A preliminary study on using line seed oil emulsion in dressing archaeological leather

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Keywords: Archaeological leather, Line seed oil, Thermal analysis (TG), pH value,
Dressing

ABSTRACT

The main goal of this study was to study and evaluate the effect of line seed oil and glycerin emulsion a surface treatment on appearance and chemical composition of archaeological leather samples, which were taken from a historical leather book binding back to 1858, 1653&1472 A.D, have been treated with line seed emulsion then a visual assessment, pH measurements , thermal analysis methods(TGA) ,infrared spectroscopy (FTIR) study and mechanical properties determination were undertaken, to see if any significant structural or chemical differences could be detected between “untreated” and “treated” leather. No dramatic changes in functional groups on the leather surface, as monitored by infrared spectroscopy, occurred in the samples before and after treatment, pH values, however, show that emulation may give good results in decreasing the

acidity of the treated leather. The emulsion enhanced thermal& mechanical properties of treated samples.

1. Aims

There are limited options for those seeking to conserve dry leather, and all with their own drawbacks. This study aims to evaluate line seed oil and glycerin emulsion to possibly introduce a fairly unused method to the conservators' repertoire. It will hopefully aid in the choice of method when confronted with a leather object that needs a surface treatment.

2. Introduction:

The leather itself represents a very complex material composition. Its surroundings are likewise a very complex and dynamic dimension constantly varying with respect to the quantity and degree of their interaction with each other and with those materials which are being stored within them. The conversion of raw animal hides and skins into durable leathers, with enhanced stability to water, bacterial degradation, heat and abrasion, was most probably the man's oldest technology combining exploitation of animals and plants (The term hide is generally used for thick natural external covering of big animals (e.g. cattle, horses) and skin for thinner natural covering of smaller animals (sheep, goats, calves, and deer); here- after we use only the term skin for both groups. The most commonly used animal skin to make leather were those of domesticated cattle, sheep, goat, and to a lesser extent pig. The natural structure of animal skin consists of different layers^[1]. The epidermis is the outermost part of the skin that

is removed in the process of leather making. Below the epidermis is the dermis, which is the layer used for making leather, and consists of two layers, the grain and corium. Fresh animal skins have limited value, because when wet and containing large amounts of readily available nutrients (e.g. carbohydrates, fats and proteins), they provide a perfect medium for rapid growth of microorganisms and susceptible to bacterial attack of the skin collagen, but if dried become inflexible and useless for many purposes such as clothing. To minimize this degradation^[2], On the other hand, the raw skins are treated through various mechanical and chemical operations, including salting, drying and tanning. Several tanning agents are known; vegetable, mineral, oil or smoke (aldehyde) tanning, and combinations thereof^[3]. The processing stages for manually convert animal skins to leather are the following. Extracting natural grease (defatting) is an important preliminary step in which excess fats are removed to avoid poor penetration of the tanning agents. The extracted fats can be used as fat liquors for finishing off the tanned leather by oiling. Traditional vegetable tanning was generally accomplished by placing alternate layers of animal skin and crushed parts of plants, including bark, wood, root, fruit pods, and leaves, or aqueous vegetable extracts in a pit, adding water, and allowing the skins to soak in the tanning bath for a certain time, often up to a year, until a satisfactory leather had formed. The plant materials contain substantial amount of vegetable tannins, characterized by complex structures containing polyphenolic compounds rich in hydroxyls and other suitable groups (such as carboxyl) to form strong complexes with macromolecules as proteins and a range of small molecules. A variety of

locally available vegetable tanning materials, as birch inner bark, willow bark, and alder bark, as well as brown rotted larch wood, were used by ancient cultures. In the prehistoric tanning practices various vegetable and animal fats, as well as mixtures of fats, were also applied in leather manufactures, either as tanning agent or for final coating of the leather fibers with a fatty film (fat liquoring) to soften tanned skin, improving the suppleness and elasticity of the tissue, and creating leather with hydrophobic properties. The fatty material used include animal adipose (cow tallow), liver, brain and milk fats, as well as fish liver oil, and the most commonly available vegetable oils – olive oil, soy oil, sunflower oil, linseed oil, rapeseed oil, and castor oil and references therein constituents decides the characteristics of the final leather^[4]. Leather lipids can be endogenous (residual lipids from animal skin) or exogenous. The endogenous lipids include 1) lipids from sebaceous glands at the side in the external layer of the skin (grain), 2) fat in globular cells in the Centre of the corium, which is made from collagen fibers, bundles of fibers, and inter-fibrillary non-structural proteins, and 3) fatty tissue from residual adipose in the internal flesh layer. Adipose fatty acids should be absent in the leather, as they are removed during leather-making procedures. The exogenous lipids come from vegetable or animal fat added for tanning during leather making or use of the leather product. Apart from tanning agents, lubrication preparations, generally vegetable and animal oils, fats and waxes, are the most important source of exogenous lipids in archaeological leather. At the end of the tannage a lubricant has to be applied before the leather is dried in order to maintain the flexibility of the leather. Earlier processes will have used natural

