RIGA TECNICAL UNIVERSITY

Faculty of Material Science and Applied Chemistry

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Doctoral study programme „Textile and clothing technologies" doctor

RAW HIDE PRESERVATION USING VACUUM UNDER LOW TEMPERATURE

Doctorate work

Scientific supervisors:

Dr., professor

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The doctoral thesis was developed at Faculty of Material Science and Applied Chemistry, Institute of Design Technologies, Riga Technical University from 2010 to 2014.

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ANNOTATION

Work of doctor's degree is worked out on the topic „Raw hide preservation using vacuum under low temperature". The choice of this subject is related to the improvement of quality of environment developing such important process of leather manufactory as hide preservation.

Within the work the significance of the history of leather manufactory has been analysed on the different stages of historical development in Latvia, the import and export data of raw hide/skin and leather in Latvia has also been clarified in time period 2001 - 2012. Different preservation methods were analysed and compared for the spotlighting of existing problems and for emphasize of necessity of development of new and more environmentally friendly preservation method.

Hypothesis: raw hide storing in vacuum prolongs its' preservation duration.

The urgency of the theme is confirmed by many scientists who are still trying to find new and cleaner short term preservation methods. Investigations have been carried on developing efficiency of preservation of raw hide/skins and reducing pollution by preservative materials. Therefore, the investigation of new and more effective short term preservation method is very welcome.

The main aim of the doctorate work is to develop simple and advanced short term preservation method of hide using vacuum, to investigate the vacuum effect on hide qualitative properties storing it at low temperature and to establish peculiarities of vacuumed hide processing into leather. Accordingly, the set of tasks, which let achievement of main aim of the work, was formed. During the research all tasks have been executed and the aim of the work has been achieved.

New short term preservation method was developed. It allows refusing from chemical materials which commonly are applied for curing of hide. The achieved preservation duration (22 days) is enough for collection of hides' amount, which processing is profitable for tanneries.

Peculiarities of vacuumed hide processing into leather were studied in laboratory and industrial conditions. It was confirmed that preservation of hides using vacuum allows produce of qualitative leather.

The author of the work:	Ilze Gudro
The theme of the dissertation:	Raw hide preservation using vacuum under low temperature
Key words:	Hide, preservation, vacuum, low t^{o}
The extent of the work:	122.pg.
The number of formulas:	9
The number of figures:	47
The number of tables:	26
The number of sources of literature:	105
The number of appendixes:	3
The content of the work:	5 chapters, 48 subunits

ANOTĀCIJA

Doktora darba izstrādātā tēma ir „Jēlādu konservēšana vakuumā zemā temperatūrā". Darba tēmas izvēle ir saistīta ar apkārtējas vides kvalitātes uzlabošanu tāda ādu rūpnīcas procesa ietvaros kā jēlādu konservēšana un uzglabāšana.

Darba ietvaros tika pētīta Latvijas ādu apstrādes rūpnīcu vēsture dažādos laika periodos, tika salīdzināti Latvijas 41/42/43 nomenklatūras grupas importa un eksporta dati laika periodā no 2001. – 2012. gadam, tika izanalizētas, aprakstītas un salīdzinātas dažādas jēlādu konservēšanas metodes, lai pierādītu nepieciešamību pēc jaunas un videi draudzīgākas jēlādu konservēšanas metodes pilnveidošanas.

Darbā izvirzītā hipotēze: jēlādu konservēšana vakuumā pagarina tās uzglabāšanas laiku.

Tēmas aktualitāti pastiprina vairāku pasaules zinātnieku pētījumi, kuru ietvaros autori mēģina atrast tīrākas īsa perioda jēlādu konservēšanas metodes. Pētniecības nozare galvenokārt saistīta ar ekoloģiskākas jēlādu konservēšanas metodes izveidi, samazinot piesārņojumu, kuru rada konservējošās vielas.

Doktora darba mērķis ir izstrādāt vienkāršu īsa perioda konservēšanas metodi lietojot vakuumu. Lai novērtētu vakuuma ietekmi uz šādi konservētām un uzglabātām jēlādām tiek pētītas to kvalitatīvās īpašības uzglabāšanas laikā, zemā temperatūrā un izpētītas tās īpatnības un parametri, kuri mainās no šāda tipa jēlādas izgatavojot gatavu ādu. Pakārtoti darba mērķim, tika sastādīti vairāki darba uzdevumi. Darba pētnieciskās daļas ietvaros visi uzdevumi tika izpildīti un darba mērķis tika sasniegts.

Doktora darbā tika izstrādāta jauna, īsa perioda jēlādu konservēšanas metode. Metodes ietvaros nav nepieciešams lietot dažādus ķīmisko konservantus, kuri vispārīgi tiek pielietoti jēlādu konservēšanā. Sasniegtais, nepieciešamais laika periods (21 dienu) jēlādu uzglabāšanai vakuumā ir pietiekams un izdevīgs ādu apstrādes rūpnīcām.

Vakuumā uzglabātās jēlādas īpašību izmaiņas tās izgatavošanā uz gatavu ādu tika pētītas laboratorijā un rūpnīcas apstākļos. Tika secināts, ka šāda jēlādu uzglabāšanas metode atļauj izgatavot kvalitatīvu gatavu ādu.

Darba autors:	Ilze Gudro
Doktora darba tēma:	Jēlādu konservēšana vakuumā zemā temperatūrā
Atslēgas vārdi:	Jēlāda, konservēšana, vakuums, zema t^o
Doktora darba apjoms:	122. lpp.
Formulu skaits:	9
Attēlu skaits:	47
Tabulu skaits:	26
Literatūras avotu skaits:	105
Pielikumu skaits:	3
Darba saturs:	5 nodaļas, 48 apakšnodaļas

АННОТАЦИЯ

Тема проведенной докторской работы – "Консервирование кожевенного сырья при низкой температуре с применением вакуума". Выбор темы связан с уменьшением загрязнения окружающей среды при проведении такого процесса кожевенного производства как консервирование и хранение кожевенного сыръя.

При проведении работы обобщены данные о развитии кожевенной промышленности в Латвии в различные исторические периоды; сравнены данные по импорту и экспорту номенклатурной группы 41/42/43 в течении периода от 2001 по 2012 год; проведён анализ, описаны и сравнены различные методы консервирования кожевенного сырья с целью доказать необходимость разработки нового и более экологически чистого метода консервирования кожевенног сирья.

Защищаемое положение работы: хранение кожевенного сырья в вакууме продлевает срок его сохранности.

Актуальность темы подтверждает ряд всемирно известных научных работ, в которых авторы приводят результаты исследований новых методов кратковременного консервирования кожевенного сырья. Исследования в основном направлены на создание более чистых методов первичной обработки кожсырья, с целью снижения уровня загрязнения окружающей среды химическими материалами. Новые, меньше загрязняющие и более простые методы консервирования кожсырья являются важными и необходимыми.

Целью докторской работы является разработка нового упрощённого метода кратковременного консервирования кожевенного сыръя с применением вакуума, изучение его влияния на качественные характеристики хранимого при низкой температуре кожсырья и изучение изменений свойств полуфабриката, при проведении процессов выработки кожи из сырья, хранённого в вакууме. Для достижения цели работы были намечены задачи, которые в рамках научной части работы были успешно решены и цель работы достигнута.

При проведении исследований был разработан новый метод кратковременного консервирования кожевеннного сыръя. Примененяя этот метод ненужны химические вещества, которые обычно используются для консервирования кожсырья. Достигнута и необходимая продолжительность сохранности кожевенного сыръя, необходимая с точки зрения технологий выработки кожи.

Качественные показатели готовой кожи, выработанной из хранённого в вакууме кожсырья, были исследованы в лабораторных и промышленных условиях. Сделан вывод о том, что предлагаемый метод консервирования кожевенного сырья позволяет производить высококачественную готовую кожу.

Автор работы:	Гудро Илзе
Тема диссертации:	"Хранение кожанного сыръя в вакууме при низкой температуре"
Ключевые названия:	кожанное сыръо, консервирование, вакуум, низкоя t^o
Объём диссертации:	122. стр.
Количество формул:	9
Количество изображений:	47
Количество таблиц:	26
Количество источников литературы:	105
Количество приложений:	3
Содержание работы:	5 разделов, 48 подразделов

CONTENT

1 INTRODUCTION

The leather manufactory is not only the oldest but also one of the most polluting branches of industry. The environmentally requirements continually become stricter and they are the main stimulus to develop new technological decisions, which allow to the decrease of pollution. One of the directions of investigation is the refusing from big amounts of materials which are commonly used for preservation of hides and skins.

The preservation of raw material in this chain plays very important role because qualitative leather cannot be produced from badly preserved hides or skins. Preservation of raw stock has the objective of rendering the flayed pelt resistant to putrefaction to allow transport and storage. Preservation is accomplished either by destroying active bacteria, by preventing bacterial activity or by preventing bacterial contamination. During preservation it is essential to avoid from usage of toxic materials as these materials are very dangerous for environment due to their chemical nature.

The literature analysis has shown that investigation of new and cleaner preservation methods goes very intensely. Two main directions can be accentuated: chemical preservation when various materials are used or physical preservation without any use of chemical materials.

Unfortunately, there are not possibilities to deliver hides or skins for leather processing directly after flaying. The analysis of leather industry in Latvia has shown same situation. The shorter or longer period is needful for the collection of enough amount of raw material for the leather industry.

The wet salting, the conventional method of curing is followed by most of the tanneries because of its practical advantages; employs approximately 40-50% sodium chloride on raw material and is subsequently removed during the soaking operation. [1] So, it is very serious reason to pursue new and more environmentally friendly preservation methods because sometimes is last 1-2 weeks for the gathering for processing enough skins or hides.

This is the main reason why investigators pay their attention for the development of short term preservation methods, which allow storage of hides/skins during 1-3 weeks without symptoms of deterioration. Many scientists are still trying to

find new short term preservation methods. Investigations have been carried on developing efficiency of preservation of raw hide/skins and reducing pollution by preservative materials. Therefore, the investigation of new and more effective short term preservation method is very welcome.

The presented work was aimed to investigate new preservation method of hide. It is known method of food preservation using vacuum. The vacuum is very good known for leather technologists because it is widely used for leather drying. [2] Attempts to use vacuum for hide preservation were made and investigations of hide preserved by vacuum processing into leather were carried out. For short term preservation of hide was chosen method of hide storing in vacuum at low temperature. The method could help to avoid the pollution by big quantities of sodium chloride. On the other hand, the vacuum preservation can be applied in practise only after thorough exploration of that method.

1.1 Aim, objectives and hypothesis of doctoral thesis

The main aim of the doctorate work is to develop short term preservation method of hide using vacuum under low temperature. Hypothesis: raw hide storing in vacuum prolongs its' preservation duration. For reaching of this aim these objectives will be solved:

- *to gather data about situation in worldwide and Latvia leather industry and carry out analysis of current methods of hides and skins preservation;*
- *to investigate the vacuum effect on hide qualitative properties storing it at low temperature (organoleptic estimation of hide quality, investigation of microorganisms activity on hide preserved by vacuum, determination of nitrogen content and collagenous proteins, measurement of shrinkage temperature) and its structural changes during storage time;*
- *to estimate the quality of hide after storage;*
- *to investigate peculiarities of vacuumed hide processing into leather;*
- *to examine technological processes of leather processing from vacuumed hide;*
- *to verify suitability of vacuumed hide for processing of leather under industrial conditions and establish leather properties.*

1.2 Scientific novelty of doctoral thesis

Thorough analysis of current situation of leather manufactory in Latvia, including data of import and export of hides, skins, leather and leather goods; data about slaughterhouses, household animals, slaughtered animal count, was carried out. On the basis of the obtained analysis results, the perspectives of leather industry in Latvia are presented.

First time was investigated synergetic effect of vacuum and low temperature on hide preservation time and properties change. It was proved that hide can be preserved during 21 day when vacuum is $10\text{-}12 \cdot 10^3$ Pa at 4^oC, and such storage changes structure of hide negligible, and this doesn't decrease the quality of produced leather.

1.3 Practical significance of doctoral thesis

New short term preservation method was developed. It allows refusing from chemical materials which commonly are applied for curing of hide. The equipment which is usually used for vacuuming of food is applied for hide preservation. The achieved preservation duration is enough for collection of hides amount, which processing would be profitable for tanneries.

Processing of vacuumed hide does not require a new equipment and new processing technologies for tanneries. The processed leather from vacuumed hide is of high quality.

1.4 Structure of thesis

The doctoral work consists of 122 pages and it consists of 5 Chapters and 48 subunits): Introduction (with 6 subsections), Chapter 2 Literature review (with 10 subsections), Chapter 3 Materials and methods (with 15 subsections), Chapter 4 Results (with 17 subsections), Chapter 5 Conclusions. There are used 105 literature sources, 9 Formulas, 47 Figures, 26 Tables, and 3 Appendixes.

1.5 Thesis for defence

1. The hide storing under vacuum (10-12·10^3 Pa) at 4^{o}Cduring 21 day does not cause significant structural changes and does not worsen properties of hide as raw material.
2. Qualitative leather is produced from that hide using conventional technology.

1.6 The approbation of the results

Participation in scientific conferences

2009

1. I.Gudro, I.Beikule, G.Strazds, A.Ulme. Ādas resursu apzināšana un izmantošanas iespēju izpēte Latvijas tautsaimniecības attīstības veicināšanai**.** RTU 50. Starptautiskā zinātniskā konference. 15. Oktobris 2009 (oral presentation)

2010

2. Gudro I., Strazds G., Ulme A. The exploration of unutilized hide resources and the research of utilization possibility of such resources for the promotion of development of national economy of Latvia, poster presentation, 41th International Symposium on Novelties in Textiles 2010, Ljubljana, Slovenia, 27th-29th of May, 2010 (poster presentation)
3. Gudro I., Strazds G., Baltina I., The exploration of unutilized hide resources and the research of utilization possibility of such resources for the promotion of development of national economy of Latvia, poster presentation, 10th World Textile Conference AUTEX2010, Vilnius, Lithuania, 21st-23rd of June, 2010 (poster presentation)
4. Gudro I., Strazds G., Ulme A. The exploration of unutilized hide resources and the research of utilization possibility of such resources for the promotion of development of national economy of Latvia, Tulcea, Romania, 8th-9th of July, 2010 (oral presentation)
5. Gudro I., Strazds G., Ulme A. The exploration of unutilized hide resources for the promotion of development of national economy of Latvia, ITC & DC, 5th International Textile, Clothing&Design Conference, Dubrovnik, Croatia, 3rd-6th of October, 2010 (poster presentation)

6. Gudro I., Ulme A., Strazds G. Jēlādas resursu apstrādes apzināšana un situācijas izpēte Latvijā. RTU 51. Starptautiskā zinātniskā konference, Āzenes iela 18-modes zinību kabinets, Rīga, Latvija 15.oktobris, 2010. gads (oral presentation)
7. Gudro I., Lejniece Z., Freivalde L. Mācību iestādes interjera nozīme mūsdienu komunikācijā. RTU 51. Starptautiskā zinātniskā konference, Āzenes iela 18-modes zinību kabinets, Rīga, Latvija 15.oktobris, 2010. gads (poster presentation)

2011

8. Gudro I., Ulme A. Augstskolu loma dizaina speciālistu konkurētspējas palielināšanā. Starptautiskā zinātniski praktiskā konference „Mūsdienu tendences un tehnoloģijas dizaina izglītības attīstībā Boloņas procesa ietvaros" Baltijas Starptautiskā akadēmija, Lomonosova ielā 4, Rīgā, Latvija, 20.- 21.janvāris, 2011 (oral presentation)
9. Gudro I., Ulme A. Opportunities of use of Latvian rapidly renewable resources in the context of sustainable development. "Telpiskā stratēģija ilgtspējīgai attīstībai", 3. Starptautiskā zinātniskā konference, 26.-28. aprīlis,2011, Kuldīga (oral presentation)

