller and Wilt extensively studied the stability of HPC due to their reported popularity in conservation. Although the stability of HPC has been disputed for long-term use, due to certain aspects of thermal stability that are poor including a tendency to discolor with age, HPC remains a popular consolidant today (Feller and Wilt 1990, Shashoua and Rugheimer 1998, Derow 1993, Skinner 2013, Kite and Thomson 2006, Haines 2002).

Preparation of Cellugel

Cellugel is a pre-made solution of HPC with an added unknown fragrance in 100% isopropanol, manufactured by Preservation Solutions Inc. It is marketed as a red rot consolidant and targeted towards book conservation. There is no indication of the concentration of the

solution or molecular weight of the hydroxypropyl cellulose on the packaging; however, personal communication with the company revealed that it is a similar molecular weight to Klucel G and comparable concentration to a 2 % solution of Klucel G (w/v) in isopropanol. The Cellugel used for this evaluation was purchased from Gaylord Brothers (www.gaylord.com). The company would not reveal any information on the fragrance but stated that it was added to counter the strong smell of isopropanol and should not have adverse effects on materials it is applied to. In this evaluation, the Cellugel was applied at the concentration it arrived in from the manufacturer.

Preparation of Klucel G

Klucel G with SC6000: Klucel G and SC 6000 were purchased from Talas. From the powdered form of Klucel G, a 2% (w/v) solution isopropanol was made. SC6000 is a blend of waxes and an acrylic resin emulsified in aqueous isopropanol. The same amount of SC6000 (v/v) compared to the Klucel G was added to the solution so that it was a 1:1 mixture. The mixture required two days on the stirplate with constant low speed stirring to become homogenous.

6. Methodology……………………………………………………………………………..

6.1. Performance

Ease of Application

Cellugel, Klucel G with SC6000, neri and chitosan in ethanol/water and isopropanol were applied to five leather samples each[5]. One leather sample was left uncoated as a control for each

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[5] The chitosan in isopropanol was applied to leather samples taken from a degrading book binding and not from the leather moccasins.

consolidant. The ease with which the consolidant was able to be applied to the surface was evaluated based on (1) the amount of pressure needed to achieve an even coating, (2) the surface wettability of the solution, (3) the ease of applying it by brush, and (4) the perceived disruption to the leather fibers as each was applied.

The ease of application is a practical aspect that is important to evaluate as it can affect the feasibility and protocol of treatment. In an attempt to standardize this evaluation, the method of application was kept the same for all consolidants. Due to the powdery nature of the leather, the use of a vaporized system or mister was not deemed appropriate as it would likely dislodge the fibers. The choice was made to apply the consolidants with a ½ inch soft bristle brush with a flat edge. The brush was drawn across the surface lightly in a single continuous stroke so that an even coat was applied to all the fibers on the surface.

Consolidating Performance

An important aspect to consider in a consolidant is its ability to adequately stabilize the surface of the leather thus reducing powdering and adding strength. The leather samples that were evaluated for ease of application were the same as those evaluated for their consolidating performance. The amount of powdering was evaluated by rolling a cotton swab across the consolidated surface of the leather three times for each leather sample and then comparing this against the control. To evaluate the strength of the leather, each leather sample was handled and gently bent to observe cracking or stiffening. It is important to note that the consolidants in this study are not equal in their concentrations. They have been prepared in the concentrations that

have been recommended in the literature for their use as a leather consolidant (Haines 2002, Kite and Thomson 2006, www.talasonline.com). [6]

6.2. Visual and Physical Changes to Leather

Optical Microscopy

Initially, the leather used for the samples was taken from a pair of donated moccasins; the leather was evaluated macroscopically and documented in the moccasin condition report (see Appendix A). When the leather was cut into samples, it was evaluated again under a Meiji stereobinocular microscope, specifically to aid in describing color and texture. Notes were taken about the overall appearance and properties of the samples both before and after consolidation, and representative photomicrographs were taken for each sample using a Nikon D70 camera.

Colorimetry

In addition to a qualitative evaluation of appearance changes to the leather, color changes created in the leather from consolidation were quantified through the use of the colorimeter function on a Spectrodensitometer. A colorimeter applies the CIE*LAB (International Commission of Illumination) system to describe reflected or transmitted color mathematically through the use of a defined light source and a response characteristic of the observer. In the CIE*LAB System, color is described in three dimensions through the values of L*, a* and b*,

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[6] The Cellugel arrived as a prepared solution of unknown concentration by the manufacturer. The distributor states that Cellugel is of comparable molecular weight and percentage as a 2% Klucel G solution. The Klucel G mixture was prepared as recommended by the manufacturer (www.talasonline.com) and an equal amount of SC6000 by weight was added as cited in the literature (Haines 2002). The neri was produced following the approximate concentrations suggested in the instructions on the packaging material (1tbsp/gallon of water (this is v/v ration; however, when weighed this produces about 0.4% as w/v ~ 0.4% (w/v)). It was then diluted further with ethanol based on an estimated concentration 0.2%.

where the L* axis measures the lightness-darkness; the a* axis measures redness-greenness (+a) is red; (-a) is green; and the b* axis measures yellowness-blueness (+b) is yellow (-b) is blue.[7]

The instrument used was an X-Rite®939 Spectrodensitometer along with X-RiteColor® Master Software. In this instrument, the illumination/detection angle is fixed to 0/45 ° and the spot site is 4mm. For this analysis, the light source used was D65, which represents the average daylight (D) with 6500 (65) degrees Kelvin color temperature; the CIE Observer was 2° for the viewer. The instrument was calibrated with white tile and black card standards. Each consolidant was applied to five leather samples and one sample was kept as the control. For each sample, 6 measurements were taken and averaged to provide a single L*, a*, and b* value. This was done before and after applications of each consolidant.

The L*a*b* values that were collected were analyzed to detect changes in each aspect, i.e. ΔL*, Δa*, Δb*. The change in each of these parameters, ΔE, is calculated before and after aging to determine color change ($\Delta E = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}}$)These values were calculated to determine the overall color change referred to as ΔE.[8] In 1976, the CIE published a color difference formula that is referred to as the CIE*76 or CIE*LAB. Since the original equation in 1976, the formula has been updated, once in 1994 (CIE'94) and again in 2000 (CIE'00). As the CIE '00 is the most updated formula aimed at representing the color change closest to the perception of the human eye this formula will be used in the study as a comparison tool (Pesme 2013). The resulting ΔE'00 values are reported and discussed in this study though the other

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[7] For more information on the CIE*LAB color system see Bern 2000 or Johnston-Feller 2001.
[8] The ΔE values for each color difference formula were calculated on the spreadsheet provided by Color Conversion Center, http://ccc.orgfree.com/.

values are provided in the appendix[9]. The perception of noticeable difference is meant to rely on a significant group of viewers systematically assessing the leather samples under the same lighting conditions to account for vision differences. However, the required amount of viewers and conditions to systematically view the samples was not possible to achieve for this evaluation. Therefore, the threshold value of 1.5 ΔE'00 will be considered a relative baseline for just noticeable difference based on the standards used by the Getty Conservation Institute (Pesme 2013).

Haptic Evaluation

The leather samples were qualitatively evaluated for their haptic properties after the consolidants were applied. The objective was to understand the changes in the feel of the leather, particularly surface after the consolidant was applied, especially with respect to the stiffness or roughness. It should be expected that some changes occur in the feel of the leather as the fibers become better bound. However, the ideal consolidant would show a minimal amount of change to the haptic properties.

6.3. Chemical Stability

In the field of conservation, there is an accepted responsibility to use only the most stable materials that are available for the treatment, exhibition, and storage of an object (AIC Code of

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[9] It is important to note that color is affected by many factors, including texture and gloss. In this evaluation, gloss is the most important factor to take into consideration. Matte objects appear less intensely colored with lower chroma and higher lightness. Instruments with 0/45 geometry, such as the X-Rite used in this analysis, reject almost all specularly reflected light. Therefore, there is no information on the gloss provided but as the gloss increases, more of the light will be reflected in the specular direction, thus contributing more than diffuse components to dilution of the color light reflected. So, glossier samples may be recording as delivering a higher perceived chroma (Dalal and Natale-Hoffman 1999, 169; Pesme 2013).

Ethics VI). As a consolidant used to stabilize red rot is typically applied rather liberally to a large area of the surface of an object, stability is especially important as it could greatly affect the object's condition overall. Stability often refers to the resistance to change in terms of physical and chemical properties under extreme conditions of heat and light or other factors, such as chemical or biological agents (Feller 1990, 37).The measurement of stability is usually measured according to the time it takes for an unacceptable change in properties to occur (Feller 1990, 37). Feller has proposed applying a general classification system for materials based on their thermolytic and photochemical stability, and his stability classification system has been generally accepted within the field (Feller 1978, Feller 1994, Caple 2000, Horie 2010, 159). In his nomenclature, Class A1(excellent) materials are those that that show excellent properties beyond 500 years; Class A2 materials(excellent) -greater than 100 years but less than 500 years; Class B (intermediate)- 20 through 100 years; Class C (temporary)-unstable or fugitive in less than 20 years (Feller 1994, 6-8). It is recommended that conservators only use materials in their treatments that are at least Class A2, though it is a reality that that often Class B materials are used because of their specific properties within a certain treatment context.

In order to classify the stability of a material, conservators often employ some form of accelerated aging. In addition to qualifying the useful lifetime of a material, the accelerated aging process provides a way to monitor the extent of deterioration and characterize the type of degradation.[10]

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[10] It is important to understand that there is some discussion in the field about whether accelerated aging provides an accurate understanding of how the materials would react over a long period of time in less extreme conditions. For example, Feller (1978) proposes that increasing temperature and intensity of light may give false indications on what will occur under natural conditions, further explaining that in polymers cross-linking may occur at high temperatures; however, in low temperatures it may experience chain breaking (4).

For this experiment, each consolidant was brushed onto glass slides and subjected to heat and light aging. The materials were then analyzed through colorimetry, FTIR analysis, and solubility testing to understand the deterioration processes that occurred.

Aging Process

Light aging

To understand their photolytic stability, Cellugel, Klucel G with SC6000, neri, and chitosan in water/ ethanol[11] were brushed onto four glass slides. Twelve of those slides (three slides per consolidant) were placed in a tray next to a south facing window where they were exposed to extended periods of sunlight without disturbance. A control for each consolidant was kept in the dark for the duration of light aging.

To establish an ideal endpoint for the aging process, the samples were exposed to a lighting dose based on standard illumination levels for museums and an estimated amount of lighting per year recommended for leather. Leather objects are typically considered an object of medium sensitivity; therefore it is recommended that they receive 150 lux of illumination. A standard estimation of exposure recommended for items of medium sensitivity has been established by Stephen Michalski as approximately 8 hours a day, and 3,000 hours per year. Therefore; each year a leather object would likely receive about 450,000 lux hours of illumination and in 100 years, they would likely receive 45 million lux hours (Mlx h). This dose became the goal of the light aging; though it became clear that time would be a limiting factor.

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[11] Chitosan in isopropanol was not light aged.

While there are accelerated aging chambers that are capable of exposing materials to a specific light dose with a controlled lighting source, none of these were available for this examination. The light source was daylight from a window with a filter that removed approximately 98% of the energy within the ultraviolet range. The amount of UV transmittance through the filter was measured using an Elsec -764 Environmental Monitor at various times throughout the day. The recorded UV levels averaged 26 µW/ lumen with the highest amount at 39 µW/ lumen. Michalski (2011) claims that UV radiation below 75 µW/ lumen will not have any adverse effects and can be considered negligible.

To estimate the dose of light absorbed by the samples through the aging process, two qualitative methods were employed—the ISO Blue Wool Standards (BWS) and a HOBO datalogger with a light meter function. [12] The Canadian Conservation Institute (CCI) website provides approximate light doses necessary to cause a "just noticeable fade" for each Blue Wool Standard number[13]. Through the use of these values, the BWS can be used as a qualitative dosimeter. The recorded doses are divided into two categories based on whether UV is present or has been removed. As the majority of the UV has been removed by filters on the windows used, the UV absent category was selected for measurement.

To complement the BWS, a HOBO datalogger was used to record incident readings of lighting levels. Since the datalogger does not calculate cumulative light energy, calculations using the incident light readings were necessary to achieve an accurate estimation of overall dose. The datalogger recorded light levels every half hour. It was decided that the lux readings of

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[12] The Blue Wool Scale is for sensitivity to light fading, based on a set of eight different dyed pieces of wool, each with its own characteristic light fastness that can be used to qualitatively understand light dose.
[13] www.cci-icc.gc.ca/caringfor-prendresoindes/articles/10agents/chap08-eng.aspx#det5

the HOBO would be averaged for each day and be added together to reach an approximate dose. It was recognized that the recordings documented significant light levels for nine hours every day and dramatically lower levels of light for the other hours, due to the southern position of the window and the shadows created by the surrounding buildings. Therefore, a decision was made to eliminate the data from the hours that recorded insignificant lux readings from the averages as they would not accurately represent the average[14]. From the dataset, it was also observed that the first three hours within the data to be included in the averaging had larger intervals in between the readings as the sun began to rise. Therefore, two sets of data were established for each day- the first three hours and the other six. The averages of these two sets were totaled for each day.

After 57 days, the aging process was stopped due to limitations of time. At this point, there was a noticeable fade apparent on the Blue Wool number 4 and possibly a just noticeable fade on Blue Wool number 5. According to the approximate doses provided by the CCI, this would indicate that the BWS had absorbed an estimated dose of 10-30 Mlx hrs. As the endpoint for 100 years aging was estimated at 45 Mlx hrs, the aging achieved during this process could be equivalent to 50 years aging, ~ 22.5 Mlx hrs. A review of the data set revealed a significant limitation in the HOBO datalogger's recordings. At this point, only an estimated dose of 3,595,430 lux hours was averaged from the recordings by the HOBO datalogger. Clearly this is a point of discrepancy with the results from the Blue Wool Standards In looking over the data, it was discovered that for several hours of many days, the datalogger recorded exactly 10, 521 lux. This is a sign that the upper limitation of the equipment was reached during those hours and therefore information on the actual lux levels was lost. To understand what the threshold of lost

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[14] Twenty of the highest recordings were taken during the peak hours and averaged. The levels outside these hours were typically recorded between 21 – 1000 lux.

levels may have been, the light meter function of the Elsec 744 monitor was used during the direct sunlight hours. It found that levels up to 43,518 lux were being absorbed by the samples during direct sunlight. When compared to the datalogger this is a difference of 33,006 lux.

Since the measurement of photolytic stability is based on changes that occur due to amount of light absorbed overtime; the inability to record the exact amount of light dose absorbed was a setback. However, the two methods of estimating the light dose were used to inform each other. Together, it is believed that a relatively close and conservative estimate of 22.5 Mlx h was absorbed by the consolidants for the equivalent of about 50 years of aging. This will be touched upon again in the discussion.

Heat Aging

There are no widely accepted standards in conservation to assess thermal stability; however, Feller (1990) proposed in his aging of cellulose ethers that 288 hours at 100°C would generate a degree of deterioration approximately equal to 100 years of natural ageing (38). In total, 16 glass slides were brushed with three coats of consolidants[15] (four slides per consolidant). Twelve of these slides were placed onto an aluminum tray into an oven preheated to 100°C ±1°C. One slide per consolidant was kept in ambient temperature conditions as a control. Care was taken to rotate the tray of slides so that the slides were being equally heated in the oven. The slides were left in the oven for 12 days (approximately 288 hours). It is important to note that this was dry heat aging and that no moisture was added. In the literature on aging, there is a discussion about whether to include conditions of extreme humidity as well as heat when assessing thermally induced degradation (Feller 1990). For this assessment, the decision was

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[15] The consolidants heat aged were Cellugel, Klucel G with SC600, chitosan in water/ethanol, and neri. Chitosan in isopropanol was not tested as it was a later addition to the evaluation.

made to not include humidity as a factor. This decision was also due to the fact that humidity is difficult to control and when it is included in the aging process, the results would include not only thermal degradation but hydrolytic, which is not part of the scope of this evaluation.

Colorimetry

The discoloration of polymers overtime is used throughout the field of conservation as an indicator of chemical instability. Discoloration is caused by chemical alterations that create new chromophores (parts of the molecule that create color). For most polymers, the significant reason for discoloration is due to yellowing. Yellowing of a consolidant not only represents chemical instability but can affect the visual appearance of the entire consolidated surface of the object. Light aging of cellulose ethers, for example, is known to discolor the material through lightening that is due to bleaching of the cellulosic materials (Feller and Wilt 1990, 43).

In order to understand the discoloration properties of these selected consolidants, color measurements based on the CIE* LAB System were taken of consolidants on the glass slides before and after heat and light aging as well as the controls for each (Cellugel, Klucel G with SC6000, neri, chitosan in water/ethanol). Due to the transparency of the glass slides, the measurements were taken against both the white and black backgrounds provided with the instrument for calibration. As the signal from the white background will be strongest, these measurements will generally be reported, however, the comparison between white and black will indicate changes in the opacity of the consolidants. For each glass slide, 6 measurements were taken in the area where consolidant was applied, and then averaged into one L*, a*, b* value.

The values for ΔL^*, Δa^*, Δb^* were calculated and then applied in the CIE* 2000 color difference equation to document the overall color changes.

Fourier Transfer Infrared Spectroscopy (FTIR)

For organic materials, Fourier Transfer Infrared (FTIR) spectroscopy is a commonly used technique to understand chemical composition. "Infrared spectroscopy is practically indispensable for studying either natural or synthetic polymers, including cellulose, and their degradation, because it offers a real insight into what happens at the molecular level" (Princi 2011, 129). The technique uses an instrument to apply radiation from within the mid-infrared spectral region of the electromagnetic spectrum to a material and then documents the reactions of the bonds within the molecules of the material as it absorbs the radiation. The result is a spectrum where specific wavelengths of energy correspond to the molecular movements, such as vibration and rotation. On its own, the analysis does not indicate what elements are present or what specific molecule has been analyzed. However, the spectrum can be interpreted to understand which functional groups are present through the presence or absence of particular bands. As the spectrum provided for the material should always be identical to the original, any changes that occur in the spectrum indicate a change in the chemical composition of the material. Therefore, the comparison of spectra of the materials before and after aging will help determine the extent and type of chemical deterioration that occurs.

