CHEMICAL AND PHYSICO-MECHANICAL CHARACTERIZATIONS OF LEATHER FOR RESTORATION

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Leather is a complex material mostly consisting of a matrix of collagen, chemically stabilized by various tannins. This matrix, sooner or later undergoes alterations as a consequence of interactions between their structure and environment. A comprehensive study based on multiple chemical and physico-mechanical standard tests regarding leather samples which were artificially aged from 7 to 112 days has been made at 70°C. The behavior in artificial aging of calf leather samples tanned at pilot level with two different vegetal tannins, mimosa and quebracho, were investigated due to its similarity to the natural degradation of historical leather samples. Physico-mechanical characteristics of historical leather can be correlated with the high impact of degree of deterioration even though there are no standard regulations. To be able to choose the proper way to achieve compatibility with an appropriate material in the restoration-conservation process, multiple sample characteristic must be known. The condition of historical leather can be assessed by a series of simple visual and physical examinations which determine the flexibility, strength and coherency of the fibers and then correlate these assessments with the condition of leather as determined by various chemical and physical-chemical analyses. Therefore, the following chemical standard tests were made: volatile substances, shrinkage temperature, extractable substances, total soluble substances and the following physico-mechanical tests: tensile strength, elongation at breaking and tear resistance.

Keywords: artificially aged leather, physico-mechanical and chemical analysis, deterioration.

INTRODUCTION

The term tannin is used for a number of compounds widely used in the plant regna. Tannins have the property of turning raw skin into tanned leather. Tanning substances consist of fairly large molecules with a high molecular weight, although it is debatable whether they can be considered as macromolecular substances that can be fragmented. (Chiriță and Chiriță, 1999).

New and artificially aged leathers are complex systems, due to the number of components introduced in the processing. For this reason, their analysis must take into account the fact that it is a system consisting polymer matrix (collagen) to which are added solid and liquid substances dispersed or dissolved in the substrate and which, in different stages of processing, interact between each other. (Miu *et al.*, 2007; Sendrea *et al.*, 2017).

In addition, due to the intervention of environmental (temperature, humidity, light, pollution), biological (bacteria, fungi, rodents, insects), and chemical (acids, bases, oxygen, ozone, ultraviolet radiation) factors, many structural changes happen and they must be known from a scientific point of view, in order to achieve compatibility with an appropriate material in the restoration-conservation process (Sebestyén *et al.*, 2015).

In museums there are a multitude of leather heritage objects in various degrees of damage. To restore these artifacts, museums need leathers processed according to traditional methods from the International Conservation and Restauration Standards (ENVIRONMENT Leather Project; Meghea *et al.*, 2002; Badea *et al.*, 2012).

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METHODS & ANALYSIS

For this study, calf hides were processed at pilot level in INCDTP-ICPI. The technological process included the specific operations of the usual leather processing. The tanning of the leather was done with 15% vegetable tanning extracts of mimosa and quebracho.

The main chemical characteristics are presented in Table 1.

Table 1. Chemical characteristics of new leathers

Sample code [tanning]	Humidity, %	Ash, %	Extractable substances, %	Dermal substance, %	Organic soluble substances, %
VM [mimosa]	14.1	0.8	9.6	66.8	4.2
VQ [quebracho]	14.8	1.2	8.7	67.1	5.8

The samples of newly processed leathers, artificially aged, were analyzed according to the actual standards specific to vegetable and/or tanned leathers.

It is found that all the determined characteristics fall within the admissible limits, including the pH of the aqueous extract, which has values in the range 4.1-5.8.

Aging behavior tries to simulate a degradation over time, similar to the natural degradation of heritage leather. According to numerous studies performed on various skin types, the temperature of 70°C was selected as the most suitable for performing accelerated aging. For this purpose, VM and VQ were selected to be aged for 7-112 days at 70°C (Table 2).

