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 tanned 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.

INFLUENŢA UNOR NOI PRODUSE DE CONSERVARE ASUPRA PIEILOR TĂBĂCITE VEGETAL DESTINATE RESTAURĂRII OBIECTELOR DE PATRIMONIU

REZUMAT. În această lucrare a fost studiat efectul a patru materiale destinate conservării obiectelor de patrimoniu pe suport colagenic. Produsele elaborate au fost aplicate pe eşantioane de piei noi tăbăcite cu tananţi vegetali precum quebracho şi mimoza, care apoi au fost supuse unui proces de îmbătrânire accelerată pentru 24, 48 şi 72 de ore, la temperatura de 50°C. Evaluarea efectelor noilor materiale ecologice aplicate pe piei a fost efectuată cu ajutorul unui protocol de caracterizare specific domeniului conservării şi restaurării obiectelor de patrimoniu pe suport colagenic. Evaluarea efectelor noilor recepturi asupra pieilor tăbăcite cu extracte tanante vegetale s-a realizat utilizând protocolul de caracterizare care cuprinde analize fizico-chimice şi organoleptice privind modificările de culoare, tuşeu, gradul de etalare, gradul de hidrofobizare (rezistenţa la picătura de apă şi timpul de pătrundere). De asemenea, determinarea şi evaluarea modificării culorii s-a efectuat cu spectrofotometrul portabil Datacolor CHECK II şi cu sistemul software CIEL*a*b* şi CIEL*C*h, obţinându-se coordonatele cromatice ale culorii pentru fiecare probă de piele tratată cu recepturile studiate. Tratamentele efectuate au produs unele modificări ale caracteristicilor pieilor, în funcţie de produsul aplicat.
CUVINTE CHEIE: piele tăbăcită vegetal, conservare, restaurare

L'INFLUENCE DE NOUVEAUX PRODUITS POUR LA CONSERVATION DES CUIRS AU TANNAGE VÉGÉTAL SUR LA RESTAURATION DES OBJETS DU PATRIMOINE

RÉSUMÉ. Dans ce travail, on a étudié l'effet de quatre matériaux pour la conservation des objets du patrimoine à base de collagène. Les produits développés ont été appliqués à des échantillons de cuir nouveau au tannage végétal tel que quebracho et mimosa, qui ont ensuite été soumis à un vieillissement accéléré de 24, 48 et 72 heures à 50°C. Les effets des nouveaux matériaux écologiques appliqués sur la peau ont été évalués selon un protocole de caractérisation spécifique pour la conservation et la restauration des objets du patrimoine à base de collagène. Les effets des nouvelles recettes sur le cuir tanné avec des extraits végétaux ont été évalués en utilisant le protocole de caractérisation qui inclut des analyses physico-chimiques et organoleptiques en ce qui concerne les changements de couleur, le toucher, l'étalement, le degré d'hydrophobisation (résistance à la goutte d'eau et le temps de pénétration). En outre, la détermination et l'évaluation du changement de couleur ont été réalisées avec le spectrophotomètre portable Datacolor CHECK II et le logiciel CIEL*a*b* et CIEL*C*h pour obtenir les coordonnées chromatiques de la couleur pour chaque échantillon de cuir traité avec les formulations étudiées. Les traitements ont produit des changements dans les caractéristiques du cuir, selon le produit appliqué.
MOTS-CLÉS: cuir tanné végétal, conservation, restauration

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

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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 INCDTP-ICPI 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 (Hidrophyl-Liophyl 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 mate-rials;
- 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 2-4% emulsifier, 13-18% distilled water	lanolin, paraffin oil, collagen hydrolysate, wax, distilled water, triethanolamine

Figure 1. Application of treatment to leather

RESULTS AND DISCUSSION

Organoleptic Assessment

To assess the degree of penetration, softening, spreading, uniformity, leather softness, and handle, 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

As Table 2 shows, organoleptic assessment (degree of penetration, softness, spreading, uniformity, handle and colour change) of the treated leather indicated that some treatments have produced changes in the characteristics of leathers. However, leather appearance was not altered in the case of T1.3 product composition, observing thus, the principles of conservation norms. This product can be successfully used in the conservation of heritage objects.

