THE INFLUENCE OF NEW PRESERVATION PRODUCTS ON VEGETABLE TANNED LEATHER FOR HERITAGE OBJECT RESTORATION

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ABSTRACT. The paper studied the effect of four materials for the preservation of collagen-based heritage objects. The products developed were applied to new leather samples treated with vegetable tanning agents such as quebracho and mimosa, which were then subjected to accelerated ageing for 24, 48 and 72 hours, at the temperature of 50°C. The effects of the new environmentally-friendly materials applied to leather were assessed according to a characterisation protocol specific for preservation and restoration of collagen-based heritage objects. The effects of the new formulations on vegetable tanned leather were assessed using the characterisation protocol that includes physical-chemical and organoleptic analyses in terms of colour change, handle, uniform spread, hydrophobisation (resistance to water drop and penetration time). Colour change was determined and assessed using Datacolor CHECK II portable spectrophotometer, and CIEL*a*b* and CIEL*C*h software, obtaining chromatic coordinates for each leather sample treated with the studied formulations. Treatments have caused some changes in leather characteristics, depending on the product applied.

KEY WORDS: vegetable tanned leather, preservation, restoration.

INTRODUCTION

Cultural heritage is an infinite source of information of historical and anthropological value. By preserving this heritage we are giving back to society a glimpse to our history and transfer our traditions to future generation. – Traditionally, conservation and restoration work was considered an empirical, handicraft activity practiced by people with manual skills who passed secret techniques and materials on to younger generations. However, under the influence of modern theories on art history and the impact of technological and scientific revolution on social life, these interventions cannot be perceived today as a process of restoration; even if they met certain requirements regarding restoration, they were not a reflection of a scientific concept.

Conservation represents the full range of measures aimed at keeping the object in good condition and maximizing its life [1]. Conservation encompasses a vast series of operations that...
do not alter the appearance of the artifact but retain its original shape.

Preventive conservation is defined by the combination of measures and indirect actions that do not interact with the physical structure of the object in question and aim at preventing the factors involved in the mechanism of deterioration processes of the object.

Active conservation is directed to the object in question, interacts with the material structure and is meant to fight the effects of physical, chemical and biological degradation.

Despite increased interest in techniques to improve conservation and decontamination, leather and parchment artifacts are not always treated with due respect and are largely neglected also because of their less interesting appearance compared to other types of artifacts.

Collagen objects and artifacts are an essential part of archival and library collections, ethnographic and military collections, furniture collections, but also of natural sciences collections (paleozoology, ornithology, mammalogy, etc.). The intrinsic resistance of historical collagenous materials determined, on the one hand, minor restoration interventions over time, and special attention in terms of aggressiveness of substances and techniques used in conservation and restoration of such objects, sometimes with dramatic consequences.

The study of deterioration mechanisms of these materials has been initiated very recently, both in European and in national studies [2-6], only in the last decade of the last century [7-8], but there are very few studies for validation of current substances, materials and protocols for conservation and restoration [9], still based on empirical knowledge, without a real scientific basis. Moreover, products for the conservation and restoration of collagen, especially leather and parchment, specified in the guidelines elaborated by the national institutions responsible for protecting cultural heritage [10, 11], are natural products (whose use has been perpetuated by tradition, but has not yet been validated by scientific methods) and synthetic substances (solvents, adhesives, insecticides and fungicides) created for the industry, which were adopted by restorers for lack of anything more appropriate or created specifically for their field.

The effect of conservation-restoration materials was analyzed in various specialized studies [12-16]. Rushdya Rabee Ali Hassan [15] evaluated the effect of linseed oil and glycerine emulsion for surface treatment on the chemical composition of archaeological leather samples, which were taken from a historical leather book cover. The samples were treated with a linseed oil emulsion (7 g glycerine, 20 ml linseed oil, 5 g cetyl alcohol, 5 g stearic acid, 100 ml distilled water) and were then visually evaluated, pH value was measured, thermal analysis (TGA) and infrared spectroscopy (FTIR) were used and physical-mechanical studies were conducted to determine structural and chemical differences between treated and untreated leather samples. Research has shown that there were no major changes in functional groups on the surface of leather, monitored by infrared spectroscopy; pH values showed that the emulsion led to improvements by reducing the acidity of the treated leather, also improving thermal and mechanical properties of treated samples.

Flavia Pinzari et al. [16] conducted a study of biodeterioration on a parchment representing an ancient manuscript. To observe the physical and chemical changes that occur in a parchment infested with bacteria and fungi, analyses (SEM-EDX) were performed and purple spots caused by bacterial attack were noticed.

In the paper “Evaluation of consolidants for the treatment of red rot on vegetable tanned leather: the search for a natural material alternative” [13], C.C. Mahony compares four consolidants: Cellugel, Klucel G with acrylic wax (SC6000), neri (consolidant extracted from aibika plant roots, traditionally used in the manufacturing of Japanese paper) and chitosan to assess their impact on vegetable tanned leather objects that had undergone red rot degradations (acid degradation of leather tanned with vegetable extracts, attacked by “red rot”). Compared to oxidative degradation of vegetable tanned leather, this acid degradation is much faster and more aggressive. Damaged leather shows low hydrothermal resistance and stability, acidity of the leather increases, often reaching pH values in the range of 3.0-4.0.