Slides of unaged consolidant and slides that were heat and light aged were used to provide sample material for the FTIR analysis. The material was collected from the slides with a scalpel and mixed with potassium bromide (KBr) with a mortar and pestle. This mixture was then pressed into a pellet. The instrument used to perform the analysis was a Jasco FT-IR-420.

The parameters for all the analyses were set at 180 runs, 4cm^{-1}, %T, range 4000-400cm^{-1}. The spectra were analyzed and processed on Spectra Manager and KnowItAll® Informatics System 9.5 software. The spectra were baseline corrected and smoothed.

Solubility (Reversibility after aging)

Retaining the properties of solubility is not only important for the reversibility of the treatment, it may also be an indicator of the chemical stability of the material. Although in most cases where a consolidant is necessary the object will be too weak to withstand removal of a consolidant, if insolubility was observed after aging, these consolidants would be immediately eliminated as a potential treatment material. An inability to solubilize in a solvent may indicate cross-linking or chemical degradation of the substance.

To assess the retention of solubility properties, each of the aged samples was placed under the microscope and a microswab that was wet with the original solvent of each respective consolidant was applied in a rubbing motion. These aged samples include heat and light aged samples for Cellugel, Klucel G with SC6000, neri, and chitosan in water/ethanol and isopropanol (heat aged only).[16] The consolidant was deemed soluble if the swab showed that the material fully solubilized with ease. It was deemed partially soluble if the consolidant swelled from the application of the original solvent and insoluble if the original solvent was unable to affect the material. For materials that showed a change in solubility parameters, then the "Teas charts" of solubility parameters of solvents was consulted (Horie 1987, 193). From the "Teas charts", four different solvents, namely water, ethanol, acetone, and mineral spirits, were chosen in an attempt to characterize the change in solubility.

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[16] There was no opportunity to light age the chitosan in isopropanol and it was a late addition to the experiment.

7. Results (See Appendices B, C, D, and E)……………………………………………………………...

Chitosan

Overall, both the chitosan in water/ethanol and in isopropanol demonstrated great ease of application, which allowed for an even distribution over the surface and a continuous coating. Yet, when applied to the leather samples, the chitosan in water/ethanol drastically altered the appearance and physical properties of the leather. It created uneven surfaces with some areas of shiny dark leather that appeared flat, crispy, rough, and no longer demonstrated the supple fibrous nature of leather. Microscopically, the samples appeared overall to be glossy and gelatinous. The color measurements before and after this solution was applied quantified the color change with a drastic ΔE'00 of 13.72. However, it was concluded that it was the solvent mixture of water/ethanol that denatured the leather and not the chitosan itself, as chitosan in isopropanol did not show the same adverse effects.

The chitosan in isopropanol had very little effect on the gloss, saturation or hue of the leather samples. Under the microscope, this consolidant appeared to have the least amount of material visible on the surface compared to the other consolidants, though the difference was minor. The overall ΔE'00 for this solution was calculated to be 4.13. Under the microscope areas of glossy material could be found but it was well dispersed and minimal. This was likely the polymer that remained on the surface from application. This single application of chitosan was found to be sufficient in stabilizing the powdering surface of the leather. However, the chitosan did not seem to strengthen the leather substrate beyond the surface cohesion. This may be due to the fast evaporate rate of isopropanol.

When chitosan was subjected to accelerated light aging, the material was found to lighten more than the other three consolidants. Comparing the unaged and the light aged sample, the chitosan was calculated to have an average ΔL^* of + 0.48. Heat aging resulted in an even higher overall change in ΔE than light aging. With a ΔE of 1.37 reported, the chitosan showed the highest amount of overall color change than all the consolidants tested. This overall change appears to be attributed to the increased yellowness of the chitosan samples. The average Δb^* for this consolidant was calculated as 1.27 compared to the -0.44 Δa^*, and -0.31 ΔL^*.

The spectra of the aged samples of chitosan show different chemical changes occurring, likely from different chemical reactions being induced. Overall, the chitosan heat aged spectrum is noisy but does not appear to change much when compared with the unaged, except for the likely loss of water being driven off by heat. The light aged spectrum seems to be noticeably altered in the 1000-1200 cm^{-1} region where C-C-O and C-O-C modes are located. As the alteration appears to be a reduction of the absorption for this band, it is possible that the glycosidic linkage between monomers is breaking, causing the chain to scission. For the light aged sample of chitosan there is also the appearance of new peaks at 1640 cm^{-1} and 1470 cm^{-1}, which is the C=O and NH region. Together these two changes may indicate a change in the acetyl groups still remaining in the unreacted chitin features of the polymer, as the acetyl group becomes hydrolyzed thus corresponding with an increase in OH. It is interesting to recall that the most discoloration measured was from the heat aged samples of chitosan, where in FTIR, it appears that the light aged chitosan shows the most alteration in chemical structure.

Finally, the chitosan in both solutions, water/ethanol and isopropanol, seemed to show a dramatic shift in solubility when aged. Both the heat and light aged samples of chitosan in deionized water/ethanol altered in a way that they were no longer soluble in ethanol and only

swelled in deionized water. The aged chitosan in water/ethanol was also found to be insoluble in isopropanol, mineral spirits, and acetone. If one considers the "Teas charts" for solubility parameters of solvent, it could be suggested that the solvent required to solubilize the material after aging was one of increasing polarity and degreasing dispersion forces (Horie 1987, 193). For this examination, only a heat aged sample of chitosan in isopropanol was tested for solubility shifts. It was found insoluble in isopropanol, but further conclusions could not be made.

Table 2: Average overall color changes calculated for leather samples after consolidants were applied

sample	ΔL*	Δa*	Δb*	ΔE'00	ΔE'94	ΔE' 76
Chitosan in H2O/ETOH	-10.80	-9.50	-18.40	13.72	15.67	23.27
Chitosan in isopropanol	-4.49	0.32	-3.21	4.13	4.86	5.55
Neri in H2O/ETOH	-9.38	-6.25	-17.02	11.91	13.28	20.54
Cellugel in isopropanol	-1.62	0.136	-1.34	1.69	1.82	2.22
Klucel G with SC6000 in isopropanol	-1.44	-0.172	-1.68	1.51	1.68	2.26
Control Variance	±0.368	±0.315	±0.845	±0.66	±0.60	±1.04

Neri

When neri was applied to the leather samples, it exhibited a stringy quality that presented application challenges. First, it was difficult to apply it to the surface without multiple applications or uneven distribution. Secondly, the strings of the neri fell onto other surfaces that were not meant to be consolidated. Like the chitosan in water/ethanol, the neri drastically altered the appearance of the leather creating uneven surfaces with some areas of shiny dark leather that appeared brittle, weak, rough, flattened and distorted. The overall color change was calculated as a ΔE'00 of 11.91. Essentially, the water in this solution denatured the leather and attempts were

made to remove the water content of neri, but they were unsuccessful. Due to the denatured appearance of the leather, it was considered futile to assess consolidation performance.

When neri was subjected to heat and light, the material showed very minor changes in color overall. The average overall ΔE '00 value calculated between unaged neri and heat aged was 0.28, between unaged neri and light aged 0.34, which averaged a 0.31 overall value. These changes can almost be considered negligible as the calculated ΔE'00 value for the controls were found to be ±0.46.Neri was found to be soluble in its original solvent after both heat and light aging.

In FTIR spectra, the most noticeable change between the unaged and aged neri is to the absorption bands that appear in the 3400-3000 cm^{-1} range where the stretching bands that correspond to the functional groups O-H and N-H lie. The peak alters from a broad peak to a narrower one in the heat and light aged samples. For neri, both the heat aged samples show an increase in this peak intensity. These changes may indicate oxidative influences due to increased O-H group stretching. In the 3200-2800 cm^{-1} range, there is also an increased intensity of the hydrocarbon absorption bands, especially in the heat aging, showing some alteration to the polymer chain.

Table 3: Average overall color changes calculated for slides after accelerated aging

sample	ΔL*	Δa*	Δb*	ΔE'00	ΔE'94	ΔE' 76
Chitosan in H2O/ETOH	0.39	0.24	0.7	0.86	0.93	0.96
Neri in H2O/ETOH	0.35	0.03	0.11	0.31	0.43	0.47
Cellugel in isopropanol	0.10	0.02	0.05	0.09	0.12	0.12
Klucel G with SC6000 in isopropanol	0.27	0.06	0.11	0.23	0.30	0.31
Control Variance	±0.25	±0.18	±0.15	±0.24	±0.33	±0.33

Cellugel

The Cellugel was applied as prepared by the manufacturer. This thick viscosity did not provide enough flow and it appeared to sit on the surface of the leather. In order to achieve a universal application, dabbing of the brush was required which disturbed the fibers more than the other consolidants. One coating of the solution on the samples was found to provide satisfactory reduction of powdering. However, the strengths of the surfaces were only slightly improved. The strength was mostly superficial and was seen in the restriction of movement of fibers where the consolidant was applied. When gently folded, the leather experienced some cracking. Macroscopically, the Cellugel appeared to have little effect on the gloss, saturation, or hue of the leather. The color changes measured showed a movement to blue and green; however, the average overall ΔE '00 value calculated between unconsolidated leather and leather consolidated with Cellugel was only 1.69, where the average control variance was calculated as ±0.66. In their haptic evaluation it was found that the samples coated with Cellugel retained a significant portion of their soft quality, though there was stiffening in the movement of the leather. This could be due to a strengthening of the surface through the cohesion created between the fibers.

After light aging, the samples of Cellugel showed the lowest color measurement changes with a 0.08 ΔE '00 value. Again with heat aging, the samples recorded the lowest overall color change with a ΔE '00 value of 0.10. However, when the measurement of color changes against a black background were compared to those seen in the white background, there was an indication of opacity change. A slight change in opacity could be indicated for light aged Cellugel samples where the average ΔL^* value was a 1.66 on a black background compared to the average -0.01 ΔL^* recorded on the white background.

All aged samples of Cellugel were found to be soluble in the original solvent, isopropanol.

FTIR revealed chemical changes for Cellugel as occurred with all four consolidants in terms of the region corresponding to the NH and OH bonds in the molecules. The peak in this range (3400-3000 cm^{-1} range) alters from a broad peak to a narrower one and increases in intensity in both the heat and light aged samples. For Cellugel, there appears to be a reduction in the intensity of the bands for the hydrocarbon absorptions in the 2900- 2700 cm^{-1} region in both the aged samples. There are also observable changes in the 1000-1200 cm^{-1} region for both aged samples of Cellugel. Together this may indicate a possible disruption in the cyclic ring structure of the cellulosic material (Herant 2013).

Klucel G with SC6000

The Klucel G with SC6000 mixture demonstrated great application properties. It demonstrated good wettability, which allowed for an even distribution over the surface and a continuous coating. One coating of the solution reduced the powdering of the leather samples sufficiently. The samples retained a significant portion of their soft quality after the consolidant was applied, though there was stiffening in the movement of the leather. This could be due to a strengthening of the surface through the cohesion created between the fibers. Like the other consolidants; however, the added strength was mostly observed to be superficial and did not show much effect on the overall strength of the leather matrix. Macroscopically, this consolidant appeared to have little effect on the gloss, saturation, or hue of the leather. According to the measured color values and calculated color changes, this mixture altered the coloring of the samples the least as the ΔE'00 value calculated between unaged Klucel G with SC6000 and heat and light aged Klucel G with SC6000 was only 1.51.

After light aging, the average color changes calculated for Klucel G with SC6000 was 0.26 ΔE'00. Heat aging also brought minimal change with a calculated average of 0.21 ΔE'00. The overall color change does not appear to be from yellowing but from a lightening that occurred as measured changes in lightening were greater than changes in either blue-yellow or red-green axes. The most significant difference recorded between white and black background, however, is with the heat aged samples of Klucel G with SC6000, where the average ΔL* is 4.12 compared with the average white background measurement of 0.2, demonstrating a great change in opacity.

All aged samples of Klucel G with SC6000 were found to be soluble in the original solvent, isopropanol.

The FTIR spectra of the aged Klucel G with SC6000 shared similarities with Cellugel. There is a reduction in the intensity of the bands for the hydrocarbon absorptions in the 3200-2800 cm^{-1} region in both the aged samples as well as in the in the 2900- 2700 cm^{-1} region. These changes could represent chain scissioning which would correlate to Feller's 1990 study where he found substantial chain scissioning for many cellulose ethers. Curiously, for the Klucel G with SC6000 mixture, the 165O cm^{-1} peak not only reduced in intensity for heat, as it did in the Cellugel, but broadened in both the heat and light aged samples. This change may have something to do with the added wax element.

8. Discussion…………………………………………………………………………………….

Performance

As all of the consolidants were easily available, affordable, and safe to handle, the practical aspects that were evaluated for overall performance were their ability to consolidate the

surface sufficiently and the ease of applying the consolidant. Overall, all the consolidants were found to stabilize the surface sufficiently with one application but the ease of application varied. The chitosan solutions (water/ethanol and isopropanol) as well as the Klucel G with SC6000 were the easiest to apply by brush. They readily wet the surface with minimal disturbance to the leather fibers. Cellugel was less convenient to apply. As it is sold as a prepared solution, Cellugel is rather thick for supple leather with fibrous texture. For book binding or saddle leathers that are commonly treated with Cellugel, this thickness may not be an issue as their surface treatment often results in a more compact surface. Yet, on the samples for this study, the consolidant required stippling after the initial stroke from the brush in order to get the consolidant evenly dispersed within the fibers of the leather. Any level of dilution with isopropanol would likely make application easier. However, it appears that the problems with the application properties of Neri cannot be mitigated. Neri has a stringy quality that makes it difficult to avoid delivering to unwanted areas, and application is therefore difficult. Attempts were made to dilute the solution with ethanol, but with no success. The properties were so undesirable that, based on this aspect of performance, it is believed that neri may be an unsuitable material for leather consolidation. This conclusion answers the question proposed by Lorenz et al in her 2012 article on the possible application of neri on leather (15). Unfortunately the unique gel-like network and dispersive effects could not be used to their full advantage due to the unavoidable water content.

Effects on Leather

According to Glen Ruzicka at the Conservation Center for Art and Historic Artifacts (CCAHA), Klucel G with SC6000 is supposed to be an overall improvement on Klucel G alone, or Cellugel, which is an equivalent, though the specific qualities being improved were not made clear. The explanation for which properties were improved was not found however, Haines

(2002) claims that the addition on SC6000 effectively retards the transmission of water vapor to the leather support, which could offer protection against hydrolysis or acidic pollutants (20). Haines (2002) also notes that Klucel G alone gives a dull finish and the coating tents to break up on repeated flexing; however, she found the finish of Klucel G with SC6000 mixtures overall aesthetically pleasing and indicated promise for the mixture seemingly indicating that the mixture would be an improvement over Cellugel (21). However, it is important to note that leather is often found in different circumstances in terms of water vapor transmission and wax may affect these properties. For book binding leather, the importance of water vapor transmittance is very little because one side is already blocked by another material, but for a leather that is unbound and free on both sides, the transmission of water vapor may be more substantial. In this type of leather, the wax component of this mixture may block this action and become cracked in appearance due to one sided pressure.

Chemical Stability

The evaluation of chemical stability is vitally important for all consolidants in this study. For neri and chitosan, the chemical stability of these materials have not been fully investigated. In order to be considered a conservation grade material and potential consolidant, an assessment of their stability deserves attention. In the cases of Cellugel and Klucel G (both hydroxypropylcellulose (HPC), their stability has been classified in previous studies (Feller 1971, Feller and Wilt 1990), however, as the museum conditions and conservation needs are consistently changing, a reevaluation into their stability classification is also warranted. Evaluating the chemical stability of a material is a complex task as there are several types of degradation reactions that occur, different agents or factors that may instigate deteriorations, such as heat, light, chemical or biological agents, and there are a variety of methods that can be

used to evaluate materials (Feller and Wilt 1990, 37). For this study, it was decided to accelerate the aging of the materials in heat (dry) and light and monitor their chemical changes in terms of discoloration, molecular changes evidenced in FTIR, and alterations in solubility. Due to the certain limitations, specific information about what type of chemical change is occurring will be brief and the focus will be more about reporting how much change has occurred within the material and how it compares to the other tested materials.

Chitosan

In terms of discoloration, both the light and heat aged chitosan demonstrated an overall yellowing and lightening that was greater than that experienced by neri, Cellugel and Klucel G with SC6000. The heat aged samples of chitosan in water/ethanol had the most notable discoloration with an overall ΔE of 1.37. Not only do these color changes indicate that the chitosan demonstrates more instability than the other samples, but the values are close enough to 1.5 ΔE'00 that there may be the possibility that it could discolor the surface appearance of the leather overtime (Pesme 2013, Druzik 2013). An important consideration is the slightly acidic nature of chitosan in solution due to its initial requirement of a pH below 6.0 to be soluble in water. For leather, this acidity is not an issue due to its inherent acidity, however, for other materials this may be an issue.

A cohesive study done on the photo- and thermodegradation of chitosan demonstrates comparable results in terms of chitosan's instabilities (Mucha and Pawlak 2002). According to this study, the degree of deacetylation of chitosan affects the stability, where higher deacetylated chitosan is more susceptible to weight loss due to higher temperatures. Mucha and Pawlak's study subjected the chitosan to short episodes of intense heat (100°C, 130°C, 160°C, 200°C) and

light (low pressure mercury lamp at $\lambda = 254$, 700 lux, 1 hr). The chitosan for the present experiment was purchased from Sigma-Aldrich and known to have a degree of deacetylation of 75%, indicating that 25% in still in its chitin form. Significant changes to the C-O-C group at 1150 -1040 cm^{-1} were also observed in the study. Additionally, Mucha and Pawlak recorded an increased absorbance for the band of amide group at 1655 cm^{-1} (in this study 1620 cm^{-1}), pointing to chitosan acetylation. Overall, they found that thermo-and photodegradation results in the scission of the main chain and a destruction of an unstable amine group, then an increase in chitosan acetylation degree, and macromolecular cross-linking.