Table 2. Tanned leathers with tanned vegetable extracts subjected to artificial aging

No.	Sample code	Sample, aging time
1	VM_0 (initial)	Calf leather tanned with mimosa, not subject to aging
2	VM_7	Calf leather tanned with mimosa, aging 7 days
3	VM_14	Calf leather tanned with mimosa, aging 14 days
4	VM_21	Calf leather tanned with mimosa, aging 21 days
5	VM_28	Calf leather tanned with mimosa, aging 28 days
6	VM_56	Calf leather tanned with mimosa, aging 56 days
7	VM_112	Calf leather tanned with mimosa, aging 112 days
8	VQ_0 (initial)	Calf leather tanned with quebracho, not subject to aging
9	VQ_7	Calf leather tanned with quebracho, aging 7 days
10	VQ_14	Calf leather tanned with quebracho, aging 14 days
11	VQ_21	Calf leather tanned with quebracho, aging 21 days
12	VQ_28	Calf leather tanned with quebracho, aging 28 days
13	VQ_56	Calf leather tanned with quebracho, aging 56 days
14	VQ_112	Calf leather tanned with quebracho, aging 112 days

For the aged leather samples, the chemical characteristics which may suffer changes due to the accelerated aging process were determined, such as: volatiles, extractable substances, free fatty acids, total soluble substances, mineral soluble substances, organic soluble substances and shrinkage temperature. The values obtained for the samples of calf leather (VM, VQ) tanned with vegetable tannins are shown in Fig.1 and Fig. 2.

Physico-chemical characteristics of aged samples, compared to the initial ones:

Figure 1. Variation of volatile compounds (a.) and extractable substances (b.)

Figure 2. Shrinkage temperature variation (c.) and variation of total soluble substances (d.)

Comparing the values of the chemical characteristics obtained for the samples of tanned calf leather with those obtained for the leathers aged at 56 days and 112 days, significant decreases in the content of volatiles and extractable substances can be observed, and the most affected is the shrinkage temperature, which shows a very accelerated decrease in the treatment of 112 days of aging.

Decreasing the content of extractable substances during accelerated aging leads to impairment of physical and mechanical characteristics (traction, tearing).

Also, the decrease of the content of total soluble substances in aged leathers denotes the involvement of tanning and lubricating materials by their binding in interfibrillary networks with the impairment of hydrogen or covalent bonds, which leads to decreased leather strength properties.

PHYSICAL-MECHANICAL ANALYSIS

The samples were analyzed from a physical-mechanical point of view, and the results are presented in Table 3.

Table 3. The main physical-mechanical characteristics of new leathers

Sample code [tannin]	Sample code	Tensile strength at tearing, N/mm ²	Elongation at breaking, %	Tear resistance, N/mm
VM [mimosa]	VM	20.9	53	86.7
VQ [quebracho]	VQ	16.6	53	102.6

Dimensional change, tensile strength (N/mm²), elongation at breaking (%) and tear resistance (N/mm) were determined. Examination of the data (Figures 3 and 4) shows:

- dimensional change, %: after 1-6 cycles (Figure 3) at 7 days there are no changes, and at the end of the experiment there are accentuated dimensional changes especially for the surface of the specimen (contraction of up to 8% at 112 days in the VM test) and its thickness (dimensional increase, maximum 3% for the VM sample).

Figure 3. Dimensional changes of aged leather samples (a.-f.)

- the tensile behavior at break (N/mm^2), elongation at break (%) and tear (N/mm), after 1–6 cycles of accelerated aging in the oven at 70°C is shown in Figure 4.

Figure 4. Physical-mechanical characteristics of calfskin (a.-c.)

According to the presented data, regarding the tensile strength, for the VM test an almost constant behavior is observed during the six aging cycles. The VQ sample registers a decrease of the resistance compared to the initial sample during the period 7-21 days (of 11-25%), and in the interval 28-112 days a minimal fluctuation is observed.

The elongation at breaking of the VM sample has an almost constant behavior over the 28 days, while at 56 days and 112 days it showed an increase of up to 61%. A similar behavior with the VM sample can be observed in the case of the VQ sample.

The tear strength of the samples shows some fluctuations throughout the period, without significant losses.

CONCLUSIONS

The same types of samples were subjected to accelerated aging for 7-112 days, at 70°C, and the samples of tanned leather with plant extracts of mimosa and quebracho did not have considerable different behaviors during the aging process, in terms of chemical analysis or physical-mechanical resistance. From the presented data result a certain scattering of the values obtained due to the fact that for the historical leathers there is no regulation of the physical-mechanical characteristics. This diversity of values can be attributed both to the complex technologies applied and to the structural (native) variety of calfskin.

Both types of leather correspond to restauration activity.

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