2012

10. Gudro I., Valeika V., Širvaitytė J. Structural changes of hide preserved for short time by vacuum. Polymer Chemistry and Technology. Proceedings of Scientific Conference. Chemistry and Chemical Technology. Kaunas University of Technology, Kaunas, Lithuania 23rd-24th of April 2012 (poster presentation)
11. Gudro I., Valeika V., Širvaitytė J. and Ulme A. Vacuum as tool for hide preservation at low temperature. 26th International conference on Surface modification technologies, June 20th-22nd 2012, Ecully, Lyon, France (poster presentation)
12. Gudro I. Sirvaityte J., Virgilijus V., Ulme A. Short term raw hide storing using vacuum preservation method. 6th International textile, clothing & design conference - Magic world of textiles, 7th-10th of October, 2012, Dubrovnik, Croatia (poster presentation)

Published scientific abstracts, proceedings and papers:

Abstracts:

2010

1. Gudro I., Strazds G., Ulme A. The exploration of unutilized hide resources and the research of utilization possibility of such resources for the promotion of

development of national economy of Latvia, Book of Absrtacts/41th International Symposium on Novelties in Textiles and 5th International Symposium on Novelties in Graphics and 45th International Vongress IFKT/ University of Ljubljana, Faculty of Natural Sciences and Engineering, Department of Textiles, Ljubljana, Slovenia, 2010 [255], p.65. (ISBN 978-961-6045-79-7)

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Newspaper:

2010

3. Vīksne I., Gudro I. Ādu bizness pussprādzis. [1.lpp. turpinājums 8.lpp.]. Latvijas Neatkarīgā Avīze. Piektdiena, 2010.gada 17.decembris. # 291 (5881) (ISSN 1407 -3463)

Proceedings:

2009

4. **Gudro I., Ulme A. Presentation of the social responsibility within the public space image of higher educational establishments. Management of technological changes. Proceedings of the 6th International Conference on Management of Technological Changes. Book 1. Democritus Uniersity of Thrace. September 3rd - 5th, Alexandroupolis, Greece, 2009, p.89-92. (ISBN 978-960-89832-7-4)**

2010

5. Gudro I., Strazds G., Ulme A. The exploration of unutilized hide resources and the research of utilization possibility of such resources for the promotion of development of national economy of Latvia. Symposium Proceedings. 41th International Symposium on Novelties in Textiles. Narodina in univerziterna knjižnica, University of Ljubljana, Faculty of Natural Sciences and Engineering, Department of Textiles, Ljubljana, Slovenia, 2010 [1224.] p.312-319. (ISBN 978-961-6045-80-3)
6. **Gudro I., Strazds G., Ulme A. The exploration of unutilized hide resources and the research of utilization possibility of such resources for the**

promotion of development of national economy of Latvia. Quality Management in Higher Education, Proceedings of the 6th International Seminar on the Quality Management in Higher Education, Book II, Gheorghe Asachi Technical University of Iasi Romania, UTC Press-Cluj Napoca, Tulcea, Romania, 2010, [716] p.689-692. (ISBN 978-973-662-566-4)

7. Gudro I., Strazds G., Ulme A. The exploration of unutilized hide resources for the promotion of development of national economy of Latvia, ITC & DC: Book of Proceedings of the 5th International Textile, Clothing & Design Conference, Magic World of Textiles, Faculty of Textile Technology, University of Zagreb, 2010 [967] p.833-838. (ISSN 1847-7275)

2011

8. Gudro I., Ulme A. Augstskolu loma dizaina speciālistu konkurētspējas palielināšanā. BSA starptautiskie zinātniskie raksti. The catcher in the lie. Communicator. Компьютерная верстка, дизайн, Rīga, 2011 -1/2 [233] p.223-228. (ISSN 1691-5356)
9. Gudro I., Ulme A. Sustainable and rapidly renewable material in design objects in Latvia. Baltic Horizons. Euroacademy. Art&Design, Tallin, Estonia, 2011 p.61-68. (ISSN 1736-1834)
10. **Gudro I., Ulme A. High School role in magnification of design specialist competitiveness in Latvia. Management of Technological changes. Proceedings of the 7th International Conference on Management of Technological Changes, book 2, Democritus University of Thrace, Alexandroupolis, Greece, 1st-3rd September, 2011 p.513-516. (ISBN 978-960-99486-3-0)**

2012

11. **Gudro I., Valeika V., Širvaitytė J. Structural changes of hide preserved for short time by vacuum. Polymer Chemistry and Technology. Proceedings of Scientific Conference. Chemistry and Chemical Technology. Kaunas University of Technology, Kaunas, Lithuania 2012 p.135-139. (ISSN 2029-2457)**
12. Gudro I., Valeika V., Širvaitytė J. and Ulme A. Vacuum as tool for hide preservation at low temperature. Surface Modification Technologies, Vol 26, Published by Valardocs, Chennai, India 2012 p.251-256. (ISBN 978-81-926196-0-6)

13. Gudro I., Sirvaityte J., Valeika V. Ulme A. Short term raw hide storing using vacuum preservation method. 6th International Textile Clothing and Design Conference "Magic World of Textiles" (ITC&DC) October 07th to 10th 2012: Book of Proceedings, University of Zagreb, Dubrovnk, Croatia, 2012 p.53-58. (ISSN 1847-7275)

Paper:

2014

14. **Gudro I, Valeika V, Sirvaitytė J. Short Term Preservation of Hide Using Vacuum: Influence on Properties of Hide and of Processed Leather. PLoS ONE 9(11): e112783. doi:10.1371/journal.pone.0112783, 2014**

RTU proceedings:

2009

15. Gudro I., Beikule I., Strazds G., Ulme A. Ādas resursu apzināšana un izmantošanas iespēju izpēte Latvijas tautsaimniecības attīstības veicināšanai.//Rīgas Tehniskās universitātes zinātniskie raksti, Materiālzinātne, Sērija 9, Sējums 4, RTU izdevniecība, Rīga, 2009 [150] 45-49.lpp. (ISSN 1691-3132)

2010

16. Gudro I., Ulme A., Strazds G. Jēlādas resursu apstrādes apzināšana un situācijas izpēte Latvijā.//Rīgas Tehniskās universitātes zinātniskie raksti, Materiālzinātne, Sērija 9, Sējums 5, RTU izdevniecība, Rīga, 2010 [198] 34-40.lpp. (ISSN 1691 - 3132)
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2011

18. Gudro I., Ulme A. Opportunities of Raw Hide Using as a Sustainable Material in Latvia.//Rīgas Tehniskās universitātes zinātniskie raksti. Ilgtspējīga telpiskā attīstība. Sērija 14/Sējums 3. RTU izdevniecība, Rīga, 2011, [115.lpp.] 103-107.lpp. (ISSN 1691-6174)

2 LITERATURE REVIEW

Despite the fact that mankind till now cannot manage without various leather articles as gloves, clothes and especially footwear, there are numerous countries in which such important and expensive raw material (fresh hides and skins) is not properly cared for after slaughter of animal and flaying and becomes not available for leather making. Fortunately, in most world countries a well-developed system of hide and skin collection exists to provide the necessary qualitative raw material for the leather industry. In Figure 2.1 is presented scheme of conventional leather processing. The preservation of raw material in this chain plays very important role because qualitative leather cannot be produced from badly preserved hides or skins.

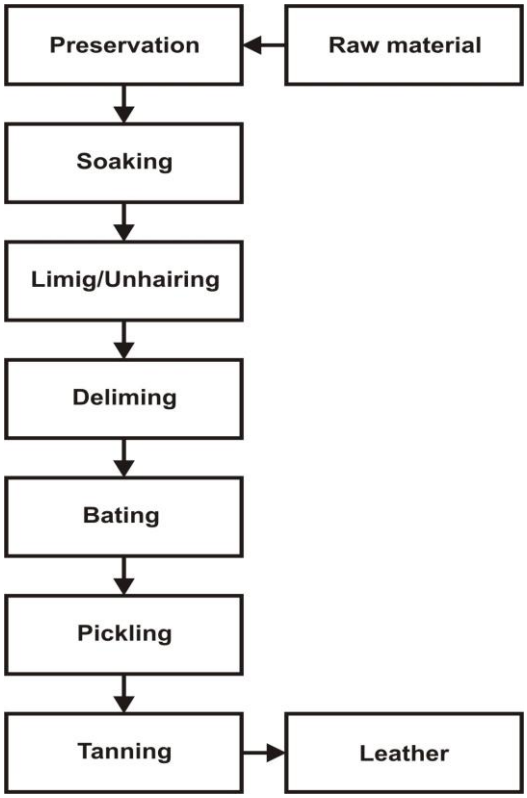


Figure 2.1 Technological scheme of leather processing [author's illustration]

According to the main aim of the dissertation a literature analysis was carried out. It is based on scientific information about hide and skin preservation. Various chemical and physical preservation methods were described especially paying attention for the methods of short term preservation. Main advantages and disadvantages of the methods were emphasized.

The structure of hides is briefly represented as well. Within the chapter factors responsible for putrefaction of hide/skin were described. Also, literature about the use of vacuum in leather manufacture was gathered.

Additionally, a situation in leather industry in Latvia is analysed as well. There are gathered facts about leather manufactory elimination and enumerated problems in yield of leather processing in Latvia. Economical aspects of leather manufactory like import and export data are described. Data about slaughterhouses, household animals in Latvia, slaughtered animal count in Latvia are presented.

2.1 Leather industry in Latvia

The raw hides and skins are widely used in the whole world tanning industry as a by-product of meat and milk industry suitable for further processing. The situation in states where leather industry is not developed or has been abolished is similar to Latvia, i.e., by-products as raw hides and skins are simply thrown away or destroyed.

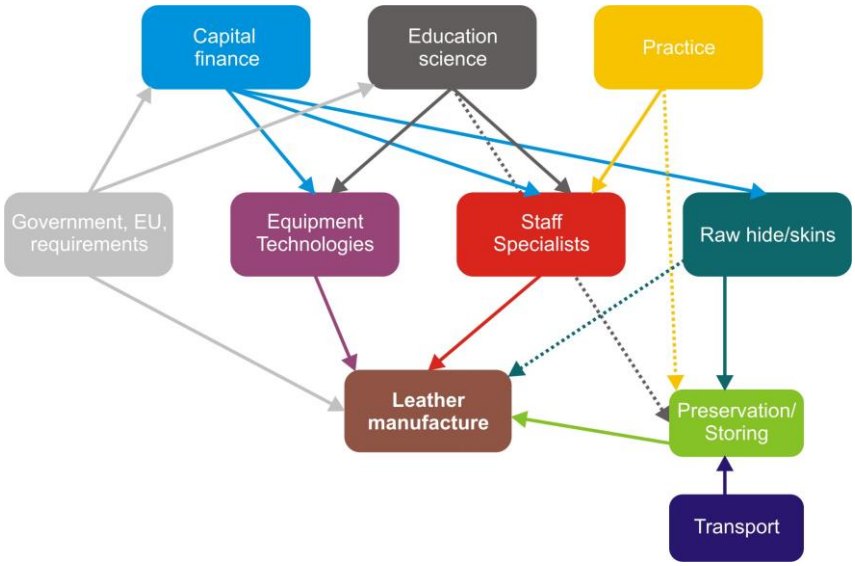


Figure 2.2 Leather manufactory basic resources and constraints [author's illustration]

Leather industry branch is impeded essentially by great amount of illicit slaughter houses, requirements of the EU, raw hide dealers, lack of professionals, no higher establishment with leather handling studies and raw hide storing possibilities (Figure 2.2).

As it can be seen from Figure 2.2, p.18, the leather industry branch in Latvia is dependent from many factors, resources and is also impendent by various constraints. For leather manufactory sustainable development it is necessary to find out factors which are impended it:

- European Union and government requirements for leather processing. These requirements are referred to leather processing pollutions. [3] [4]
- Education and science: there are no higher educational establishment which prepares specialists for leather industry (especially for hide tanning). If there are no any specialists in this area (except employees of joint-stock company Ritales) it could be a real end of leather manufactory in Latvia. For this reason it is necessary to do urgent activities and to work out principles for rescuing of this branch of manufactory as soon as possible.
- Staff, specialists in leather manufactory: in Joint-stock company Ritales works 50 employees, only 3 of them has higher education in leather tanning speciality (they got their education in Russia). It is necessary to find out ways how they could transfer their practical skills to other-future specialists.
- Capital, finances play important role in whole system together it affects equipment purchasing, education possibilities, science and specialists supporting and also raw material acquisition (including prices, transport etc.).
- Raw material: the most important problem with raw hides and skins is to store them for longer period organizing the possibility to produce leather in Latvia. But other factors such as lack of professionals, money and technological and laboratory equipment impede it. If the raw hides and skins are not properly stored, they start to deteriorate and no longer factory fit. Nowadays for raw hide preservation NaCl salt is widely used (but it is a waste use of salt). That is the reason other manufactories and slaughter houses try to use other raw hides and skins preservation methods. As an example, in slaughter houses in Lithuania do not salt raw hides but keep them in fridge in appropriate temperature (storing time is shorter in such case).

Leather tanning manufactory is strategically important for promotion of development of national economy of Latvia.

In order to implement the requirements of people in the conditions of population growth from nature available resources and services should be efficient as

possible within the society. Social efficiency means that resources will need to be used where they are necessary the most.

2.1.1 History of leather manufacture in Latvia

Tanning is the process of leather making which converts animal hide/skin into leather without decomposing of its structure. Animal skin has been used for different purposes in human society and the tanning process itself is known since the Paleolithic era. [5] In Late Iron Age leather became as an export product and served as a symbol of human's position in society. The wide availability of instruments for tanning in the period of Late Iron Age testified about that, as well as medieval archaeological monuments and written sources.

Nowadays manufacturing of leather and leather production is a branch of national economy (a section of international standard classification of economical branches; DC) which integrates all enterprises dealing with hide tanning and manufacturing, production of different leather products, for example, suitcases, bags, harness, footwear etc.

Even in the twenty first century, the manufacture of leather retains an air of the dark arts, still somewhat shrouded in the mysteries of a millennia old, craft based industry. Despite the best efforts of a few scientists over the last century or so, much of the understanding of the principles of tanning is still based on received wisdom and experience. [6]

Leather industry is one of the oldest industries in Latvia. The first leather manufactories were formed at the end of 18th century gradually competing with different handicrafts of leather processing which were established during Middle Ages.

In 1910 there were 46 manufactories which were concerned with leather processing and production of articles from leather with 3405 workers in Latvia, and at 1913 the number of workers involved in leather and leather articles industry had grown up to 6800 workers. [7] The most prominent and the biggest manufactories were L.Jacobson footwear factory (established in 1889), leather and footwear factory Riga city Bufalo (2000 workers), Vildenberg leather factory in Riga (500 workers) (Figure 2.3, p.21), M. Grebner wax cloth and hat factory in Jelgava city (375

workers), H.Grilih leather factory in Daugavpils city (300 workers) (Figure 2.4), Mercury footwear factory in Riga city (220 workers). [8]

OSKARA VILDENBERGA

SAVIENOTO ĀDAS FABRIKU AKCIJU SABIEDRĪBA

Valdes priekšsēdētājs Jānis Ekserts
„ „ vietn. inž. tehn. kīm. Herberts Rozenfeldts

B/M

RĪGĀ (Torņakalnā), 1939. g. 2. septembrī.
Bauskas ielā 16.

Figure 2.3 Document from Vildenberg leather factory [9]

Ll-63 ARHĪVA KOPIJA

ĀDU FABRIKA G. M. GRILICHES ĀDU FABRIKA

DAUGAVPILĪ — LATVIJĀ

Telefoni: 3-179, 2-194
Pasta kastīte 1

Telegrammu adrese
»GRILICHES«

Daugavpilī, 1940. g. "16" novembrī.

Figure 2.4 Document from H.Grilih leather factory [10]

In 1915 all Latvia's manufactories were relocated to Russia. In 1918 when Latvia became as independent state, the leather manufacturing had to start from the beginning. At that time the number of small footwear workshops (1-2 workers) increased, where both the production and the repair of shoes were realized.