An aspect of the treatment that was not evaluated in this experiment was the interaction between chitosan and the leather. The molecular interactions between chitosan and collagen have been documented extensively as it is an interest to the medical field (Sionkowska 2004,). To date, there have been several successful cases where blends of chitosan and collagen have been made into various films for different applications. Furthermore, it has been observed that the chitosan aspect of the blend adds instability to the collagen in terms of resistance against ultraviolent radiation (Sionkowska 2004, 551). This molecular interaction that occurs between collagen and chitosan puts into question the appropriateness of use as a consolidant, especially when the combination appears to increase the instability of the materials.

Neri

Overall, neri seemed to show a relatively high level of thermal (aged ~100 years) and photolytic stability (aged ~50 years). As there have been no previous studies on the stability of neri, comparisons with findings in other studies cannot be made as can be done with the other consolidants. As there is current interest in paper conservation to use neri for applications outside

of paper production (Lorenz et al 2012, 14), this stability that is observed may support the promise of its appropriateness as a conservation material, though it may have limitations due to the application properties observed.

Hydroxypropylcellulose (Cellugel and Klucel G with SC6000)

In terms of solubility, all of the aged samples of both the Cellugel and Klucel G with SC6000 were found to retain their solubility in isopropanol, showing that they provide an aspect of retreatability if present on an object. The overall color change for Cellugel was the least of all the consolidants, though Klucel G with SC6000 was also considered to impart negligible change. Although it was not an initial aim of the color measurements, the comparison between the measurements made on the black and white surfaces provided valuable information on opacity changes. Most significantly, the Klucel G with SC6000 showed a significant change in opacity from heat aging. It is likely that this is an alteration in the wax component of the consolidant mixture. This aspect is important to consider as the opacity changes could affect the appearance of the leather surface with changes in temperature overtime.

The changes in the FTIR spectra between the aged and unaged samples of Cellugel and Klucel G with SC6000 may represent chain scissioning which would correlate to Feller's 1990 study were he found substantial chain scissioning for many cellulose ethers. For cellulose ethers (Cellugel and Klucel G) an important aspect of thermal aging is that it should bring a gradual increase in the peroxide content, which can lead to a chain of chemical reactions resulting in weight loss, discoloration, an degradation of molecular weight. However, for Cellugel and Klucel G, both of the heat aged spectra show after approximately 100 years of aging, a reduction of C=O band that would signify peroxide formation. As touched on briefly before, the stability of

hydroxypropyl cellulose has been evaluated previously. Feller and Wilt's 1990 publication has become an authority for cellulose ether stability.

Before the discussion of stability continues to a comparative ranking or establishment of a grade level, it is important to discuss certain aspects of the experiment that affect the interpretation of the results. The aging processes selected for this evaluation have a major role in the chemical changes that have been demonstrated. Currently, in the conservation field, there is no universal method of accelerated aging for conservation materials; however, attempts were made to design the aging process so that the results could be compared to relevant studies. For example, the design of the dry heat aging experiment was modeled after the parameters discussed in Feller's examination of cellulose ethers (1990). The light aging method was informed by the standards set forth by the Canadian Conservation Institute (Michalski (2011) and again by Feller's study (1990). However, there were limitations of time and equipment. Both the methods for monitoring the light dose proved to be somewhat inadequate. A significant setback was the HOBO datalogger which could not accurately document the light levels that were being absorbed by the material throughout the testing period. A maximum level of light at 10512 lux was reached for multiple hours and multiple days. A comparison with an Elsec Environmental Monitor revealed up to 38000 lux was being absorbed at times by the object. The second tool used as a dosimeter, the Blue Wool Standards, proved to have its own flaws. The end point of the light aging was a just noticeable fade on BWS 4, which approximates 10-30 Mlx hrs with a possible deviation of 3-30 Mlx hrs (Michalski 2011). As the amount of lux estimated by HOBO datalogger was approximately 3.6 Mlx hrs, between the two doses there is clearly a large amount of uncertainty. Therefore, it is possible that the light aging conducted for this study represents about 50 years of light aging.

A major aspect of this study was to discover which chemical changes correlate with those presented in the Feller and Wilt publication, which condemns hydroxypropylcellulose (HPC) to a temporary use category within his standards of material stability for conservation purposes. Feller's findings with respect to HPC are that HPC's typically have little tendency to form peroxides, have excellent photochemical stability, yet they have significant reduction of degree of polymerization and have the potential to discolor at around 20 years. The chain breaking which causes the reduction of polymerization causes a loss of strength meaning that there may be the need to retreat an object overtime. Most importantly, Feller comments that for a thin film made from low percentage of HPC, the effects of negligible discoloration and chain breaking may not be serious as there is not a real tendency for HPC to become insoluble, react with collagen, or form harmful byproducts (Feller and Wilt 1990, 94). Feller does comment that the molecular weight grade of the HPC plays a significant role in the stability. He found, for example, that Klucel G, which has a lower molecular weight than Klucel H and M, exhibits more stability. So while most HPC's are deemed only acceptable for temporary use (less than 20 years use), Klucel G is considered intermediate stability (use 20-100 years). Feller also emphasizes that the specific brand of Klucel G plays a role in its stability. It's unclear whether this point it still relevant 23 years after the publication as there may have been developments or standardizations of quality since then, yet the importance of paying attention to the brand should be noted.

As with this study, the specific aspects of Feller's experimental design must be understood in order to interpret the results. For example, Feller aged both powder samples (bulk samples) and films on glass and most of his crucial finding that were provided negative results for cellulose ethers were based on the results from the aging of the powder samples. It is

important to know that for his evaluation, Feller uses the standard of 300 lux a day and 1 million lux hours of illumination a year to create and end point for accelerated aging in his assessment of cellulose ethers. However, current practices and standards in conservation are much different from when this assessment was made. Michalski (2011) estimated that museum objects receive about 3,000 hours a year of illumination in a museum. Also, it is currently typical to expose leather to 150 lux when lighting for exhibition due to its classification as a Medium Sensitivity object. This sets the standard of 450,000 lux hours of illumination per year, which is less than half of Feller's estimation.

9. Treatment of Apache Bag (Appendix G)………………………………………………

Based on the results of this examination, the two natural materials did not exhibit enough stability and desired properties as the well-known consolidant materials. Therefore, Cellugel was selected to consolidate the powdering leather of the Apache bag suffering from red rot deterioration. Isopropanol was added to the Cellugel to dilute it from a ~2% solution to a 1% solution. This solution demonstrated improved wettability and lessened stiffening of the surface. This solution was applied universally to the exterior surfaces of the bag. No adverse effects were observed and the surfaces were sufficiently stabilized. However, testing on the leather thong and interior side of the leather revealed that the consolidant darkened, caused some embrittlement, and did not sufficiently stabilize the flaking that was associated with powdering on the thong. It was discovered that the polarity of the isopropanol was the cause. Two important points were realized at this time. One is that the flesh versus the grain side of the leather may react very differently, and only the flesh side was consolidated in this experiment. The exterior surfaces of the bag were identified as the flesh side, where the thong and interior were the grain side. It was also realized that the hydroxypropyl cellulose had restricted solubility in common non-polar

solvents. The most practical solution was to switch to a consolidant that had solubility in a

solvent that did not create adverse effects. The solvent of choice was toluene; therefore, the

consolidant BEVA 371 was selected. The BEVA 371 still caused darkening to the surface but

penetrated the matrix to stabilize the flaking further. Overall, the treatment of the powdering was

successful to an extent; however, the reality of red rots ability to completely leave the matrix

without structural strength was realized. The surface was stabilized but the leather matrix still

lacked enough strength to fully repair the tears. In the end, the treatment to apply mends to tears

was stopped as it became clear that the bag could not be stabilized further.

10. Conclusion………………………………………………………………………………

In this study, four consolidants were compared for their effectiveness in the consolidation

of red rot as well as their chemical stability. Of the four consolidants chosen, two currently find

widespread use as consolidants for leather: the Cellugel and Klucel G with SC6000, and two are

novel materials as they have not been used for this application: neri and chitosan. It was

discovered that chitosan showed some undesirable properties with respect to chemical stability

especially in heat that may result in significant yellowing and insolubility overtime. A literature

review of the uses of chitosan in the medical field revealed that chitosan may have interactions

with the collagen in leather and therefore lacks the inert quality that is sought for a conservation

material. Therefore, chitosan is not recommended for use as a consolidant for leather until more

research is done on this interaction. While neri showed a great chemical stability during

accelerated light and heat aging, it does not have the desired application properties and has a

water content that is unavoidable. Therefore, the neri is also not recommended for leather,

though its stability makes it a potential conservation material for other materials and uses.

Klucel G with the SC6000, the popular "red rot cocktail" was found to be easy to apply and did

not bring adverse effects to the visual and haptic properties of the leather; however, the wax

component may bring a change in opacity over time as was seen in the heat and light aging. This

is a concern to take into account when using this mixture. Cellugel was found sufficient in

stabilizing the surface of red rot, but it was found not to penetrate the matrix of the leather to

provide strength to leather that is severely deteriorated by red rot (as with the Apache bag). The

stability of Cellugel and Klucel G was found to be appropriate for use as a diluted consolidant as

its deterioration retained solubility, inertness, and the majority of its translucent and colorless

properties.

Appendix A: Condition Report of Moccasins Used for Leather Samples

Condition Report

Object: child's leather moccasins with beading

Cultural attribution/provenance: Unknown. Likely American Indian or First Nations attribution.

Dimensions: 4 in x 5.5 in, (10 cm x 14 cm)

       3.75 in x 5.4 in, (9.5 cm x 13.5 cm)

Identification (or accession, registration, or catalog) number: fragmentary "88.8" inked onto one sole, "88.8.1/2" (?) on the other

Medium: leather (likely vegetable tanned), machine-manufactured un-dyed fabric, brown pile/velvet (?) fabric, brown twill fabric, red ribbon of a course material, glass seed beads in various colors

Current/past owners: Deaccessioned from the Eiteljorg Museum. Donated to the UCLA/Getty Program in Conservation.

Date of examination: 11/09/2012

Conservator: Caitlin Mahony

First page, object description:

The objects are a pair of child's leather moccasins with floral beading design on the vamp and a brown cloth ankle cuff with light blue beading in a zig-zag design. The shoes are secured to the wearer with red ribbon ties.

Materials and techniques:

Structure

The moccasins are constructed with an interior lining of machine-made fabric and an exterior of tanned leather. One piece of leather is used to make the sole and part of the upper. It comes together at a seam along the back heel. The tongue or vamp is a separate piece of leather. This piece is lined on the exterior side with a heavy brown twill fabric that appears to be wool. Each shoe has an ankle cuff that begins at the tongue and covers most of the lateral sides. This cuff is sewn down to the leather on all edges with a brown thread. The cuffs are constructed of a thick leather interior that provides structure and are covered by a brown velvet fabric. A coarsely

woven red ribbon is wrapped and sewn around the edge of each cuff. These ribbons extend past the cuff to provide a length to be tied.

Surface

Both the vamp and the cuff have glass beaded designs. The vamp has two boarders of white beads surrounding a floral design interior with red, dark blue, and light blue buds. The cuffs have a zig-zag design of blue beads. The beading is sewn with a natural-colored thread that appears fibrous and not to be sinew.

Condition:

      Structurally, the object is unstable due to the pervasive deterioration of the leather presumably due to red rot. Red rot is an acidic deterioration of the collagen fibers that results in friable brittle red/brown colored leather. Due to the brittleness, the leather is split on each shoe along the line that divides the upper part of the shoe and bottom sole. This split is associated with losses and fragmentation. Aside from the leather deterioration, other elements of the structure such as the stitching appear intact.The next most significant condition issue is the damage exhibited to the fabric that covers the exterior of the ankle cuffs. Each cuff is suffering significant loss to the velvety piling on the surface. The only areas where the piling survives are those in close proximity to the beading. The edges of the fabric on one shoe has loss along the edge nearest to the leather. It is possible that the fabric is constructed of a cellulosic material and is suffering due to the acidic nature of the deteriorating leather. It is also possible that the damage is from wear. The brown twill fabric on the vamp is mostly intact, which could be due to the fact that it appears to be wool which is more compatible with acidic environment than cellulosic material. The edges of red ribbon are fraying. Overall, the surfaces are extremely dirty and covered with the powder of the deteriorated leather substrate.

Condition summary:

Both moccasins are in extremely poor condition due to the failing leather substrate. The leather exhibits red rot on all surfaces. It is structurally unstable due to splitting and continued loss of the leather substrate due to its brittle nature.

Testing, analysis:

The pH was measured using colorpHast® indicator strips ph 0-6. The pH was a 4.

The shrinkage Temperature (T_s) was measured using a Physitemp T3-4ER Controller with needle probe. The T_s was recorded as 39.1-41°C.

Proposed treatment:

The deteriorated leather will be used in a study for testing consolidants for red rot. The material will be cut and prepared into 24 samples.

Condition Images:

4: General view of moccasins at the time they were received from the Eiteljorg Museum.

5: General view of the obverse side of the moccasins. The fragmentary and brittleness of the leather is evident.

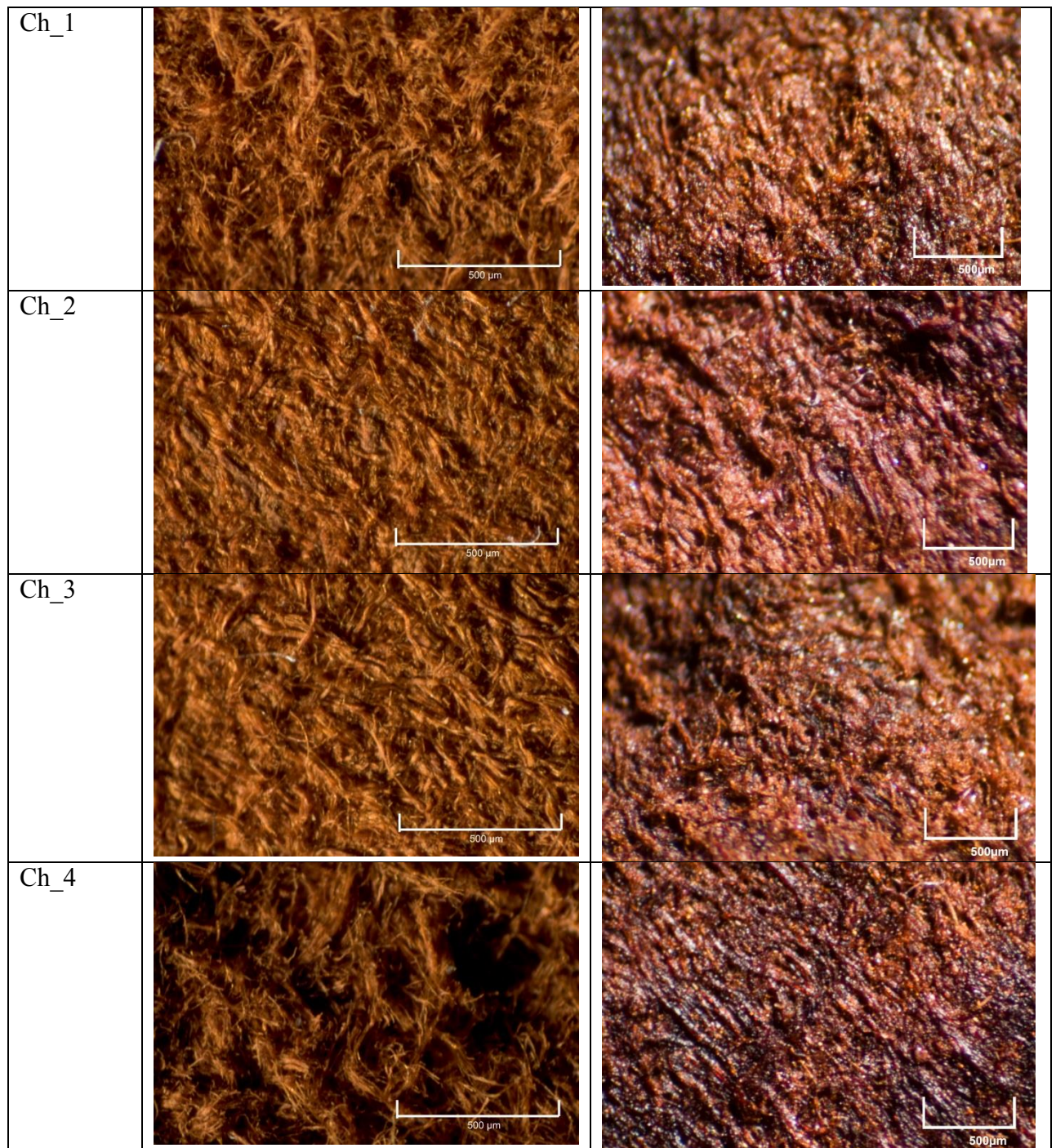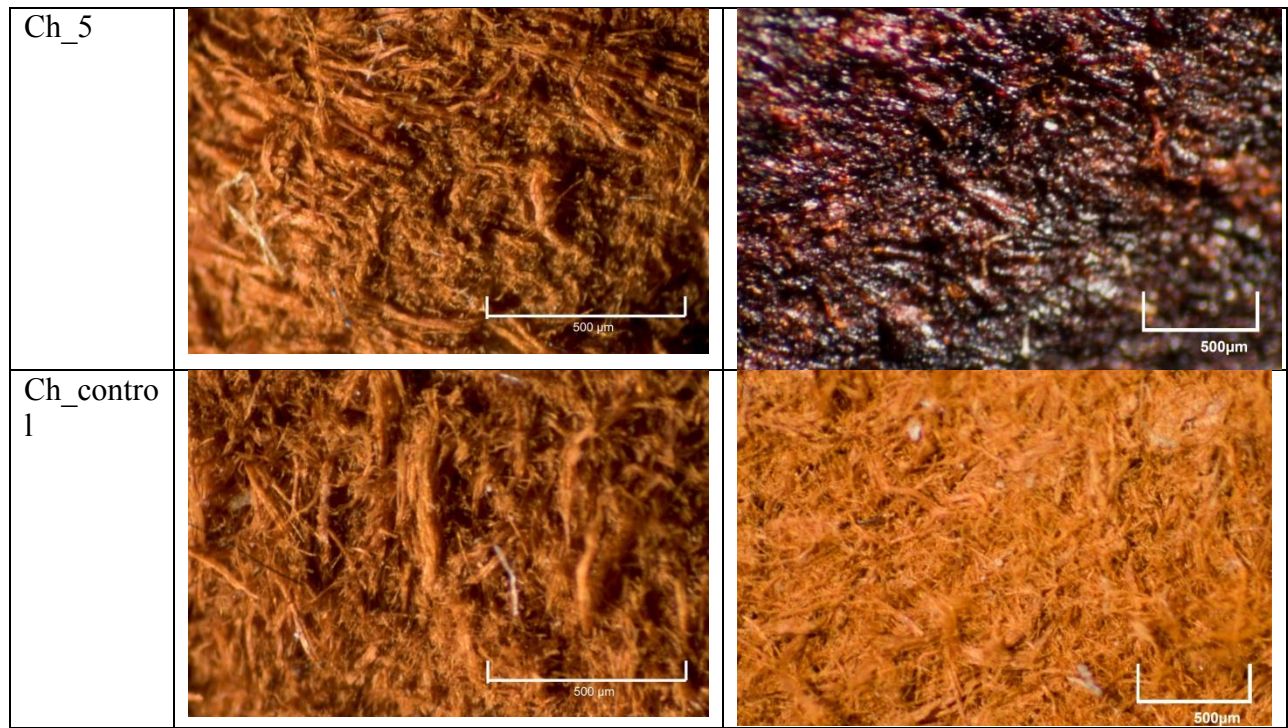6: Detail of the damage to the velvet fabric on the ankle cuff.

