THE BEHAVIOR OF SHEEP LEATHER PARCHMENT TO ARTIFICIAL AGEING

Lucreția MIU[1*], Elena BADEA[1,2], Claudiu ŞENDREA[1], Maria-Cristina MICU[1], Simona Maria PĂUNESCU[1], Iulia Maria CANIOLA[1]

[1]INCDTP – Division: Leather and Footwear Research Institute, 031215 Bucharest, Romania, lucretia.miu@icpi.ro

[2]Department of Chemistry, Faculty of Sciences, University of Craiova, Calea Bucureşti 107 I, 200585 Craiova

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ABSTRACT. Parchment used for restoration, book binding and art requires special performance on physical-chemical, organoleptic and aesthetic characteristics, but also good long-term stability. In this sense, the parchment is ecologically processed, with features that ensure firmness, fullness, light resistance, dimensional stability, thermal stability, malleability, flexural/pressure bending resistance. For a good behaviour in time and to artificial ageing, it is found that in the case of parchments made/obtained from sheepskin, the fat or volatile matter content must be as low as possible. The parchment with these qualities allows for the creation of new covers or historical replicas, complements for the integration of old covers, hot and/or cold stamping modelling, incision, entrainment, deposition of gold and silver foil, colouring and decoration with pigments and dyes. Some niche areas such as book bindings and art require a dedicated craftsmanship that promotes the survival of artisanal forms of production and the perpetuation of local creativity and identity. The parchments have undergone artificial ageing treatments based on the concomitant action of temperature and relative humidity for up to 16 days. Chemical (volatile matter, extractable substances, total ash, total nitrogen, dermal) and physical-chemical (measurement of colour variation and shrinkage temperature) analyses were performed to evaluate colour parameters and collagen hydrostability. The fat content of the parchment leads to oxidation reactions that cause the bathochromic effect, closing the colour, but also the deterioration over time of the fibrillar structure by depreciating the contraction temperature.
KEY WORDS: parchment, heritage object, colour change

COMPORTAMENTUL LA ÎMBĂTRÂNIRE ARTIFICIALĂ A PERGAMENTULUI DIN PIELE DE OAIE

REZUMAT. Pergamentul utilizat pentru restaurare, legătoria de patrimoniu și de artă necesită performanțe speciale privind caracteristicile fizico-chimice, organoleptice și estetice, dar și o bună stabilitate pe termen lung. În acest sens, pergamentul se prelucrează ecologic, cu caracteristici care asigură proprietăți de fermitate, plinătate, rezistență la radiațiile luminoase, stabilitate dimensională, stabilitate termică, maleabilitate, rezistență la flexiune/îndoire sub presiune. Pentru o bună comportare în timp și la îmbătrânire artificială se constată că în cazul pergamentelor realizate/obținute din piei de oaie, conținutul în grăsime sau materii volatile trebuie să fie cât mai mic. Pergamentul cu aceste calități permite realizarea de coperți noi ori replici istorice, completări pentru integrarea coperților vechi, modelare prin poansonare tip timbru sec la cald și/sau la rece, incizare, intarsie, depunere de foiță de aur și argint, colorare și decorare cu pigmenți și coloranți. Pergamentele au fost supuse unor tratamente de îmbătrânire artificială bazate pe acțiunea concomitentă a temperaturii și a umidității relative timp de până la 16 zile. S-au efectuat analize chimice (materii volatile, substanțe extractibile, cenușă totală, azot total, substanță dermică) și fizico-chimice (de măsurare a variației culorii și temperaturii de contracție) pentru evaluarea parametrilor de culoare și a hidrostabilității colagenului. Conținutul de grăsime din pergament conduce la reacții de oxidare care favorizează efectul batocrom, de închidere a culorii, dar și deteriorarea în timp a structurii fibrilare prin deprecierea temperaturii de contracție.
CUVINTE CHEIE: pergament, obiecte de patrimoniu, modificarea culorii