Only few of above mentioned manufactories were able to continue their existence. For example, L.Jacobson footwear factory remained the same, factory Riga city Bufalo was split into few small footwear manufactories. In 1935 there were 152 factories (tanneries, harness workshops, hide and leather production enterprises) with 1401 workers, 12 footwear factories with 605 workers and 1541 shoemakers with 2409 workers in Riga. In 1938 the leather industry of Latvia contained 97 enterprises with 1650 workers, which accordingly made a 1.6% of total amount of enterprises and 1.4% of factory workers. 53 of 97 enterprises were located in Riga city. [11]

In 1937 the holding company Skin and Wool Central was founded (capital asset 0.3 millions of Lats), which held a state monopoly of wool and raw hide import and export. In 1938 the company had bought hides and skins, the value of which was

measured in 6.8 millions of Lats, at the same time the export (for the most part to Soviet Union, the USA, Germany, Sweden) of hides/skins was measured in 2.8 millions of Lats. The company functioned till the 1940. About 60% of raw material was domestic origin, and accordingly 40%-imported. The total asset of leather production was 21 million of Lats, 91% of production was used by domestic consumption, 9%-for exportation.

As regards to soviet times of Latvian Republic at that time all main sub-branches of the leather industry were developed. In 1940 3.3 thousand of workers were engaged in production of leather goods, the modernization was realized and the production line for footwear manufacturing was introduced. The biggest enterprises were such as Riga city leather factory (with 136 workers), Jelgava city leather factory (101 workers) (Figure 2.5), Liepaja city footwear factory "Apavi" (162 workers), Riga city leather factory "Uzvara" (110 workers).


A/S. A.V.C.
JELGAVAS ĀDU FABRIKA
JELGAVĀ, DOBELES ŠOSEJĀ № 2. TĀLR. 523.
JELGAVĀ, 1940. g. 4. decembrī.

Figure 2.5 Document from Jelgava city leather factory [12]

In 1964 15 thousand workers were involved in manufacturing of different kind of leather goods. The most prominent enterprises at that time were leather processing factory (production association) "Kosmoss" (982 employees), footwear factory "Pirmais Maijs" (2158 employees), footwear factory "Blazma" (1424 employees), footwear factory "Rekords" (782 employees), fur factory "Elektra" (608 employees). In 1964 in comparison with 1958 the total production of leather goods had risen for 39%. [13]

The electrical supplying technology had also risen for 45%. In 1965 the total amount of fixed assets of manufactured goods in the field leather production had reached 19 millions of Soviet Union rubles. The comparison of total amount of production in main directions of leather industry in 1960, 1970 and in 1980 was such: production association "Kosmoss" supplied the main part of domestic footwear and fancy goods manufacturers with leather as well as 42.5% of its hard leather production and 19.9% of soft leather production was sent to other republics of the

Soviet Union. Approximately 50% of domestic raw materials were used by domestic leather industries, the other 50% were used by or imported to other republics of the Soviet Union. Later the artificial leather substitutes were used increasingly in the manufacturing of fancy goods and footwear. The main producers of such substitutes in the Soviet Latvia were experimental leather factory "Ozolnieki", which during the 1982 had produced 201 millions square decimetres of artificial leather. [7]

In the eighties the main manufacturers of leather goods were such enterprises as leather company "Kosmoss", integrated plant "Somdaris" of production of such leather haberdashery as bags, suitcases, briefcases, gloves, belts, souvenirs (the production of that plant was very popular abroad), fur factory "Elektra" which manufactured collars, caps etc. goods from natural and artificial leathers. [13]

In 1985 the specific weight of branch of production of leather goods within the total industry of Latvia was 2.6%, the amount of involved people in that branch was 3.3% of total number of employees. In 1990 these numbers were accordingly 2.1% and 2.5%, in 1994-1.5% and 3.1%, in 1995-1.0% and 2.4%, in 1996-0.9% and 2.2%.

During the 1st quarter of 2001 605 employees were involved in the processes of leather processing, in production of suitcases, bags and such type of goods, and in manufacturing of footwear and harness (for 574 of employees it was principal work).

The specific weight of leather production within the total amount of production of Latvia was 0.1-0.2% in 2000, and 0.1% in the 1st quarter of 2001. In the beginning of 2001 34 companies were involved in the raw hide and skin and leather goods production in Latvia. The biggest ones were such companies as "Rital", "Trilari", "Akots", "Dabiska ada", "Adas galanterija", "Somdaris" etc. Currently only company "Ritales" is still functioning. [13]

From Middle Ages till nowadays all experts in hide handling got their education in different world countries, mostly in Russia and Lithuania.

Currently, there is only one currently functioning leather producing enterprise in Latvia: joint-stock company Ritales (located in Jelgava city) with approximately 50 employees. Employee’s age is between 40 and 60 years. Many of them got the leather technologist specialty in Russia (due to the lack of professionals which could spread knowledge about leather processing in Latvia). Ritales tannery is dealing with Latvia’s livestock (mostly the cattle (cows and oxen) is used) from definite slaughter houses. [14] Joint-stock company Ritales exports 95% 41th combined nomenclature

group products: raw hides and skins (other than furskins) and leather. 5% from all production stays in Latvia as a leather for other goods.

If there is no any specialist in this area (except employees of joint-stock company Ritales) it could be a real end of leather manufactory in Latvia. For this reason it is necessary to do urgent activities and to work out principles of rescuing this branch of manufactory as soon as possible.

Latvia has marvellous reserves of skin materials: a lot of livestock (cows and oxen) are being tended till nowadays. It is self-explanatory due to the old traditions people have been leaving on eating meat. Another question is what to do with such packing-house by-product as raw hide/skin. It is absolutely clear that specialists of many branches in Latvia should raise awareness of this problem. Latvia essentially needs both professionals and manufacturers of leather production. Thinking about the future and the improvement of economical situation the chain of measures must be planned and must be done, therefore giving a space of activities for slaughterers, leather manufactures, and scientists and so on.

The first reason of those manufacture elimination is non-effective hide/skin delivery from slaughter houses. The second reason is hide/skin preservation problems both in slaughter houses and tanneries. Thee third reason is the lack of hide/skin handling specialists in Latvia. For this reason it is necessary to do urgent activities and to work out principles of rescuing this branch of manufactory as soon as possible.

2.1.2 Export and import of raw hide material in Latvia from 2001 till 2012

As was mentioned previous, hides and skins are widely used in the whole world tanning industry as a by-product of meat and milk industry which is suitable for further processing. The situation in states where leather industry is not developed or has been abolished is similar to Latvia, i.e., by-products as hides and skins are simply thrown away or destroyed.

All raw materials for leather manufacture gets from slaughterhouses of Latvia. From PVD (Food and Veterinary Service) data till 2012 were 82 slaughterhouses and one mobile slaughterhouse for sheep slaughtering.

According to currently situation Government has approved the law to allow to slaughtering of animals in own households. Due to this fact it is very difficult to

precise data about slaughtered animals in territory of Latvia. Slaughtering in own households can be done if [15]:

- *It is made according to PVD regulas; Only 3-30 animals are slaughtered; Special chambers for slaughtered animals are built.[16]*

Table 2.1

Number of animals in the territory of Latvia at the end of the year (in thousands) [15]

	2010	2011	2012
Cattle	379	381	393
i.e. dairy cows	164	164	165
Pigs	390	375	355
Sheep	77	80	84
Goats	13	13	13
Horses	12	11	11
Fowls	4949	4418	4911

The main part of legal slaughterhouses are oriented to the slaughtering of fowls, pigs, cattle (mostly calves, cows and bulls) and sheep [17].

Table 2.2

Slaughtered animals in Latvia's slaughterhouses (2010/2011) [18] [19]

Year	Cattle	Pigs	Sheep	Goats	Horses	Fowls
2012	92 588	329 919	11 281	50	519	14 748 099
2011	90 760	246 236	8528	27	424	15 081 405
(%) from total amount	**0,599**	**1,882**	**0,065**	**0,0003**	**0,003**	**97,451**

As it can be seen from the Table 2.2 the main part of slaughtered animals contains from fowls (97%), pigs (1.8%) and cattle (0.59%). Only cattle hides (hides of cows, bulls and calves) are used for the leather manufacturing. Nowadays leather is and industrial intermediate product which is used by branches of industries of consumer products. Within the EU the most significant production market for leather is manufacturing of footwear, clothing, leather goods and also automotive industry [20].

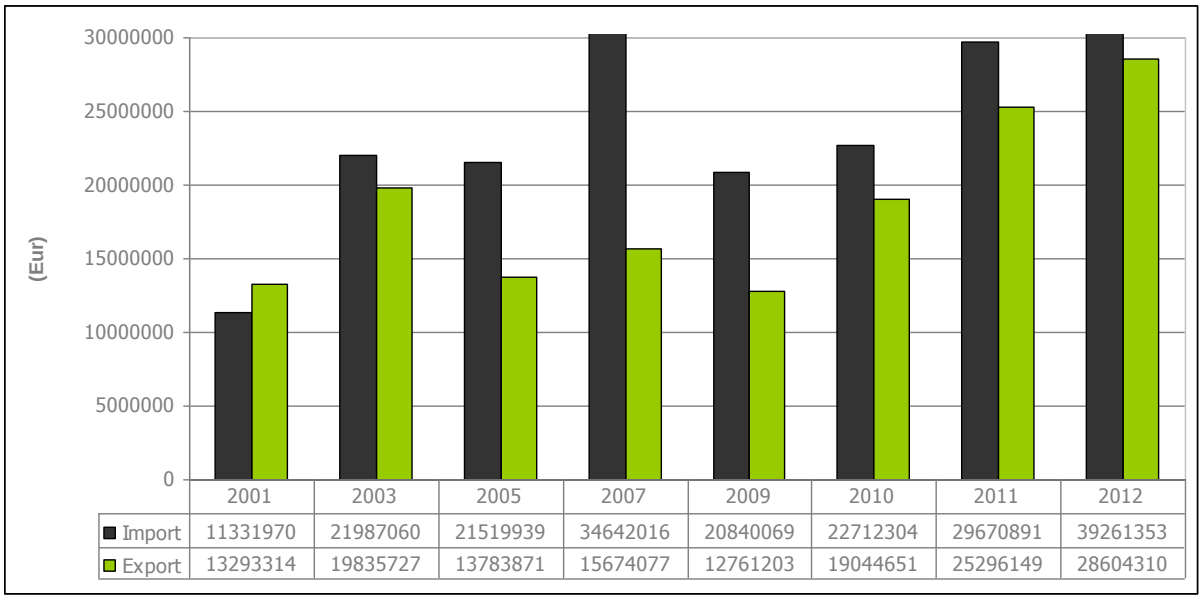
Every year in Latvia thousands of cattle (total number could be 100 000) are slaughtered, total mass is 200 tons of hide per month. [17]

The amount of hides and skins processed monthly by company Ritales is 100 t producing about 14 300 square meters of semi-finished leather for the exporting to other European countries. [14]

Joint-stock company Ritales exports 95% products, which are incorporated into 41th combined nomenclature group products: raw hides and skins (other than furskins) and leather and only 5 % from all production stay in Latvia as a leather for other goods. [14]

From 2001 till 2008 chapter 41 [20] product level have been decreasing since year 2003. Till 2003 this production export and import grew very fast because there were more hide/skin treatment manufactures ("Ritales", "Trilari", "Akots") as nowadays. As was mentioned, today is working only one manufactory "Ritales".

After Latvia joining to EU (European Union) in 2004 export and import started to decrease. The reason of this decreasing was numerous EU regulations and laws for leather processing materials, hide storing and other export regulation. Export decreasing also was influenced by hide/skin treatment enterprises elimination from market (Figure 2.6, Figure 2.7, p.27) [21].



	2001	2003	2005	2007	2009	2010	2011	2012
Import	11331970	21987060	21519939	34642016	20840069	22712304	29670891	39261353
Export	13293314	19835727	13783871	15674077	12761203	19044651	25296149	28604310

Figure 2.6 All Leather Chapters (41;42;43) import and export data in Latvia from 2001 - 2012 (EUR) (2001, 2003, 2005, 2007, 2009, 2010, 2011, 2012) [21]

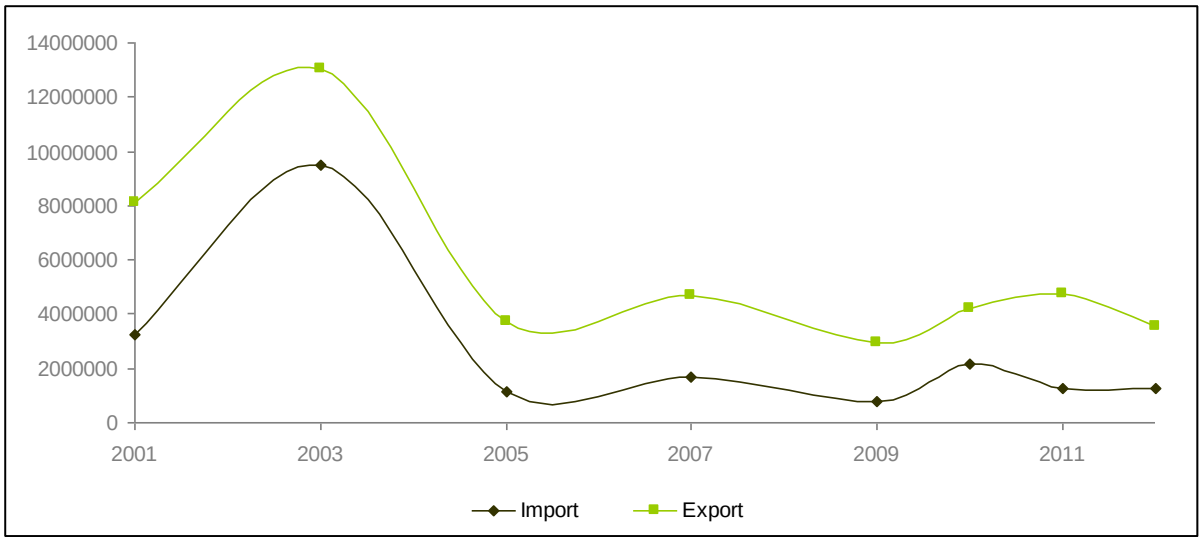


Figure 2.7 Chapter 41 (Hides and skins (other than furskins) and leather) (EUR) export and import in Latvia (2001, 2003, 2005, 2007, 2009, 2010, 2011, 2012) [21]

For example in 2001 major Chapter 41 import groups were: 410121000 (34.6%-784991 Ls/1121415,7 EUR): whole hides and skins, unsplit, of a weight per skin not exceeding 8 kg when simply dried, 10 kg when dry-salted, or 16 kg when fresh, wet-salted or otherwise preserved; 410439100 (21.3%-484754 Ls/692505 EUR): tanned or crust hides and skins of bovine (including buffalo) or equine animals, without hair on, whether or not split, but not further prepared: In the dry state (crust).

Comparing with 2012, where major Chapter 41 Import groups were: 41152000 (26.8%-239490 Ls/342128 EUR): Parings and other waste of leather or of composition leather, not suitable for the manufacture of leather articles; leather dust, powder and flour; 41015030 (19.6%-175516 Ls/250737 EUR): Raw hides and skins of bovine (including buffalo) or equine animals (fresh, or salted, dried, limed, pickled or otherwise preserved, but not tanned, parchment-dressed or further prepared), whether or not dehaired or split: Wet-salted.

In 2001 major Chapter 41 export groups were: 410110100 (32.1%-1827419 Ls/2610598 EUR): raw hides and skins of bovine (including buffalo) or equine animals (fresh, or salted, dried, limed, pickled or otherwise preserved, but not tanned, parchment-dressed or further prepared), whether or not dehaired or split; 410121000 (24.1%-1373069 Ls/1961527 EUR): Whole hides and skins, unsplit, of a weight per skin not exceeding 8 kg when simply dried, 10 kg when dry-salted, or 16 kg when fresh, wet-salted or otherwise preserved.