7: Detail showing the intact twill fabric, beading, and interior seams.

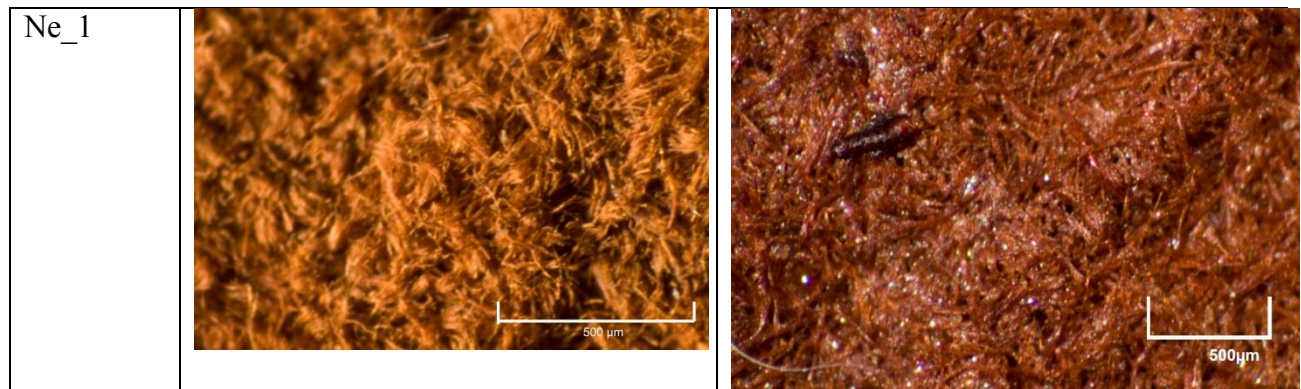**Appendix B: Photomicrographs of Leather Before and After Consolidant Treatment**
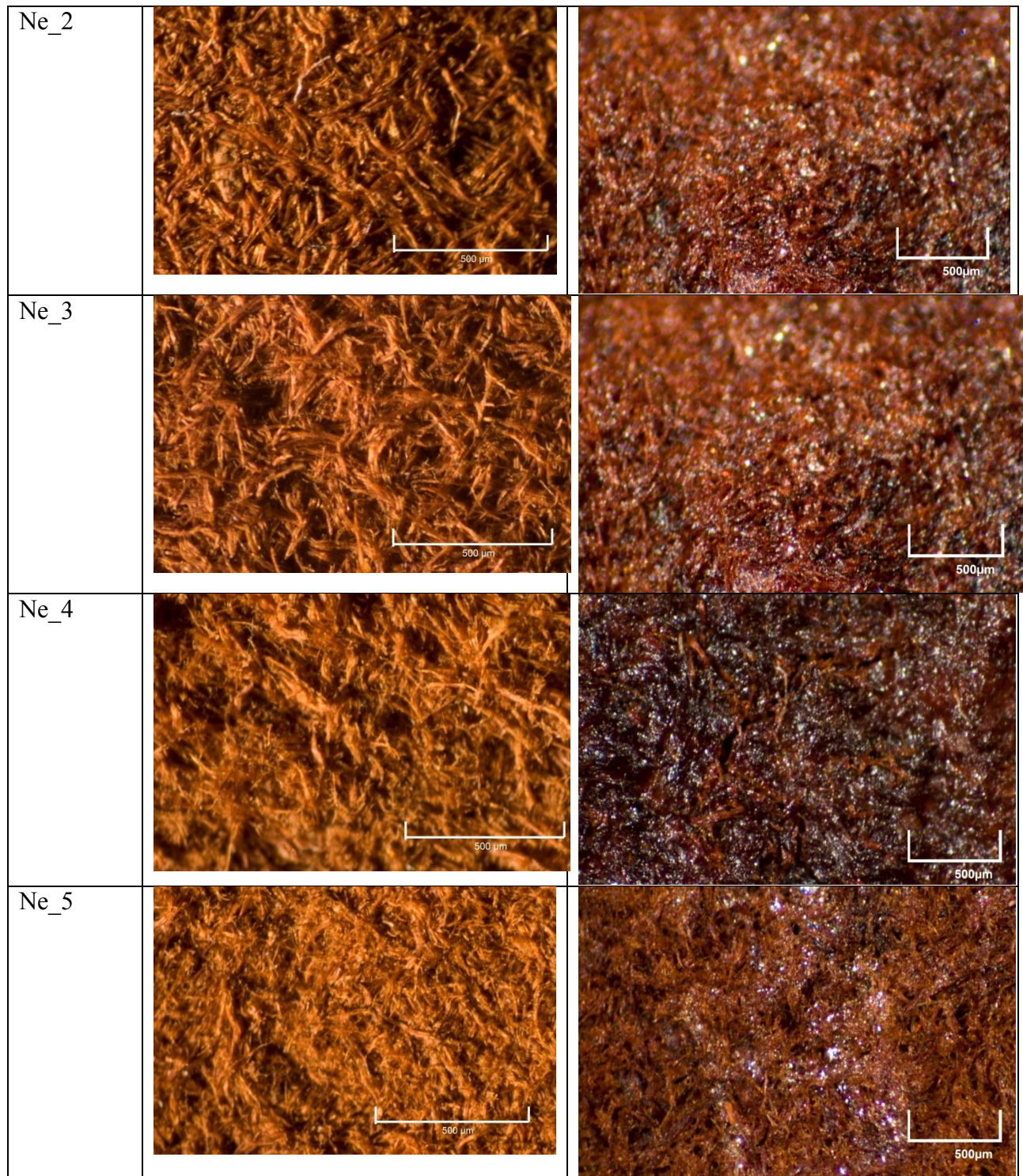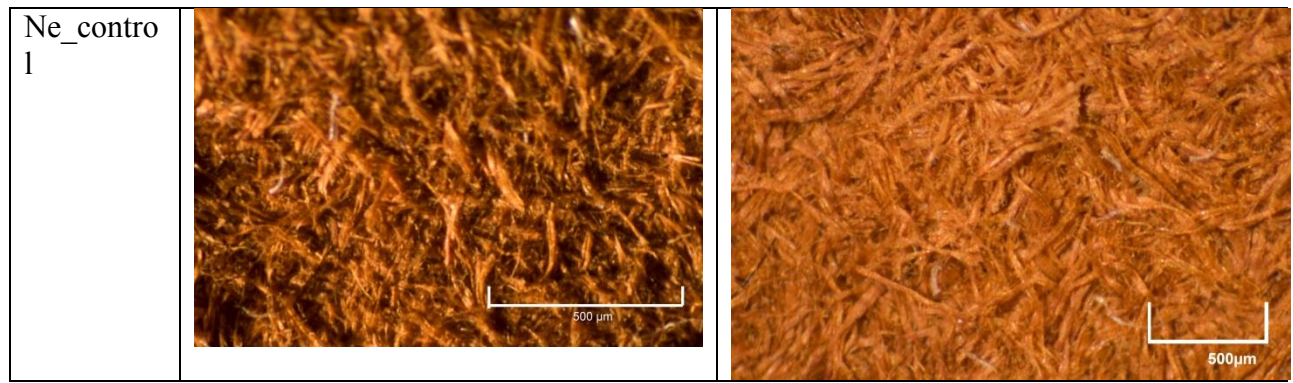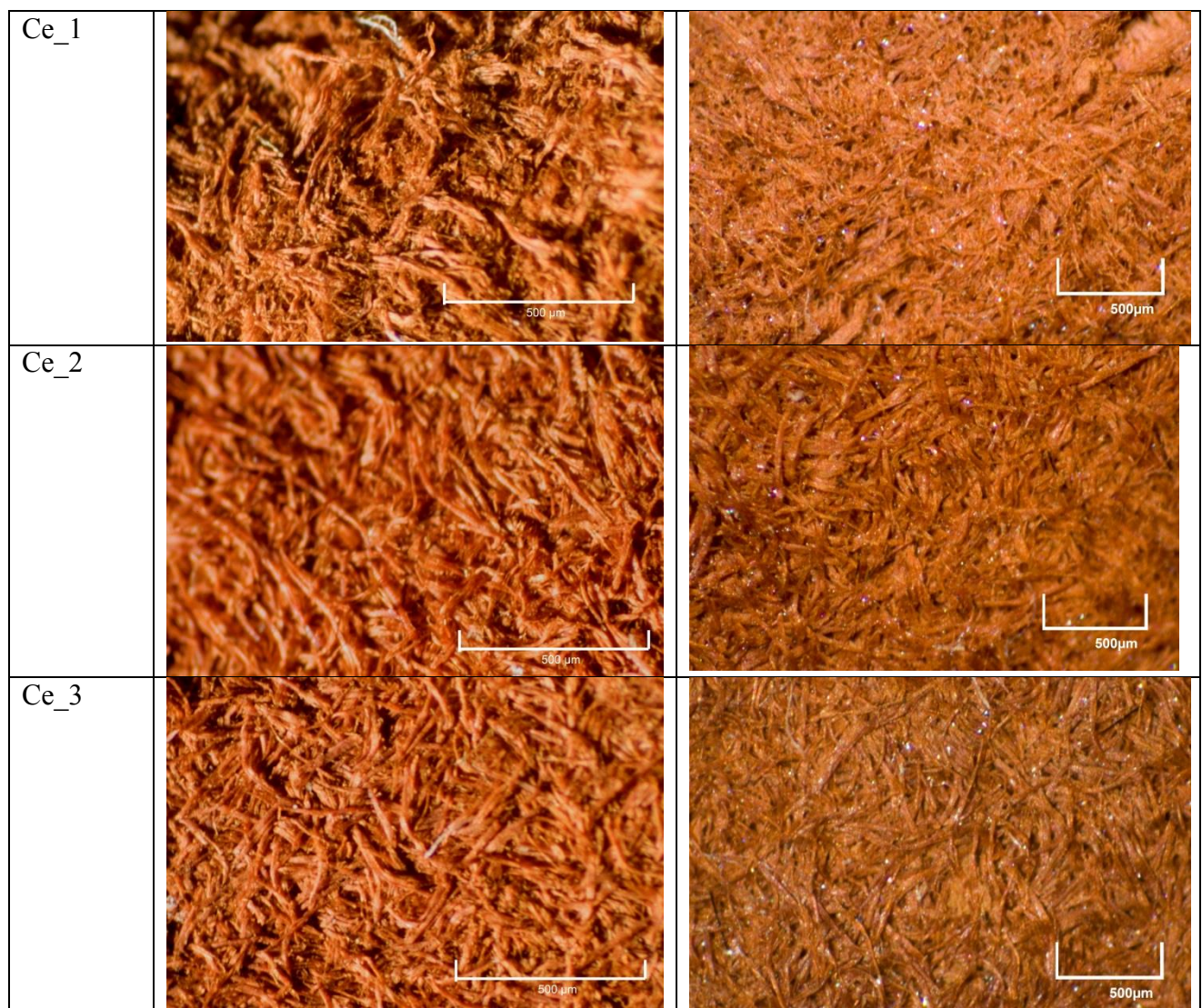
Chitosan in water/ethanol