LE COMPORTEMENT AU VIEILLISSEMENT ARTIFICIEL DU PARCHEMIN EN CUIR DE MOUTON

RÉSUMÉ. Le parchemin utilisé pour la restauration, la reliure héritage et des œuvres d'art nécessite des performances particulières en ce qui concerne les caractéristiques physico-chimiques, mécaniques, organoleptiques et esthétiques, mais également une bonne stabilité à long terme. Dans ce sens, le parchemin est traité de manière écologique, avec des caractéristiques qui assurent les propriétés de fermeté, de plénitude, de résistance au rayonnement lumineux, de stabilité dimensionnelle, de stabilité thermique, de malléabilité, de résistance à la flexion sous pression. Pour un bon comportement dans le temps et un vieillissement artificiel, on constate que dans le cas de parchemins réalisés/obtenus à partir de peau de mouton, la teneur en matières grasses ou en matières volatiles doit être la plus faible possible. Ces qualités permettent la création de nouvelles couvertures ou de répliques historiques, des ajouts pour l'intégration des anciennes couvertures, la modélisation par poinçonnage à chaud et à froid, la gravure, la marqueterie, le dépôt de feuille d'or et d'argent, coloration et décoration avec des pigments et des colorants. Les parchemins ont été soumis à des traitements de vieillissement artificiels basés sur l'action concomitante de la température et de l'humidité relative pendant 16 jours. Des analyses chimiques (matières volatiles, substances extractibles, cendres, azote total, substance dermique) et physico-chimiques (pour la mesure de la couleur et de la température de retrait) ont été effectuées afin d'évaluer les paramètres de couleur et l'hydrostabilité du collagène. La teneur en matière grasse du parchemin conduit à des réactions d'oxydation qui favorisent l'effet bathochrome, assombrissant, mais aussi endommagent dans le temps la structure fibrillaire en dépréciant la température de retrait.
MOTS-CLÉS : parchemin, objets de patrimoine, changement de couleur

* *Correspodence to: Lucreția MIU, INCDTP – Division: Leather and Footwear Research Institute, 031215 Bucharest, Romania, lucretia.miu@icpi.ro*

INTRODUCTION

Roman historian Plinius reports that the origin of the use of parchment as a support for writing is attributed to the existing cultural competition between the king of Pergamon (now Turkey), Eumenes II (197-159 BC) and Ptolemy V of Egypt. The king of Egypt, fearing that Eumenes II will create a library that could overshadow the fame of Alexandria, suspended the export of papyrus. The king of Pergamon was forced to find alternative writing materials; this is supposed to have led to the invention of the parchment [1]. The parchment was mainly used for writing, initially on rolls - as is still the case in Israel - and from the second-century in the form of a book. The advantages of this material relative to the other supports was its durability, whiteness and flexibility. In addition, the processed skin absorbs less ink than the papyrus and could be written on both sides, the corrections were lighter, and several parchments could be sewn together; for these reasons, the use of parchment as a support for writing has become more and more frequent. Thus, parchment was the main support for writing from the Roman Empire to the Middle Ages. The development of the Christian Church played a fundamental role in its adoption throughout Europe. It is supposed that between the tenth and the sixteenth centuries, the use of parchment was predominant in Europe and its production qualities were the best. During this period, parchment was used for ecclesiastical texts, for legal and financial records, and for royal courts and for book covers [2-6].

Heritage objects from parchments kept in old monasteries, libraries, archives and museums are most often exposed to uncontrolled environmental conditions. Unsuitable environmental conditions are a serious threat for the artefacts' conservation and greatly reduce their lifespan as frequently the induced damage may remain invisible for a long period, while the inner structures may already have been seriously weakened. Therefore, their conservation condition requires a strict monitoring.

Parchment preservation has been an important concern in the work of modern researchers and conservators. There are numerous studies in literature [7-16] of artificial ageing that contain information about the various structural damages that occur in parchment. These are highlighted through complex micro-destructive or non-destructive analyses. Moreover, Ghioni *et al.* [17] show, by complex methods (X-ray diffraction, gas chromatography, solid state NMR), that the fats (lipid fraction) of the parchments causes in time the deterioration of the hierarchical structure of collagen. Compared to the data presented in the literature, this study brings in addition to accelerated ageing, a correlation of the amount of fat from parchments with the decrease of their shrinkage temperature but also a change of colour.