fat and greases and natural emulsifiers found in materials such as egg yolk and brains .Leather recovered from the archeological sites presents a variety of challenges for the conservators. Landsite recovered leather may be brittle with cracks and shrinkage excessively. Mold, fungi and exposure to ultraviolet light and airborne contaminants such as sulphur dioxide all act to undermine the integrity of leather ,finally, as leathers age they can become firm, hard and cracky. At the same time, it has therefore been assumed that the fatty materials added during processing have been lost. This concept of "feeding" the leather with new oil and fat mixtures to replace this lost material and restore the original properties has therefore grown up^[5]. In most cases, archeological leather requires some degree of cleaning before conservation procedures are undertaken^[6]. Leather dressings are applied as lubricants to leather, particularly items that are in use, rather than on static display. They are beneficial when a leather item has lost its flexibility, or when it must be protected from future variations in humidity. A large number of oils, greases and waxes are employed in the archaeological leather dressing^[7]. British Museum Leather Dressing has been used by many conservators since its publication to protect and conserve leather^[8]. The basic formulation of British Museum Leather Dressing is 200 g anhydrous lanolin, 30ml cedar oil (acts as a fungicide), 15 beeswax (optional) , 330 mlX-4 solvent or diethyl ether or hexane^[9]. However, dressings, or finishes, are usually oil or wax based and surface applied with the intent to restore flexibility, protect from deterioration and enhance appearance. For a long time, dressings used to be the standard treatment used in conservation of leather. This has proved to be the

cause of many problems, as there are a myriad of drawbacks with dressings as a conservation method. Since the base components are fatty substances, overuse can cause oxidization and stiffening, discoloration and staining, a tacky surface that attracts dust and dirt, encouraging of microorganism-growth, and hampering of future conservation efforts. Over applying can also result in the depositing of spew on the surface, a white substance of free fatty acids, sometimes looking like mold. As well as oils and waxes, dressings often include some type of solvent. These bring with them potential problems of their own, such as dissolving of original surface treatments, adhesives or paint and wetting, swelling and deforming^[10]. Despite these drawbacks, dressings are still commonly used, mainly due to aesthetic reasons, giving the object a finished look^{[11] [12]}. Finally, this experiment was conducted to study and evaluate line seed oil and glycerin emulsion as a new surface treatment for dry archaeological leather.

3. Materials and methods

3.1. Archaeological leather samples

For this study three types of leather were acquired, to simplify, the types of leather will be called 1, 2 and 3.

Leather type 1 comes from a historical leather book binding back to 1858 A.D. Period of Mohammad Ali Basha .

Leather type 2 is a book binding from Dar El kotob dating back approximately to 1650- 1653 A.D, which had been exposed to weathering factors.

Leather type 3 is a stamped leather binding dating back (1472 A.D. / 876 A.H.) from the store of Azhar mosque.

All samples in dry condition and item have lost its flexibility. Information on the samples types are listed in Table 1.

3.2. Dressing emulsion

The new recipe for dressing archaeological leather as a following:

1-7g Glycerin (glycerol have been used successfully on brittle and/or desiccated leather), glycerol, which is soluble in water and alcohol, acts as a humectant for leather^[13].

2- 20 ml of line seed oil (this is drying oil and can be used as surface dressing and was the basis of japanned or patent leather).

3- 5g acetyl alcohol (Anionic agents to modify the particle size of oil in water emulsion and to increase the stability of the emulsion to electrolytes, acetyl alcohol is used as an emollient, emulsifier or thickening agent in the manufacture of skin creams)^[14].