Ch_1		
Ch_2		
Ch_3		
Ch_4		

Ch_5		
Ch_control		

Neri

Ne_1		

Ne_2		
Ne_3		
Ne_4		
Ne_5		

Ne_control		

Cellugel

Ce_1		
Ce_2		
Ce_3		

Ce_4		
Ce_5		
Ce_contr ol		

Klucel G with SC6000

Kg_1		

Kg_2		
Kg_3		
Kg_4		
Kg_5		
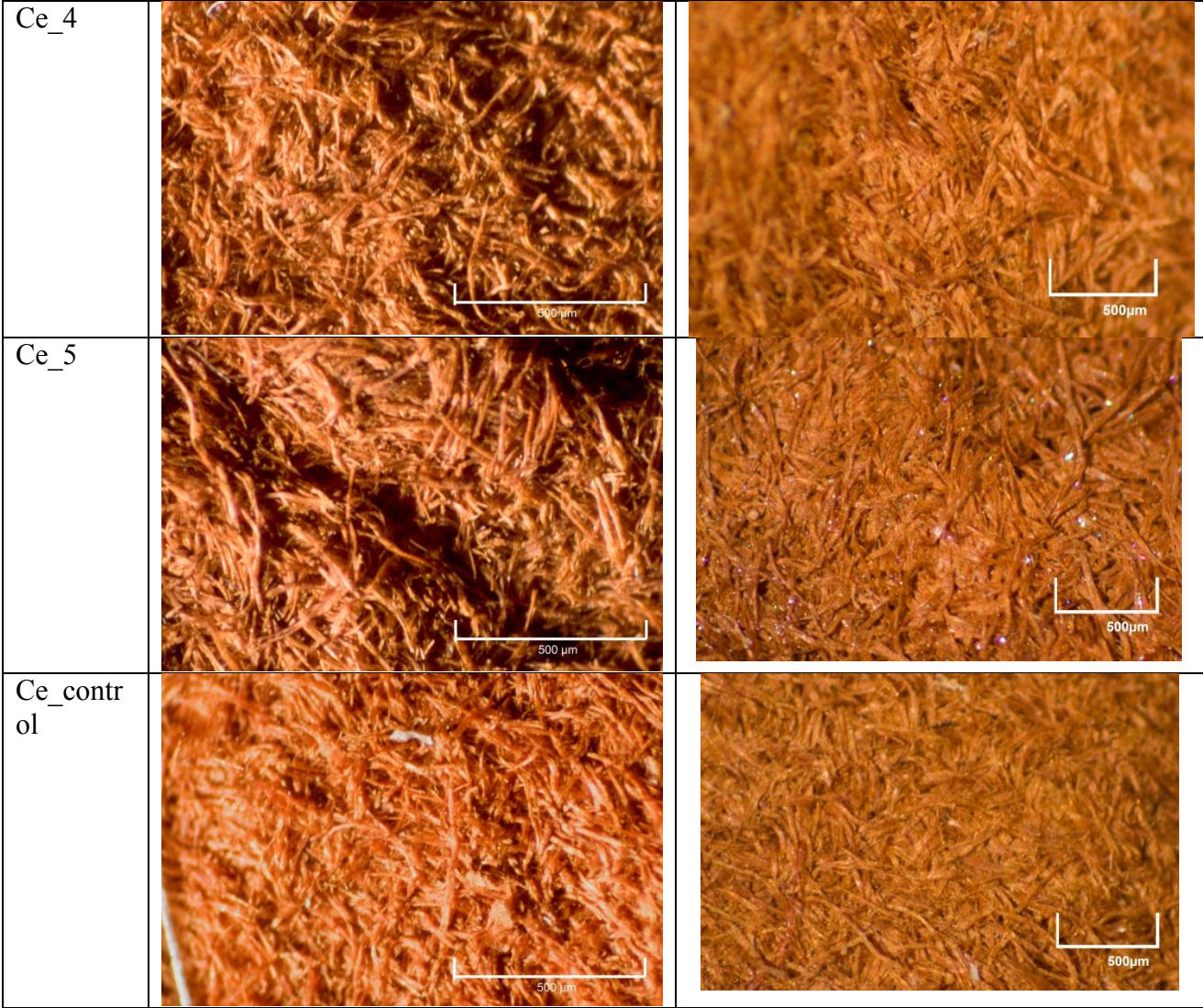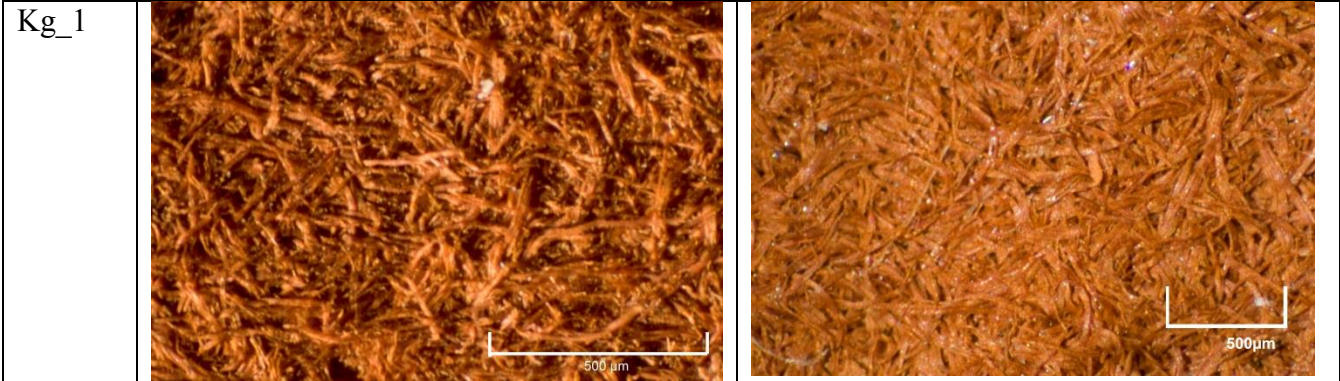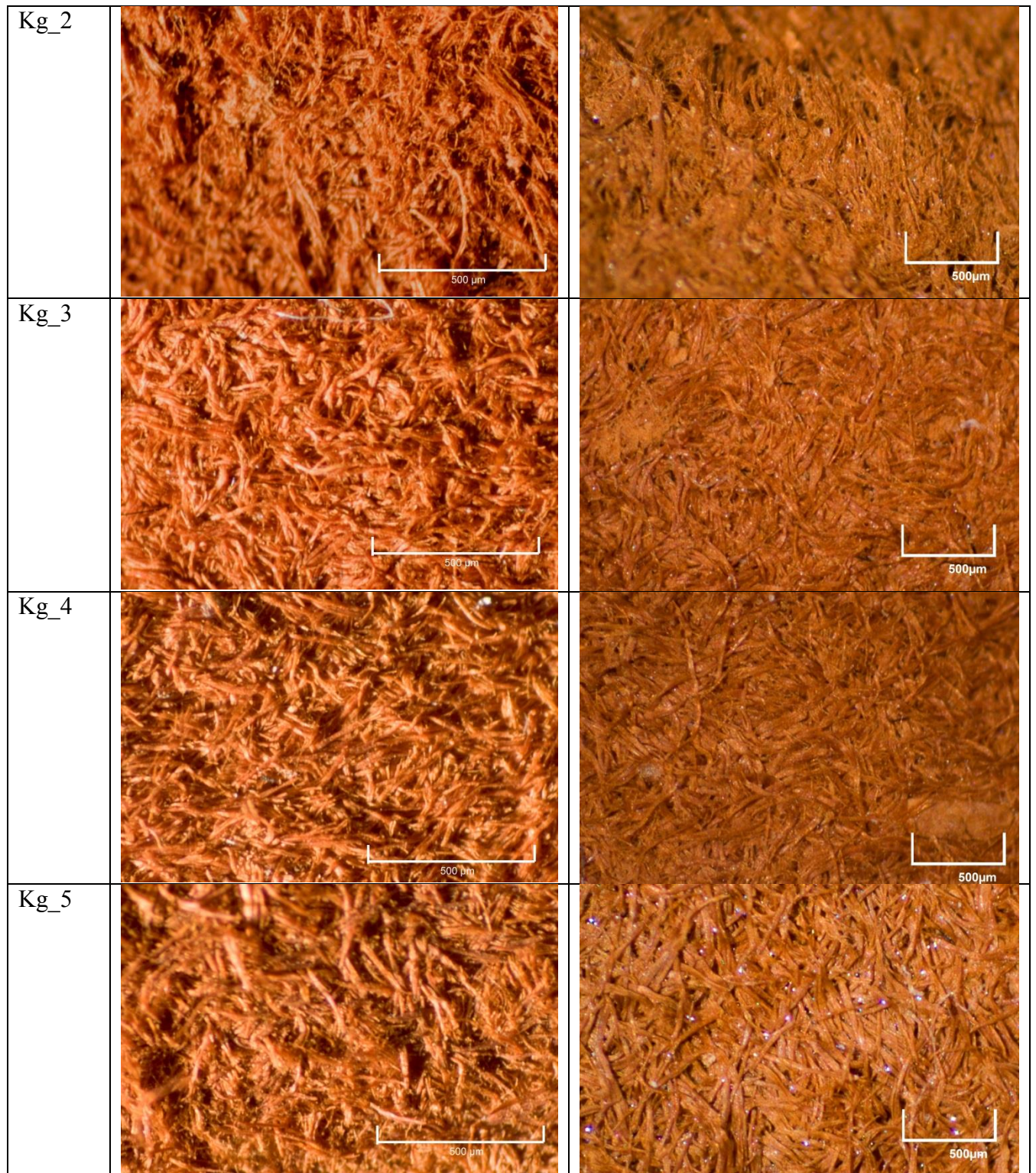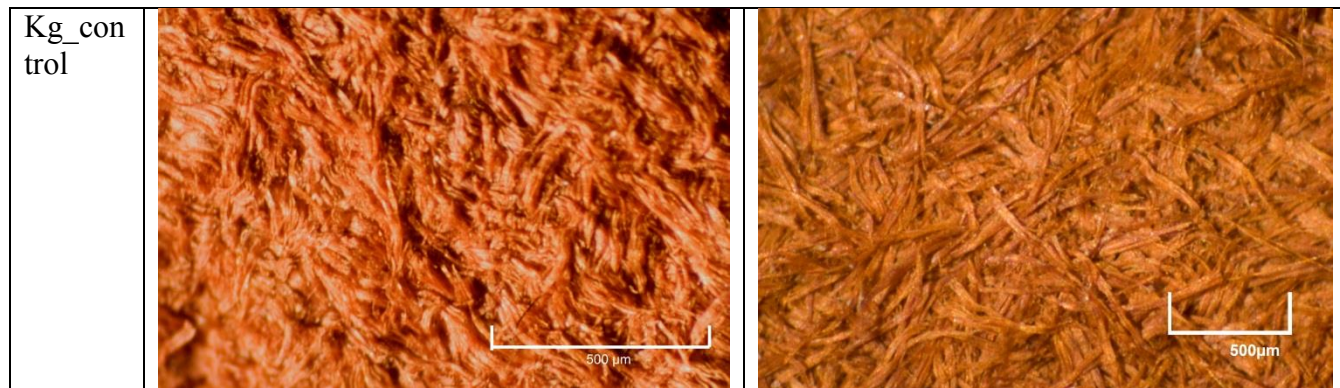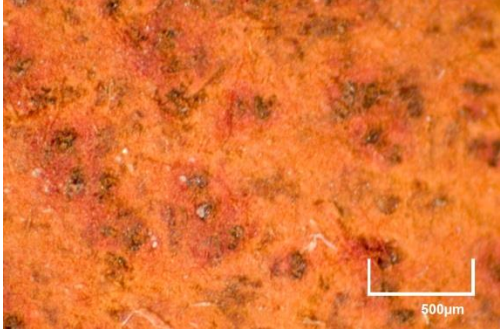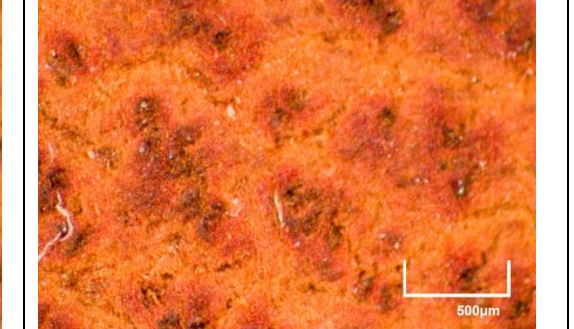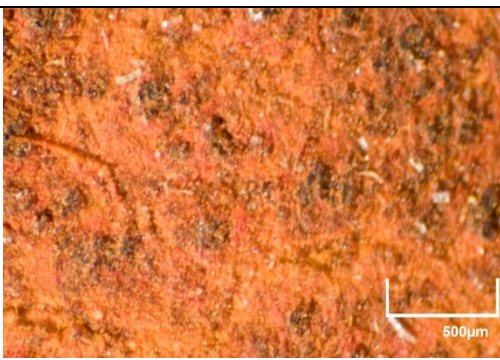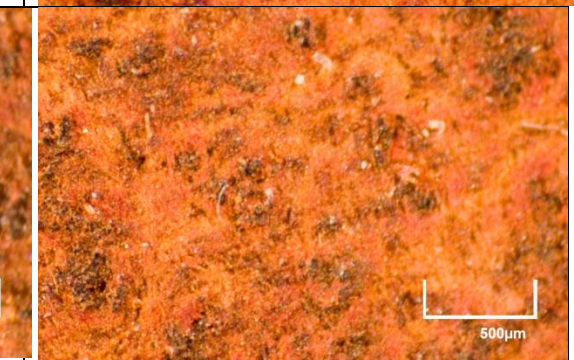
Kg_control		

Chitosan_isopropyl alcohol

Ch_is_1		
Ch_is_2		
Ch_is_3		
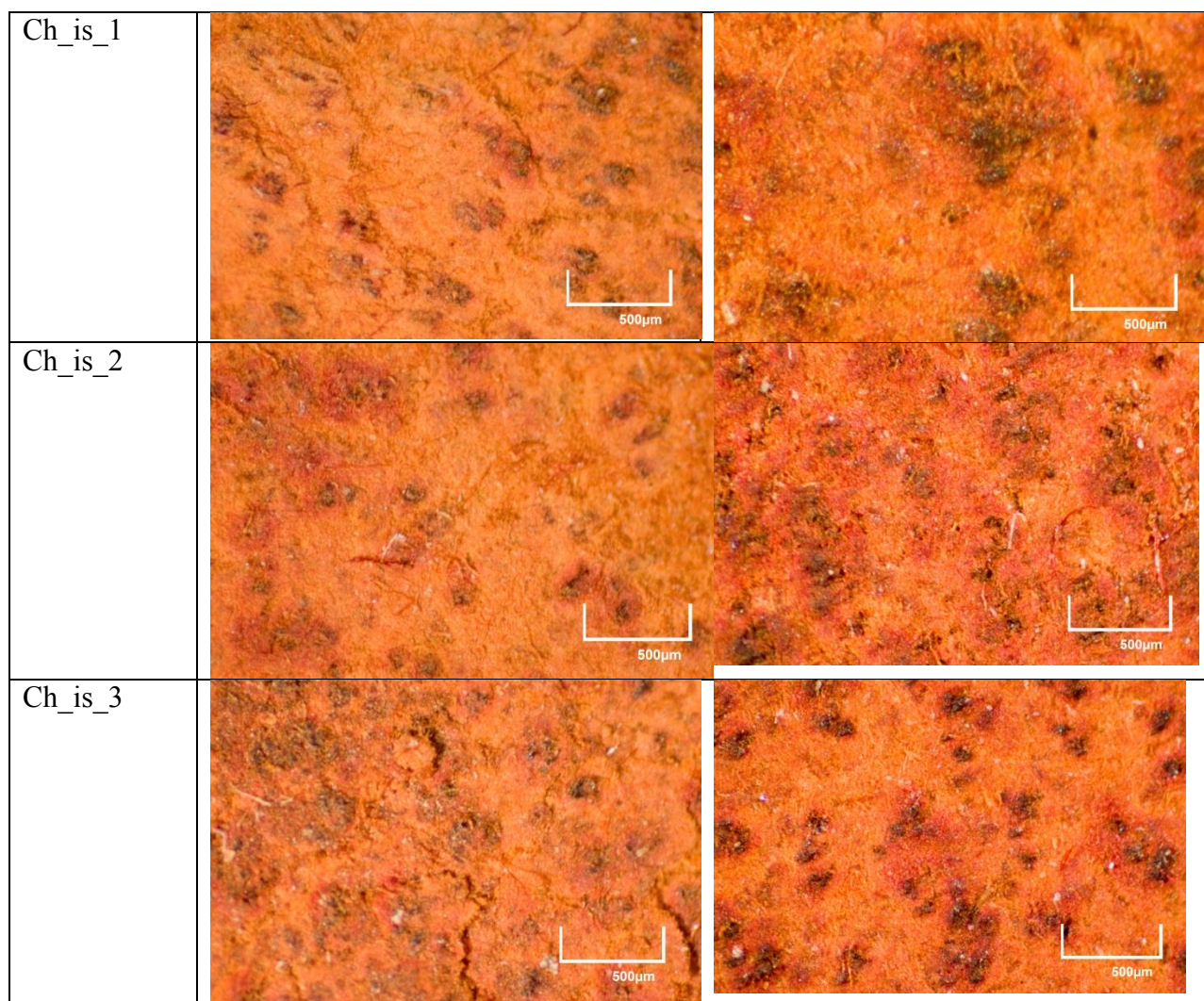
Ch_is_4		
Ch_is_5		
Ch_is_control		

Appendix C: Color Measurements of Leather Before and After Consolidant Treatment

Measured Color L*a*b* Values of the Leather Before and After Application of Consolidant

sample	consolidant	AT L*	initial L*	ΔL*	AT a*	initial a*	Δa*	AT b*	initial b*	Δb*	ΔE '00	ΔE '94	ΔE '76
ce_1	cellugel	34.87	36.67	-1.8	20.66	19.86	0.8	26.04	26.52	-0.48	1.66	1.9	2.03
ce_2	cellugel	34.52	37.3	-2.78	21.8	22.02	-0.22	26.31	28.11	-1.8	2.5	2.91	3.32
ce_3	cellugel	31.82	32.98	-1.16	18.78	18.82	-0.04	21.49	22.76	-1.27	1.19	1.35	1.72
ce_4	cellugel	35.59	37.1	-1.51	22.91	22.88	0.03	26.6	28.49	-1.89	1.65	1.8	2.42
ce_5	cellugel	31.54	32.38	-0.84	19.04	18.93	0.11	21.59	22.94	-1.35	1.09	1.15	1.59
ce_c	control	36.35	36.42	-0.07	22.36	22.01	0.35	28.73	28.39	0.34	0.2	0.2	0.49
AVERAGE Δ				-1.62			0.14			-1.34	1.62	1.82	2.22
ch_1	chitosan/water/ETOH	22.57	34.87	-12.3	7.52	20.02	-12.5	4.64	25.98	-21.34	16.51	18.95	27.62
ch_2	chitosan/water/EtOH	25.56	36.97	-11.41	12.3	19.78	-7.48	11.2	27.86	-16.66	12.82	14.69	21.02
ch_3	chitosan/water/ETOH	25.69	35.09	-9.4	13.25	19.59	-6.34	12.14	27.06	-14.92	10.97	12.63	18.74
ch_4	chitosan/water/ETOH	23.88	32.66	-8.78	11.3	19.66	-8.36	9.12	25.78	-16.66	11.78	13.21	20.6
ch_5	chitosan/water/ETOH	24.05	36.1	-12.05	8.42	21.23	-12.81	5.08	27.33	-22.25	16.58	18.88	28.36
ch_c	control	34.15	34.74	-0.59	19.31	19.79	-0.48	25.55	26.3	-0.75	0.6	0.69	1.07
AVERAGE Δ				-10.80			-9.50			-18.40	13.72	15.67	23.27
kg_1	klucelG/sc6000	33.24	34.65	-1.41	20.25	20.14	0.11	23.34	24.76	-1.42	1.44	1.62	2
kg_2	klucelG/sc6000	33.4	34.37	-0.97	18.9	19.55	-0.65	23.66	25.53	-1.87	1.21	1.32	2.2
kg_3	klucelG/sc6000	36.07	37.61	-1.54	21.81	22.24	-0.43	26.1	28.27	-2.17	1.69	1.85	2.7
kg_4	klucelG/sc6000	26.21	37.66	-11.54	22.56	22.39	0.17	27.14	28.55	-1.41	1.49	11.48	11.54
kg_5	klucelG/sc6000	35.64	37.46	-1.82	21.65	21.71	-0.06	27.16	28.71	-1.55	1.74	1.97	2.39
kg_c	control	31.99	32.29	-0.3	19.33	19.33	0	22.74	24.34	-1.6	0.98	0.92	1.63
AVERAGE Δ				-1.44			-0.172			-1.68	1.51	1.68	2.26
ne_1	neri	22.8	34.37	-11.57	12.22	17.45	-5.23	11.51	35.09	-23.58	15.08	16.87	26.78
ne_2	neri	26.9	34.4	-7.5	15.71	20.01	-4.3	12.49	24.42	-11.93	8.95	10.02	14.73
ne_3	neri	26.68	35.64	-8.96	15.05	21.27	-6.22	11.36	26.25	-14.89	10.92	12.2	18.46
ne_4	neri	26.13	38.13	-12	14.04	21.19	-7.15	11.36	28.83	-17.47	13.46	15.31	22.37
ne_5	neri	28.72	35.61	-6.89	12.32	20.66	-8.34	10.09	27.34	-17.25	11.14	12.01	20.36
ne_c	control	37.04	36.53	-0.51	21.82	21.39	0.43	28.56	27.87	0.69	0.53	0.6	0.96
AVERAGE Δ				-9.38			-6.25			-17.02	11.91	13.28	20.54