EXPERIMENTAL

For this study, 5 parchments were prepared at the Leather and Footwear Research Institute (ICPI), Division of the National Research and Development Institute for Textiles and Leather (INCDTP), Bucharest. The sheepskins were processed according to a traditional recipe of obtaining parchment. The skins preserved by salting were soaked in clean water of about 22°C to rehydrate the skins to a minimum, at least equal to the time of skinning. After soaking and fleshing, the recipe is using solution of lime for 3-4 days for removal of hair. The fleshing operation is used before the second liming operation (2-3 days). Then, other operations are deliming, washing and at the end the skin is stretched tensioned on a wooden frame and left to dry [18-20]. Frequently, during the processing of the sheepskins, the entire amount of fat cannot be removed because the fibrillar structure of the dermis is very fine and dense (it also depends on the breed of the animal, the type and state of preservation of the raw hides).

Samples were cut from the sheep parchments (Table 1) from the spine area and marked from 1 to 5, i.e. S1, S2, S3, S4 and S5. The parchment samples underwent artificial ageing treatments based on synergic action of relative temperature and humidity. The artificial ageing treatments have the following parameters:

- Duration: one day, 2 days, 4 days, 8 days and 16 days;
- Temperature: 85°C;
- Relative humidity: 60%.

The samples exposed to the artificial ageing treatment were subjected to chemical tests, shrinkage temperature and colour determination and assessment.

Chemical characteristics were determined according to standardised methods for obtaining volatile matter, extractable substances, total ash, total nitrogen and dermal substances [21-24].

Shrinkage activity was evaluated using a recently developed automated instrument (imageMHT) incorporating image analysis and diagnostic software [25]. The fibres samples, about 0.1-0.2 mg, taken from the corium side, were conditioned with demineralized water, for 10 minutes on a concave microscope glass. After separation of the skin fibers, the glass covered with a cover glass was inserted into the hot table and heated. The temperature rise rate was kept constant (2°C/min), and the maximum temperature level was set at 100°C. Collagen fibres' shrinkage activity was recorded and the Ts was measured. By heating in water, the fibers contract in different temperature intervals, their contraction depends on the quality and the degree of deterioration of the collagen structure.

In order to determine and assess colour changes, parchment samples were measured using a portable Datacolor CHECK II spectrophotometer, equipped with software for colour measurement [26, 27]. Using CIEL*a*b* and CIEL*C*h dedicated software, chromaticity coordinates were obtained for each parchment 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;

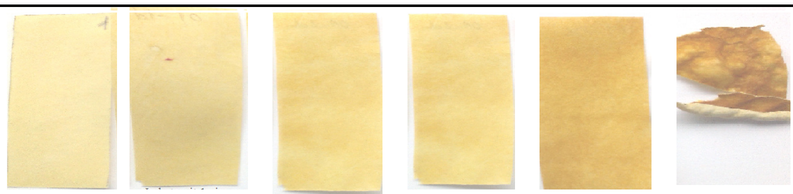
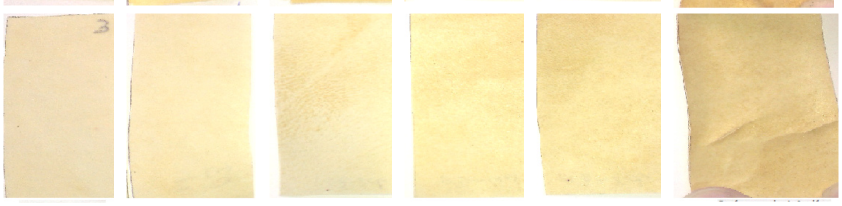
- C* (chroma) provides clues on purity (higher values) or complexity (lower values) of the mixture;

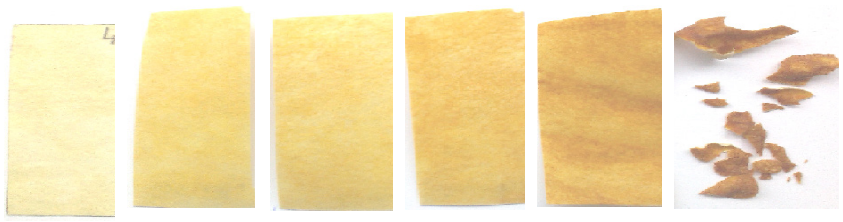
- h is the hue angle, reflects the proportion of the chromatic components a* and b*.

