Journal of Cultural Heritage xxx (2016) xxx–xxx

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Original article

A preliminary study on using linseed oil emulsion in dressing archaeological leather

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ARTICLE INFO

Article history:
Received 28 March 2015
Accepted 12 October 2015
Available online xxx

Keywords:
Archaeological leather
Linseed oil
Thermal analysis (TG)
pH value
Dressing

ABSTRACT

The main goal of this study was to study and evaluate the effect of linseed oil and glycerine 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 linseed 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 linseed oil and glycerine 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); hereafter, 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 becomes 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

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http://dx.doi.org/10.1016/j.culher.2015.10.001

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:

- lipids from sebaceous glands at the side in the external layer of the skin (grain);
- fat in globular cells in the Centre of the corium, which is made from collagen fibers, bundles of fibers, and interfibrillary non-structural proteins;
- 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, 30 ml cedar oil (acts as a fungicide), 15 beeswax (optional), 330 ml X-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. Overapplying can also result in the depositing of spew on the surface, a white substance of free fatty acids, sometimes looking like mold. As well as oils and waxes, dressings often include some type of solvent. These bring with them potential problems of their own, such as dissolving of original surface treatments, adhesives or paint and wetting, swelling and deforming [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 linseed oil and glycerine 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 are as follows:

1 7 g glycerine (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 linseed oil (this is drying oil and can be used as surface dressing and was the basis of japanned or patent leather);
3 5 g 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 5 g stearic acid (this acid give highly viscous; stearic acid is not very reactive acid and does 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 emulation

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 continually, 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

Table 1
Description of samples.

Sample code	Skin type	*Tannage*	Thickness (mm)
Leather type 1	Goat	*Sumac*	0.69
Leather type 2	Sheep	*Oak bark*	1.02
Leather type 3	*Calf*	*Acacia Arabica*	0.26