A STUDY OF ARTIFICIALLY AND NATURALLY AGED LEATHER BY USING THERMAL ANALYSIS

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Introduction

The structural stability of collagen based museum objects is crucial to their preservation and for carrying out the functional and artistic rôle which they were intended as texts reading, binding, decorative objects, wall tapestries, upholstery, shoes and clothing, etc.

Currently, the hydrothermal stability of collagen fibres is widely determined by measuring the shrinkage temperature (T_s) using the Micro Hot Table (MHT) method. However, the survey of the MHT method results showed strong inherent limitations in the use of this qualitative parameter for the historical materials diagnosis. Shrinkage activity, defined as a sequence of 5 temperature intervals in which collagen fibres distinctly move, provides a better characterisation of structural heterogeneity and stability of leather and hence of its damage.

The use of differential scanning calorimetry (DSC) for specific damage markers detection and identification of sensitive materials can help to resolve the important question of the stability of the artefacts.

DSC and MHT data correlation proved to deliver an improved diagnosis for a better preventive conservation of historical leather.

Results obtained by MHT and DSC on both artificially aged and historical vegetable-tanned leathers indicate that:

- **Shrinkage activity is influenced by time exposure, temperature and relative humidity, as well as by UV irradiation.**
- **Shrinkage activity is correlated with the age, function and individual history of the individual artifacts.**
- **Melting temperature of the collagen crystalline fraction discriminates between accelerated aged and naturally aged leather.**

Samples

- **6 Newly obtained vegetable-tanned leather** obtained from sheep and calf hides. Vegetable extracts were from mimosa, quebracho and chestnut.
- **72 Artificially aged leather samples** obtained by exposure to
  - UV light (radiation source: Xenon SOL 2 Light) for 1, 2, 4, 8, 16, 32 h
  -Heating at 80 °C at 80% RH (in a desiccator over saturated KCl solution placed in a thermo-controlled oven) for 1, 2, 4, 8, 16, 32 days
- **34 Historical leather samples** from various Romanian museums.

Experimental

Micro Hot Table (MHT) (**Fig. 1**): Shrinkage is visualised through a stereo microscope using reflected light as a motion of fibres in aqueous medium under 2°C min^{-1} heating rate. The film is recorded by a camera and observed by an operator which defines the shrinkage temperature intervals (**Fig. 2**):

no activity – A1 – B1 – C – B2 – A2 – complete shrinkage

Differential Scanning Calorimetry (DSC) in dry nitrogen flow (20 mL/min) Samples (1–3) mg in open Al pans are heated at 10 K min^{-1} from 25 to 280 °C.

Results

New vegetable-tanned leather

T_s values ranges from 67.8 to 81.1 °C while ΔT ranges from 15.3 to 49.6 °C depending on the tannin type and production technology.

Artificially aged leather

UV irradiation and humid heating resulted in a progressive T_s decrease with exposure time increasing (**Figs. 3a and 3b**) .

Melting temperature of collagen crystalline fraction T_m did not vary during accelerated ageing (**Fig.4**).

Historical leather

T_m, directly related to crystalline network strength, show almost constant values specific for both new and old leather (**Fig.5**).

Shrinkage activity highly varies confirming the much higher heterogeneity of natural ageing (**Figs.6a and 6b**).

Final remarks

In situ evaluation of hydrothermal stability of heritage objects is highly sought, hence the automated MHT method, which is now developing within the research project COLLAGE (www.collage.com.ro), will encourage conservators to adopt this method as a mainstream analytical tool for parchment and leather artifacts assessment. It provides (i) more reliable results, (ii) inter-laboratory comparison, (iii) dramatic reduction of operator's work time.

The first and second are secured by the quality of the motion algorithms producing results not influenced by human error. Besides, the operator will no longer visually analyse the records.

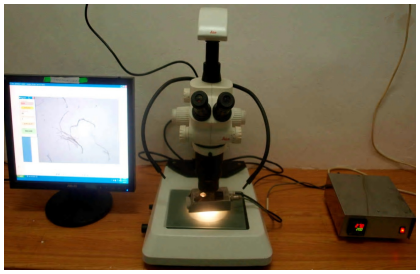

Fig. 1 *MHT equipment comprises of a steromicroscope coupled with a camera and a Hot Table equipped with a Central Processer both from Caloris (Romania).*

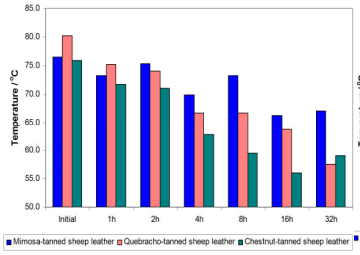

Fig. 3a *Shrinkage temperature variation for vegetable tanned leathers during UV irradiation exposure*

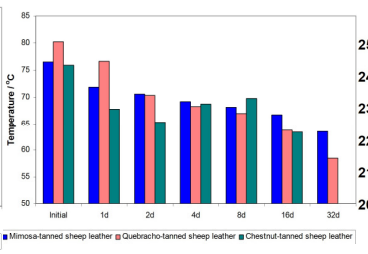

Fig. 3b *Shrinkage temperature variation for vegetable tanned leathers during heating at 80 °C iand 80% RH*

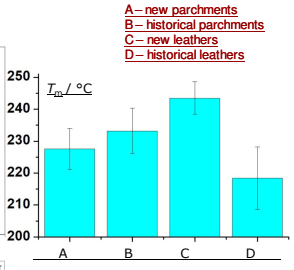

Fig. 5 *Melting temperature of collagen crystalline fraction for new and historical leathers compared with new and historical parchments*

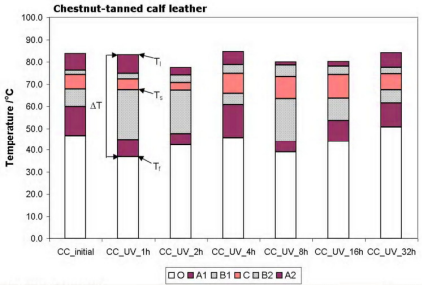

Fig. 2 *Shrinkage intervals for chestnut-tanned calf leather during UV light exposure. Shrinkage temperature T_s is defined as the start of C interval. T_f is the temperature at which the very first fibre motion is observed, whereas T_l that of the very last motion observed.*

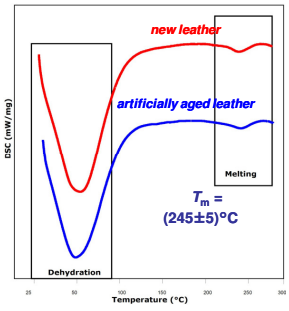

Fig. 4 *Melting temperature of collagen crystalline fraction for new (**red**) and accelerated aged (**blue**) vegetable-tanned leather*

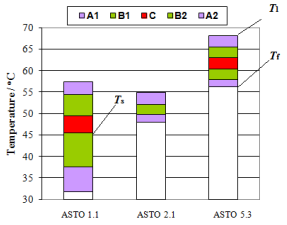

Fig. 6a *Illustration of shrinkage intervals for 3 historical parchment rolls from the State Archives of Turin (XIV-XVI century). ASTO 2.1 sample does not show the main shrinkage interval C, and thus has no defined T_s.*

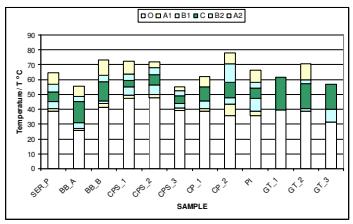

Fig. 6b *Shrinkage intervals of historical leathers from various collections*