RESULTS AND DISCUSSIONS

The behaviour of the parchment samples after the artificial ageing cycles can be seen in Table 1.

Table 1: Images of S1-S5 sample parchments before and after ageing cycles

No.	Initial parchment	Artificially aged parchment 1 day	2 days	4 days	8 days	16 days
Sheep 1						
Sheep 2						
Sheep 3						

No.	Initial parchment	Artificially aged parchment 1 day	2 days	4 days	8 days	16 days
Sheep 4						
Sheep 5						

Any changes that occur in the parchment during the technological process are related to the changes that occur in its constituent substances. Therefore, in order to understand the processes, the chemical composition of the parchment and the properties of its component parts must be known. With the help of chemical analysis, the following can be determined directly or indirectly: volatile matter and values for total ash, total nitrogen and dermal substances.

Table 2: Chemical characteristics of sheep parchments

No.	Characteristics	MU	Sample code/Values S1	S2	S3	S4	S5	* Uncertainty	Method Standard
1	Volatile matter	%	13.89	15.09	14.72	14.43	13.70	± 0.42	SR EN ISO 4684 – 2006
2	Extractable substances	%	6.61	2.39	3.69	5.83	8.81	± 0.87	SRENISO 4048 – 2008
3	Total ash	%	7.30	4.27	5.61	4.22	4.83	± 0.27	SR EN ISO 4047 – 2002
4	Total Nitrogen	%	15.29	14.76	14.38	14.48	14.42	± 0.66	SR ISO 5397 – 1996
5	Dermal substance	%	89.45	86.35	84.12	84.71	84.36	± 2.26	SR ISO 5397 – 1996

**Values for extracts are reported as free from volatile matter and values for total ash, total nitrogen, dermal substances are reported as free from volatile matter and extracts.*

From Table 2 it is observed that the big value variations of extractable substances, and the samples S1, S4 and S5 presents bigger amounts than S2 and S3 samples. The other chemical characteristics have similar values.

The variation of the shrinkage temperature is shown in Fig. 1.

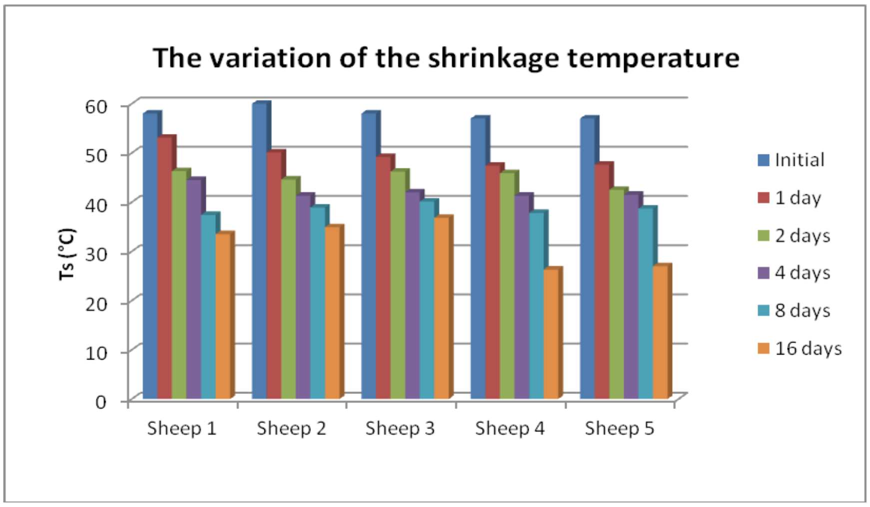


Figure 1. Variations of the shrinkage temperature after the ageing treatments

Shrinkage temperatures, Ts, showed a rather good hydrothermal stability for the untreated parchment samples, in good agreement with the data in the literature [15]. All samples show a major decrease of 5-9°C in the shrinkage temperature after a day of artificial ageing. In the following periods/ageing cycles, an approximately linear decrease of the shrinkage temperature is observed, by approximately 3-4°C. After the ageing period of 16 days at 80°C and RH 60%, there is an accentuated decrease of the shrinkage temperature for samples S4 and S5, according to Fig. 1 and at the same time, the images presented in Table 1.

