

# Low-pickle Processing of Leather: Assessment of Leather Tanning Quality by Methods of Thermal Analysis

Virgilijus VALEIKA \*

Department of Physical and Inorganic Chemistry, Kaunas University of Technology, Radvilėnų pl. 19, Kaunas LT-50254, Lithuania

**crossref** <http://dx.doi.org/10.5755/j01.ms.26.3.22509>

Received 15 January 2019; accepted 31 March 2019

Pelt obtained by delimiting with peracetic acid can be chromed after additional treatment with sodium chloride or oxalic acid solution, or directly tanned using synthetic tannins. The results of differential scanning calorimetry and thermogravimetric analyses have suggested that any tanning increases thermal stability of leather collagen. The produced chrome-free leather, despite its high tensile strength, is not characterized by high shrinkage temperature what indicates insufficient thermal stability of such leather. This fact contradicts the results of differential scanning calorimetry and thermogravimetric analyses results which show the high thermal stability of the chrome-free leather. It has been concluded that scanning calorimetry and thermogravimetric analyses are not sufficient for the appropriate assessment of leather obtained by the methods of various tanning, and the conclusions about changes in leather structure and quality of leather can not be drawn only upon results of the mentioned analyses.

*Keywords:* delimiting, leather, tanning, crosslinking, differential scanning calorimetry, thermogravimetric analysis.

## 1. INTRODUCTION

The conventional leather processing technology is based on strong alkaline treatment of hide or skin with the purpose to remove hair and open up of derma structure. Subsequent delimiting aims at removal of calcium compounds and reduce alkalinity of unhaired hide/skin. Next step, which is pickling, significantly reduces pH of pelt down to 2–4, and thus the pelt characterised by such pH value becomes suitable for subsequent chrome tanning process.

Development of beamhouse processes such as unhairing [1, 2] or delimiting leads to production of almost neutral [3] or even acidic pelt [4, 5]. Accordingly, the parameters of further processing steps such as pickling and chrome or vegetable tanning can be changed seeking to diminish their impact on environment. Thanikaivelan et al. have demonstrated the possibility of chroming of pelt having pH 8 without conventional pickling overall [6].

The attempts to develop new pickling methods for conventional alkaline pelt have been made trying to replace commonly used materials: sodium chloride and sulphuric acid by other materials such as synthesized new materials rich in sulfonic acid groups [7] or a novel pre-tanning agent Q16 synthesized from cyanuric chloride and *p*-aminobenzoic acid [8]. Unfortunately, the authors do not comment the impact on environment of the new methods.

Chromium has been used as primary tannage for many leathers for over 100 years [9]. Though chromium is considered as the best mineral-tanning agent to date it has its own negative image as well. Search for substitutes for chrome tanning has been undertaken by many researchers all over the world. The alternative tanning agent could be

organic or inorganic based. Inorganic [10] or organic non-chrome tannages have gradually become preeminent in leather production [11]. An organic tanning system as a substitute for chrome tanning is considered as a suitable alternative owing to the limitations of inorganic tanning agents [12]. Since the quality of current chrome-free leather is lower due to, for example, lower resiliency and hydrothermal stability [13] new combinations of subsequent processing of pelt obtained by delimiting with peracetic acid (PAA) have been explored: a) less pickle + chrome tanning; b) organic tanning directly after delimiting.

The aim of this research was to investigate the possibility to use chrome-free tanning agent directly after delimiting with PAA and bating, and to assess the accordance of the leather properties and results of differential scanning calorimetry (DSC), thermogravimetric (TG) and physical-mechanical analyses.

## 2. EXPERIMENTAL

### 2.1. Parameters of processes

Cattle hide (mass 22.8 kg) preserved by NaCl was used for experiments. The hide was processed up to tanned leather with the aim to produce tanned leather (“wet white” or “wet blue”) as follows:

Soaking (% based on hide mass): H<sub>2</sub>O 100%, at 18–22 °C, Na<sub>2</sub>CO<sub>3</sub> 1.4 %, duration 8.5 h, run continuously.

Washing: H<sub>2</sub>O 200 %, temperature 20–22 °C, duration 15 min, run continuously.