But major Chapter 41 export groups in 2012 were: 41015030 (55.5%-1378744 Ls/1969634 EUR): raw hides and skins of bovine (including buffalo) or equine animals (fresh, or salted, dried, limed, pickled or otherwise preserved, but not tanned, parchment-dressed or further prepared), whether or not dehaired or split: Wet-salted; 41041951 (29.5%-731610 Ls/1045157 EUR): tanned or crust hides and skins of bovine (including buffalo) or equine animals, without hair on, whether or not split, but not further prepared: Whole hides and skins, of a unit surface area exceeding 28 square feet (2,6 m²). Detailed import and export information can be seen in appendixes: 1;2.

In 2006 in whole world leather manufacture branch included about 3700 enterprises with turnover of 10.6 milliards of euro. In the enterprises of 27 EU member states about 52 thousands of people were employed. Tanneries in the EU mostly are family-owned enterprises and small or medium factories. Quite strong regional concentration in the EU is existing, in some states leather industry plays a very significant role in the national economy due to the source of wealth and working places.

In the context of providing general competitiveness the special attention is drawn to the possibilities of European tanning industry and to the risk factors in the situation of enlarged EU. Considering the integration of enterprises of leather industry of so called newly EU member states it is foreseen (and it is being seen currently to some extent) that these processes will rise a structural adaptation due to the several reasons, including the fact that one of advantages of newly EU member states: law costs on human resources, would gradually diminish.

Preservation of rawstock has the objective of rendering the flayed hide/skin resistant to putrefaction to allow transport and storage. Preservation is often referred to as “curing”, but this implies some form of chemical treatment, although the terms are often used interchangeably.

Preservation is accomplished either by destroying active bacteria, by preventing bacterial activity or by preventing bacterial contamination.

It is important to recognize the effect of "salting", defined as the delay between flay and cure, when bacterial activity may proceed. It has been shown that a delay of as a little as 24 hours will guarantee some grain damage. That is why hide and skin preserving is made by salt. This use for preserving foodstuffs is ancient: globally it is still the most common way of hides and skins preserving.

There is mostly used wet salting in Latvia. “Wet salting” is easy and convenient: the term refers to the application of dry sodium chloride to the freshly flayed hide or skin, which is wet with the natural moisture content. Sometimes hides and skins are salted in slaughterhouses but sometimes just in tannery A/S Ritales. This causes a problem, because non-salted hide structure can be damaged till it gets to the processing. And as a result: leather quality level decreases.

As it was mentioned before, Joint Stock Company Ritales is able to process only 100 t of hides per month. The other part of hides (100 t) becomes useless due to the fact that neither Ritales nor other companies are able to store unprocessed hides and skins. It indicates that a half of raw material of slaughtered stock and cattle are liquidated. Thereby, the conclusion could be done about the fact that the question of raw hide and skin processing and utilization in Latvia has not been solved yet.

As it is known European Union has worked out many regulations (directives) regarding hide and skin preservation. The requirements of these legal acts, especially regarding to special hygiene conditions and separate chambers for hide and skin storage impacted essentially the situation with hide and skin preservation in slaughter houses of Latvia due to the increase of expenses. For this reason hereafter it is not possible to secure the durable storage of hides and skins in slaughter houses of Latvia.

2.2 Skin structure

Skin as a natural material is required to perform different functions, to deal with different stresses over its area.

Skin is anisotropic, its structure and properties vary over its area. The parts of hide or skin can be defined in terms of the "butt", the "belly" and the "neck".

The butt is defined by the region up to half way from the backbone to the belly edge and two-thirds of the way from the root of the tail to the neck edge: within this region the fibre structure is relatively consistent and hence the physical properties of the skin or leather are consistent.

The remaining regions to the side of butts are called belies and the remaining region the butt towards the head is the neck (Figure 2.8, p.30).

The regions can be characterized as follows. The butt has a tight fibre structure, making the skin relatively firm and stiff: it is thick compared to the belly, but thin compared to the neck.

Belies of all skins are the thinnest parts, with an open structure, making them relatively weak. The neck is the thickest part, also with relatively open structure. It is an important aspect of the technology of leather making to try to make the non-uniform skin structure as uniform as possible in the final leather product.

The butt region contains the Official Sampling Position: because of the anisotropic nature of skin, to accommodate its physiological functions, it is necessary to make best comparisons of leather properties. It is also important to note how the anisotropy varies over the whole skin. [5]

For this reason, sampling for physical testing is routinely done in two ways, parallel and perpendicular to backbone.

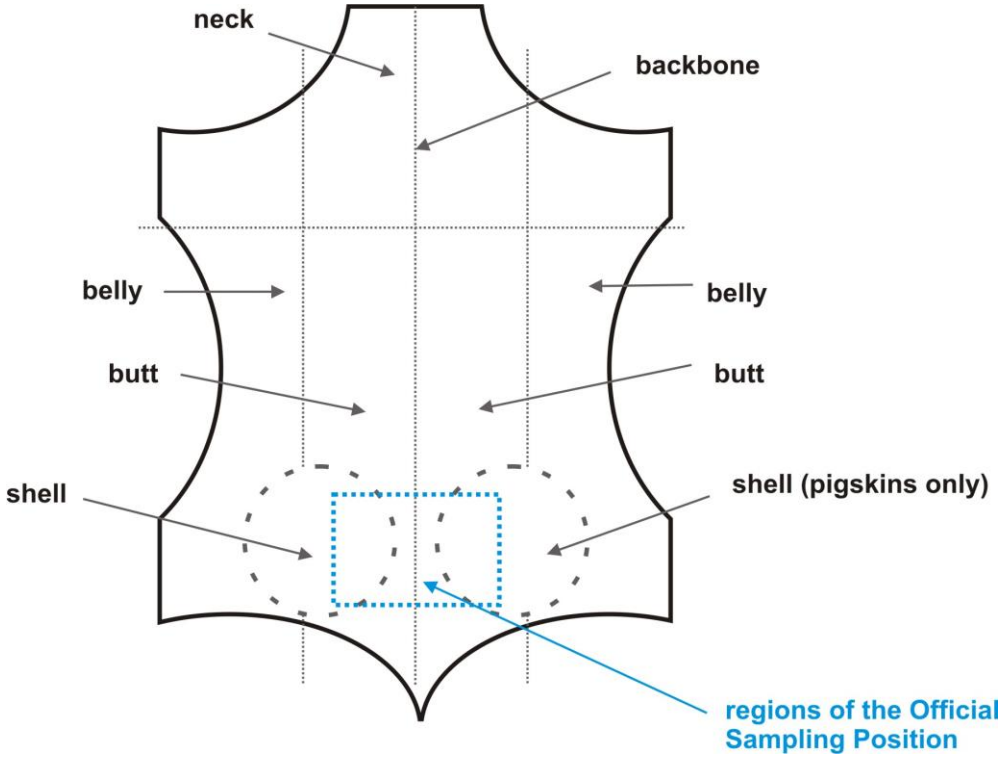


Figure 2.8 Defined regions within the hide: butt, belly, neck [5]

The direction of the fibre weave, indicated in Figure 2.9, p.31, demonstrate the influence of the direction of physical testing. Because the skin has to stretch to accommodate stomach filling, skin and its derivatives exhibit greater strength perpendicular to the backbone than parallel to he backbone. Another notable feature is the symmetry features in the skin about the backbone. This is useful in

experiments or testing, when samples are matched from the two sides of the same hide.

The appearance of the grain layer is generally consistent over the skin, with the exception of the neck region, where "growthiness" may be encountered. The incidence and degree of this effect depends strongly on species and breed, being most apparent on bull cattle hides and merino sheepskins. It takes the form of ripples in the skin, across the neck region, held in places by the elastin content.

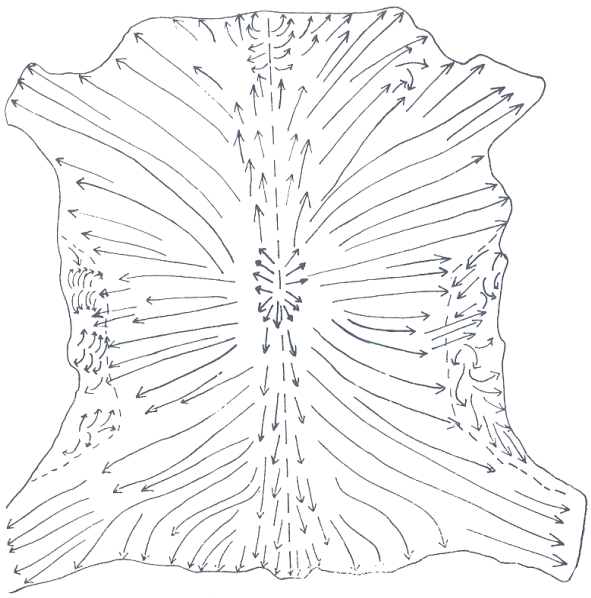


Figure 2.9 Anisotropy of fibre structure over the hide or skin [5]

The area of piece of hide, skin or leather depends primarily on the angle of weave of corium. The angle of weave is fixed within the structure by two controlling elements of structure, the flesh layer and the grain (see Figure 2.10).

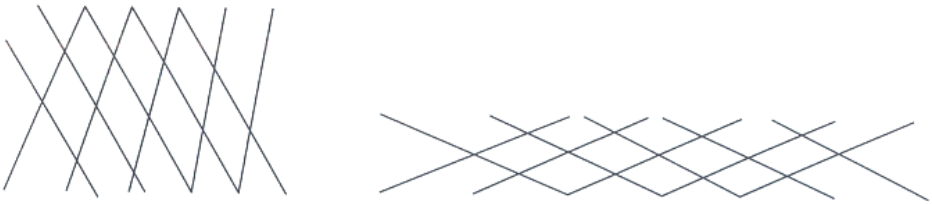


Figure 2.10 Representation of the influence of fibre angle of weave on area [5]

Chemical skin composition is presented in Figure 2.11, p.32, The most important constituent in skin is protein collagen which covers about 90% of absolutely dry hide weight. Quality of leather depends on effect of chemical materials on the collagen during leather processing.

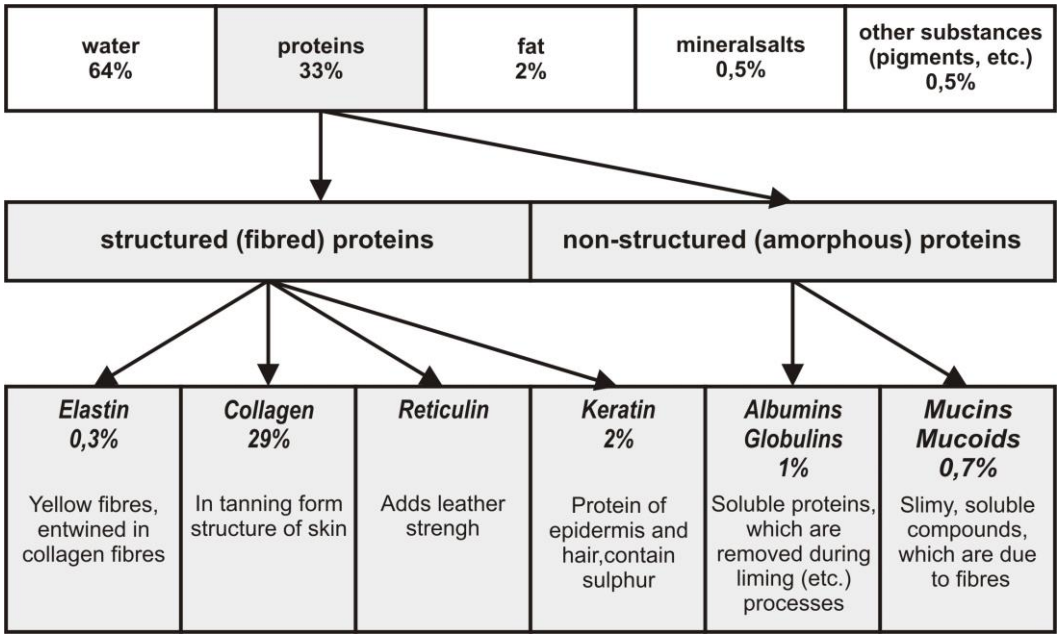


Figure 2.11 Chemical compositions of skins [22]

Hide structure is presented in Figure 2.12.

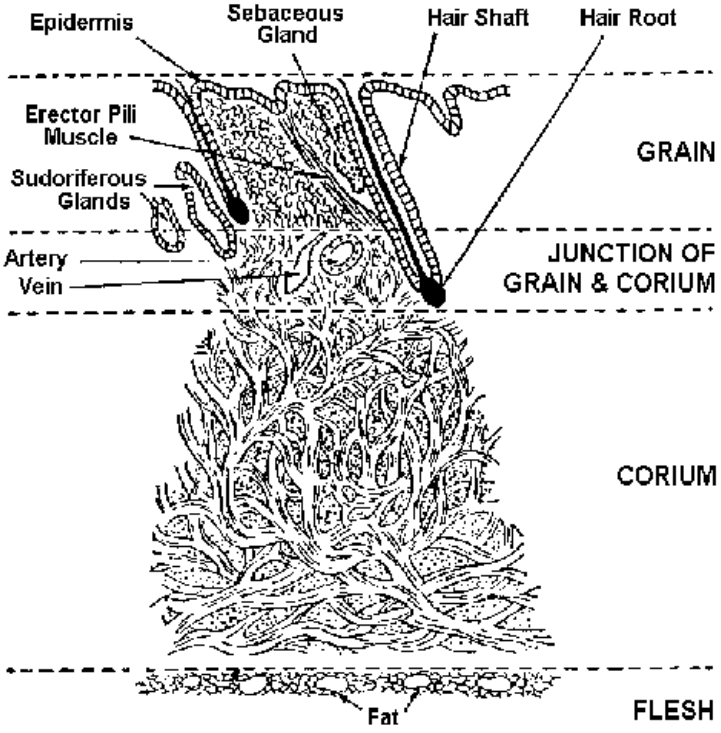


Figure 2.12 Illustration of the structure of skin (cross - section) [5]

Epidermis is the outermost layer of the raw skin, the barrier between the animal and its environment: it is composed of so-called "soft keratin", characterised

by a relatively low content of cystine compared to cysteine, i.e. less oxidation of the thiol groups to the crosslinking disulfide group.

In the early stages of processing, when hair or wool is removed from the skin, particularly by chemical dissolving techniques, the epidermis is also removed.

Grain is the uppermost layer in unhaired or dewooled pelt, the corium minor, is also referred to in the jargon as the grain layer. The structure is fibrous, but the fibres are so fine the appearance is more like a solid. The lack of fibre interaction in a comparison with lower layer of the skin, makes grain week. The macro-structure is a convoluted sheet, because the grain layer is larger in area than the lower layers, so it has to be folded.

There is a layer of collagen on the grain surface, known in the jargon as the grain enamel: the structure may be based on type III collagen since it is known to concentrate in the grain. [23]

This is the most valuable part of the skin, because it provides the desired appearance of the grain: in particular, the enamel confers the appearance to the naked eye of a continuous, reflective surface.

Damage to the grain enamel reveals the underlying fine fibres of the grain which scatter light more than the enamel, therefore altering the perceived colour and appearing dull. Breaks in the enamel may create paler or darker areas, because coloured molecules either penetrate more easily through the surface or coloured particles lodge in the exposed fibre structure. This can occur with dyes: the water soluble, hydrophilic dyes penetrate more easily to confer paler appearance, the less water soluble or insoluble dyes cause colour build up in the faults, to appear darker. Chemically, the grain is the same as the more obviously fibrous corium, so the impact of chemical modification is the same. However, because the grain has a more solid structure, filling it with stabilising chemicals can embrittle it, allowing it to crack when stressed, especially, if it is not adequately lubricated. [23]

Junction. The grain-corium junction is the transition zone between the very fine fibres of the grain and the much larger fibres of the corium. It is an open structure, consisting of relatively small fibres and carrying other structural components of the skin: these include the veinos system and, in the case of sheepskins, lipocytes, which are the cells that contain triglyceride fat. [5]

Corium. The main part of the skin is the obviously fibrous structure called the corium or the corium major. The fibre structure varies trough the cross section of hide

or skin: the fibres increase in size, reaching a maximum fibre diameter in the centre of the corium and then decreasing a little as they approach the next lower layer.