**EXPERIMENTAL PART**

**Materials**

In order to test new materials for the conservation of collagen-based heritage objects, new leathers were tanned with vegetable tanning agents such as quebracho and mimosa.

The effect of new formulations on leather
was assessed by characteristic physico-chemical and organoleptic methods.

Technological operations were performed in the pilot station of INCERTP-I CPI on goat skins of B category, in accordance with the technological principles of patent RO122098 (2007) - “Method for producing natural leather for heritage bookbinding”. The starting point for the preliminary study was patent 127958/2016 “Active and preventive conservation product for treating heritage leather” and four new compositions were developed for preventive conservation of collagen objects, presented in Table 1.

The developed products were applied to vegetable tanned goat skin samples which were then subjected to accelerated ageing for 24, 48 and 72 hours at 50°C.

As seen in Table 1, the four variants proposed are based on natural oils (cedar, wax), natural waxes (beeswax), natural fats (lanolin), emulsifiers, solvents/thinners (distilled water, hexane) protein components (hydrolyzed collagen) and essential oils (lavender, melilot, basil).

T1.1 and T1.2 products contain no water and were made by modern principles of treating old leather objects, using only natural ingredients to ensure both penetration of treatment into leather structure and good behavior over time.

T1.3 and T2 products are water-in-oil emulsions (have low water content) that were made for uniform spreading, dermal penetration and distribution of the greasing/emulsifying active substance in the substrate.

Fatty materials were selected taking into account both the HLB value (Hydrophil-Lipophil Balance) indicating material affinity to fat and water, and the surface electrical charge of the material to be treated (old leather objects).

In creating formulations for conservations, the principles of obtaining cationic, anionic, amphoteric and “multicharge” emulsions (combining compatible anionic and cationic oils) were taken into account.

**Characterisation Protocol**

The protocol for characterization and assessment of the effects of new environmentally-friendly materials applied on leather samples was carried out after accelerated ageing at different time intervals, namely 24, 48 and 72 hours.

This characterization protocol included the following:
- Assessment of grain handle;
- Uniform spreading/penetration of materials;
- Emulsification / softness;
- Hydrophobisation;
- The degree of colour change.

The compositions were applied by dabbing the leather samples (Fig. 1) and, after drying and ageing, tests were performed according to established protocol.

### Table 1: Framework formulations for development of new products for conservation

| Code variations recipes | T1.1 | T1.2 | T1.3 | T2 |
|-------------------------|------|------|------|----|
| Materials used          | Basic formulation: lanolin, cedar oil, beeswax, hexane, volatile oils (melilot, basil, lavender) | T1.1+15-25% hexane | T1.1+15-25% hexane | lanolin, paraffin oil, collagen hydrolysate, wax, distilled water, triethanolamine |
|                         |      | T1.1+15-25% hexane | 2-4% emulsifier, 13-18% distilled water | |

Figure 1. Application of treatment to leather
RESULTS AND DISCUSSION

Organoleptic Assessment

To assess the degree of penetration, softening, spreading, uniformity, handle, and colour changes, assessments were conducted at various time intervals, after 1, 2, and 3 days of ageing (Table 2).

Table 2: Assessment of penetration, softening, spreading, uniformity, handle and colour change of treated leather samples

| Treatment/Observations | T1.1                          | T1.2                          | T1.3                          | T2                        |
|------------------------|-------------------------------|-------------------------------|-------------------------------|---------------------------|
| **Initial**            | Weak spreading,               | Weak spreading,               | Good spreading,               | Very good spreading,      |
|                        | Moderate penetration,         | Moderate penetration,         | Moderate penetration,         | Good penetration,         |
|                        | Sticky handle,                | Sticky handle,                | Sticky handle,                | Slightly greasy handle,   |
|                        | Weak uniformity               | Moderate uniformity           | Moderate uniformity           | Moderate uniformity       |
| **After 24 h**         | Weak spreading,               | Weak spreading,               | Good spreading,               | Very good spreading,      |
|                        | Moderate penetration,         | Moderate penetration,         | Moderate penetration,         | Very good spreading,      |
|                        | Sticky handle,                | Sticky handle,                | Slightly sticky handle,       | Dry handle,              |
|                        | Moderate uniformity           | Moderate uniformity           | Moderate uniformity           | Good uniformity           |
| **After 48 h**         | Moderate spreading,           | Moderate spreading,           | Moderate spreading,           | Very good spreading,      |
|                        | Moderate penetration,         | Moderate penetration,         | Good penetration,             | Good penetration,         |
|                        | Good uniformity,              | Good uniformity,              | Good uniformity,              | Good uniformity           |
|                        | Uniform handle,               | Uniform waxy handle           | Uniform waxy handle           | Uniform slightly greasy   |
|                        | strongly waxy                 |                               |                               | handle                    |
| **After 3 days**       | Good spreading,               | Good spreading,               | Good spreading,               | Very good spreading,      |
|                        | Good penetration,             | Moderate penetration,         | Moderate penetration,         | Good penetration,         |
|                        | Sticky handle,                | Slightly sticky handle,       | Slightly sticky handle,       | Dry handle,              |
|                        | Good uniformity,              | Good uniformity,              | Good uniformity,              | Good uniformity           |
|                        | Uniform waxy handle,          | Uniform waxy handle           | Uniform slightly waxy handle  | Uniform slightly greasy   |
|                        | Slightly intense colour       | Slightly intense colour       | Very slightly intense colour  | handle                    |