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, Moderate penetration, Sticky handle, Weak uniformity	Weak spreading, Moderate penetration, Sticky handle, Moderate uniformity	Good spreading, Moderate penetration, Sticky handle, Moderate uniformity	Very good spreading, Good penetration, Slightly greasy handle, Moderate uniformity
After 24 h	Weak spreading, Moderate penetration, Sticky handle, Moderate uniformity	Weak spreading, Moderate penetration, Slightly sticky handle, Moderate uniformity	Good spreading, Moderate penetration, Slightly sticky handle, Moderate uniformity	Very good spreading, Good penetration, Dry handle, Good uniformity
After 48 h	Moderate spreading, Moderate penetration, Good uniformity, Uniform handle, strongly waxy	Moderate spreading, Moderate penetration, Good uniformity, Uniform waxy handle	Good spreading, Moderate penetration, Good uniformity Uniform waxy handle	Very good spreading, Good penetration, Good uniformity Uniform slightly greasy handle
After 3 days	Good spreading, Good penetration, Sticky handle, Good uniformity, Uniform waxy handle, Slightly intense colour	Good spreading, Moderate penetration, Slightly sticky handle, Good uniformity, Uniform waxy handle, Slightly intense colour	Good spreading, Moderate penetration, Slightly sticky handle, Good uniformity Uniform slightly waxy handle, Very slightly intense colour	Very good spreading, Good penetration, Dry handle, Good uniformity Exudate handle, but with powdery surface Very slightly intense colour

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);

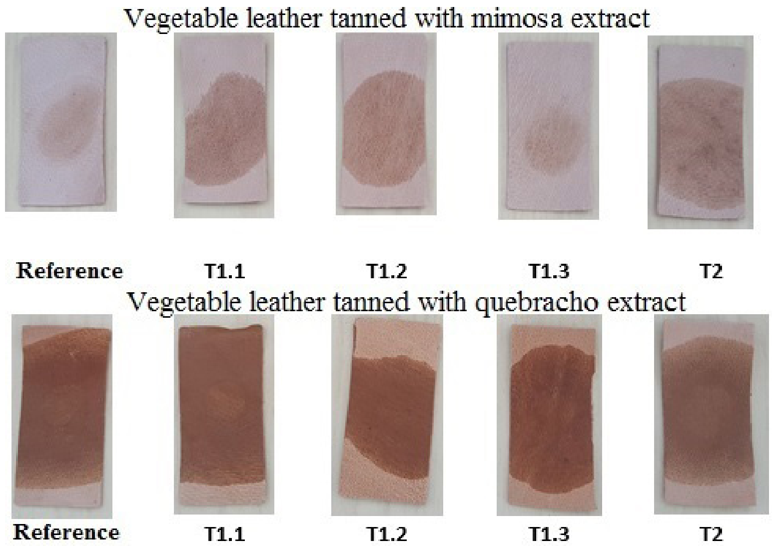

Figure 2. Leather samples during hydrophobisation degree determination

Table 3. Hydrophobisation degree assessment tests

Treatment/Characteristics	Reference	T1.1	T1.2	T1.3	T2	/UM
Leather tanned with mimosa extract						
Penetration time (STAS 8259/3-68)	1	15	10	4	2	min
Initial colour change, contrast between control sample and treated samples	-	2	2	1/2	2/3	Marks 1-5
Colour change after 24 h, contrast between drop mark and the rest of the sample	3	4/5	4	4/5	4	Marks 1-5
Leather tanned with quebracho extract						
Penetration time (STAS 8259/3-68)	2.5	9	10	5	1,5	min
Initial colour change, contrast between control sample and treated samples	-	3/4	2/3	1	4	Marks 1-5
Colour change after 24 h, contrast between drop mark and the rest of the sample	4/5	3	4/5	3/4	3/4	Marks 1-5