The network of fibres, often referred to as the weave, consist of fibres dividing a recombining with other fibres. This makes the corium strong, able to resist stresses placed on it: the distribution of a stress imposed on the fibre structure from the point of stress over the surrounding area is reflected in resistance to the stress, observed as strength.

An important feature of the corium structure is the angle of weave: experienced observes of corium structure can estimate the average angle-magnitude of the angle can provide useful information regarding the process history of pelt. The average angle of weave in raw skin is about 45^{o}; a lower value indicates greater depletion or relaxation of the corium and a higher value indicates a degree of swelling. [24]

Flesh layer is the layer of the skin closest to the flesh of the animal: although it has a distinct fibre structure, it is still part of the corium. Its structure is characterized by the low angle of weave, always lower than the corium angle of weave.

Flesh, hides and skins are inevitably presented to the tanner with adhering flesh (muscle) and fat. This must be removed at the earliest stage possible in the processing programme, because it creates a barrier to the uniform penetration of chemicals, which would cause non-uniformity of leather properties. The traditional method of fleshing was to place the hide or skin over a wooden beam, inclined at about 45^{o}, then manually scrape off the flesh and fat with a sharp, double handled knife. This is the derivation of the term “beamhouse processes”, referring to the process steps conducted on the beam, leading to the tanning step. In modern tanneries this process is done by machine, using a blade fixed to a rotating cylinder.

2.3 Hide and skin preservation

Leather industry is probably the oldest industry in the whole world. Also, in nowadays it takes a big role in whole world economic system.

Despite of incomes, leather industry is also very pollutant industry not only in raw material production but in preserving as well. [25] Preservation of raw stock has the objective of rendering the flayed pelt resistant to putrefaction to allow transport and storage. Preservation is accomplished either by destroying active bacteria, by

preventing bacterial activity or by preventing bacterial contamination. During preservation it is essential to avoid from usage of toxic materials as these materials are very dangerous for environment due to their chemical nature.

The raw hides and skins are flayed from the animal and processed further into leather. Curing or other preservation of hides/skins is performed as the primary step of leather processing. As the main constituent of the raw skins and hides is protein, they are much susceptible for bacterial degradation. Thus, it is essential to preserve the protein matrix and also to arrest microbial attack temporarily. [26] Despite that several chemical, biocidal and physical methods have been advocated and adopted, the preservation using salt remains the popular curing technique worldwide due to ease, cost-effectiveness and the quality of the finished leather produced. Common salt is employed as the conventional agent for curing purpose. It is also not very safe and useful method because of waste of natural materials (salt) and damage to nature (during processing all salt is washed out). Use of the salt enhances the pollution load of tannery effluent which becomes highly contaminated with increased total dissolved solids (TDS) and chlorides (Cl^-). [27]

Preservation of rawstock has the objective of rendering the flayed pelt resistant to putrefaction to allow transport and storage. The mechanism of putrefaction is the production of proteolytic enzymes by bacteria. Following the death of the animal, these bacteria cause autolysis of the collagen. This breaks down the protein to amino acids, which further break down to produce ammonia. Other reactions include the hydrolysis of triglyceride fat to free fatty acids and glycerol by lipases and the breakdown of carbohydrates into sugars by carbohydrase enzymes. [28]

Ideal practice in the abattoir would be to spread the newly flayed pelt onto concentrate, to remove the body heat as rapidly as possible, then put it into cure or into processing as soon as possible. It has been shown that a delay of as little as 24 h will guarantee some grain damage. This can be appreciated when it is known that the bacteria on hides can double in numbers in less than 4 h at 25^{o}C. [29]

In reality, hides and skins are typically held in piles prior to curing or processing, so they are effectively kept warm-this is a reflection of the abattoirs view that hides and skins are only a byproduct of the meat industry, with little associated value to them compared to the value of the carcases. Consequently, because some

incipient damage is often caused, whatever curing system is used, the process can only halt bacterial action and the damage caused after flaying remains. [30]

Hence, efforts should be harnessed to search and adopt cost effective and environmentally safer curing methods which will not affect the quality of the resultant adversely.

2.3.1 Physical preservation methods

Leather industry requires copious amount of water and a plethora of chemicals for leather processing to arrive to a final form of usable leather, which makes the industry one of the most polluting industries in the world. [31]

Unfortunately, conventional method of hide preservation by sodium chloride is the first which begins the chain of leather manufacture processes and which characterises by high environmental pollution.

Therefore, the ideal is doing not any preservation method: immediately after flaying to deliver fresh (green) hide for leather processing. A green hide needs only to be rinsed to remove dirtiness: blood, dung etc. But word "immediately" means not later than 2 hours after flaying. The specificity of the leather processing is simultaneous treatment of comparatively big quantity of hides (no by one), Due to this, long period (significantly longer than 2 hours) is needful for collection of enough hides for processing. [32]

Other simple method which does not require any chemicals is drying. Drying can be divided into two ways: natural in sun or controlled drying. The simplest and cheapest method is to dry hides/skins by evaporation under the sun. The use of drying is limited to those countries where the climate is conductive to drying. [27]

Dried hides or skins must be folded while damp, to avoid cracking the dried pelt. This preservation wherever practised is often poorly controlled resulting in either overdrying leading to subsequent problem in further processing of leather or under drying leading to deterioration of skin. Air drying reduces the water content of the hide, often to below 15% and leaves the interfibrillary proteins intact. In this case rehydration becomes longer because the fibres stick together.

When the hide has been dried too quickly the water in the outer layers evaporates leaving a crust which makes further extraction of water, from the centre of fibre structure, difficult. The centre is then still moist and ideal for putrefaction. The

damage is to be seen after rehydration when holes appear when the collagen has degraded. Generally, sun dried skins produce inferior quality leathers and there are difficulties in wetting back of skins/hides while processing into leather.

The fresh skin can be dried in a controlled environment within 24 hour by using drying chamber at 26^{o}C. Skins are toggled on the perforated metal frame, flesh side out, prior to drying.

In this method, a much greater control over moisture content is possible, thereby resulting in a more consistent product. Spoilage due to putrefaction has been virtually eliminated, and the rate of rehydration of the skin is similar to that of salted skins. This method provides long term preservation.

However this method requires high installation and running cost. In the wet seasons due to high humidity drying time may be increased which results in putrefaction of hides and skins. In such cases pretreatment of hides and skins with bactericides may be necessary.

Summarising, such disadvantages of drying must be mentioned: drying problems during the monsoon; growth of bacteria, causing putrefaction; susceptibility to damage by insects, rats, etc; difficulty to rehydrate; difficulty to assess quality of cure; storing in dry conditions required.

In many countries, industrial application of cooling system for hides and skins is being practised. A temperature between +2 and +5^{o}C is employed and the results are reported to be satisfactory. However, preservation time is limited and Table. 2.3 summarizes the dependence of preservation time on the storage temperature.

Quality of the preservation depends on the temperature during the transfer period. Cooled hides and skins should be kept in a well insulated store room and in piles to get the best results. In practice, one of the following methods is adopted to bring about refrigeration of the skins and hides.

Table 2.3

Preservation time as a function of temperature [27]

Temperature, ^{o}C	Time
0	3 week
5	2 week
10	1 week
15	2 days
20	1 day
25	2 hour

The cooling effect can be achieved using cooled air treatment. This technology is adapted to large slaughterhouse where it is possible to automate and therefore cool and store large quantities of hides without handling. By this technique it is possible to process 300 hides/h on a continuous conveyor. Hides are cooled at 5^{o}C for about 45 min. The hides after cooling are piled on palettes. In the case of hot weather, some ice is added between the hides. [5]

Next method of cooling is to add ice. It is possible to cool hides and skins in a continuous way in a mixer by using some ice cubes, cakes or flakes, just after flaying. Within 2 h, hides are collected from 3^{o}C to 1^{o}C and can be stored for 24 h without further treatment. This method is being followed on large-scale in Switzerland, Germany and Austria. The cost of an ice making machine is low compared to a cold room investment. The limitation of the process is the draining of liquor containing high concentration of preservative. [33]

Also dry ice can be used for this purpose. Compared to the normal ice, the hides and skins are cooled to -35^{o}C and cooling is achieved rapidly in the whole area of skin/hide. The method does not suffer from the problems with the use of ice, as given earlier, such as re-wetting problem and brine draining from melting of normal ice. It gives a uniform cooling and preserves the hides or skins for a minimum of 48 h. However, special care has to be taken because of the suffocation risks by the use of carbon dioxide. The cold conditions and the high pressure of carbon dioxide storage must be taken into account. [34]

The disadvantages of cooling are: high investment cost; special equipment for trucks; limited protection in time; risks with carbon dioxide.

The above mentioned cooling systems provide only short term preservation for 24-48 h. When it is necessary to store hides or skins for a longer period of time, it is possible to process it in much colder conditions down to -10 or -20^{o}C. At -10^{o}C, it is possible to preserve hides for 3 month without any problem. Sometime the tissue fibres may be damaged, therefore, it does not appear to be reliable. It is also reported that at the end of the freezing period, bacterial degradation is faster than with the cooled hides. Any hindrance in the freezing step may promote bacterial growth. Advantages of this chilling system are the good grain quality of the resultant leathers, fewer environmental problems because of no use of salt, safer handling of the cooled and chilled hides. The disadvantages are the high investment and

operation costs and high power consumption, especially in warm climates and higher slipperiness of the pelt during fleshing. [34]

Radiation processing (irradiation) is a safe method involving systematic exposure of materials to ionising energy to effect specific chemical or biological changes. While sufficiently energetic to drive chemical reactions, the radiation does not induce radioactivity. Consequently exposed products can not pose any radiation danger. [35] [36]

The two principle radiations used by industry are gamma rays and electron beams. For hide processing, for reasons of efficacy, safety, versatility, speed and cost, electron beams are superior to gamma rays. In electron beam processing, ionizing energy is produced without the use of any radioactive materials. [35]

High-speed electrons are used to sterilize the hides. If the hides are sterile and the enzymes in them are inactivated and they are not allowed to be re-infected, the hides will retain the properties of fresh green hides.

Despite of significantly decreased salinity of effluents, the electron beam method has only theoretical value due to need of very expensive equipment and full protection of the workers operating the equipment.

Overall, the chilling, cooling preservation or treatment by radiation practically are not used because these methods are too complicated for little slaughterhouses. Drying as preservation method is also used seldom due to significant decrease of leather produced from dried hides or skins. Usually, small suppliers of hides and skins need cheap, simple and fast preservation method.

2.3.2 Chemical preservation methods

Curing by sodium chloride is most common method for preservation. Sodium chloride is used amounting 30-40% of total flesh weight. The salt is not a real preservative, because it works on abstracting water from hide so that living condition for bacteria changes. The method is cheap, reliable, available, simple, non-toxic, and hygienically acceptable. On the other hand, the use of the salt enhances the pollution load of tannery effluent which becomes highly contaminated with increased total dissolved solids (TDS) and chlorides (Cl^-) [37]. The high salinity can not be removed by any physical, chemical or biological methods. To overcome this hurdle,

researchers are in constant search of alternative preservation techniques which are either totally void of salt or use only a meagre amount of salt. [38]

Attempts to change sodium chloride by potassium chloride (KCl) were made. The preservation of animal hides and skins with potassium chloride in place of common salt has been carried out with steer hide by brine curing method. The cured stock cannot be distinguished from that cured with common salt except that the potassium chloride hides are considerably drier on the surface. The method prevents from "red heat" defect, and potassium is nutrient to the plant. Unfortunately, potassium chloride is markedly more expensive and characterizes by strong dependence of solubility on temperature. [39]

John Sundar and Muralidharan developed a low salt–MgO substituted skin preservation methodology has been developed meeting the requirements of preservation. The methodology employs less than 25% of salt on the weight of the skin used and is suitable for all conventional raw material resources. [40]

Study on sodium sulphate mediated buffalo hide preservation was carried out. After rigorous laboratory experimentation on moisture content, SEM of hide, pure sodium sulphate as well as sodium sulphate in addition with sodium chloride (i.e. 10% w/w and 20% w/w) proved as most preferable option for curing of buffalo hide which gives effective preservation. [41]

Attempts for hide and skin preservation using powder biocide compositions (Liricure) have been made. [27] The powder preservatives are applied to freshly flayed sheep skins for effecting curing. Minimum effective dosages and relative activities of various preservatives have been worked out. In this method, a mixture of antiseptics with medium coarse sawdust (pine) is applied uniformly to cover the flesh surface.

The powder preservatives used are chlorinated phenol (PCMC) and EDTA (ethylene di-amine tetra acetic acid). Finished leathers are manufactured from the sheep skins and cattle hides after the storage period of 12 months. The physical properties are reported to be comparable with sodium chloride cured system. A powder which may cause difficulties in Liricure powder in precipitating chromium compounds in effluent treatments.

Benzalkonium chloride (BAC) is tested for the short time preservation of hides and skins and as an adjunct for use with salt in brine-curing and green salting. The percentage of (BAC) used for the preservation of fresh calf skin ranges from 0.1-

0.4%. There is no difficulty in processing hides treated with this material and no adverse effect on the leather is found. BAC is a widely used household and industrial antiseptic. There are no toxicity problems at the recommended concentration but BAC may be unacceptable in some by-products. [42]

Temporary preservation of hides using a saturated aqueous solution of boric acid (approximately 4.5%, v/v) both alone and in conjunction with saturated sodium chloride solution has been investigated. Hides soaked in saturated acid solution alone had storage life of only 5 days. [43]

In place of the salt which functions mainly because of its ability to dehydrate the hide/skin below critical moisture content from its bacteriosatic property, a dehydrant silica gel is used to preserve the raw hide/skin. Silica gel at the level of 15 % alone and the level of 10% with biocide Para Chloro Meta Cresol (PCMC) could bring about effective preservation of the hide/skin. Similarly silica gel at the level of 5 % with minimum amount of salt 5% with or without PCMC also established a preservation effect in the raw hide/skin. The results showed that the leather obtained is comparable in properties with a potential to reduce pollution load in terms of TDS by 70-75% and chlorides 80-85% over salt curing system. [27]

A short term preservation with aryl alcohol has been reported. It was found that aryl alcohol a total dosage of around 2-3% (on green weight) gave satisfactory preservation for about two months. It was also found that hypo at the level of 5% was able to preserve the buffalo hide and goat skin for 10 days. The zinc sulphate at the level of 5% and a mixture of benzaldehyde (0.5%) with B-napthol (0.5%) could also preserve the stock for 3 days and 1 week, respectively. [44]

It has been found that the wide range of materials, both organic and inorganic, can be used for the preservation of skin/hide without employing common salt. They include sodium chlorite, sodium carbonate, propionic acid and per acetic acid as well as organic antiseptic reagents such as teborit and hyamine. [45]

Preservation of skin by using sulphites, bisulphites and meta-bisulphites used in conjunction with an acetic acid are also present. [41] Fresh cowhides were treated with solutions of sodium sulphite and acetic acid by two different methods. Some of the hides were treated by drumming in a 20% float; the others were treated with a more concentrated solution in a spray tunnel. After storage for seven days the hides were processed into side upper leather without modification of standard tannery processes.

The hides treated by drumming produced leather equal or superior in quality to the controls. This method provides the tanner with an alternative to fresh or salt cured hides.