Liming (total duration 24 h): a) H<sub>2</sub>O 100%, at 20–22 °C, detergent 0.1 %, duration 30 min, run – continuously; b) Na<sub>2</sub>S 1.2 %, Ca(OH)<sub>2</sub> 2.3 %, duration 1.5 h, run continuously; c) Ca(OH)<sub>2</sub> 2.3 %, duration 1 h, run

\* Corresponding author. Tel.: +370-37-300189; fax: +370-37-300152.  
E-mail address: [virgilijus.valeika@ktu.lt](mailto:virgilijus.valeika@ktu.lt) (V. Valeika)

continuously; d) H<sub>2</sub>O 100%, at 20–22 °C, duration 30 min; run continuously. Leave stand until morning.

Washing (two times): a) H<sub>2</sub>O 200 %, temperature 20–22 °C, duration 30–min, run – continuously, drain.

Delimiting (% based on pelt mass):

1<sup>st</sup> variant: conventional delimiting-bating (control): a) H<sub>2</sub>O 40 %, at 33–38 °C, NH<sub>4</sub>(SO<sub>4</sub>)<sub>2</sub> 2.2 %, duration 30 min, run continuously; b) NH<sub>4</sub>(SO<sub>4</sub>)<sub>2</sub> 1.5 %, duration 30 min, run continuously; c) H<sub>2</sub>O 100%, EP Oropon ON2 (Röhm GmbH & Co, Germany) 0.15 %, duration 1 h, run continuously.

2<sup>nd</sup> variant: delimiting with peracetic acid (PAA) and bating (experimental): a) H<sub>2</sub>O 40 %, temperature 36–38 °C, PAA 0.75 %, pH of PAA solution 4.0, duration 1 h, run continuously; b) EP Novo Bate WB (Novozymes, Denmark) 0.30 %, duration 1 h, run continuously (pH of solution at end of the process 4.86).

Washing (two times): H<sub>2</sub>O 100 %, temperature 20–22 °C, duration 20 min, run continuously, drain.

Treatment before tanning (% based on pelt mass):

1<sup>st</sup> variant: pickling (control): a) H<sub>2</sub>O 40 %, temperature 20–22 °C, NaCl–5.5 %, duration 15 min, run continuously; b) HCOONa 1%, duration 20 min, run continuously; c) H<sub>2</sub>SO<sub>4</sub> 0.5 %, duration 15 min, run continuously; d) H<sub>2</sub>SO<sub>4</sub> 0.5 %, duration 15 min, run continuously; e) H<sub>2</sub>SO<sub>4</sub> 0.5 %, duration 15 min, run continuously; f) H<sub>2</sub>SO<sub>4</sub> 0.5 %, duration 5 h, run continuously (final pH of solution 3.18).

2<sup>nd</sup> variant: treatment with NaCl: H<sub>2</sub>O 40 %, at 20–22 °C, NaCl 6 %, duration 2 h, run continuously (final pH 4.84).

3<sup>rd</sup> variant: treatment with oxalic acid: H<sub>2</sub>O 40 %, HOCCOOH 0.1 %, temperature 20–22 °C, duration 1 h, run continuously (final pH 4.65).

Chrome tanning (in pickling or other treatment before tanning solution (% based on pelt mass): a) Cromeco EXTRA (Gruppo Chimico Dalton, Italy) 1.5 % (counting to Cr<sub>2</sub>O<sub>3</sub>), temperature 20–22 °C, duration 12 h, run continuously; b) Neutrargene MG-120 (Codyeco s.p.a., Italy) 0.25 %, duration 2 h, run continuously; c) Neutrargene MG-120 0.25 %, duration 2 h, run continuously; d) H<sub>2</sub>O 40 %, temperature 55 °C, duration 1 h, run continuously.

Organic tanning: H<sub>2</sub>O 110 % (% based on pelt mass), temperature 25–26 °C, synthan *Blancotan W* (*Silva*, Argentine) 20 %, duration 48 h, run continuously.

Hide or leather samples used for investigation:

1<sup>st</sup> – limed pelt;

2<sup>nd</sup> – conventionally delimited, pickled and chromed leather (control leather);

3<sup>rd</sup> – delimited with PAA, treated with NaCl solution before chroming and chromed leather;

4<sup>th</sup> – delimited with PAA, treated with oxalic acid solution before chroming and chromed leather;

5<sup>th</sup> – delimited with PAA and directly tanned with synthetic tannin *Blancotan W* leather.