4- 5g stearic acid (this acid give highly viscous. stearic acid is not very reactive acid and do not oxidize on ageing .

5- 100 ml of distilled water (which forms the continuous phase for the emulsion and usually constitutes from 40 to 70% by weight)^[15] .

3.2.1. Preparation of dressing emulsion

Warm the first two ingredients together at about 60°C. Cool the mixture to 20°C and add acetyl alcohol and stearic acid. Mix thoroughly and rapidly^[16]. While stirring continuously, add the distilled water bit by bit. When all the water has been added, pour the mixture in to glass cylinder. Paint the cooled emulsion on to the leather using a clean swab. Allow the leather to dry between coats, after 7 days^[17], the leather may be polished with a soft cloth.

3.2.2. Chemical aspects of emulsion components

Linseed oil is a triglyceride, like other fats. Linseed oil is distinctive for its unusually large amount of α -linolenic acid, which has a distinctive reaction with oxygen in air. Specifically, the fatty acids in a typical linseed oil are of the following types (i) The triply unsaturated α -linolenic acid, (ii) The saturated acids palmitic acid, (iii) The monounsaturated oleic acid, (iv) The doubly unsaturated linoleic acid^[18] (see Fig.1) Having a high content of di- and tri unsaturated esters, linseed oil is particularly susceptible to polymerization reactions upon exposure to oxygen in air. This polymerization, which is called drying, results in the rigidification of the material. On the other hand, linseed oil has been used as a wood finish, linseed oil dries slowly and shrinks little upon hardening. Linseed oil does not cover the surface as varnish does, but soaks into the (visible and microscopic) pores, leaving a shiny but not glossy surface that shows off the grain of the wood^[19]. A linseed oil finish is easily repaired, but it provides no significant barrier against scratching. Only wax finishes are less protective. Liquid water

penetrates a linseed oil finish in mere minutes, and water vapour bypasses it almost completely, but there is no previous study concerning the use of Linseed oil on leather. Conservators are often concerned about behavior of Linseed oil. It is generally known that like some other drying oils, linseed oil exhibits fluorescence under UV light after degradation^[20].

The second component is glycerol; glycerol is a simple polyol (sugar alcohol) compound. It is a colorless, odorless, viscous liquid that is widely used in pharmaceutical formulations. Glycerol has three hydroxyl groups that are responsible for its solubility in water and its hygroscopic nature. The glycerol backbone is central to all lipids known as triglycerides. Triglycerides found in fats and oils are by definition esters of glycerol with long-chain carboxylic acids; the hydrolysis (saponification) or transesterification of these triglycerides produces stoichiometric quantities of glycerol. Like ethylene glycol and propylene glycol, glycerol is a non-ionic kosmotrope that forms strong hydrogen bonds with water molecules, competing with water-water hydrogen bonds. This disrupts the crystal lattice formation of ice unless the temperature is significantly lowered. In other studies, Elize Dienst^[21] has recently shown that glycerol has proved successful in the following formulations of lubrication archaeological leather (i) Castor oil (1.5- 2.5 parts), Glycerol (1 part) & Methylated spirit (8 parts), (ii) Lanoline (10g), Castor oil (5cc), Glycerol (5cc), White spirit b.p. 190-250°C (70-75cc) & Distilled water (5-max. 10cc). The first formulation is used as a bath; the second is applied to one side of the leather, by brush. Addition of water as a major component in

combination with one of the other base oils, commonly used in engineering processes.

3.3 Analysis

3.3.1. Visual assessment

Visual examination with plain sight was done to detect any changes in color or sheen, or any notable distortion. The samples were also examined under a stereo microscope, on the grain side and in a cross section. The samples surface feels were compared by simply feeling them, noticing any stickiness or smoothness. The surface morphology of the samples was examined by Compact Video Microscope (CVM) SDL, international Ltd. England.

3.3.2. Measurement of pH

The analyses are performed on between 2200 and 1000 mg of leather (grain and corium) cut into 1 mm² fragments. The leather fragments are extracted in water for 24 h at room temperature, under constant agitation in a closed polyethylene vessel. The measurements were performed directly on the aqueous extract using a pH meter (PHM62, Radiometer, Copenhagen) with a combination electrode and calibrated between pH 3 and 7, at 28°. To make the method available to small samples, the dilution condition of the leather extract (1 g/50 ml)^[22], differs by a factor of 2.5 from the standard procedure (2.5 g/50 ml). This makes the present pH readings of strong mineral acid solutions about 0.4 higher as compared to the standard procedure.