It is possible to effect short term preservation employing a mixture consisting of 2% sodium sulphite and 4% sodium bisulphite which is applied on the flesh side of raw hides. The authors claimed that the hides are kept free of bacterial contamination by treatment for at least four weeks and that the leather produced from the treated hides is of equal standard with that produced from regular wet salted stock. An incidental disadvantage encountered by Nathan using the process, however is that the Swedish acceptable limit for atmospheric sulphur dioxide (2 ppm) is exceeded. [29]

It has been reported that sodium sulphite can be used to avoid pollution associated with the use of sodium chloride. The effective preserving agent is the sodium sulphite. Its use is claimed to meet the requirements for a low cost, non-polluting, easy to apply curing system that does not have any adverse effect on the leather quality produced. [41]

It is also reported that enhanced antiseptic activity is obtained when some commercial antiseptic materials, including merpin TKE, Nercolan GLO and vantocil CL are applied to washed fleshed hides at levels of sodium chloride 10-15%, all treatments being based on green hide weight. The leather quality is comparable with conventional salt curing method. [27]

It is possible to hold wool sheep skins at 25^{o}C for 20 days in good condition after treatment with a combination of sodium chlorite, sodium silico fluoride and boric acid. Sodium silico-fluoride (SSF) is mainly used as a slat additive but it was recommended that hides and skins should be dipped for 30 min in a saturated solution of SSF prior to shade drying. Controversy arose on leather making quality of treated hides, mainly the sheep skins. Although SSF has LD 50 of 125 mg/kg, it has been considered safe. The chemical is stable to heat, light and air and is non-volatile. As fluoride is precipitated by calcium, effluent treatment in the tannery will precipitate out most of the fluoride used. [41]

Chlorites and hypo chlorites are effective bactericides but they may cause adverse effects on leather making qualities. More grain blemishes are present than are normally seen on leathers produced from wet salted skins.

It has been found that a further alternative to the traditional salt cure, advocating the use of formaldehyde at a concentration of 0.25% on hide weight. They added the reagent through the hollow axle of a rotatory drum containing the flayed hide, with no float. With increasing concern about the formaldehyde in the leather due to its toxicity the use of formaldehyde for preservation is ruled out at this stage. [46]

The development of salt less preservation by the use of neem oil with alcohol has also been reported. The neem extracts were applied to both flesh and hair sides at a rate of about 1 % on the green weight. After the treatment the experimental skins are allowed to dry in the shade. The skins, by this method can be preserved for more than 6 months but the resultant leathers were of inferior quality. [47]

In India, immersion of hides and skins for 4-8 h in a mixed solution of zinc chloride and sodium penta chloro phenate (PCP), at 0.15 and 0.16% respectively, prior to salt curing is found to preserve hides and skins for at least 7 days. But due to pollution concern the use of PCP is banned. [27]

Use of antibiotics to control green hide biodegradation has been also reported, where *tetracycline, streptomycine* have been examined. The author has developed microbiological bioassays to determine the antibacterial activity of selected B-*lactams tetracyclines* and *aminoglycosides* against *Vibrioaliginolytious*, used as collagenolytic test bacterium. Results indicated that the tetracycline type antibiotics are most effective at 1%, w/v, with *B-lactam* to a lesser extent. [43]

A short term preservation technique for the cattle hides using a combination of *sodium chloride and hydrolysed starch-poly acrylo nitrile graft co-polymers after* washing with 4 % acetic acid has been reported. Vantocil IB, a polymeric biguanidine hydrochloride is widely used as food bactericide. This has been tried as a preservative on hides in admixture with another ventocil produce CL. A short term preservation for 8 d at 25^{o}C has been possible with this curing method. However, storage at lower temperatures is preferred. A short term preservations by using Busan 30, 2 (Thiocyano methyl thio-benzothiazole) (TCMTB) are used in conjunction with boric acid. The recommended treatment is 2 h drum application of busan 30 (0.3%) plus boric acid (0.9%) in 10% float, based on green hide weight. Cost and quality are comparable with conventional salt curing process. [33]

By using Busan 52, a product based on a mixture of sodium 2-mercapto benzo thiazole and potassium N-hydroxy-N-Methyl dithiocarbamate, the short term

preservation of hide has been carried out. Good result is reported when this product is used in conjunction with boric acid, naphthalene and a wetting agent. [27]

Another short term preservation of cattle hide using 20%, w/v, soda ash has also been reported. The treatment may be used for preserving raw cattle hide for 8 days. Because of limited effectiveness, sodium carbonate against bacteria, particularly strains of halophilic bacteria, sodium carbonate (1%) has usually been used a salt additive in combination with naphthalene (1%) .

For the short term preservation of hides by the use of zinc chloride or calcium hypo chlorite as alternative to sodium chloride have been reported. [34] Three options for carrying out the preservation have been suggested-zinc chloride (0.3-0.5%) with 0.05 % biocide, or 0.05-0.1% phenol with 20-25% float-for drumming about 2 h will preserve hides for a maximum of 5 or 6 days at 25^{o}C. The second option is 1 % application of 30% sodium chlorite eg, Imprapel CO, Hoechst (equivalent to 0.375% solid sodium chloride, 80% active) with 0.05 biocide or 0.05-0.1% alcohol with float 20-30% drumming for 2 h gave better result.

Such materials as like neem oil [47], potassium chloride [39], polyethylene glycol [1], and ozone [48] are investigated. Also was found use of sodium sulphite with acetic acid [49]. There has also been explored the possibility of using Semecarpus anacardium (S. anacardium) nut extract as an alternative to salt for the curing process [50], Didato, D.T have been charecterizing recent developments in the short-term preservation of cattle hides in USA [51], the scientists from India tried to use cetyltrimethylammonium bromide as a potential short-term preservative agent for stripped goat skin [52].

Summarising chemical preservation methods analysis can be proposed that in most of them relatively dangerous materials are suggested for the use: various antibiotics, zink chloride, naphthalene, thiocyano methyl thio-benzothiazole etc. Therefore, the use of presented preservation methods is limited due to complicate use, high cost or toxicity of suggested materials.

2.4 Factors responsible for putrefaction of hide/skin

The raw hides and skins consist mainly of water and protein, which make them vulnerable to attack by microorganisms. The microorganisms decompose the protein and it is technically called putrefaction of hide/skin and eventually makes the

hide/skin unsuitable for the manufacture of good quality leather. [53] The process or the treatment, which is followed in preventing attack by various kinds of bacteria on raw hide and skin is termed as curing. [28]

The various factors to be considered in curing process are:

(a) Loss of structural fibre. As bacterial anzymes attack the skin components, particularly the protein, there is an increase in both volatile and soluble nitrogen: the former is essentially ammoniacal nitrogen and the leather is degraded protein. [54]

(b) Damage to grain. Damage to grain occurs if bacteria reach the grain corium junction, because enzymes can extend through the grain to the enamel - epidermis junction. Hence, the signs of damage include: lifting of the epidermis, loosening of the hair and loss of enamel, only visible after unhairing.

(c) Increase in free fatty. Increase in free fatty acid seen as yellowing of the fat. Fat breakdown has been proposed by Koppenhoeffer as a measurement of pelt quality. Within 30 days, the phospholipids is completely hydrolised, in 30 days there is 15% loss of triglyceride and in six month there is 67% loss of triglyceride. The degree of hydrolysis of the triglyceride fat may give an indication of the history of the pelt, but does not yield information about the status of the protein. Oxidative rancidity does not become apparent until after 6 month storage.

(d) Bacteriological aspects of curing. The hide/skin once flayed is deprived of oxygen and nutritional components. The removal of the metabolites from the cell is stopped leading to the accumulation of toxic products, this in turn leads to breaking of the part of the enzyme controlled process starts. In this process intercellular enzyme *cathepsin* is involved. The various bacteria are involved in the degradation of collage. But the most dangerous bacteria are anaerobic type that deteriorates proteins into the stage of amino acids. [53][55]

(e) Moisture. The moisture content of the raw hide/skin is an important factor to be considered those controls the bacterial activity. Bacteria cannot grow unless there is critical moisture in the hide/skin. The moisture content present in the raw hide/skin is found to be 70%. Hence, in the curing process the moisture content decreases. The critical moisture content for the bacterial activity was found to be 50%. [54] Above this level of moisture content, the hide/skin is conducive for bacterial attack and the control over moisture content is an important factor.

(f) Temperature. The higher temperature during curing always play negative role in the curing process. If the temperature is more, the efficiency is affected by bacterial

damage or by the loss of hide substance. Hence, it is necessary that even the skin is being preserved by chilling (+2 to +5°C) and freezing (-10 to -20ºC) may injure the hide/skin by freezing the ice crystals around the material and cause rupture of tissue. Hence keeping the raw material at optimum temperature is an important factor. Most of the bacteria in living condition showed optimum temperature between 15ºC to 37ºC. It has also been reported in literature that better reservation would be established at temperature range between 10-18ºC. [56]

(g) Humidity. It is very difficult to control the moisture content without controlling the atmospheric humidity. Elevated humidity, especially in the monsoon induces sodium chloride or curing agents to absorb more moisture and thereby helping bacterial growth. Hence, elevated humidity is not suitable for the curing process. [56]

(h) pH. pH is an important factor to be considered in any curing process of the hide/skin the reason is that bacteria or enzyme is active at the pH of neutral or slightly alkaline conditions. Hydrolysis of collagen by *proteolytic bacteria shows a maximum at pH 7.5.* At pH 9.0, the activity is weaker, while at pH 5.5 to 6.5, the activity is practically negligible. But the precautionary measure has to be taken in the case of alteration of pH, once the pH goes below 4.0, there is a change of swelling of collagen and in turn would weaken the fibre, which would make the hide/skin unsuitable for leather making. [51]

(i) Procuring period. The procuring period is time between the actual slaughtering of animal and commencement of curing process. It is an important factor as the hides/skins become putrefied to some extent due to delay in curing. If the condition of the hide/skin is sufficiently fresh and without the onset of bacterial action, the aim of curing simply lies in quick dehydration of water from the material. It has been found that if the precuring period delay for about 5 hours is slight degenerative changes takes place in the cells lying around the sweat glands. After 11 hours, the remaining skin structure also gets affected leading to breakdown of the polypeptide into dipeptide level. [43]

2.5 Use of vacuum for leather processing

The vacuum is widely used in leather processing for leather drying. Vacuum drying offers fast speed at a low temperature, which would be advantageous to heat-vulnerable chrome-free leather. [57] [2]

Several attempts were made trying to use vacuum for other leather processing steps. It could be mentioned investigations of the vacuum employment for leather tanning. Acquired results show that, on the premise of increasing the overall quality of leather tannage, the working time is greatly shortened and the discharge of waste liquid is decreased by more than 50%. [58]

Investigation was carried out adopting vacuum in leather manufacturing by vacuum. The chromium tannage process was chosen as a model and influence of the factors such as thickness of pelt, temperature, concentration of Cr_2O_3 in the chroming solution and additionally, the use of pressure on the rate of solution penetration and qualitative indexes of leather was investigated. The use of 0.01 MPa vacuum reduces the duration of chroming down to 3-20 minutes depending on the thickness of pelt. [59]

2.6 Summarization of literature review and motivation of the aim of dissertation work

The literature analysis has shown that investigation of new and cleaner preservation methods goes very intensely. Two main directions can be accentuated: chemical preservation when various materials are used or physical preservation without any use of chemical materials.

Unfortunately, there are not possibilities to deliver hides or skins for leather processing directly after flaying. The analysis of leather industry in Latvia has shown same situation. The shorter or longer period is needful for the collection of enough amount of raw material for the leather industry.

The wet salting, the conventional method of curing is followed by most of the tanneries because of its practical advantages; employs approximately 40-50% sodium chloride on raw material and is subsequently removed during the soaking operation. [1] So, it is very serious reason to pursue new and more environmentally friendly preservation methods because sometimes is last 1-2 weeks for the gathering for processing enough skins or hides.

This is the main reason why investigators pay their attention for the development of short term preservation methods, which allow storage of hides/skins during 1-3 weeks without symptoms of deterioration. Many scientists are still trying to find new short term preservation methods. Investigations have been carried on developing efficiency of preservation of raw hide/skins and reducing pollution by preservative materials.

For short term preservation of hide was chosen method of hide treatment by vacuum and storing of treated hide under low temperature. The method could help to avoid the pollution with the salt and buried raw hides. The vacuum is widely used in leather processing for leather drying. [57] On the other hand, the vacuum preservation can be applied in practise only after thorough exploration of that method. For reaching of this aim these tasks will be solved:

- to gather data about situation in Latvia leather industry and carry out analysis of current methods of hides and skins preservation;

- to investigate activity of microorganisms on preserved by vacuum hide and its structural changes during storage time; estimate the quality of hide after storage;
- to examine technological processes of leather processing from vacuumed hide;
- to verify suitability of vacuumed hide for processing of leather under industrial conditions and establish leather properties.

3 MATERIALS AND METHODS

3.1 Scheme, object and materials of investigation

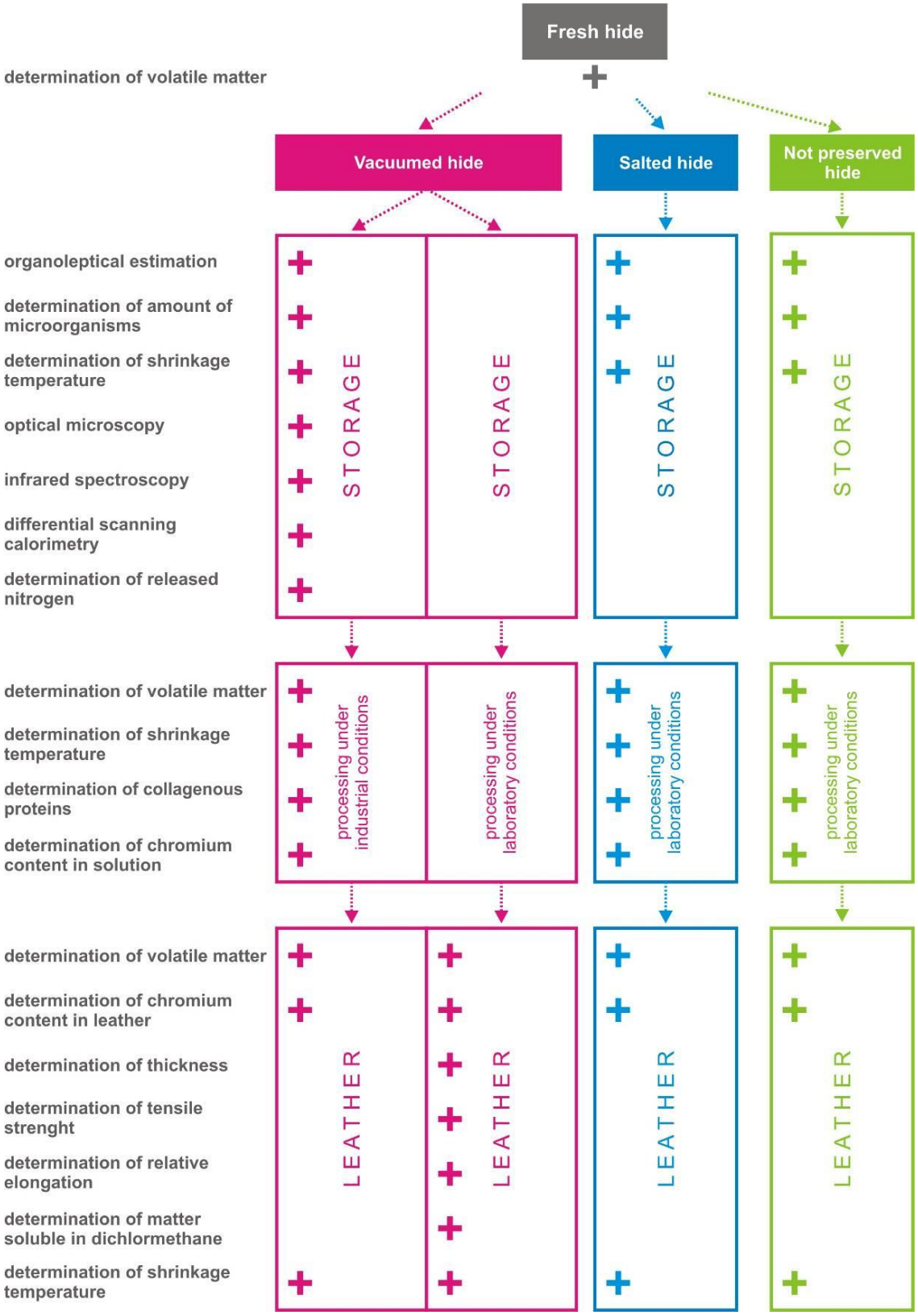


Figure 3.1 Scheme of investigation [author's illustration]*experiment time - 22 days

Two fresh calf hides had been purchased from the local slaughterhouse, and immediately after flaying cut into pieces.