The variations of the a* parameter is reported in Table 3 and in Fig. 2.

Table 3: Colour values of a* parameter for sheep parchments

Sample/Days of ageing	S1	S2	S3	S4	S5
			Parameter: a		
0-Initial	-0.28	-0.08	-0.18	-1.29	-1.09
1 day	2.36	4.15	-0.11	3.95	5.49
2 days	3.63	5.43	1.78	4.52	6.35
4 days	6.07	10.16	2.44	5.47	9.28
8 days	11.39	10.74	5.35	12.96	14.9
16 days	11.13	10.27	5.25	15.73	13.87

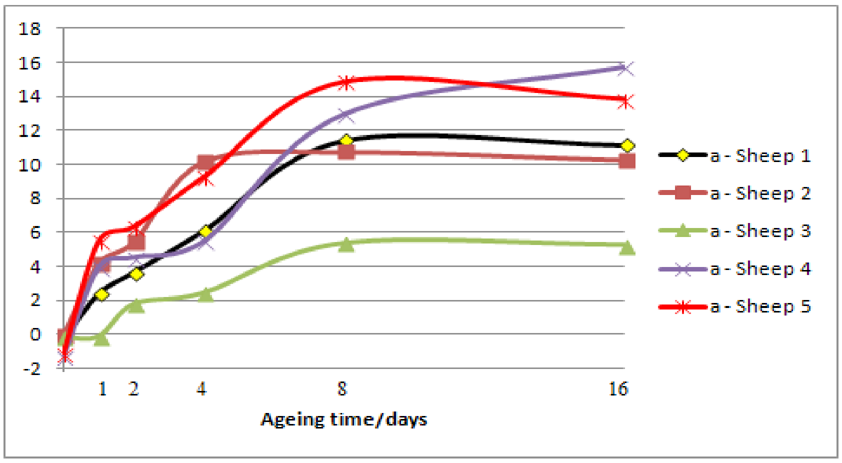


Figure 2. Variations of the a* parameter after the ageing treatments

According to Fig. 2, the smallest changes of the parameter a* were obtained for samples S3 and S2, both at 8 days and at 16 days of artificial ageing. For samples S1, S4 and S5 there is an intensification of the colour from yellowish white in initial state to creamy yellow after 4 days, and after 8 and 16 days to brownish cream, simultaneously with the deformation, embrittlement and rupture of the samples.

For the other measured colour parameters changes are presented in Fig. 3, 4, 5 and 6.

The variation of the colour parameter b* (from blue to yellow) during artificial ageing is shown in Fig. 3.