3.3.3. FTIR spectroscopy analysis.

The IR spectra of treated and untreated samples were recorded by means of Nicolet 380 (FTIR) spectrometer with Attenuation Total Reflection (ATR) mode with a zinc selenide crystal, in the wave length range $650\text{-}4000\text{ cm}^{-1}$. The IR absorbance frequencies for the samples under test were recorded with an average of 128 scans using a resolution of approximately 4 cm^{-1} .

3.3.4. TG measurement

The influence of dressing emulsion on the thermal properties of derma collagen was studied by differential thermal analysis. TG& DTG analysis was carried out by using Shimadzu TGA-50 Japan over the $22\text{-}760^{\circ}\text{C}$ temperature range in static nitrogen atmosphere with heating rate of $10^{\circ}\text{C}/\text{min}$. The temperature ranges of the Specimens under study were evaluated from differential mass loss curves.

3.3.5. Mechanical Properties determination.

All leather samples were conditioned according to ISO 187 before measurements at a temperature of 23°C and a RH of 50% over 24 hours^[23]. The measurement which were focused on the mechanical properties of leather, were performed in compliance with DIN 53354- Artificial leather tensile test, using Zwick tensile testing machine Z010, Germany at a constant crosshead speed of $100\text{ mm}/\text{min}$. The mean values of tensile strength and stretch were calculated from 5 measurements with a precision in the $\pm 10\%$ range.

4. Results and discussion

4.1. Visual assessment

When first applying the line seed oil and glycerin emulsion, a distinctive darkening could be observed, especially on the flesh side of the leather samples. After finishing the treatment, the color of the type 1 and 2 leather had returned to a shade indistinguishable from the original samples. Besides that, no great changes in color were observed. The type 3 samples darkened considerably after the treatment due to the cleaning effects of the treatment removing the white residue and the dirt. When compared to a control sample from a part of the strap that was in very good condition (i.e. no white residue and quite clean) the coloration is very similar. Not observed in any of the treated samples was a drastic change in the sheen. The type 1 sample retained its slightly glossy surface, and no difference could be optically observed between the treated sample and the control. The single coated type 2 sample did obtain a very slight sheen on the grain side. The type 3 samples, although cleaner, have retained a mainly matte surface, with only a tiny bit of sheen. No discernible difference was observed between the treated samples and the controls when viewed in a stereo microscope.

The feel of the grain surfaces on the treated samples was a bit more slippery than the control. Especially on the type 1 sample, these could be that leather is a fibrous material; the fibre structure consists of collagen protein fibres stabilized with cross links of various kinds by the process known as tanning. It is necessary to control the internal friction of this structure with oils, such as line seed oil in current recipe, finally the durability of leather is increased by the presence of oils,

there was a little bit less friction when rubbed. On the type 2 and type 3 leather, this effect was only just discernible. No tacky feel of the surface could be felt on any of the samples. Not observed in any of the treated samples was a drastic change in the sheen. The type 1 sample retained its slightly glossy surface, and no difference could be optically observed between the treated sample and the control. The samples all retained their flexibility, no additional stiffness was observed. On the type 1 leather the bend in the sample kept its shape, not flattening out. The type 2 sample was even a bit more flexible than its control counterparts, and the surface did not crack more when bent, though the original cracks were left unchanged. The type 3 sample retained the flexibility that it had before the treatment (See figure 2). Figures (3, 4 &5) show Video micrographs of the samples before and after treatment. The micrographs showed differences in surface patterns between treated and untreated leather under this study, untreated leather was firm, hard and cracky, These phenomena have disappeared after treatment It is seen that the line seed oil and glycerin emulsion give more pleasing appearance ,the surface feel of leather has been improved by actions of line seed oil and glycerin especially for type 1.The sealing of the surface in this way greatly reduced the absorption of harmful atmospheric pollutants and adds to life of the artifact.