Test pieces for further processing and analysis were taken according to standard [60]. Little samples (10-15x20 cm) were prepared for laboratory investigations from one hide and the big samples (42x36 cm) were prepared for test in industrial conditions from second one (Figure 3.2).

Figure 3.2 Sample locations for investigation [author's illustration]

All samples (excepting eight little pieces) were enveloped into bilayered laminate material using vacuum (10-12·10^3 Pa). Deepness of vacuum was chosen as appropriate for foodstuff (meat). Those hide samples titled as "vacuumed" were stored in a fridge at 4ºC. Temperature was chosen from average appropriate grade from literature analysis, p.37.

Four little pieces were enveloped into simple polyethylene film and stored in a fridge at 4ºC ("not preserved" samples).

Four little pieces were salted by the use of 50% NaCl and stored at 20±1ºC ("salted" samples).

All chemicals used for the analysis were of analytical grade (Table 3.1, p.52) For leather processing under laboratory conditions the chemicals used were of

analytical grade as well. Obtained from various enterprises technical products designed for leather processing were employed as well.

Table 3.1

Chemicals used for investigation [61]

Nº	Identification code	Formula	Purity class
1	Acetone CAS 67-64-1	CH_3H_6O	p.a./G.R. 99,5%
2	Hydroxide Calcium CAS 1305-62-0	$Ca(OH)_2$	p.a./G.R. 99,5%
3	Hydrogen peroxide CAS 7722-84-1	H_2O_2	p.a./G.R. 29,0 – 32,0%
4	Sodium formate CAS 141-53-7	HCOONa	p.a./G.R. 98,0%
5	Sodium sulfide CAS 1313-82-2	Na_2S	Technical product 60,0%
6	Sulfuric acid CAS 7664-93-9	H_2SO_4	p.a./G.R. 96,0%
7	Sodium Chloride CAS 7647-14-5	NaCl	p.a./G.R. 99,9%
8	Sodium hydroxide CAS 1310-73-2	NaOH	p.a./G.R. 98,5%
9	Potassium iodide CAS 7681-11-0	KI	p.a./G.R. 99,5%
10	Ammonium Sulfate CAS 7783-20-2	$(NH_4)_2SO_4$	p.a./G.R. ≥99.0%
11	Enzyme preparation OROPON ON2 (Röhm GmhH, Germany)	-	Technical product
12	Methylene blue CAS 7220-79-3	$C_{16}H_{18}N_3SCl \cdot 3H_2O$	Dye content, ≥82%.
13	Cromium extract Chromal, ("Alwernia" S.A., Poland)	-	basicity 33 – 34%, ~25% Cr_2O_3
14	Neutrogene MG120 (Codyeco s.p.a., Italy)	-	Technical product for increasing of chromium compounds basicity
15	Prevocel NG-12 (surfactant) CAS 9062-77-5	$C_{19}H_{32}O_3$	60%
16	Nickel Sulfate CAS 10101-98-1	$Ni_2SO_4 \cdot 7H_2O$	p.a./G.R. 99,0%
17	Sodium thiosulfate CAS 7772-98-7	$Na_2S_2O_3$	p.a./G.R. 99,0%
18	Hydrochloric Acid CAS 7647-01-0	HCl	p.a./G.R. ≥36,5%
19	Copper(II) sulfate CAS 7758-98-7	$CuSO_4$	p.a./G.R. 98,0%
20	Starch CAS 9005-25-8	$(C_6H_{10}O_5)_n$	puriss. p.a.
21	Carbamide CAS 57-13-6	NH_2CONH_2	≤0.1% Insoluble matter
22	4-(Dimethylamino)benzaldehyde for the determination of hydroxyproline CAS 100-10-7	$(CH_3)_2NC_6H_4CHO$	≥99.0% (HPLC)
23	Potassium Sulfate CAS 7778-80-5	K_2SO_4	p.a./G.R. ≥99.0%
24	Dichlormethane CAS 75-09-2	CH_2Cl_2	ACS reagent
25	Ethyl alcohol (“Stumbras”, Lithuania)	C_2H_5OH	Technical product, rectificate ≥96.0%
26	(1-((4-(phenyldiazenyl)phenyl)azonaphthalen-2-ol) CAS 85-86-9	$C_{22}H_{16}N_4O$	purity dye content, ≥85%
27	Nitric Acid (70%) CAS 7697-37-2	HNO_3	ACS reagent, 70%
28	Perchloric Acid (60% to 70 CAS 7601-90-3	$HClO_4$	ACS reagent, 60%
29	Orthophosphoric Acid CAS 7664-38-2	H_3PO_4	p.a./G.R. ≥85.0%
30	Sodium thiosulfate CAS 72-98-7	$Na_2S_2O_3$	purum p.a. ≥98.0%

3.2 Equipment for packing in vacuum

Hide samples were packed in vacuum using special vacuum equipment MULTIVAC C300 (manufacturer: MULTIVAC, Germany, supplier: Multivac Oy branch office in Latvia).

Chamber Machine C 300 is a floor-standing machine, the compact C 300 single-chamber machine features a powerful vacuum pump. This delivers fast, reliable operation even in the most demanding environments. The C 300 is one of the most popular models in the meat industry because of its generous dimensions to accommodate large portion sizes with a small machine footprint. [62]

Table 3.2

MULTIVAC C300 Technical data [62]

Chamber machine MULTIVAC C300	**Parameters**	**Technical data**
	Chamber height	160 mm
	Chamber width	450 mm
	Chamber depth	470 mm
	Sealing length	440 mm
	Power supply	3x400V 50Hz, 3x220V 60Hz
	Weight	approx. 160 kg

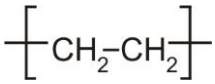
MULTIVAC C300 features: compact size; stainless steel construction; powerful pump; safety glass window; quick change seal bar; filler plates; microprocessor control; automatic progressive ventilation; vacuum "quick-stop". [62]

MULTIVAC C300 standard specifications: stainless steel chamber housing; composite lid with safety-glass viewing window, lid height: 160 mm; stainless steel tilted insert for liquid products; slide-in sealing bar; double-seam sever-sealing at bottom (1x3.1x1mm); insert plates for sealing height adjustment; control unit: MC 06, stores up to 29 programs, 18 menu language. [62]

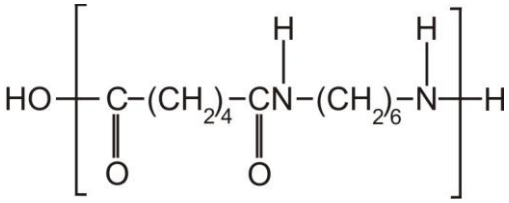
MULTIVAC C300 options: Modified Atmosphere Packaging system; Pack at atmospheric pressure - Locking Lid; Pouch holding clamp; Double-seam sealing at bottom (2x3mm); Double-seam sealing at top and bottom (2x3mm each); Stainless steel lid with safety-glass viewing window, chamber height: 230mm; Vacuum Throttle;

Vacuum pumps: 40 m³/h (Busch), 63 m³ (Busch); External glass pot separator with controlled drain for liquid or very wet products;

In this vacuum machine MULTIVAC C 300 low (1×10^5 to 3×10^3 Pa) or medium vacuum (3×10^3 to 1×10^{-1} Pa) can be reached. Hide samples were enveloped into bilayered laminate material PE/PA (polyethylene/polyamide). [63] Average thickness of this film is 65±3 μm (micrometers). Used packing film dimensions: 300 x 300 mm.



Chemical formula. PE (polyethylene)



Chemical formula. PA (polyamide) 66

PE films are widely used for packaging in composition of various multi-layer materials. PE films are lightweight, economical, elastic, have moisture resistance and low vapour permeability. PE Films are cheap packaging material. These films have small mechanical strength, but high flexibility.

PA is widely used in film production. For packaging of food products PA 6 film is widely used (for casing sausages mono- and multilayer PA films are used). The welding temperature of this film is from 121 till 177°C. PA is often used in multilayered material compositions, because of material strength these films surpass almost all synthetical material films. Special polyamide feature is its ability to form resistant fibres from a melt.

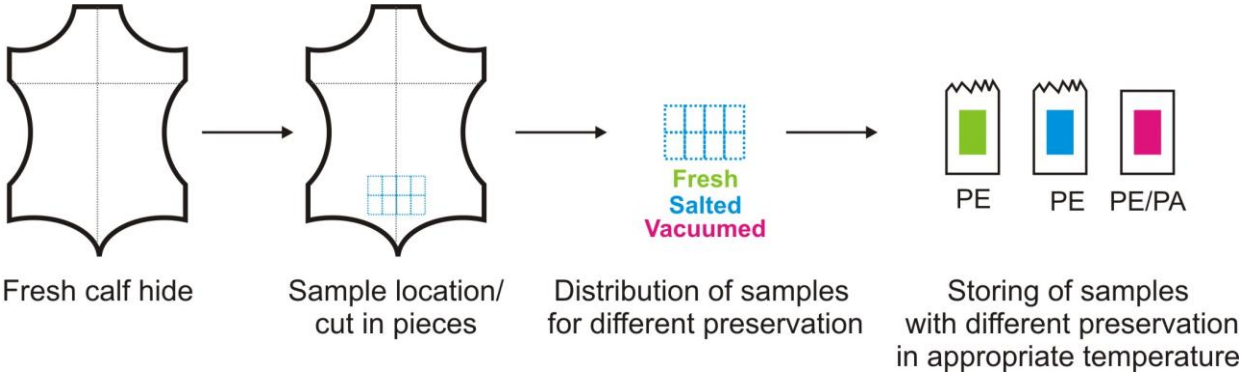


Figure 3.3 Scheme of sample preparation [author's illustration]

3.3 Statistical analysis

Determinations of shrinkage temperature, amount of nitrogena and amount of bacterias characteristics were carried according to methods or standards described below and the data were expressed as the average values of triplicate measurements. Confidence limits were set at $P<0.05$. Standard deviations did not exceed 5% for the values obtained. Statistical analysis was performed using Student's t-test.

3.4 Processing of samples under laboratory and industrial conditions

A part of little samples was processed into wet blue under laboratory conditions described in Table 3.3. The processing was performed in a laboratory drums with capacity of 3 litres.

Table 3.3

Parameters of hide processing in laboratory conditions

Process title	Process parameters		
	Material title and amount, % from hide/unhaired hide mass	Temperature, °C	Duration and regimen
Washing	H_2O - 200	20±2	1 h, run continuously
Liming-unhairing	a) H_2O - 100;PAM - 0,1 b) $Ca(OH)_2$ (60%) - 2,3; Na_2S (60%) - 2 c) $Ca(OH)_2$ (60%) - 2,3 d) H_2O - 100	20±2	a) 30 min., run continuously b) 1 h, run continuously c) 1 h, run continuously d) 21 h, 30 min run continuously, later 5 min. every 4 h, drain in the process end
Washing	a) H_2O - 200 b) H_2O - 200	37±1	a) 30 min., run continuously, drain b) 30 min., run continuously, drain
Deliming-bating	a) H_2O - 40;$(NH_4)_2SO_4$ - 2 b) $(NH_4)_2SO_4$ - 2 c) H_2O - 100; Enzyme Oropon ON2 - 0,15	37±1	a) 30 min., run continuously b) 30 min., run continuously c) 1 h, run continuously, drain
Washing	a) H_2O - 200 b) H_2O - 200	20±2	a) 20 min., run continuously, drain b) 20 min., run continuously, drain
Pickling	a) H_2O - 40; NaCl - 5,5 b) HCOONa - 1 c) H_2SO_4 - 0,5 d) H_2SO_4 - 0,5 e) H_2SO_4 - 0,5	20±2	a) 15 min., run continuously b) 20 min., run continuously c) 15 min., run continuously d) 15 min., run continuously e) 5 h, run continuously
Chroming	a) Chromeco - 6 b) Neutragene MG-120 - 0,35	20±2 c) 60±1	a) 20 h, run continuously b) 2 h, run continuously c) 2 h, run continuously, drain
Washing	H_2O - 100	44±2	1 h, run continuously, drain

Big samples were processed into wet blue under industrial conditions in tannery “Kedainiu oda” (Lithuania) according to technology of upper leather processing, which was valid in this enterprise.

3.5 Methods of investigation of hide properties

According to literature analysis such methods of investigation of hide properties were employed: organoleptical estimation of hide quality; determination of amount of microorganisms in hide, nitrogen extracted from hide, collagenous proteins, shrinkage temperature, leather physical tests (determination of thickness, tensile strength and percentage extension); determination amount of chromium; of matter soluble in dichlormethane and free fatty acid content; determination of volatile matter; optical microscopy, infrared spectroscopy and differential scanning calorimetry.

3.5.1 Organoleptical estimation of hide quality

The quality of hide was assessed organoleptically observing any hair slip, appearance of bad odour and appearance of mucous surface of skin and by using analytical methods. Three different experts estimated all chosen characteristics. The hide was considered as deteriorated when any symptom of decay appeared: hair slip, bad odour, or mucous surface of skin.

3.5.2 Calculation of amount of microorganisms in hide

For determination amount of bacteria method of Feldman and Lishansky was used [64]. Three parallel samples were made for each kind of preserved hide.

10 g of shaved hide was cut into pieces (3x3 mm), put into a porcelain dish and poured with 10 ml of physiological solution (0.9% NaCl solution) (Figure 3.4, p.57). The pieces were soaked in physiological solution mixing them by glass stick during 3 minutes (all equipment must be sterilized before analysis) and extract of microorganisms obtained. Afterwards, the dish was put 45^{o} angle (Figure 3.5, p.57) and extracted solution accurately drained from hide pieces by pushing them to the

top of dish and pressing by glass stick. The solution was collected in lower part of the dish and left for 10 minutes.

Figure 3.4 Hide samples in 10 ml of physiological solution in angle 45^{o} [APF]

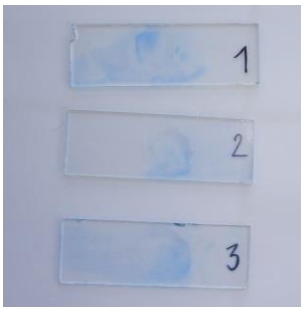


Figure 3.5 Methylene blue solution on fixed/finished specimens [APF]

Afterwards, one drop (0.04 ml) of the obtained solution had been taken and spread on microscopic glass forming square 2x2 cm. The glass was placed into thermostat for 10 min at 35^{o}C and left for drying. The dried specimen was 2 seconds kept on the flame for the fixation of microorganisms, and immediately dyed slide with solution must be placed in thermostat at temperature till the rest of solution will be dried out. Acquired prepared specimen was kept in a flame at least for 2 sec and coloured with a methylene blue solution. The solution was prepared dissolving 2 g of methylene blue ($C_{16}H_{18}N_3SCl \cdot 3H_20$) in 32 g pure (96%) ethyl alcohol and diluting 1 ml of this solution with 5 ml of distilled water. For the coloration of bacteria the methylene blue solution was poured on fixed specimen and left for 2-3 min. After this, the dye was washed with distilled water, and specimen dried in thermostat at temperature 35^{o}C till it became dry.

The observation of bacteria was performed with optical microscope Olympus CX 31 using magnification 1000 times and cedar oil for immersion medium formation. 10 photographs from various places of specimen surface were made and used for the calculation of microorganisms in the specimen.

The amount of microorganisms in each picture was reckoned up and average value of amount of microorganisms in one picture calculated. The amount of microorganisms in specimen was calculated according to formula:

$$\mathbf{m} = \frac{\mathbf{n} \cdot \mathbf{b} \cdot \mathbf{v_2}}{\mathbf{a} \cdot \mathbf{v_1} \cdot \mathbf{10}} \qquad \textbf{(3.1)}$$

where:

m amount of microorganims in hide, units/1 g of hide;

n average amount of microorganisms presented in one photograph, units;

a square of specimen, which is seen in one photograph, mm^2;

b square of specimen, in which one drop with bacterias was spread, mm^2;

v_1 volume of one drop of solution with bacterias, ml;

v_2 total volume of solution with bacterias, ml.