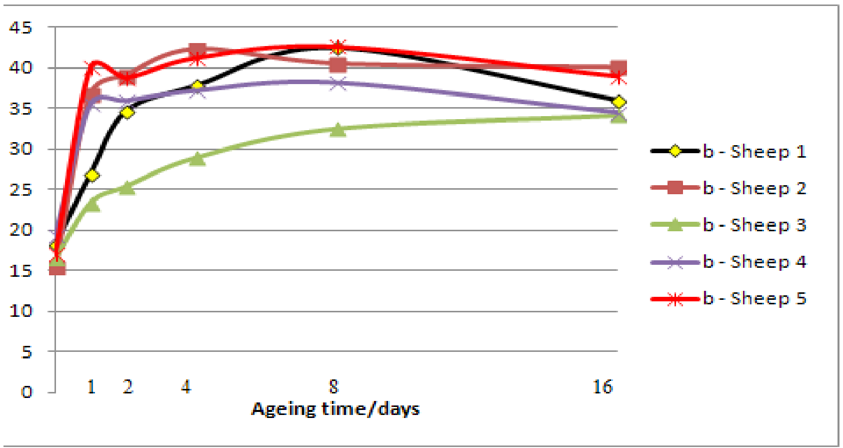


Figure 3. Variations of the b* parameter after the ageing treatments

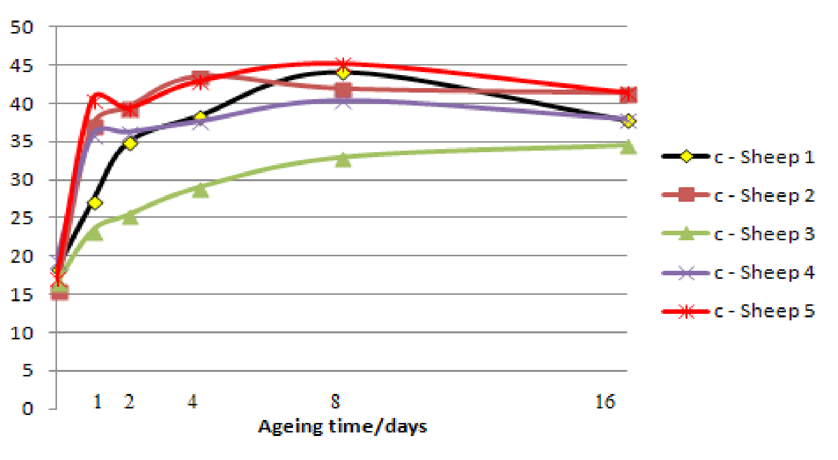


Figure 4. Variations of the c* parameter after the ageing treatments

The variations of the c* parameter after the ageing treatments is reported in Fig. 4.

From Fig. 4 it is observed that the best behaviour, from the point of view of c* parameter, is shown by sample S3, which has a small increase. Also, the significant growth takes place in the first period of artificial ageing, respectively after 1 day to 4 days inclusive.

The variations of the h parameter after the ageing treatments is reported in Fig. 5.

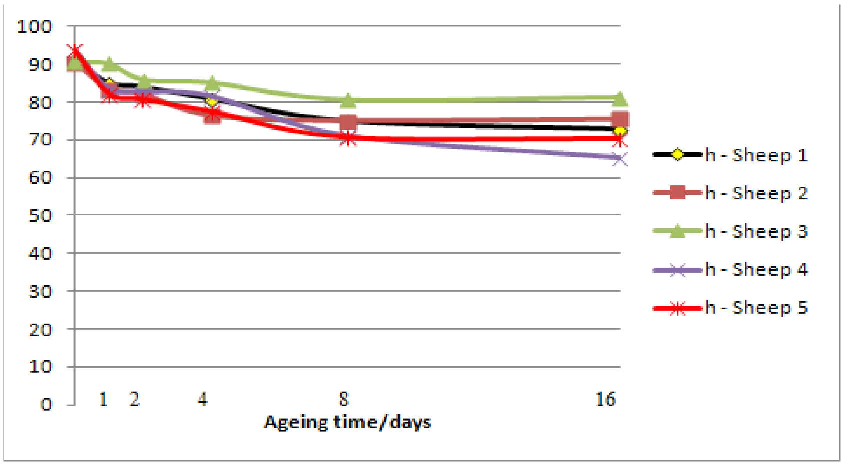


Figure 5. Variations of the h parameter after the ageing treatments

Fig. 5 shows that the parameter h for samples S2 and S3 has the smallest changes, which attests the good behaviour of these parchments during artificial ageing. The variations of the L parameter after the ageing treatments is reported in Fig. 6.

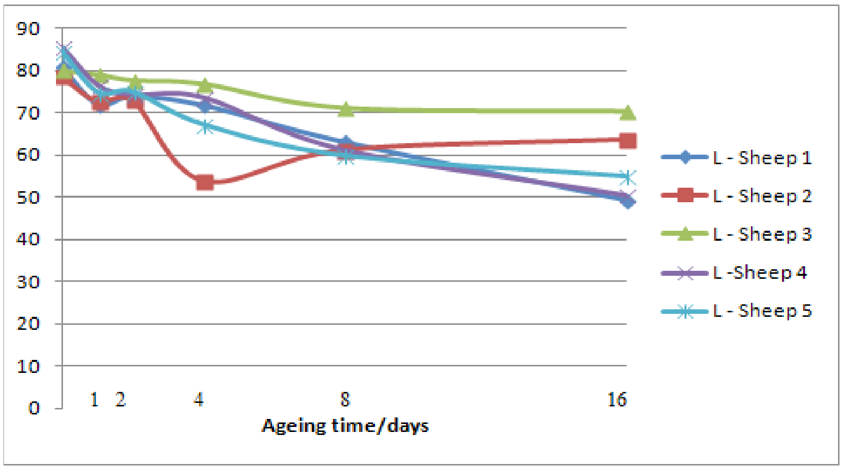


Figure 6. Variations of the L parameter after the ageing treatments

And from Fig. 6, as in the case of Fig. 5, it is observed that parameter L for samples S2 and S3 has the smallest changes after 16 days of artificial ageing, which confirms the good behaviour of these parchments during artificial ageing.