4.2. Measurement of pH

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

The measurements seem to indicate that the type of leather is more significant to the pH than the treatment methods, but the results are so diverse that it is difficult to determine positively. Seen is that the type 1&3 sample treated with line seed oil and glycerin emulsion has a slightly higher pH than the other untreated type samples, here indicating that the treatment has given a less acidic leather, which in turn is less prone to degradation, the less acidity of treated leather may be due to migration of water and steric acid from the emulsion to the internal structure of treated samples, but the margins are too small to be conclusive. Also, line seed oil and glycerin emulsion treated type 2 sample has the lowest pH of that type, contradicting the indication that the treatment lessens the acidity.

When preparing the samples for the pH measurements, it was observed that all the samples treated with line seed oil and glycerin emulsion drew up water very quickly and sank to the bottom of the test tubes almost instantly, while the other samples had to be vigorously shaken for the sample pieces to wet properly. This could indicate that leather treated with line seed oil and glycerin emulsion will wet easily and draw up water into the object. . In other studies, V. Fuchs^[23] has reported that leather contains a large amount of voids in the structure, either naturally occurring spaces or produced by modifications of the fibre structure by chemical and enzyme action. These can be filled with high molecular weight fat, waxes and other polymeric consolidation agents, giving the leather increased support and solidity.

4.3. FTIR

Leather samples were also studied by FTIR spectroscopy before and after treatment and results were compared to monitor changes.

4.3.1. Untreated leather

The infrared spectra of three types of leather show the same basic structure as all leather samples^{[24] [25] [26]}, as assigned in [Table 3](#). Powdered samples taken from untreated leather surface showed a typical profile in FTIR (Figure 6, 7&8). The protein material is detected by broad bands at 3320 cm⁻¹ (due to N-H) and 2925.48 cm⁻¹(C-H stretching bands) as well as at 1642.09, 1529.27cm⁻¹ (amide bands I, II, III, correspondingly). Tanning agents also have a significant print with broad peaks at 1033 cm⁻¹ link (C-O-C=O in tannin ester) and broad bands at 2340 cm⁻¹ (sulfur ion stretching band, Sulfur may act as a contaminant from the surrounding environment or from the manufacturing process of leather bookbinding) in the type 1. The relative intensities of bands at 342.85, 1529.27, 1638.2 and 1443 cm⁻¹are higher in the type 2, whereas bands at 3410, 1542, 2920 and 1648 cm⁻¹ are stronger in the type 3.

4.3.2. Type 1 after treatment

No dramatic changes are observed before and after treatment (Fig. 6), but it is interesting to note that after treatment with line seed emulsion there are some differences in the increase of the relative intensity of the N-H group at 3408 cm⁻¹

and disappeared of the peak at 2340 cm^{-1} (sulfur ion stretching band) may be an indication of the role of emulsion in cleaning leather. The other fingerprint bands remain somewhat similar to that seen for the control sample.

4.3.3. Type 2 after treatment

After treatment with line seed oil and glycerin emulsion (fig.7) a slight increase in the relative intensity of the 3420 cm^{-1} peak is observed, In addition, the 1646 cm^{-1} and 1543 cm^{-1} bands which represent the C=O carbonyl group and C-N-H bending band have increased in relative intensity, this could be interpreted as change some of C-O group to C=O group. We can also observe the existence of the strong peak at 1037 cm^{-1} .

4.3.4. Type 3 after treatment

There were no significant differences can be seen in the FTIR spectra of type 3 before and after treatment (Fig. 8), however, the effect of treatment appear to result in an increasing in the relative intensity of the 3414 cm^{-1} peak. No dramatic changes in the aromatic peaks after treatment are observed but the area ($1684\text{--}2926\text{ cm}^{-1}$) increased in the relative intensity. Generally, no major changes in the leather samples are observed before and after treatment except for disappearance of sulfur ion stretching band group, which is not normally seen in leather spectra, probably due to may act as a contaminant, so the new treatment was useful for leather to remove this ions. On the contrary, chemical surface treatment which is often applied, using different reagents causes serious changes like ethanol which

is capable of removing the small quantities of carbonyl compounds and bulk proteinaceous material carbohydrate components and may accelerate further degradation^[27]. The current study proved that treatment could be a promising method. Finally, we can say that Infrared spectroscopy is a useful method for studying and understanding the chemical changes in leather, but since the chemical composition of leather varies with different animals, animal part (neck, upper middle, lower middle or across butt), or type of skin (I. e., goat, calf), etc. The spectra also change a little if recorded in different positions. This means that any changes have to be quite pronounced for us to be sure that it is really from the treatment and not the leather.