## 2.2. Methods of analyses

The shrinkage temperature of pelt was measured according to standard [14]. The shrinkage temperature of chromed leather samples was determined as described in the literature using special equipment and replacing the distilled water with glycerol [15].

The tensile strength and relative elongation of pelt and chrome-tanned leather were measured with dynamometer according standard [16].

DSC and TG analyses were performed with the Netzsch Gerätebau GmbH (Germany) thermal analyzer in nitrogen atmosphere at the heating rate of 10 °C/min. The reference was an empty aluminium pan. Before the DSC and TG analyses the samples of pelt and leather were dehydrated using acetone [17].

## 3. RESULTS AND DISCUSSION

Chrome-free leather such as the one tanned with synthetic or natural tannins behaves very differently from chrome tanned leather [18]. Accordingly, in order to assess the difference between these leather types, physical, mechanical indexes, and shrinkage temperature (*T<sub>s</sub>*) of samples were determined (Table 1) first.

The chrome-free samples are characterised by the highest tensile and grain strength (Table 1). This phenomenon is described in literature [18]. Synthetic tannins fill better leather matrix, therefore, tanned leather has better strength properties. Unfortunately, structure of the chrome-free leather structure is not as elastic as that of the chromed leather: the elongation of chrome-free leather is markedly lower comparing with the chromed one. Additionally, a value of shrinkage temperature shows low thermal stability of the chrome-free leather. The chrome-free tanning has increased shrinkage temperature only by 6 °C comparing with *T<sub>s</sub>* of the limed pelt.

The results of DSC and TG analyses allowed obtaining more detailed information about thermal behaviour of differently tanned leather. The thermograms are presented in Fig. 1. The peak of the first temperature effect is at 82 °C for the limed pelt and in the range of 86–90 °C for variously tanned leather. Therefore, tanning has increased the temperature of this effect in all cases.

Mostly, this effect is attributed to elimination of capillary moisture [19]. The moisture evaporates as at higher temperature as capillaries are narrower. Of course, due to swelling effect the capillaries in derma are larger after liming than after tanning.

**Table 1.** Qualitative indexes of limed pelt and chromed leather

Indexes	Sample				
	1 <sup>st</sup>	2 <sup>nd</sup>	3 <sup>rd</sup>	4 <sup>th</sup>	5 <sup>th</sup>
Tensile strength, N/mm <sup>2</sup>	13.5 ± 0.84	19.2 ± 1.08	20.1 ± 1.51	20.0 ± 1.78	21.3 ± 1.17
Grain strength, N/mm <sup>2</sup>	–	16.4 ± 1.12	15.5 ± 1.08	12.0 ± 0.94	20.0 ± 1.02
Relative elongation when load is 10 N/mm <sup>2</sup> , %	54.5 ± 4.01	45.2 ± 2.30	52.5 ± 3.30	48.5 ± 2.30	31.5 ± 2.15
Shrinkage temperature ( <i>T<sub>s</sub></i> ), °C	56.0 ± 0.62	101.0 ± 1.12	101.7 ± 1.14	104.0 ± 1.18	62.0 ± 0.70

Other explanation of the first effect is based on the number of hydrogen bonds [19–22]: the higher temperature and larger area of peak can be observed when more hydrogen or cross-linking bonds are formed in the collagen. According to this point of view, it can be proposed that treatment with Blancotan W is a good way to increase the stability of leather, but the value of shrinkage temperature of the sample tanned with Blancotan W does not confirm this assumption. Temperature interval of 200–220 °C is attributed to melting point of crystalline part of collagen, i.e. transition of collagen from high elasticity state to viscous-flow state [23]. This peak is characteristic to limed pelt or chrome-free leather only (Fig. 1, 1<sup>st</sup> and 5<sup>th</sup> sample), i.e. the peak disappears during chrome tanning. This dependence can be explained by deep penetration of chromium compounds into collagen matrix [23]. Presence of this peak indicates the other behaviour and structural properties of chrome-free leather in comparison with chrome-tanned one. It could be proposed that chrome-free leather has properties of tanned leather and pelt simultaneously.