Appendix D: Color Measurements of Slides Before and After Accelerated Aging

Measurements of L*a*b* Color Changes of the Consolidants on Slides after Accelerated Aging (Measured on a White Background)

sample	consolidant	Aged w/	AT L*	initial L*	ΔL*	AT a*	initial a*	Δa*	AT b*	initial b*	Δb*	ΔE '2000	ΔE '94	ΔE '76
s_ce_1	cellugel	Light	90.91	90.77	0.14	-1.2	-1.2	0	-0.63	-0.64	0.01	0.09	0.17	0.14
s_ce_2	cellugel	Light	91.05	91.04	0.01	-1.19	-1.18	0.01	-0.63	-0.61	0.02	0.02	0.02	0.02
s_ce_3	cellugel	Light	91.01	91.19	0.18	-1.19	-1.18	0.01	-0.58	-0.64	0.06	0.13	0.19	0.19
s_ce_4	cellugel	Heat	91.03	91	0.03	-1.24	-1.19	0.05	-0.65	-0.66	0.01	0.07	0.06	0.06
s_ce_5	cellugel	Heat	90.92	90.99	0.07	-1.21	-1.17	0.04	-0.7	-0.63	0.07	0.1	0.1	0.11
s_ce_6	cellugel	Heat	91.04	90.89	0.15	-1.2	-1.22	0.02	-0.67	-0.77	0.1	0.14	0.18	0.18
s_ce_c	cellugel	Control	91.17	90.99	0.18	-1.21	-1.17	0.04	-0.6	-0.58	0.02	0.13	0.18	0.19
Average Light					0.11			0.01			0.03	0.08	0.13	0.12
Average Heat					0.08			0.04			0.06	0.10	0.11	0.12
Overall Average					0.10			0.02			0.05	0.09	0.12	0.12
s_ch_1	chitosan	Light	90.71	90.59	0.12	-1.22	-1.26	0.04	-0.52	-0.69	0.17	0.19	0.21	0.21
s_ch_2	chitosan	Light	90.81	89.66	1.15	-1.24	-1.17	0.07	-0.58	-0.55	0.03	0.73	1.15	1.15
s_ch_3	chitosan	Light	90.76	90.6	0.16	-1.22	-1.25	0.03	-0.61	-0.69	0.08	0.13	0.18	0.18
s_ch_4	chitosan	Heat	90.74	90.98	0.24	-1.48	-1.22	0.26	0.16	-0.63	0.79	0.86	0.85	0.87
s_ch_5	chitosan	Heat	89.88	90.28	0.4	-1.41	-1.14	0.27	0	-0.51	0.51	0.67	0.69	0.7
s_ch_6	chitosan	Heat	90.46	90.75	0.29	-2.03	-1.25	0.78	1.9	-0.6	2.5	2.58	2.52	2.63
s_ch_c	chitosan	Control	91	90.81	0.19	-1.22	-1.26	0.04	-0.52	-0.68	0.26	0.2	0.25	0.25
Average Light					0.48			0.05			0.09	0.35	0.51	0.51
Average Heat					0.31			0.44			1.33	1.37	1.35	1.4
Overall Average					0.39			0.24			0.7	0.86	0.93	0.96
s_kg_1	klucel G/sc6000	Light	90.18	89.77	0.41	-1.15	-1.16	0.01	-0.64	-0.37	0.27	0.37	0.49	0.49
s_kg_2	klucel G/sc6000	Light	90.24	89.86	0.38	-1.17	-1.2	0.03	-0.53	-0.66	0.13	0.27	0.4	0.4

s_kg_3	klucel G/sc6000	Light	90.25	90.44	0.19	-1.14	-1.17	0.03	-0.58	-0.6	0.02	0.13	0.19	0.19
s_kg_4	klucel G/sc6000	Heat	90.47	90.16	0.31	-1.19	-1.12	0.07	-0.62	-0.49	0.13	0.25	0.34	0.21
s_kg_5	klucel G/sc6000	Heat	90.17	89.98	0.19	-1.23	-1.15	0.08	-0.36	-0.42	0.06	0.17	0.21	0.3
s_kg_6	klucel G/sc6000	Heat	90.39	90.25	0.14	-1.21	-1.08	0.13	-0.42	-0.35	0.07	0.21	0.2	0.2
s_kg_c	klucel G/sc6000	Control	90.08	89.94	0.14	-1.2	-1.18	0.05	-0.02	-0.54	0.18	0.2	0.22	0.22
Average Light					0.34			0.02			0.14	0.26	0.36	0.36
Average Heat					0.21			0.09			0.09	0.21	0.25	0.25
Overall Average					0.27			0.06			0.11	0.23	0.30	0.31
s_ne_1	neri	Light	90.97	91.85	0.88	-1.21	-1.24	0.03	-0.6	-0.87	0.27	0.6	0.92	0.92
s_ne_2	neri	Light	90.87	90.67	0.2	-1.2	-1.21	0.01	-0.65	-0.59	0.06	0.14	0.21	0.21
s_ne_3	neri	Light	90.70	90.27	0.43	-1.2	-1.27	0.07	-0.59	-0.58	0.01	0.29	0.44	0.44
s_ne_4	neri	Heat	91.14	90.55	0.59	-1.19	-1.21	0.02	-0.67	-0.7	0.03	0.37	0.34	0.59
s_ne_5	neri	Heat	90.94	90.8	0.14	-1.21	-1.2	0.01	-0.64	-0.72	0.08	0.12	0.16	0.16
s_ne_6	neri	Heat	91	90.53	0.47	-1.2	-1.22	0.02	-0.62	-0.8	0.18	0.34	0.5	0.5
s_ne_c	neri	Control	91.11	90.46	0.65	-1.17	-1.22	0.05	-0.63	-0.76	0.13	0.43	0.66	0.66
Average Light					0.5			0.04			0.11	0.34	0.52	0.52
Average Heat					0.4			0.02			0.10	0.28	0.33	0.42
Overall Average					0.45			0.03			0.11	0.31	0.43	0.47
Control Variance					±0.25			±0.18			±0.15	±0.24	±0.33	±0.33

Appendix E: Consolidant Chemical Information

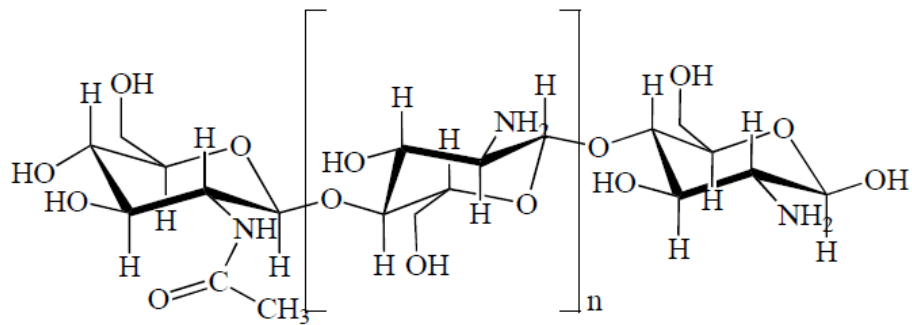Chitosan
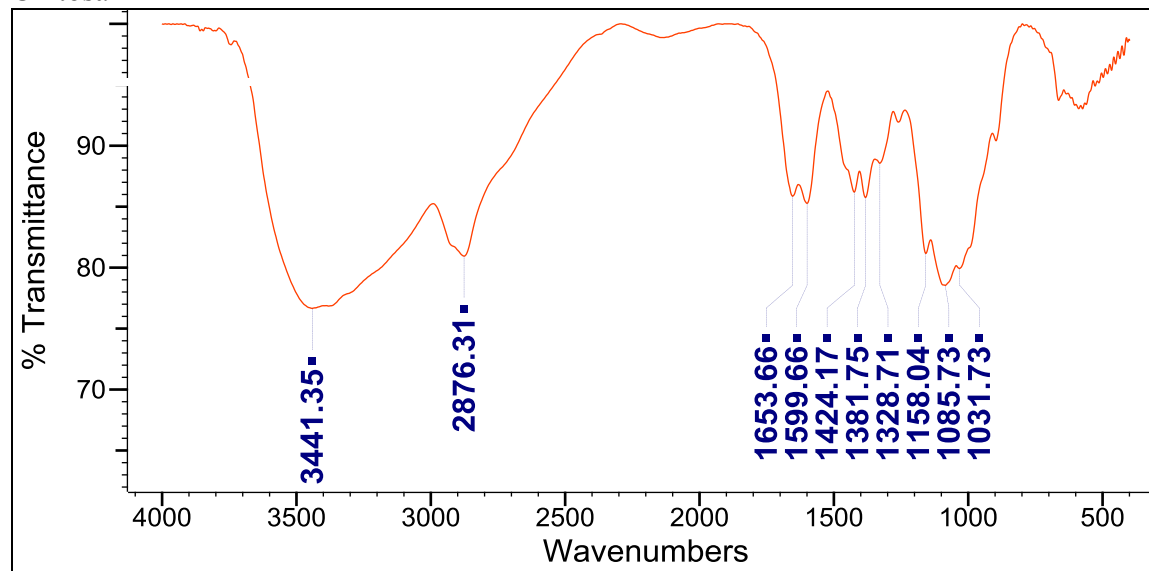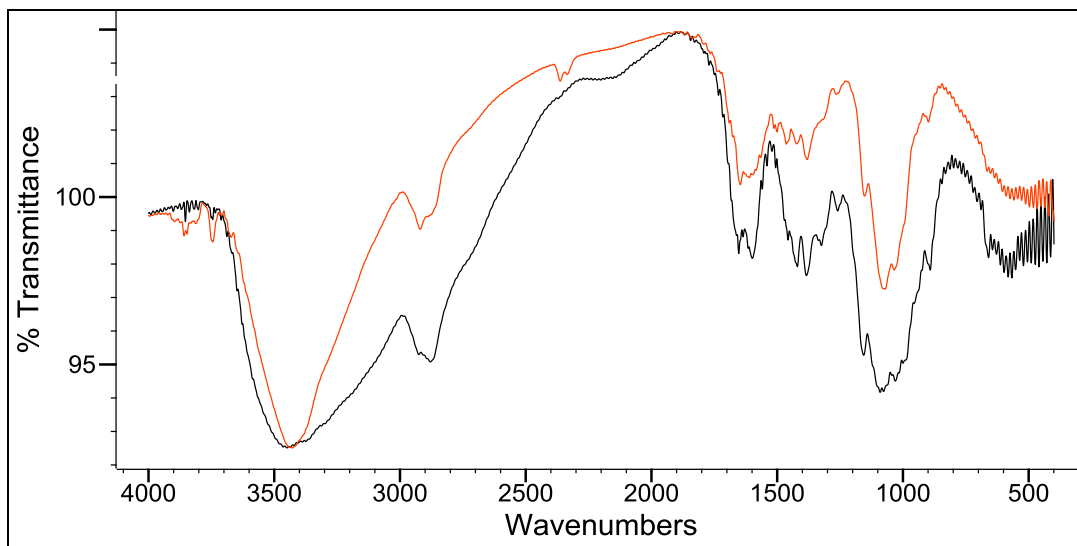

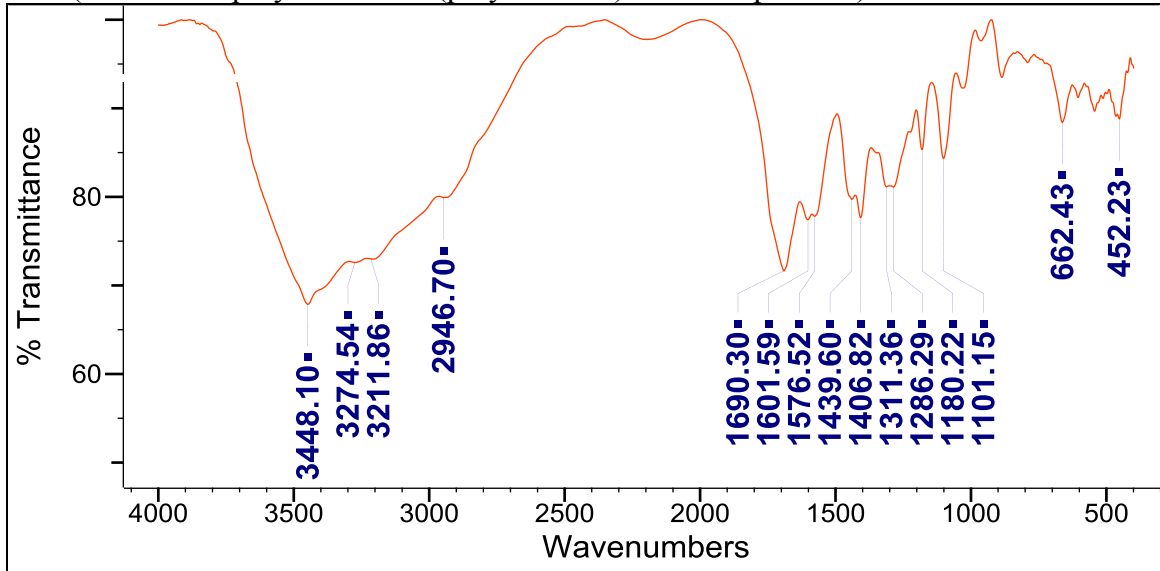| Band (cm-1)	Group	Characteristic	Strength
The Identification of the functional groups in FTIR of Chitosan (polysaccharides 75% 1-4,2-amino-2-deoxy-β-D-glucan and 25% chitin)			
3450	OH	Stretching	Broad, strong
3360	NH	s=Stretching	Broad, strong
2920, 2880, 1430, 1320	CH$_2$	Symmetric or asymmetric stretching vibration attributed to pyranose ring	Weak
1730	C=O	Stretching	
1655	C=O in amide I band, acetyl group	Amide I band	Strong, broad
1560-1500	NH	Bending	Moderate, weak
1380	CH$_3$	In amide group	
1150-1040	C-O-C	In glycosidic linkage	

(From Polymery 47 2002. Mucha and Pawlak.)

Chemical Structure of chitosan showing the deacytlated groups in the center and right pyranose rings that would represent 75% of the structure and the acetyl group on the left pyranose ring that would represent approximately 25%.


Chitosan powder (dark blue) with chitosan in water/ethanol solution dried film (red).

Neri (82% acidic polysaccharides(polyuronides) and 17% proteins)

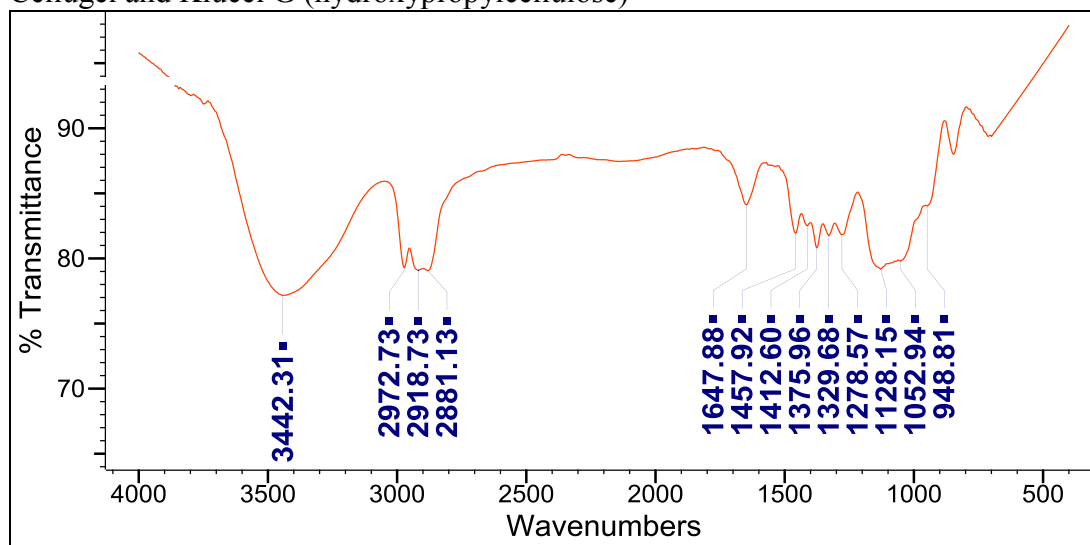| The Identification of the functional groups in FTIR of Neri (acidic polysaccharides and proteins)			
Band (cm^{-1})	Group	Characteristic	Strength
3600-3200	OH	Stretching	Broad, strong
3400-3200	NH	Stretching	Broad, strong
3000-2800	CH	Stretching	Weak
1700-1600	C=O	Stretching	
1650	OH	Bending	weak
1565-1500	C-N-H	Bending	
1480-1300	CH	Bending	Weak
1150	OH	Bending	Weak
1300-900	C-O-C	Stretching	Broad, moderate
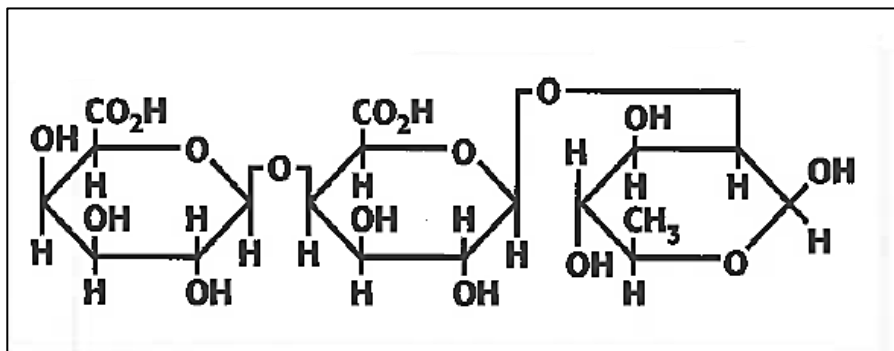
Chemical structure of the main component of Neri, rhamnogalacturonan-di-galacturonic acid (from Lorenz et al 2010,10).
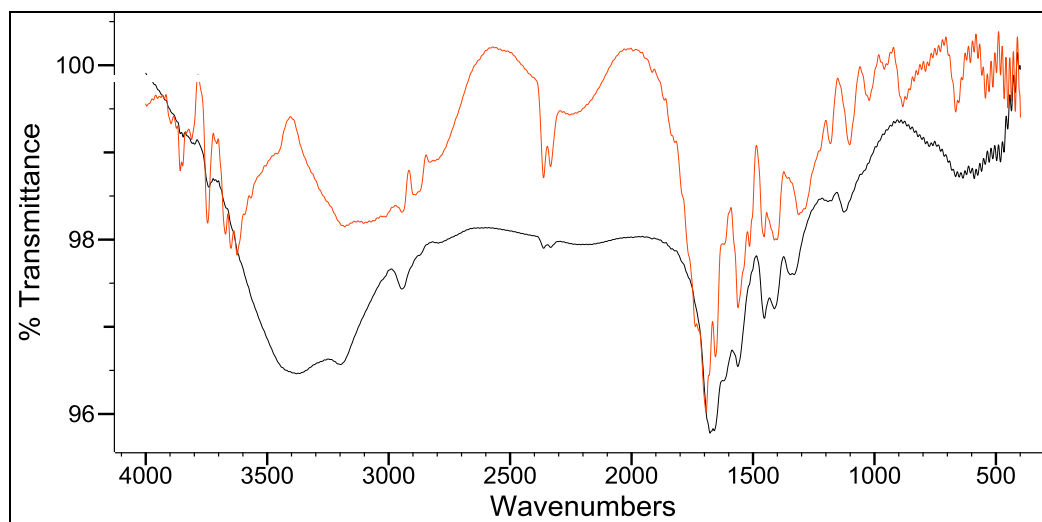
Spectra of Neri as a powder (red) and dried as a film from the neri in water/ethanol (dark blue).