Table 2 shows that the most hydrophilic sample is T2, which fully absorbs water in 2 minutes, and hydrophobic samples are T1.1 and T1.3, with a water absorption time of 10-15 minutes. The best values for colour change after 24h were obtained for leather samples T1.1 and T1.3 tanned with mimosa and leather samples T1.2 and T1.3 tanned with quebracho, respectively. The most pronounced contrast between the control sample and the treated samples is best seen in sample T1.3.

Assessment of the Hydrophobisation Degree

The degree of hydrophobisation was assessed using standard 221, STAS 8259/3-68, which refers to the method for determining the resistance of leather to the action of water droplets in order to measure penetration time, assess colour contrast between the control sample and treated samples using the greyscale and to assess the contrast between the portion where the water drop fell and the rest of the specimen, also using the greyscale. The tested leather samples were treated with the formulations T1.1, T1.2, T1.3 and T2 and aged at 50°C. The results are shown in Figure 2 and Table 3.

Table 3 shows that the most hydrophilic sample is T2, which fully absorbs water in 2 minutes, and hydrophobic samples are T1.1 and T1.3, with a water absorption time of 10-15 minutes. The best values for colour change after 24h were obtained for leather samples T1.1 and T1.3 tanned with mimosa and leather samples T1.2 and T1.3 tanned with quebracho, respectively. The most pronounced contrast between the control sample and the treated samples is best seen in sample T1.3.

Colour Determination and Assessment

In order to determine and assess colour, leathers were measured using a portable Datacolor CHECK II spectrophotometer, equipped with software for colour measurement [17-18]. Using CIEL*a*b* and CIEL*C*h dedicated software, chromaticity coordinates were obtained for each leather sample.

The significance of the parameters is as follows:
- L* represents the lightness, the maximum value for L* is 100 (perfect white), while the minimum is 0 (perfect black);
- \( a^* \) represents the shade between green (-\( a^* \)) and red (+\( a^* \));
- the negative value of \( b^* \) is blue, while the positive one, yellow;
- \( C^* \) (chroma) provides clues on purity (higher values) or complexity (lower values) of the mixture;
- \( h \) is the hue angle, reflects the proportion of the chromatic components \( a^* \) and \( b^* \).

As Figures 3-4 show, values have a linear direction without significant changes, although the decrease of parameter \( L^* \) and increase of \( a^* \) indicate a slightly darker shade, particularly of leather treated with the formulation T1.1.

**CONCLUSIONS**

Leather conservation is a constantly changing area as new methods of research and evaluation of artifacts are developed. This research illustrates the difficulties specialists in the field are facing and the need to find new suitable materials for conservation of heritage leather objects.

Developing environmentally-friendly products for conservation and restoration of historical collagenous materials will enable a substantial reduction in exposure to risk factors for workers and the environment, limiting or eliminating the use of mixtures of chemicals responsible for possible toxic or carcinogenic effects.

As a result of experiments to obtain and use new formulations for the conservation and
Figure 3. Colour parameters for mimosa-tanned leather - treatment T1.1 (a), T1.2 (b), T1.3 (c) and T2 (d)

Figure 4. Colour parameters for quebracho-tanned leather - treatment T1.1 (a), T1.2 (b), T1.3 (c) and T2 (d)
restoration of collagen-based heritage objects the following were found:

- The proposed formulations meet the requirements of national conservation and restoration standards;

- Four variants of formulations were developed and tested (T1.1, T1.2, T1.3, T2) based on oils, natural waxes and fats, with the addition of emulsifiers, solvents, volatile oils, and protein components;

- T1.1 and T1.2 variants do not contain water;

- T1.3 and T2 variants are water-in-oil emulsions with low water content;

- All of the proposed formulation variants can be categorized as eco-friendly;

- The effects of the new formulations on leather tanned with vegetable tanning extracts were assessed using a characterization protocol that includes physical-chemical and organoleptic analyses regarding the colour changes, handle, uniform spreading, hydrophobisation degree (resistance to water droplets and time penetration). Also, colour change was determined and assessed using the portable Datacolor CHECK II spectrophotometer and CIEL*a*b* and CIEL*C*h software, yielding chromaticity coordinates of colour for every leather sample treated with the studied formulations.

- After applying the characterization protocol, T1.3 was found the best variant for the conservation of heritage leather objects.

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