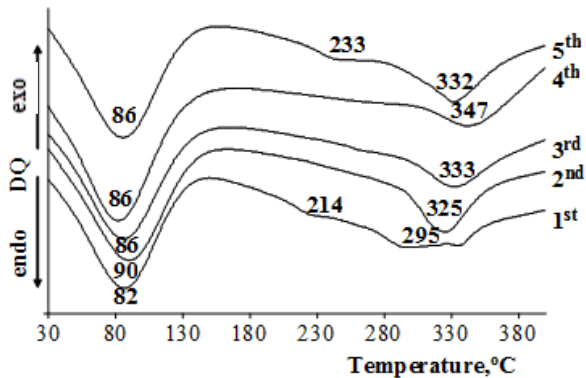


Fig. 1. DSC curves of samples

The third peak is attributed to leather collagen destruction [19–22]. The results show (Fig. 1) that tanning increases the destruction temperature ( $T_D$ ) independently of the tanning method. The limed pelt sample has the lowest  $T_D$  (295 °C) and sample delimed with PAA, treated with oxalic acid solution and chromed has higher  $T_D$  (347 °C). The  $T_D$  values correlate with shrinkage temperature (Fig. 2), but DSC analysis shows too high thermal stability of chrome-free leather. High  $T_D$  value can be attributed to big amount of used synthetic tannins in the tanned leather and, accordingly, this high value does not approve high thermal stability of the leather but rather is related with high thermal stability of the used synthetic tanning agent.

Table 2. The influence of sample weight loss on treatment method

Temperature, °C	Sample weight loss, %				
	1 <sup>st</sup>	2 <sup>nd</sup>	3 <sup>rd</sup>	4 <sup>th</sup>	5 <sup>th</sup>
50	3.4	3.1	3.0	2.5	2.4
100	13.5	13.1	14.0	13.1	12.0
150	17.4	17.9	19.7	17.9	15.5
200	17.9	18.2	21.5	19.2	15.6
250	20.3	18.9	23.6	20.9	16.8
300	28.0	22.7	27.6	24.7	21.2
350	52.2	46.0	45.0	40.3	42.8
400	62.5	55.5	58.3	61.1	55.9

The TG analysis is used in many fields of material research. Due to complexity of leather materials, there are a variety of thermal degradation behaviours of modified collagen fibres in different leathers [24]. TG analysis could give some useful guidance for improvement the leather-making technology and confirm DSC analysis results in the same time.

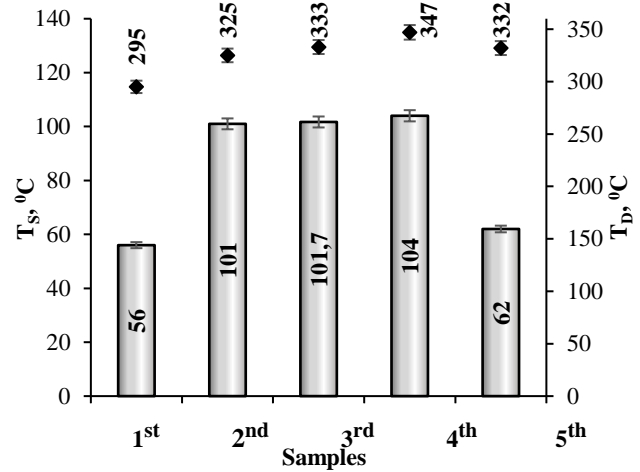


Fig. 2. The  $T_S$  and  $T_D$  temperature dependence on leather tanning method

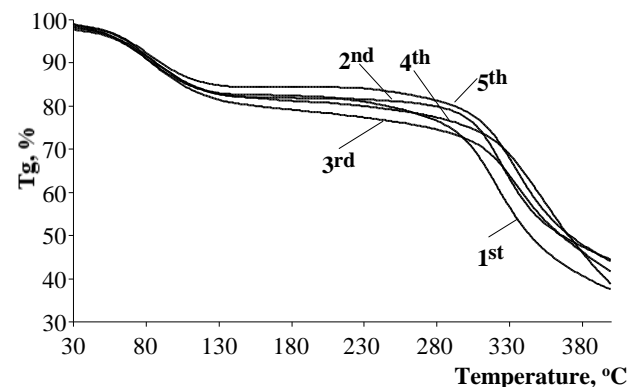


Fig. 3. TG curves of samples

On the other hand, the thermal stability comparative studies between wet-white (chrome-free) and wet-blue (chromed leather) carried out by Rosu et al. [25] exhibited a similar general thermal behaviour of the both leathers. It was observed that, for the wet-blue leather, the presence of Cr slightly increased the thermal stability, due to the formation of more stable characteristic metal–collagen complexes [25].