Cellugel and Klucel G (hydroxypropylcellulose)

The Identification of the functional groups in FTIR of Cellugel (hydroxypropylcellulose)			
Band (cm^{-1})	Group	Characteristic	Strength
3442	-OH	stretching	Broad, moderate
2970, 2920, 2880	CH$_2$	Asymmetric stretching	Sharp, Moderate
1640	C=0		moderate
1457, 1413, 1374, 1327, 1269	CH$_3$	bending	Sharp, Weak/moderate
1126, 1088	C-O	stretching	Slightly broad, Strong
988, 950			Weak/moderate

From FTIR graph Evaluation of Cellulose Ethers for Conservation, Feller 1990 and identification myself from Derrick 1999, Infrared Spectroscopy for Conservation.
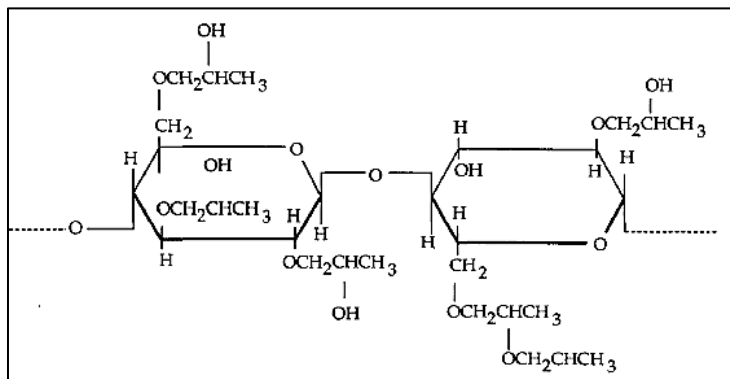
Chemical Structure of Hydroxypropylcellulose (structure of Cellugel and Klucel G) (from Feller 1990, 16).

SC6000-(acrylic and natural wax blend in isopropanol)
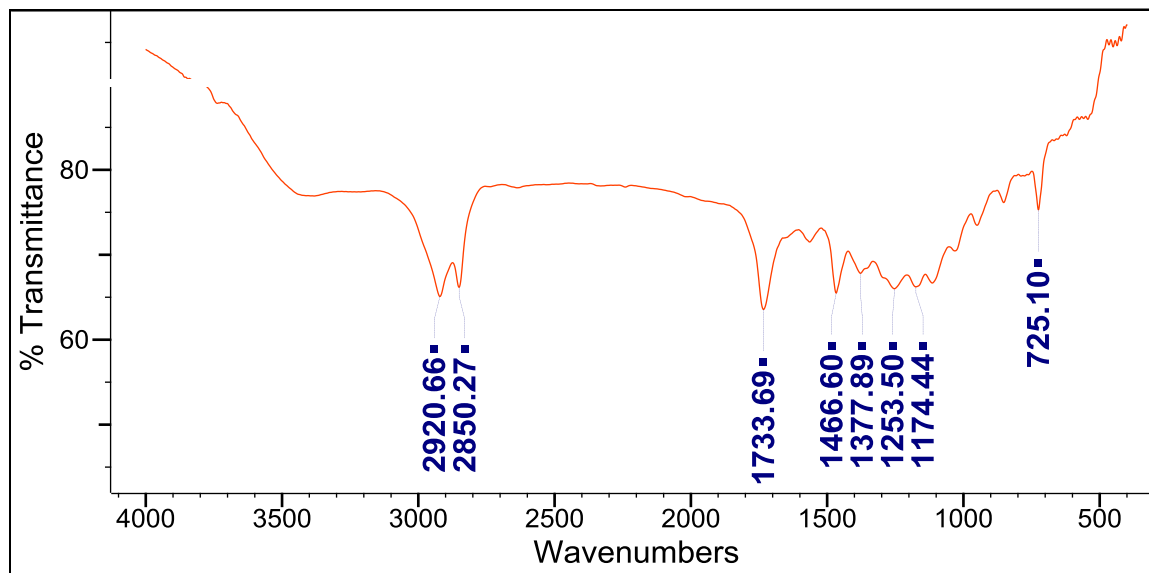
| The Identification of the functional groups in FTIR of SC600 (natural and acrylic wax mixture)			
Band (cm^{-1})	**Group**	**Characteristic**	**Strength**
2926, 2850	CH$_2$	Stretching bands	Strong
1740	C=O	Stretching	Present in natural waxes(fatty esters) and strong for

			acrylics
1466	CH$_2$	bending	Weak
1175	C-O	Bending	Weak (in natural waxes, if contains ester of fatty acid)
730-720 (doublet)	CH$_2$	Rocking	Weak (indicates at least four methylene groups in the chain)

Appendix F: FTIR Spectra of Consolidants Before and After Accelerated Aging

FTIR Spectra for each consolidant. For each spectrum, the blue represents the unaged sample, the red represents the heat aged sample, and the yellow represents the light aged sample.

Chitosan Spectra
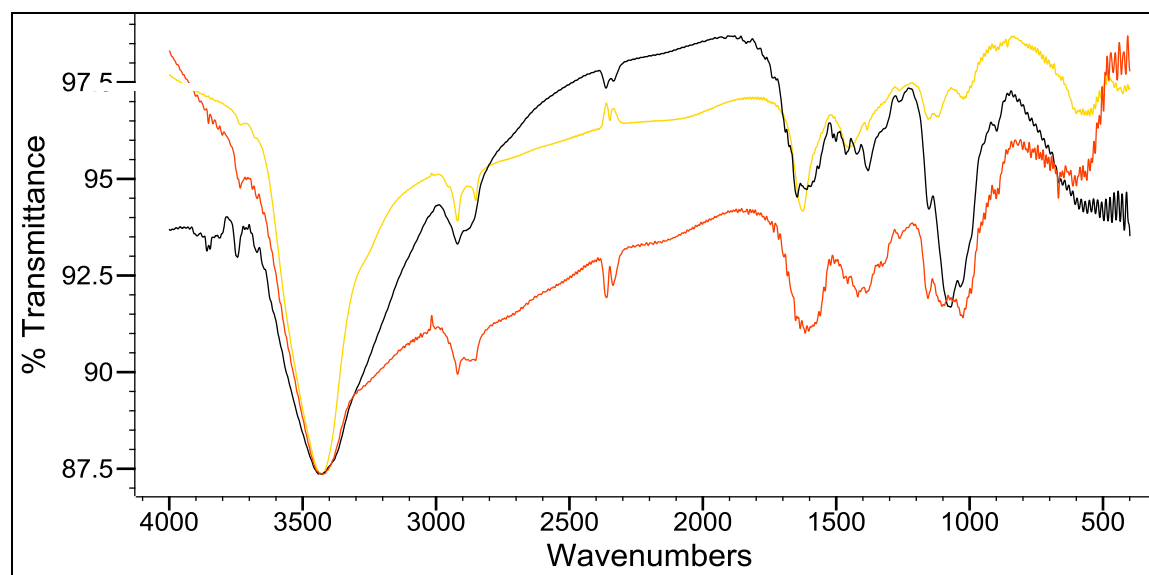
Band (cm^{-1})	Group	Changes in the FTIR spectra of chitosan in water/ethanol
3427	OH or amide	Band increased strength in light aged sample and became narrower. In heat aged sample, band became weaker and broader.
2886	CH$_3$	Shoulder band became somewhat of a split peak (2876 +2852) in the heat aged sample and a sharp single peak in the light aged sample (also shifted to 2850)
Group 1650-1520	C=O(amide) and NH$_2$	Band altered from a sharp peak followed by several shoulder to a single strong peak at 1620 in the light aged sample. It also shows minor changes in the heat aged sample.

| Group 1520-1230	NH$_2$, CH$_3$	Group of peaks do not appear to correspond to the stair step configuration in unaged sample. Light aged sample has one broad peak and a shoulder. Heat aged samples should broad peak with indistinct shoulders.
Group 1150-950	C-O	Dramatic alteration. Group of peaks are greatly reduced in size in light aged samples and does not resemble peaks in either heat or light aged samples.
1073	C-O	Band is no longer present in light and heat aged sample

Neri Spectra
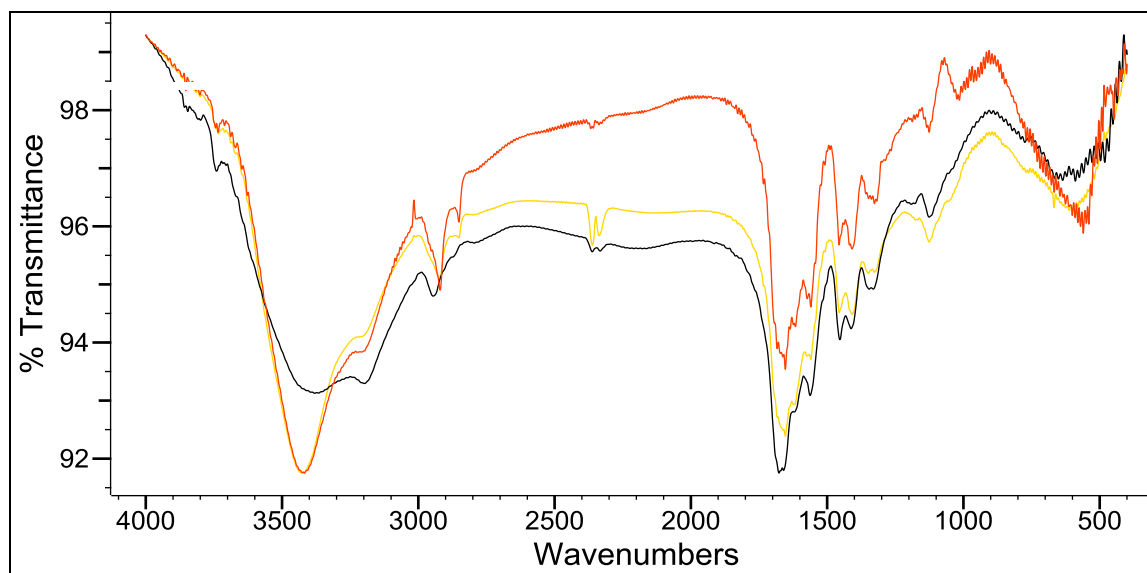
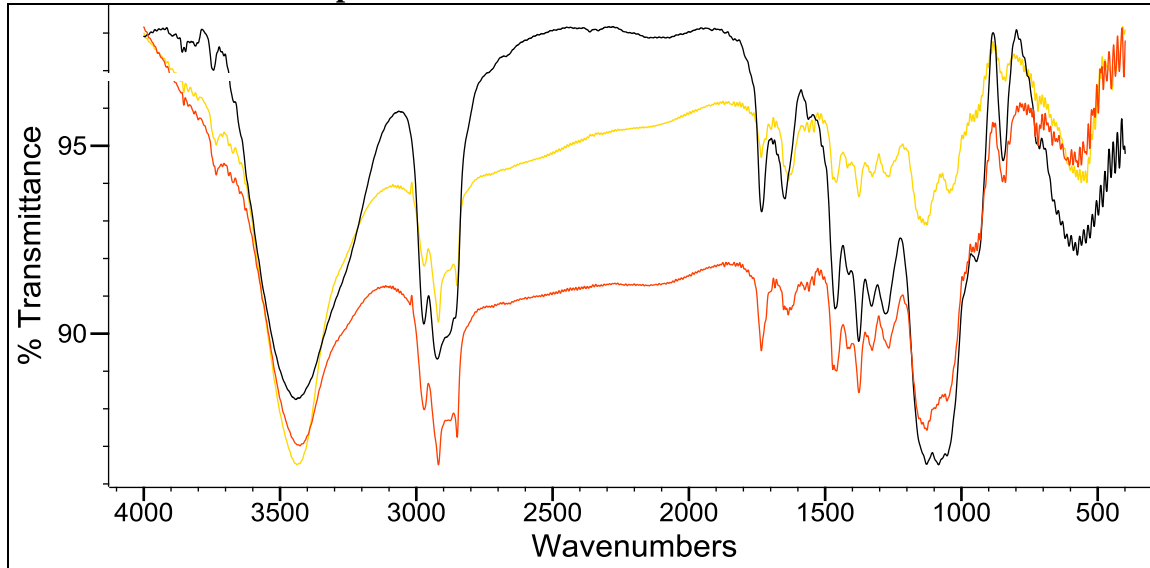| Band (cm^{-1})	Group	Changes in the FTIR spectra of neri in water/ethanol
3364	OH or amine	Band altered from a moderate strength broad peak to a stronger narrower peak at 3420 in both light and heat aged samples.
2943	CH$_3$	Weak band became a sharper stronger band in the aged samples, especially in heat. They also shifted (2912 in heat, 2919 in light.
2870	CH$_3$	Band was a shoulder in unaged sample and beak a weak sharp peak shifted to 2852 for both heat and light aged samples.
Group 1680-1560	C=O? NH-?	Group of peaks are stronger overall in heat and light aged samples.
1680	C=O?	Band became weak in light and heat aged samples.

Cellugel Spectra
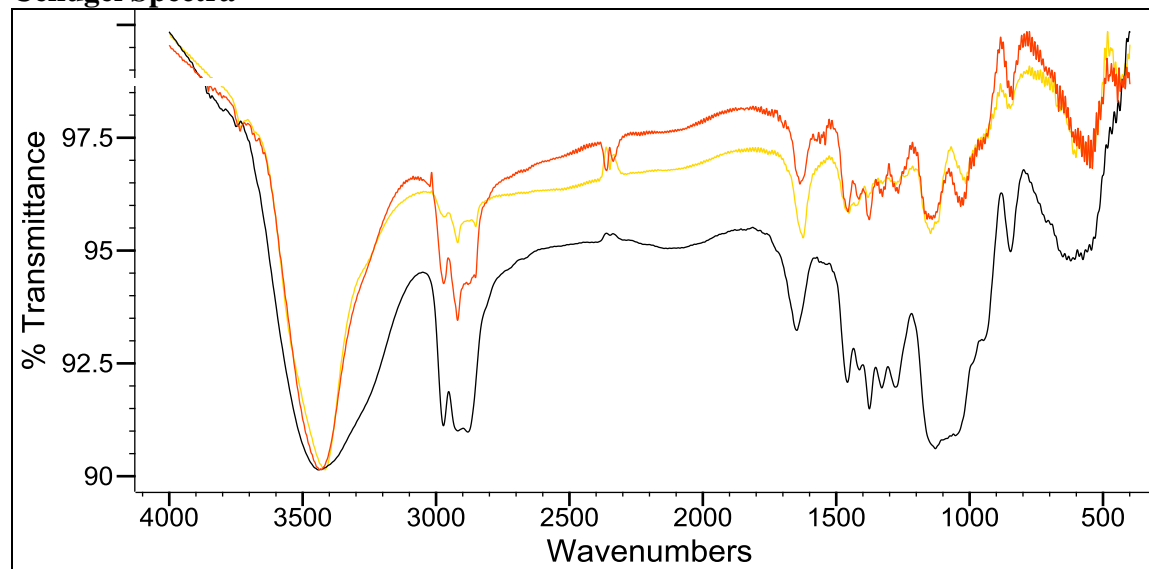
Band (cm⁻¹)	Group	Documented Change for Cellugel Samples
3434	OH	Band became stronger and sharper in heat and light aged samples
Group 2975-2800	CH₂, CH₃	Group of peaks became dramatically reduced in strength.
2970	CH3	Band became slightly weaker in the heat aged sample and dramatically weaker in light aged sample.
2933	CH2	Band altered from a moderate strength shoulder to a moderate sharp peak in both the heat and light aged samples.
2882	CH3	Shoulder band appears to have split into two weak shoulders in the heat aged sample. In the light aged sample, it became a weak sharp peak that is shifted to a lower wavenumber.
1649	C=O	Band shifted in light (1616) and heat(1636) aged samples to a lower wavenumber, also decreased in intensity for heat aged sample.
1462	CH3	Band was reduced in strength for both heat and light aged samples
Group 1500-1250	CH₃	General reduction of peak strengths in light and heat aged samples
Group 1150-950	C-O	General reduction of peak strengths in light and heat aged samples
1079	C-O	Band is no longer present in light and heat aged sample.

Klucel G with SC6000 Spectra

Band (cm^{-1})	Group	changes in FTIR spectra of Klucel G with SC600 Samples
3434	OH	band decreased in size in heat and light aged samples and shifted in both (heat, 3420 and light, 3414) to a slightly lower wavelength
Group 2975-2800	CH$_2$, CH$_3$	Dramatic reduction of band intensity
2972	CH$_3$	band reduced intensity in light
2922	CH$_2$	Band altered from a moderate strength shoulder to a more intense sharp band in heat and light aged samples
2856	CH$_3$	In unaged material, band was a moderate strength shoulder symmetrical to 2922 shoulder. But in heat and light aged samples, it became a sharp peak.
1740	C=O(wax)	In heat and light aged, peak reduced in intensity, especially in light, and in both cases gained a small shoulder at 1700.
1650	C=O	Band altered from sharp and moderate to broad and weak in both heat and light.
Group 1500-1250	CH$_3$	General reduction of intensity of all peaks in this group.
Group 1150-950	C-O	Significant decrease in light aged sample
1079	C-O	Band is no longer present in light and heat aged sample

Appendix G: Treatment Report of Leather Bag from the Autry Museum

Condition Report

Object: Leather bag with beaded decoration
Cultural attribution/provenance: Apache (?), late 19th century

Dimensions: 24.0 cm x 20.4 cm x 6.4cm (9.5 in x 8.0 in x 2.5 in)

Identification (or accession, registration, or catalog) number: 5082.G.18

Medium: vegetable tanned leather (unknown animal); blue, red, and white glass seed beads; sinew

Current/past owners: Autry National Center, Donated from the Collection of Vernette Ripley Tatum to the Southwest Museum of the American Indian

Date of examination: 1/24/13

Conservator: Caitlin Mahony

Materials and techniques:

Structure

      The object is a beaded leather bag that has been dated to the late 19th century and tentatively attributed to the Apache (Autry Condition Report 2012). The bag is constructed of three pieces of leather—two somewhat rectangular pieces that function as the faces and one long thin strip that runs along the sides and bottom edge, between the two faces, constituting the width of the bag (figures 1 & 2).