- 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

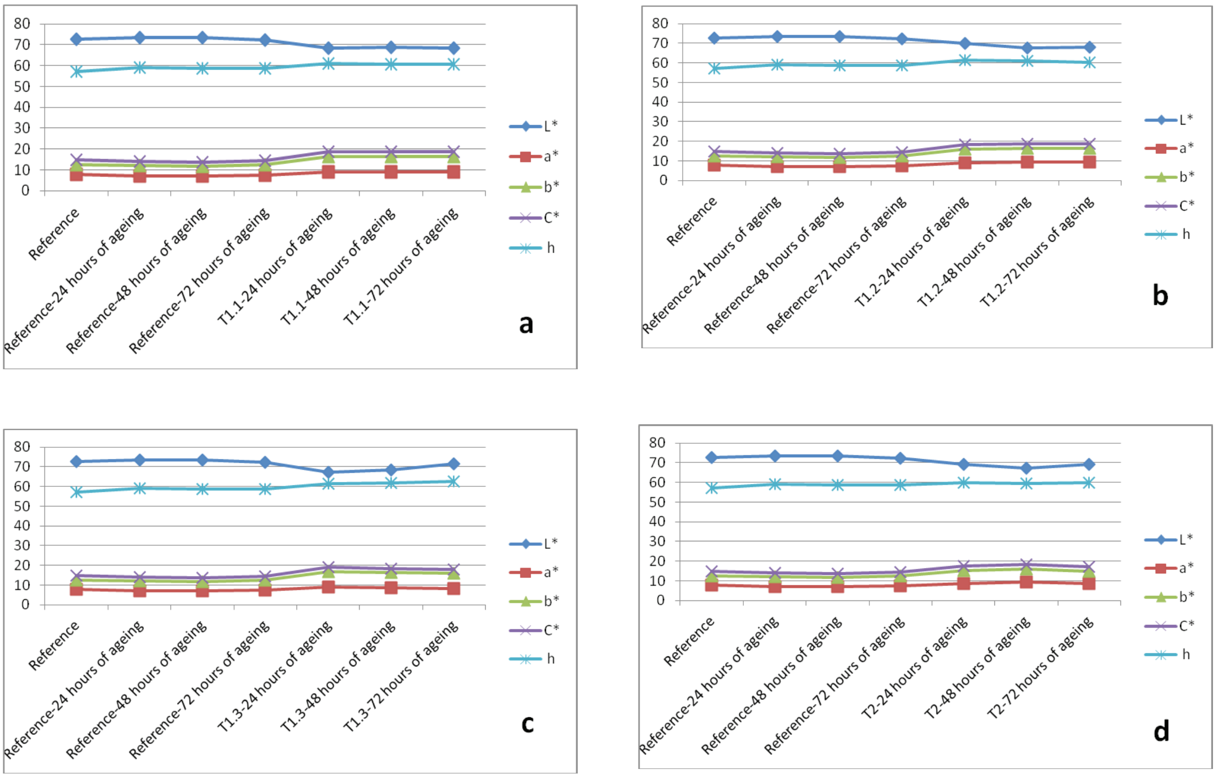

Figure 3. Colour parameters for mimosa-tanned leather - treatment T1.1 (a), T1.2 (b), T1.3 (c) and T2 (d)

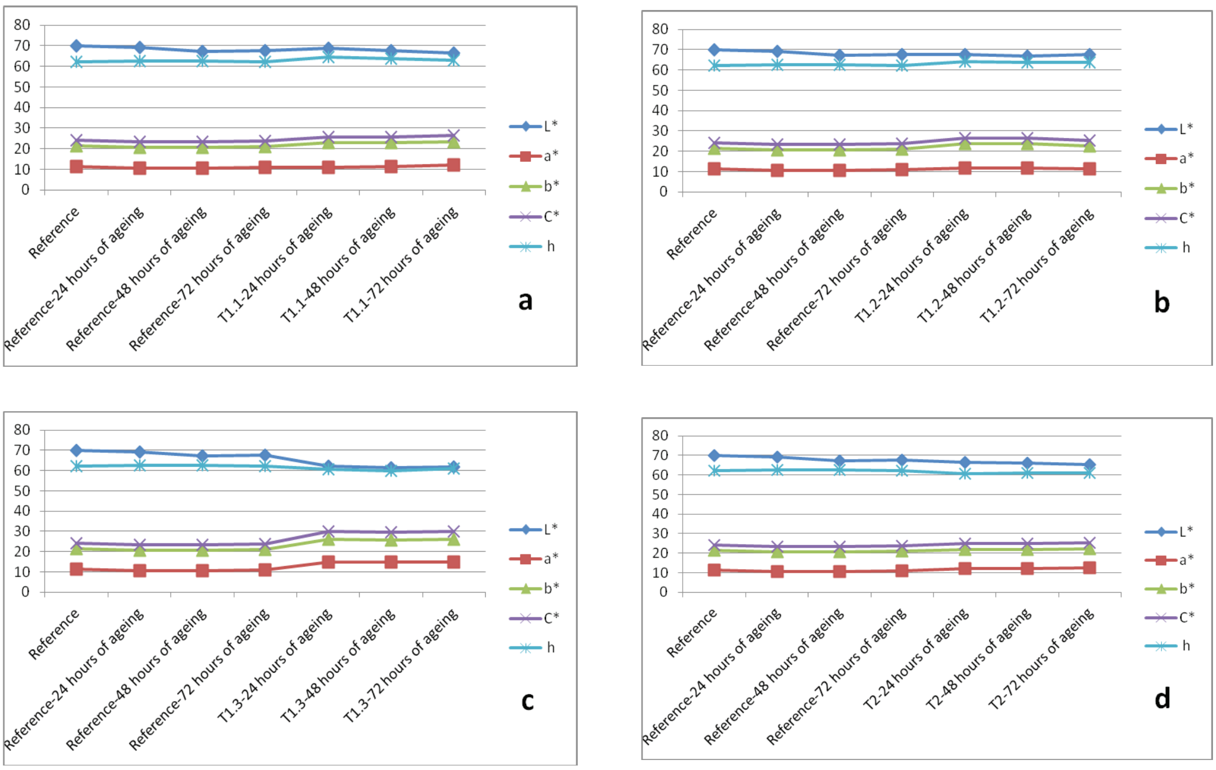

Figure 4. Colour parameters for quebracho-tanned leather - treatment T1.1 (a), T1.2 (b), T1.3 (c) and T2 (d)

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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