Because the 5 parchments obtained from 5 sheepskins were processed by the same process, it was expected that the results would show the same trend. However, the results obtained by evaluating the shrinkage temperature and colour parameters, resulted in a different behaviour after artificial ageing. This required correlations in terms of volatile matter (especially fats) and parchment's thickness. From our practice, it is known that the "quality" of parchment obtained from sheepskin is influenced by the fat content during the life of the animal, which cannot be completely eliminated during processing by specific chemical and mechanical operations.

In order to highlight the characteristics that influence the change of parchment colour during artificial ageing, a correlation of chemical and physical characteristics was performed, respectively the ratio of extractable substances (which are especially fats) and the thickness of parchments and colour parameters obtained by using CIE L*a*b* and CIEL*C*h, according to Table 4.

Table 4: Correlations between the ratio of extractable substances and the thickness of the parchments and the colour parameters obtained by using CIE L*a*b* and CIEL*C*h for the 16 days of ageing treatment

Sample	Volatile matter, %	Thickness, mm	Extractable substances/ Thickness	CIE L*a*b* and CIEL*C*h parameters				
				a*	b*	c*	h	L*
S1	6.61	0.28	23.607	11.13	36.05	37.72	72.84	49.23
S2	2.39	0.29	8.2414	10.27	40.04	41.34	75.61	63.7
S3	3.69	0.26	14.192	5.25	34.11	34.51	81.25	70.22
S4	5.83	0.29	20.103	15.73	34.46	37.88	65.47	50.51
S5	8.81	0.34	25.912	13.87	39.05	41.44	70.45	54.88

From the point of view of the colour changes we can conclude that after 16 days of accelerated ageing it is observed that for h parameter, the highest difference was recorded for sample 4, followed by sample 5 and sample 1. The smallest difference was recorded for sample 3. In the case of b and c parameters, the highest differences after 16 days were recorded for samples 2 and 5 followed by samples 1, 4 and 3.

After 8 days of accelerated ageing, the parameter a of the sample S5 is the biggest difference with a fat content of 8.81 and a thickness of 0.34, followed by the S4 sample with 5.83 grams and 0.29 thick, S1 sample with 6.61 fat and 0.28 thickness, S2 sample with 2.39 grams and 0.29 grams and sample 3, the smallest change with 3.69 grams and 0.26 thick.

For b and c parameters the greatest difference was recorded for the S1 and S5 samples with the highest fat content followed by the S2, S4 and S3 samples.

For parameter h, the largest variation was recorded in the S4 and S5 samples and the smallest difference was recorded for the S3 sample.

CONCLUSION

In this study we investigated the influence of accelerated ageing treatments on parchment samples exposed to 85°C temperature and 60% relative humidity with duration of one day, 2 days, 4 days, 8 days and 16 days and assessed the generated effects. The 5 sheepskins were technologically processed in the same way. The artificial ageing treatments affected the treated parchment samples compared to the untreated samples.

The chemical characteristics have similar values for all the parchment samples, except for the big value variations of extractable substances which showed great differences due to the way of preserving the skins by salting and to the biological characteristics of animals. Shrinkage temperatures, Ts, showed a rather good hydrothermal stability for the untreated parchment samples, but all samples show a major decrease of 5-9°C in the shrinkage temperature after a day of artificial ageing and continued to decrease in correlation with the exposure time. The most damaged samples were S4 and S5 after 16 days of ageing treatment. The results obtained by evaluating the shrinkage temperature and colour parameters, culminated in a different behaviour after artificial ageing. While the shrinkage temperature caused an accentuated decrease in Ts, the colour changes analyses results reported small differences in b*, c*, h parameters and substantial changes in a* and L* parameters for the samples S1, S4 and S5. We can conclude that the best behaviour to the artificial ageing was the sample S2 which presented small difference in colour in correlation with the smaller quantity of extractable substances (fat content).

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