      The intact areas of the leather reveal a warm brown color that would have been the original coloring of the bag. It appears that the flesh side of the hid has been used exclusively for the exterior surfaces of the bag. On the interior, the grain shows a dense, non-uniform patter of small follicles in random grouping (figure 13). These characteristics are very similar to those of deerskin. Comparable bags attributed to the various Apache groups at the National Museum of the American Indian are also listed as deerskin (NMAI Collections Search, 2013). The severe deterioration occurring on the leather known as "red rot" signifies that it was vegetable tanned, as this type of deterioration is exclusive to this tanning method. In an attempt to confirm the vegetable tannin type, a sample of collagen fibers was collected from associated loss fragments and was analyzed using an iron sulfate mircochemical tests (Odegaard et al. 2000, 150-152).

When compared against a known positive and known negative, the results were inclusive as none resulted in the identifiable blue green color that is a positive (See Testing and Analysis). This could possibly be due to the highly deteriorated state of both the known positive and the collagen sample of this leather.

The leather pieces are constructed into a bag through the use of a single piece of untwisted sinew that is used in a whip stitch along an interior seam (figure 14). The bag closes through the use of the leather thong that is woven through the leather near the opening. This thong is about 1 cm wide, appears to be also vegetable tanned, and is knotted at one end. It may have originally incorporated fringe as there is a polyethylene bag with fringe fragments associated with this object.

Decoration

There is beadwork throughout the surfaces of the bag and on the leather thong. The beading on the faces and strip was most likely completed prior to the construction of the bag due to limited access that the artisan would have once it was constructed. The beadwork is made entirely using the lane stitch (lazy stitch) technique. Throughout all of the designs, blue is used as the primary color and red and white are used to accent or emphasize areas. In the center of both faces, there is a circle with diamonds extending from the circle at the four cardinal directions. Within the circle, four diamonds meet in the center and point towards the four cardinal directions (figures 1 & 2). Along the leather strip that is the sides, the beadwork is again done mostly with blue beads though white and red beads are used in five places to create a geometric (>l<) design (figures 3 & 4). The leather thong has a small amount of beadwork after the knot (figure 3). Finally, there is a beaded trim around the opening of the bag made entirely of white beads (figure 6). It consists of little hoops of five beads that are individually stitched to the leather in a continuous fashion.

Condition:

Structure

Overall, the bag is in poor condition due to the significant instability of the leather substrate and the structural tear between along the seam between face 2 and the beaded strip.

The leather is unmistakably suffering from an acidic degradation commonly known as red rot, that is caused by the interaction of sulfates with the leather that are introduced either from the residues of sulfuric acid from the tanning process, sulfur dioxide from air pollution, or both. This deterioration has resulted in a discoloration of the leather and a significant reduction of the leather's cohesion and strength, which has led to continual powdering, tears, and some loss. Microchemical tests to characterize the acidity of the leather and the sulfur content were conducted (see Testing and Analysis). The pH was found to be 3.9, which is not considered particularly acidic for leather and therefore does not accurately represent the extent of deterioration on this object. The sulfate content was found to be slightly elevated at 800mg/L (see Testing and Analysis).

Due to loss of strength in the leather, there are several tears and losses of leather, which are contributing further instability to the structure. The most significant tear located on face 2 is structural as it extends across the bottom edge of the bag along the seam between one of the faces and the beaded strip (figures 5, 6, 7,). It is possible that the weight of the beaded strip was exerting stress on the leather in this area causing it to tear or that the wear of this area from use has made it especially susceptible to red rot. Overall, the leather along the tear is thin and weak. As a result, there are several perpendicular tears along this long tear and areas of loss and an adjacent split in the leather near the tear beginning (figure 8). On face 1, there is a 6 cm split in the leather along the side that runs parallel to the seam (figure 19). On the beaded strip, there is a split in the leather between rows of beading and one along the edge (figure 17). These splits may be from the stress of the weight of the beads or from the stress of the sinew thread stitching through the leather.

Furthermore, there are tears at the opening of the bag where there is a beaded trim (figure 12). The beaded has become unstable in some areas due to these tears and associated loss (figure 6).

Finally, there has been loss to one of the ends of the leather thong after the knot and possibly fringe. It is believed that the lost fragments are in a fragment bag associated with the object. The deterioration of the thong has resulted in delamination of the surface in sections rather than powder (figure 18)

Surface

The surfaces of the leather are discolored from the red rot and appear mottled due to various stages of powdering (figures 1 & 2). Small fragments of leather have accumulated randomly on the face surfaces. There is a light-colored streak of accreted material on face 2 near the knot of the leather thong that is most likely a stain from use.

Overall, the beads appear stable and do not show any signs of crizzling or deterioration associated with glass bead disease. The beadwork appears securely fastened to the substrate; however, there are only minor losses and instabilities. The areas where bead losses have occurred are along the opening of the bag where the leather is torn or lost (figures 6 & 12). A significant portion of the beads' surfaces appear to have a "sticky" surface (figures 9, 10, 11). The sticky surface has caused these beads to accumulate leather fibers, giving them a discolored appearance. Under microscopic analysis, the sticky surface appears to be associated with a yellow brown coating. This coating may be hygroscopic, and with fluctuations of relative humidity overtime, water may have accumulated on the surface, creating a sticky surface. Solubility and microchemical tests were conducted to help characterize the material (see Testing and Analysis). The coating material is soluble in water but not proteinaceous. The coating does not appear to be affecting the condition of the beads. When the material is removed from an area with water and a cotton swab, the beads looks intact.

The location of the coated beads does not appear to be random but rather to occur in groupings. They sometimes appear to be by row, because the next row of beads will not be affected. Other times it is the beads grouped near the edge of the row (figure 11). The pattern of this coating does not appear to be random enough to have occurred during the bag's use. One

possible explanation could be linked to the manufacture of the beadwork. The artisan could have done something to the beads during the beading process or handling of the materials that would half left some beads unaffected while others became deposited with this unknown material. Another theory could be that there is some condition issue with sinew thread in places that is somehow affecting beads in these areas.

Condition summary:

The object is in poor condition overall due to the severe deterioration of the leather substrate and the structural tear along the bottom seam.

Testing and Analysis:

Test	Results
Leather	
Iron (III) Sulfate test to determine the presence of phenols that would be a positive for vegetable-tanned leather (Odegaard et al. 2000, 152).	Inconclusive. Compared against a known-positive and known negative for vegetable tanned, none of the samples indicated the presence of phenols.
pH measurement of solution of a sample of leather powder in deionized water using Beckman ϕ 340 pH/temp Meter.	pH within normal range. A pH of 3.9 was recorded for the solution with leather samples compared to the deionized water alone that was reported as 6.0
Qualitative measurement of the sulfate content using Meckoquant EM Science Sulfate strip using solution prepared in the pH test.	Slightly raised sulfate content. Strip reported over 800 mg/L ppm of sulfates in the solution but less than 1200 mg/L. The deionized water was reported as over 400 but less than 800 mg/L.
Beads	
Solubility testing on affected bead surfaces.	Soluble in water. Insoluble in ethanol and acetone.
Protein microchemical test on collected bead surface material using Copper Sulfate ($CuSO_4$) (Odegaard et al. 2000)	When compared against a known positive, the sample was considered a negative for protein.

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Kite, Marion, and Roy Thomson (2001). *Conservation of Leather and Related Materials*. San Diego: Butterworth and Heinemann.

"NMAI Collections Search" www.americanindian.si/edu/searchcollections. Accessed 2/28/13.

Odegaard, Nancy, Scott Carroll, and Werner S. Zimmt (2000). *Material Characterization Tests for Objects of Art and Archaeology*. London: Archetype Publications.

Proposed treatment:
1. Reduce the powdering and continual loss of the leather through the use of a consolidant. Consolidant choice will rely on performance of consolidant, ease of application, chemical stability, and effect on leather appearance. Possible consolidants include Cellugel, Klucel G with SC6000, chitosan, and neri.
2. Stabilize tears in leather that are at risk for further damage through the use of hinges applied with adhesive. Selection of the hinge material and adhesive will be based on their appropriate strength and compatibility with the weakened leather. It will be informed by solvent testing and mock-up mends.
3. Address the instability in the structure by creating an exterior mount system that will provide support for the area that is structural weak and prevent further damage/distortion to the bag.

Approvals: (Placed in file)

Treatment Procedure:
 1 **Cleaning**: The exterior surfaces were cleared of debris using an air blower bulb prior to consolidation.
 2. **Consolidation of exterior surfaces**: Prior to consolidation, an area of the surface along the side of the bag was applied with ~2% Cellugel to test for any adverse effects. The leather surface immediately darkened; however, most of the darkening disappeared once the solvent evaporated. It was decided, however, that this concentration caused too much stiffening to the leather. The Cellugel was then diluted to approximately 1 % with isopropanol with the idea that it would still consolidate sufficiently but cause less alteration to the leather. The reduced strength Cellugel was found to be sufficient strength for the consolidation of the surfaces. This concentration also proved to be easier to apply due to its greater wettability. All the surfaces of the exterior faces of the bag were consolidated with ~1% Cellugel in isopropanol using a flat edge soft bristle brush. Areas of beading and sinew thread were avoided. Only minimal alterations to the physical properties of the leather were observed and were deemed acceptable.
     Consolidation of thong and interior surfaces: Cellugel was found to darken, cause tidelines, and embrittled the interior flesh side of the leather and the thong (also the flesh side). Solvent tests were conducted and it was discovered that the isopropanol was the problem.
     Hydroxypropyl cellulose, the main component of Cellugel is soluble in a variety of polar solvents, but has limited solubility in non-polar organic solvents. The organic solvents such as pyridine and dioxane that it is soluble in were not available during the time of treatment. Therefore, BEVA 371 was selected as the consolidant for the thong and the interior surfaces as it is soluble in non-polar solvents such as toluene, which when tested on the flesh side of the leather of this bag did not cause any adverse effects. A 3% solution of BEVA 371 (w/v) in toluene was made and tested on a discrete area of the interior and on the thong. The application appeared to cause some darkening on the thong but noticeably less than the Cellugel and without an embrittlement. The thong and the strap were consolidated with 3% BEVA 371 (w/v) in toluene. Interior surfaces that were accessible through the tear along the bottom seam were consolidated. This included the interior of the lower portion of face 2 and interior area of the beaded strip. In areas along the tear, several coats of consolidant were needed in order to stabilize sufficiently for a patch repair. Some areas of darkening and minor tide lines were

observed; however, embrittlement did not occur. Other areas of the interior were left unconsolidated.

*During this step of the treatment the strap portion of the thong came broke off of the thong due to a lack of any strength left in the leather substrate.

3. **Stabilizing the delamination**: Areas on the strap and on the interior of the torn edge of face 2 had leather than was delaminating and required adhesive to stabilize. Testing with 2.5% B-72 in ethanol/acetone (8:2) was done initially and found to darken and embrittled the leather. As with the consolidant testing, it was discovered that only non-polar solvent would be appropriate. A 2.5% and a 5% B72 (w/v) in toluene were applied to the underside of lifting flaps of leather and weighted until the toluene evaporated.

4. **Repairing tears in leather**: Due to the weakness of the leather and the application of the consolidant, and the sensitivity of the leather to solvents, the tears were repaired using a relatively weak substrate for the mend with a film of adhesive that would be set with heat. A light-weight Kozo Kashmir Japanese tissue paper was selected to mend the tears. Lascaux acrylics (acrylic dispersions based on *methyl methacrylate* and *butyl acrylate*) were selected as the adhesive for their ability to form a film. After testing several combinations of Lascaux 360 HV and Lascaux 498 HV, a 1:1 ratio of Lascaux 360 HV and Lascaux 498HV was selected as it provided adequate strength, minimal tackiness, and an appropriate amount of heat to set. The Lascaux combination was brushed onto the tissue paper over double sided silicone release Mylar and allowed to dry overnight. The film was cut to the desired size and shape for each mend. Once the Mylar was removed from the mend and the mend set over both sides of the tear, a large piece of Mylar was placed over the mend and the heat spatula, set at 60 °C, was applied for approximately 10-20 seconds over the entire area of the mend to adequately and evenly reactivate the adhesive with heat. Three tears extending from the tear along the bottom seam were mended in this technique. Other tears in the leather were located in positions that were more difficult to access and would require more strength in a mend. However, it was decided that mending of these tears would result in extensive damage; therefore, this step of the treatment was not continued further.

5. **Adjusting the stuffing and mount**: When the bag arrived for treatment, there was archival material placed in the interior of the bag to support the structure. However, the volume of the interior stuffing was so voluminous that it was stressing the leather. The same material was used for supporting the structure but the amount was reduced. The stuffing material that was visible through the tear along the bottom seam of the bag was covered with terracotta colored synthetic felt that is backed with an acrylic tape adhesive (purchased at www.benchmarkcatalog.com).

A pallet for the bag was constructed with unbuffered acid-free board covered with Volara. Using Ethafoam and Volara, an exterior support for area along the long tear and buffers for the sides of the bag were formed. Cotton twill tape was used cut and slipped through the foam to provide ties to secure fragments that area associated with the bag.

Before Treatment Images

Figure 1: Before treatment, general view of face 1 of the bag. The different qualities of the surface, resulting from the ongoing deterioration, are evidenced in this photo by the various shades of brown.

Figure 2: Before treatment, general view of face 2 of the bag. The lighter spots on this surface are accumulated bits of lost leather demonstrating the pervasive nature of the red rot.

Figure 3: Before treatment, general view a side of the bag. The several tears in the leather originating from the beaded strip of leather are evident in this image.

Figure 4: Before treatment, general view a side of the bag. This image shows the structural damage caused by the large tear in the leather that leaves one side of the bag sagging, distorted and stressed.

Figure 5: Before treatment, general of the bottom of the bag. This image shows the tear along the bottom edge of the seam that connects one of the faces with the beaded strip.

Figure 6: Before treatment, detail of the bag opening where the beads have become unstable due to the failing strength of the leather
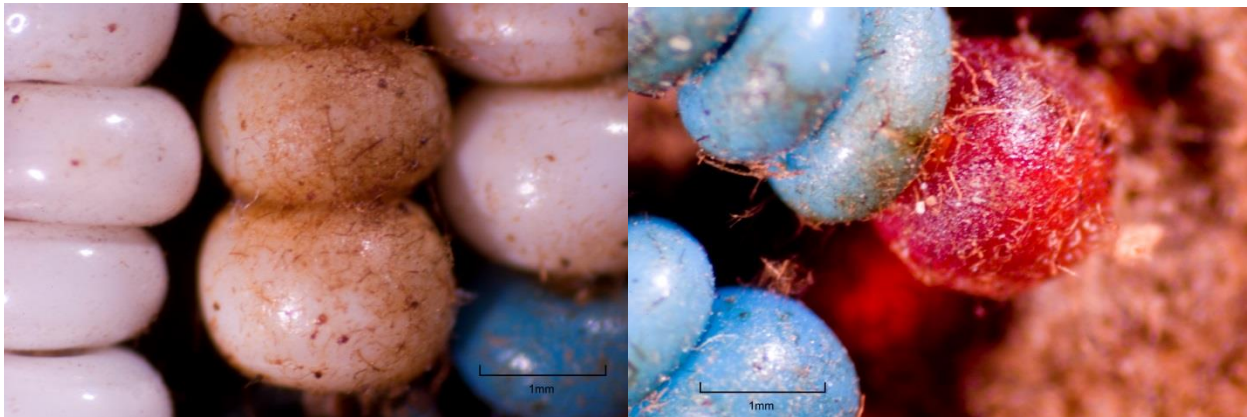

Figure 7: Before treatment, detail of one end of the structural tear along the seam.

Figure 8: Before treatment, detail of the other end of the large structural tear in the bag. Two smaller tears emanating from the large tear are visible as is an adjacent tear that continues to the beaded strip.

Figures 9 & 10: Before treatment, photomicrographs of the beads that exhibit a sticky surface due to a suspected coating that is yellow brown in color and hygroscopic. Powdering leather has adhered to the surfaces of these beads.

Figures 11 & 12: Before treatment, photomicrographs of the beads covered in powder from the leather (Left). Before treatment, photomicrograph of a tear along the opening of the bag that is creating an instability for the beaded element (right).

Figures 13 & 14: Photomicrographs of the interior side of the bag. The grain pattern of the leather has characteristics similar to deerskin (left). Image of the sinew stitching along the interior seam of the bag (right).

Figures 15 & 16: Before treatment, photomicrographs of the delaminating leather along the structural tear.

Figures 17: Before treatment of the tear in the leather in the along the seam between the beaded strip and the leather face. This tear turns and continues between a row of beading

Figures 18: Before treatment, detail of the delamination and area of loss on the leather thong.

Figures 19: Before treatment, detail of the tear in the leather on face 1 that is parallel to the strip of beads.

After Treatment Images

Figure 20: After Treatment, general view of face 1. Image shows the surfaces of the face and thong after debris has been removed and consolidant applied.

Figure 21: After treatment, general view of face 2. Image shows the surfaces of face and thong after application of consolidant.

Figure 22: After treatment, general treatment of one side of the face. Image shows the bag after the adjustment of the interior stuffing to reduce stress on the tears.

Figure 23: After treatment, general view of the one side. Image shows the loss of the strap on the thong that occurred during treatment.

Figure 24: After treatment, detail of face 2. Image shows two tear mends and the interior felt covering the stuffing.

Figure 25: After treatment, detail of beaded strip at the bottom of the bag. Image shows the opening tear along the seam that expanded during treatment.

Figure 26: After treatment, detail of the side where the strap detached from the thong during treatment.

Figure 27: After treatment, detail of the tear along the bottom seam. Image shows the alignment of the leather after the mends.

Figure 28: After treatment, detail of the strap where darkening occurred during the application of consolidant.

Figure 29: After treatment, general view of the bag after treatment on the newly designed storage system.

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