4.4. TG measurement

Thermogravimetric analysis TGA is a simple and accurate method for studying the decomposition pattern and the thermal stability of leather after dressing treatment. Figures (9, 10&11) show the primary thermo grams& derivatograms for the native and leather treated with line seed oil and glycerin.

4.4.1. TG measurement of untreated samples

As is evident the native leather sample (type 1) has an initial weight loss of 12.6% around 100°C, which is mainly due to the evaporation of absorbed moisture^[28]. The main decomposition proceeds in two steps (RF)^[29], the first one with weight loss of 30.4 occurs at decomposition temperature (Td) of 348 °C and the second with weight loss of 13.5% occurs at Td of 452°C. The types 2&3 samples show a behavior similar to the type 1(Table 4). Thermal gravimetry studies allowed a conclusion to be drawn that thermo oxidation destruction of archeological leather before and after treatment, a multistage process which involves at least three stages (Figs 9, 10&11). The maximum rate of the first stage of thermal oxidation, $d\Delta m/dt$, min⁻¹ relates to the degree of leather destruction. The data from the Table 4 show that it is the samples of archeological leather with the highest degree of destruction that reveals the highest rate of destruction at the first stage. The lowest mass loss for the samples of archeological leather at the II stage of destruction is related to partial splitting of collagen macromolecules and, therefore, increasing heterogeneousness of its structure^[30].

4.4.2. TG measurement of treated samples

The results on the TGA carried out by determining the decomposition temperature (T_d) as the maximum of the derivative curve of untreated and treated leather with Linseed oil have been shown in Figs. 9, 10&11. In accordance with the literature^[31] it has been established that there is no degradation taking place until 200°C. Above this temperature thermal stability is gradually decreasing and decomposition of the fibres occurs. Treated leathers show two different steps: one peak below 400 °C, and another one around 400 °C. The first peak is assigned to the decomposition of line seed oil and it shifts to higher temperature in comparison with untreated leather. While the second inflection with the sharp peak records the same T_d of native leather. The data illustrated in Figures (9, 10&11) show the effect of treatment on total initial weight loss; it is obvious that the treatment decreased total initial weight loss especially for type 2 and 3. However there is a change of the destruction mechanism from hydrolytic to hemolytic which might be due to Stearic acid which it is believed to enhance the hydrophobicity of the negative active material. It also reduces the extension of oxidation in the open atmosphere^[32]. Moreover, the loss of free water in leather results in a loss of softness, while the loss of bound water results in its deterioration, due to changes that occur in its chemical structure and physical properties^[33].

4.5. Mechanical Properties.

In order to estimate the effect of emulsion on mechanical properties of leather, the tensile properties, which are tensile strength (T.S) and Extension (mm) were measured. Fig 12 shows the effect of line seed oil and glycerin emulsion on mechanical properties of archaeological leather. Substantial increase of extension was observed after treatment with emulsion. Extension can be related to the leather's ability to conform and maintain conformance to a particular contour, and is also regarded as one of the most important criteria for the satisfactory behavior of leather in applications. The data from the Fig 12 shows that the incorporation of line seed oil controls the degree of cross linking, thus increasing the softness and extensibility of leather.

5. Conclusions

Using line seed oil and glycerin emulsion in dressing archaeological leather have been investigated using different experimental techniques including Visual assessment, pH measurements, FTIR spectroscopy and Thermo gravimetric analysis (TG). The conclusions that can be reached from this research can be summarized as follows:

Although the data obtained from both the Visual assessment, pH measurements and infrared techniques were completely compatible, it is useful to note that

sometimes there are changes in the chemical composition of archaeological leather observed using infrared spectroscopy, whereas they didn't appear in the structure.

Line seed oil and glycine emulsion need further research to evaluate their use in dressing archaeological leather. Moreover; the emulsion results are so diverse that it is difficult to determine positively for acidity of archaeological leather are another point to consider, especially after aging.

Lin seed emulsion treatment could be a promising method in dressing archaeological leather comparing to the traditional method.