The thermo-gravimetric curves of limed pelt, chrome tanned, and chrome-free leather are presented in Fig. 3. The weight loss dependence on treatment method is presented in Table 2. It is seen (Fig. 3 and Table 2) that limed pelt sample loses weight faster (1<sup>st</sup> sample). This can be explained by lower thermal stability of limed pelt collagen comparing with chromed leather. The tanning increases stability independently on the method of tanning (Table 2).

#### 4. CONCLUSIONS

Pelt obtained by delimiting with peracetic acid can be chromed after additional treatment with sodium chloride or oxalic acid solution, or directly tanned using synthetic tannins. Based only on the results of differential scanning calorimetry and thermogravimetric analyses it has been proposed that any tanning increases thermal stability of collagen of leather. Unfortunately, the produced chrome-free leather despite its high tensile strength is not characterized by high shrinkage temperature what indicates insufficient thermal stability of such leather. This fact contradicts results of differential scanning calorimetry and thermogravimetric analyses showing the high thermal stability of the chrome-free leather.

Accordingly, the results obtained by scanning calorimetry and thermogravimetric analyses are not sufficient for the appropriate assessment of leather obtained by the methods of various tanning, and the conclusions about changes in leather structure and quality of leather cannot be drawn only upon results of the mentioned analyses.

#### REFERENCES

1. **Aravindhan, R., Saravanabhavan, S., Rao, J.R., Nair, B.U.** A Bio-driven Lime and Pickle Free Tanning Paves Way for Greener Garment Leather Production *Journal of the American Leather Chemists Association* 99 (2) 2004: pp. 53–66.
2. **Valeika, V., Beleska, K., Širvaityte, J.** Alkaline-free Method of Hide Preparation to Tanning *Brazilian Journal of Chemical Engineering* 29 (2) 2012: pp. 315–323. <http://dx.doi.org/10.1590/S0104-66322012000200012>
3. **Zeng, Y.H., Lu, J.H., Liao, X.P., He, Q., Shi, B.** Non-ammonia Delimiting Using Sodium Hexametaphosphate and Boric Acid *Journal of the American Leather Chemists Association* 106 (9) 2011: pp. 257–263.
4. **Širvaitytė, J., Valeika, V., Beleşka, K., Valeikienė, V.** Action of Peracetic Acid on Calcium in Limed Pelt *Journal of the Society of Leather Technologists and Chemists* 91 (3) 2007: pp. 123–127.
5. **Širvaitytė, J., Valeika, V., Plavan, V.** Peracetic Acid Delimiting. Part II: Pickle-free and Low-pickle Processing of Peracetic Acid Delimited Pelt *Journal of the Society of Leather Technologists and Chemists* 93 (2) 2009: pp. 40–45.
6. **Thanikaivelan, P., Rao, J.R., Nair, B.U.** Development of Leather Processing Method in Narrow pH Profile: Part 2. Standardisation of tanning process *Journal of the Society of Leather Technologists and Chemists* 85 (3) 2001: pp. 106–115.
7. **Zhang, H., Chen, X.X., Wang, X.C., Qiang, X.H., Li, X.N., Li, M.** A Salt-free Pickling Chrome Tanning Approach Using a Novel Sulphonic Aromatic Acid Structure *Journal of Cleaner Production* 142 (4) 2017: pp. 1741–1748. <https://doi.org/10.1016/j.jclepro.2016.11.113>
8. **Cui, L., Qiang, X.H., Yu, L., Wei, X., Li, C.T.** A Cleaner Method for Low-Chrome Tanning with No-Salt Pickling *Journal of the Society of Leather Technologists and Chemists* 101 (5) 2017: pp. 219–226.
9. **Musa, A.E., Gasmelseed, G.A.** Semi-Chrome Upper Leather from Rural Goat Vegetable Tanned Crust *Journal of Applied and Industrial Sciences* 1 (1) 2013: pp. 43–48.
10. **Plavan, V., Valeika, V., Kovtunenکو, O., Širvaityte, J.** THPS Pretreatment before Tanning (Chrome or Non-chrome) *Journal of the Society of Leather Technologists and Chemists* 93 (5) 2009: pp. 186–192.
11. **Prentiss, W.C., Siegler, M., Brown, E.M.** Chrome Free Tanning Compositions and Processes *Journal of the American Leather Chemists Association* 98 (2) 2003 pp. 63–69.
12. **Saravanabhavan, S., Raghava Rao, J., Unni Nair, B., Thanikaivelan, P., Chandrasekaran, B.A.** A New Leather-making Process for Meeting Eco-label Standarts: Processing of Goatskins *Journal of the American Leather Chemists Association* 101 (5) 2006: pp. 192–205.
13. **Valeika, V., Širvaityte, J., Beleska, K.** Estimation of Chrome-free Tanning Method Suitability in Conformity with Physical and Chemical Properties of Leather *Materials Science (Medziagotyra)* 16 (4) 2010: pp. 330–336.
14. Standard ISO 3380: 2002. Leather – Physical and mechanical tests – Determination of shrinkage temperature up to 100 degrees C.
15. **Golovteeva, A.A., Kutsidi, D.A., Sankin, L.B.** Laboratornyj Praktikum po Khimiyi i Tekhnologiyi Kozhy i Mekha. Legkaiya i Pischevaiya Prom. Moscow, 1982. (in Russian).
16. Standard ISO 3376:2002. Leather – Physical and Mechanical Tests – Determination of Tensile Strength and Percentage Extension.
17. Pat. USSR 767649. Method of Determination of Leather Quality.
18. **Liu, C.K., Latona, N.P., DiMaio, G.L., Cooke, P.H.** Viscoelasticity Studies for a Fibrous Collagen Material: Chrome-Free Leather *Journal of Materials Science* 42 (20) 2007: pp. 8509–8516. <https://doi.org/10.1007/s10853-007-1744-1>
19. **Mano, V., Scarpelli Ribeiro e Silva, M.E.** Bioartificial Polymeric Materials Based on Collagen and Poly(N-isopropylacrylamide) *Materials Research* 10 (2) 2007: pp. 165–170. <http://dx.doi.org/10.1590/S1516-14392007000200012>
20. **Yao, Q., Chen, H.L., Huang, H.H., Liu, B.L.** Mechanism and Effect of Hydroxyl-terminated Dendrimer as Excellent Chrome Exhausted Agent for Tanning of Pickled Pelt *Journal of Cleaner Production* 202 2018: pp. 543–552. <https://doi.org/10.1016/j.jclepro.2018.08.164>
21. **Onem, E., Yorgancioglu, A., Karavana, H.A., Yilmaz, O.** Comparison of Different Tanning Agents on the Stabilization of Collagen via Differential Scanning Calorimetry *Journal of Thermal Analysis and Calorimetry* 129 (1) 2017: pp.615–622. <https://doi.org/10.1007/s10973-017-6175-x>
22. **Hui, C., Zhi-Hua, S.** Changes in Hydrothermal Stability of Collagen with Several Catechin-Metal Compounds: A DSC Study *Journal of The Society of Leather Technologists and Chemists* 92 (3) 2008: pp. 93–95.
23. **Ostachenko, L.S., Kutiatin, G.I.** Termograhicheskoe i Termogravimetricheskoe Isledovaniye Chromovych Kozh Razlichnoy Intensivnosti Dubleniya *Kozhevenno-obuvnaya promyshlennost* 8 1973: pp. 51–55. (in Russian).
24. **Tang, K., Wang, F., Liu, J., Liu, J., Wang, Q.J.** Preliminary Studies on the Thermal Degradation Kinetics of Cattlehide Collagen Fibers *Journal of the American Leather Chemists Association* 99 (10) 2004: pp. 401–408.
25. **Rosu, L., Varganici, C.D., Crudu, A.M., Rosu, D.** Influence of Different Tanning Agents on Bovine Leather Thermal Degradation *Journal of Thermal Analysis and Calorimetry* 134 (1) 2018 pp. 583–594. <https://doi.org/10.1007/s10973-018-7076-3>