6. Practical applications

Lin seed oil and glycine emulsion has been shown to be effective in dressing dry archaeological leather. It must be clear that the knowledge of the type and the chemical composition of dressing material, which used on the archaeological leather, in addition to its properties lead to good results during treatment; as contributes in the selection of the best ways to dress it, also reduces the amount of dressing materials used in the dressing process, the length of time the leather is exposed to the emulsion and the amount of mechanical action necessary to polished and increases the chances of good dressing.

Acknowledgements

The author would like to thank Dr. Hamed Sead, Department of Tanning and protein Chemistry, National Research Center, Dokki, Cairo-Egypt, for his help in preparation the emulation.

Table 1
Description of samples

<i>Sample code</i>	<i>Skin type</i>	<i>Tannage</i>	<i>Thickness</i>
Leather type 1	Goat	<i>Sumac</i>	0.69mm
Leather type 2	Sheep	<i>Oak bark</i>	1.02mm
Leather type 3	<i>Calf</i>	<i>Acacia Arabica</i>	0.26mm

Table 2 Results of the pH testing

	<i>Sample type</i>	<i>Control</i>	<i>Treated samples</i>
	Type 1	pH 5.3	pH 5.7
	Type 2	pH 4.9	pH 4.8
<u>Tables</u>	Type 3	pH 4.5	pH 4.9

Table 3 The functional groups in leather.

Wave number cm^{-1}	Functional group
3600-3200 cm^{-1}	(O-H) stretching band
3100-2800 cm^{-1}	C-H stretching bands
1740-1640 cm^{-1}	C = O stretching band
1650-1600 cm^{-1}	C-C stretching band
1480-1300 cm^{-1}	C-H bending band
1565-1500 cm^{-1}	C-N-H bending band
1663 cm^{-1}	Amide I band of leather protein
1551 cm^{-1}	Amide II band of leather protein
1237 cm^{-1}	Amide III band of leather protein

Table 4 Parameters of the thermo oxidation destruction for archeological leather before and after dressing.

Leather	Stage I		Stage II		Stage III	
	$\Delta m, \%$	$d\Delta m/dt.min^{-1}$	$\Delta m, \%$	$d\Delta m/dt.min^{-1}$	$d\Delta m/dt.min^{-1}$ $\Delta m, \%$	
Type 1	12.6	1.1	30.4	5.2	13.5	1.4
Type 1 after treatment	10.2	1.0	27.9	7.2	11.6	1.3
Type 2	12.3	0.6	32.7	2.6	15.7	1.5
Type 2 after treatment	9.8	0.6	19.6	2.1	12.8	1.2
Type 3	11.5	1.2	25.8	6.1	15.5	1.5
Type 3 after treatment	10.9	0.8	23.6	5.0	13.8	1.1

Figures

Fig . 1. Representative triglyceride found in a linseed oil, a triester (triglyceride) derived of linoleic acid, alpha-linolenic acid, and oleic acid

Fig . 2. Line seed oil and glycerin emulsion: control samples and post treatment. Samples to the left are control samples. Top: type 1, middle: type 2, bottom: type 3.

Fig . 3. Video microstructure (zoom x 35) of type 1, untreated leather (A) & treated leather (B) the arrows refer to slight sheen on the grain side after dressing.

Fig . 4. Video microstructure (zoom x 35) of type 2 showing the surface after & before dressing with line seed oil and glycerin emulsion, and there are major differences, the leather was firm, hard and cracky, These phenomena have disappeared after treatment

Fig . 5. Video microstructure (zoom x 35) of type 3, untreated leather (A) & treated leather (B)

Fig . 7. FTIR Spectra of Leather type 1 before and after treatment with a line seed oil and glycerin emulsion, (a) before and (b) after treatment.

Fig.6. FTIR Spectra of *Leather type 2* before and after treatment with a line seed oil and glycerin emulsion, (a) before and (b) after treatment.

Fig.8. FTIR Spectra of leather type 3 before and after treatment with a line seed oil and glycerin emulsion, (a) before and (b) after treatment

Fig.9. TGA curves & weight loss% of archaeological leather type 1 before & after dressing

Fig.10. TGA curves & weight loss% of archaeological leather type 2 before & after dressing

Fig.11. TGA curves & weight loss% of archaeological leather type 3 before & after dressing

Fig.12. Effect of line seed oil and glycerin emulsion on mechanical properties of the different leather types

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