3.5.3 Preparation of hide samples for nitrogen content determination

The level of hide preservation can be assessed measuring amount of released ammonia in hide tissue. The ammonia forms as product of proteins degradation resulted by the action of microorganisms [53]. When extracting a hide, the formed ammonia together with other nitrogen containing (soluble collagenous or non collagen proteins) materials is removed from hide tissue. Since the content of removable by extraction proteins does not depend on the hide storage time, the change of the amount of the nitrogen containing materials in the hide extract can depend only on the formed ammonia. Usually Kjeldahl method is used for nitrogen amount determination. The weighted piece of hide (about 5 g) is cut into small pieces 3x3 mm. These pieces are placed into glass flask and poured with 25 ml of distilled water. Two parallel samples were prepared for each kind of preserved hide.

Flask is embedded into shaker (Figure 3.6) and is agitated 30 minutes. Acquired liquid must be filtrated.

Figure 3.6 Flasks with samples into shaker [APF]

Figure 3.7 Heating of Kjeldahl bulbs [APF]

After filtration 10 ml of the filtrate is poured into Kjeldahl bulbs. Approximately ~5 mg of Kjeldahl catalyst (mixture of K_2SO_4 and Cu_2SO_4) and 5 ml of concentrated H_2SO_4 are put additionally into Kjeldahl bulbs. The samples are heated up to complete hydrolysis of samples (Figure 3.7). During hydrolysis a chemical reaction takes place:

$$COO^-–R–NH_3^+ + H_2SO_4 \rightarrow (NH_4)HSO_4 + CO_2 + SO_2 + H_2O$$

Do not let too intense boiling because ammonia can be oxidized up to nitrogen anhydride and evaporated. After the hydrolysis the samples are suitable for the ammonia amount determination.

Nitrogen amount determination according to Kjeldahl method. The content of Kjeldahl bulb is cooled, diluted with distilled water, cooled again and poured into bulb of Kjeldahl distillation apparatus. Kjeldahl bulb is washed three times with distilled water collecting it into the bulb of Kjeldahl apparatus (Figure 3.8) as well. After that, 35 ml of NaOH solution (35%) is added and apparatus is closed hermetically.

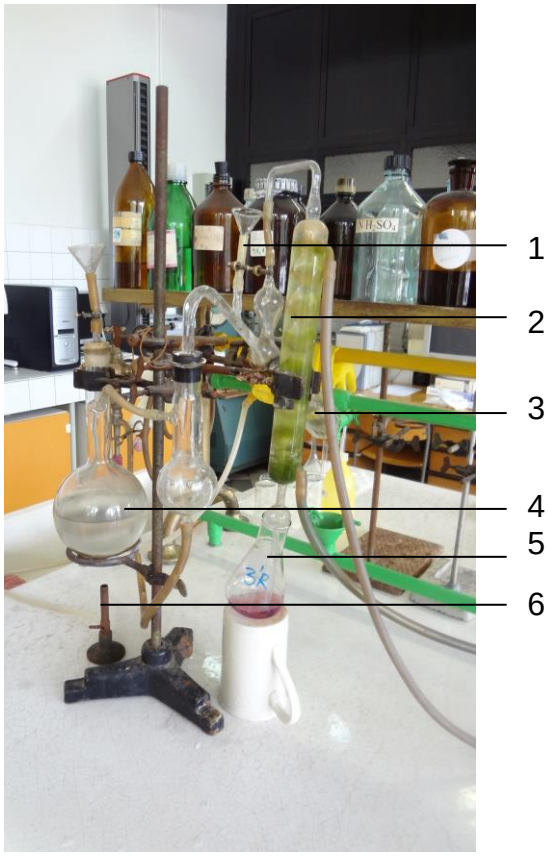


Figure 3.8 Kjeldahl apparatus. 1 – gap for pouring of test sample; 2 – cooler; 3 – bulb for distillation; 4 – bulb with distilled water; 5 – flask for distillate; 6 – burner. [APF]

The alkali added reacts with products of hydrolysis of nitrogen containing materials in such way:

$(NH_4)HSO_4 + 2NaOH \rightarrow NH_4OH + Na_2SO_4 + H_2O$

Afterward the test mixture is distilled with water steam. The distillate with ammonia is collected into Erlenmeyer flask, in which 25 ml of 0.01 mol/l H_2SO_4 and Kjeldahl indicator (solution of methylene red and methylene blue mixture) are poured.

Process of distillation is finished when about 50 ml of distillate is obtained. Afterward, the rest of acid is titrated with 0.01 mol/l NaOH. Two parallel tests were made for one sample.

Amount of nitrogen is calculated according to formula:

$$w = (v_1 - v_2) \times 0{,}00014 \times K_{NaOH} \qquad (3.2)$$

where:

v_1 is the volume, in millilitres (ml), of 0,01 mol/l NaOH solution used for the titration of blank test (for the titration of 25 ml of 0,01 mol/l H_2SO_4 solution);

v_2 is the volume, in millilitres (ml), of 0,01 mol/l NaOH solution used for the titration of investigative sample;

0,00014 amount of nitrogen (g), which corresponds to 1 ml of 0,01 mol/l NaOH solution;

K_{NaOH} correction coefficient to titre of 0,01 mol/l NaOH solution.

3.5.4 Determination of collagenous proteins

The determination of the collagenous proteins amount is based on the evaluation of amount of hydroxyproline, which forms after hydrolysis of hide tissue or hide treatment solutions. The hydroxyproline is specific amino acid of collagen, and its amount in collagen is uniform and known. Modified Neiman-Logan [65] method was used for the determination of hydroxyproline content. The colorimetric method is based on a formation of coloured compound when products of hydroxyproline oxidation and 4-(Dimethylamino)benzaldehyde react. For the hydrolysis of collagenous proteins were taken 5-50 ml of treatment solution (solution after hide processing process, during which collagen proteins are removed from hide tissue into treatment solution), poured into porcelain dishes, and evaporated till dryness upon water bath. The dry residue waswashed with HCl 6 mol/l and quantitatively transferred into test-tube. The test-tube was hermetically closed by melting and leaved in an oven for 10 h at 125±2^{o}C.

After hydrolysis the test-tube was opened, the hydrolisate cleaned adding absorbent carbon, filtered into porcelain dishes, and evaporated till dryness upon water bath. The dry residue was quantitatively transferred into 100 ml volumetric flask and made up to the mark with distilled water.

2 test test-tubes were taken and 1 ml of the obtained solution was poured into each test-tube. Into third test-tube was poured 1 ml of distilled water (blank solution).

Into all test-tubes were poured: 0.5 ml of 0,05 mol/l $CuSO_4$ solution, 0.5 ml of 2,5 mol/l NaOH solution, and 0.2 ml of 4 % H_2O_2 solution. Test-tubes were shaken 5 min., and left for rest for 5 min. After that, the test-tubes were placed into water bath

and left for 10 min. at 70°C. Test-tubes were cooled down, and 0.5 ml of 0.01 mol/l carbamide solution poured into each. The content of test-tubes was shaken for mixing and left in rest for 5-10 min.

Afterward, 0.8 ml of 4 mol/l H_2SO_4 solution and 2.5 ml of 5% 4-(Dimethylamino)benzaldehyde solution in isopropyl alcohol were poured into each test-tube. Then, all test-tubes were put into water bath, left for 22 min. at 70°C, taken out and cooled down to ambient temperature.

The optical densities of the obtained solutions were measured at wavelength 560 nm. Spectrophotocolorimeter Genesis 8 (Spectronic Unicam, USA was employed for the measurement. The solution from the third test-tube was used as blank solution (Figure 3.9).

a **b** **c** **d** **e**

Figure 3.9 Sample preparing for determination of the collagenous proteins: **a**-hermetically heated samples; **b**-filtration process; **c**-shaking process before heating in 70°C; **d/e**-samples after heating [APF]

The values of hydroxyproline concentration were found using a calibration curve, which was drawn using 0.0005-0.003 % pure hydroxyproline solutions.

Since the content of hydroxyproline in cattle hide collagen is equal to 12.8 %, the amount of collagenous proteins was calculated multiplying the amount of hydroxyproline on 7.8 (100/12.8).

3.5.5 Measurement of shrinkage temperature

Shrinkage temperature was determined for raw and preserved hide, for hide during storage, for hide after technological processes (after liming, deliming, bating etc.) and for produced leather.

Measurement of shrinkage temperature of hide and leather up to 100^{o}C. Shrinkage temperature was determined after liming, deliming and pickling processes according to the method described in standard [66]. Three parallel samples were prepared for each kind of preserved hide. Principle of this method is following. Test piece is heated at a specified rate in water until a sudden shrinkage occurs. Used apparatus is shown in Figure 3.10.

a **b** **c**

Figure 3.10 Shrinkage temperature apparatus (**a**-schematic [66]: 1-pulley; 2-3g force; 3-pointer; 4-temperature measuring device (Thermometer shown and used); 5-fixed test piece holder; 6-vessel; 7-test piece; 8-movable test piece holder; **b**-real situation; **c**-test piece for determination shrinkage temperature [APF]

Apparatus consists of the following parts:

- *Vessel, minimum volume 500 ml and minimum working depth 110 ml. the vessel may be pressurised to operate temperatures in excess of 100^{0}C.*
- *Fixed test piece holder, for example a pin or clip, 30 mm +/- 5 mm above the base of the vessel.*
- *Moveable test piece holder, for example a hook or clip. One end is attached to the top of the test piece. The other end is attached to a thread which passes over a pulley and terminates in a mass 3 g heavier than the moveable holder.*
- *Pointer, with means of monitoring its movement. In the instrument shown, the relative dimensions of the pulley and pointer shall be such that any movement of the moveable holder is magnified by a factor of at least 5.*
- *Temperature measuring device, graduated to 1^{0}C and shown to be accurate to +/- 0.5^{0}C with the sensor placed close to the centre of the test piece and a working range suitable for the sample under test.*
- *Distilled or de-ionized water, confirming to the requirements of grade 3 of ISO 3696:1987*
- *Heater, capable of heating the vessel filled to its working depth with distilled or de-ionized water at a rate of 2^{0}C +/- 0.2^{0}C/min.*
- *Stirrer, capable of sufficiently agitating the water in the vessel such that the temperatures at the top and bottom of the test piece do not differ by more than 1^{0}C.*

Samples were prepared in such way. Hide was cut in rectangular test pieces 50 mm +/- 2mmx3.0 mm +/- 0,2mm. For each measurement 3 parallel test pieces were taken. One end of test piece was embedded on fixed test piece holder and

second end of test piece embedded on moveable test piece holder. When test piece had been fixed in apparatus it was put into vessel with distilled water. The vessel was stood on heater with agitator. When the process of heating is initiated it is strongly recommended to fix equipment for length changes to zero.

The speed of temperature changes should not exceed 2^{o}C +/- 0,2^{o}C during the heating. At 30 s intervals temperature and corresponding position of the pointer (in method is used electronic device) was noted. The heating was continued until the test piece shrinks considerably or the desired temperature is reached. The plot pointer position against temperature was inspected to find the temperature corresponding to the movement of the pointer which is equivalent to a shrinkage of the test piece of 0.3% from its maximum length. This temperature was recorded as the shrinkage temperature.

Measurement of shrinkage temperature of leather over 100^{o}C. The shrinkage temperature of chromed leather samples was determined as described in literature [67] using a special equipment and glycerol instead of the distilled water. It is because chromed leather shrinkage temperature is higher than 100^{0}C. From the samples of leather were cut strips 3 mm x 60 mm and used for shrinkage temperature determination. Three parallel samples were prepared for each tested hide. The shrinkage temperature was determined using the equipment shown in Figure 3.11.

a **b**

Figure 3.11 Equipment for determination of shrinkage temperature over 100^{o}C: **a**-scheme of shrinkage temperature apparatus (1-jaws; 2-pot with glycerol; 3-lower regulative screw; 4-heaver; 5-upper regulative screw; 6-contacts; 7-indicating lamps; 8-thermometer.) [67] **b**-wet blue test piece and strips for shrinkage temperature determination [APF]

The test strips were fixed into jaws of apparatus and using regulative screws was adjusted such tension of strips under which the strips became stretched out without disconnection of contacts. The fixed test strips were submerged into glycerol. The speed of temperature change should not exceed 5^{o}C +/- 0,2^{o}C during the heating.

When the test strip shrinks the corresponding contact disconnects and indicating lamp switches on. Corresponding to this moment temperature was recorded as shrinkage temperature of test strip. The shrinkage temperature was recorded for each test strip. The shrinkage temperature of leather was calculated as arithmetic average of shrinkage temperature values of three test strips.

3.5.6 Leather physical-mechanical tests

Strength properties were determined according to standard [68]. Thickness of samples was measured as described in literature [69].

5 and 19 days hide samples stored under vacuum were processed under the industrial conditions in the tannery “Kedainiu oda” (Lithuania) into shoe upper leather.

Measurement of thickness. Before determination of tensile strength and percentage extension-sample thickness was measured. The leather is placed in a gauge under a specified load for a specified time and the thickness read directly. 3 measurements have to be taken, distributed across the sample. The results have to be expressed as the arithmetic mean and range to the nearest 0.01 mm.

Determination of tensile strength and percentage extension. A test piece is extended at a specified rate until the forces reach a predetermined value or until the test piece breaks. In this experiment test piece was extended till it broke. The shape of test piece was cut by special machine according to standard (using standard designation) - see Figure 3.12, Table 3.4, p.65.

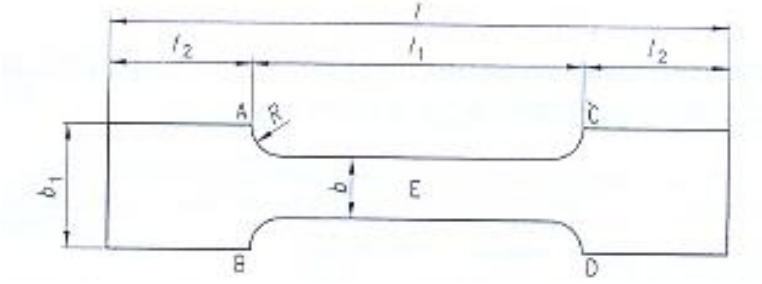


Figure 3.12 Shape of test piece [68]

Table 3.4

Shape of test piece [68]

Designation	l	l_1	l_2	b	b_1	R
Standard	110	50	30	10	25	5
Large	190	100	45	20	40	10

Samples for determination of tensile strength and percentage extension were taken according to standard (Figure 3.13). Two parallel tests of each samples were made.

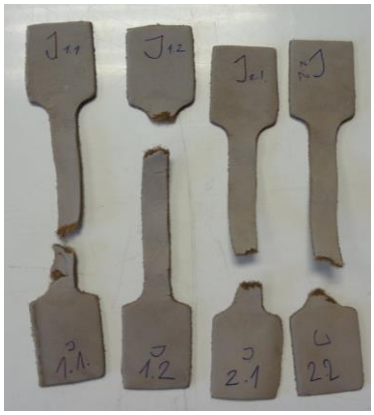


Figure 3.13 Samples after test ⇑ [authors PF]

Tensile strength T_n in Newtons per square millimetre shall be calculated using the equation:

$$T_n = F/w \cdot t \qquad (3.3)$$

where:

F is the highest force recorded in Newtons, N;

w is the mean width of the test piece in millimetres, mm;

t is the mean thickness of the test piece in millimetres, mm.

3.5.7 Determination of chromium amount

Determination of chromium oxide concentration in solution was made according to literature [67] Two parallel determinations were made for each kind solution hide. Chromic oxide content in leather was determined according to standard. [70] Two measurements were made for each tested hide.

Determination of chromium oxide concentration in solution. The method is designed for the determination of chromium oxide content (concentration) in

solutions before or after chroming, wastewaters after chroming etc. Usually two parallel determinations are carried out.

Procedure. 5 ml of solution were poured into laboratory flask (volume 100-200 ml), and added 10 ml NaOH (1 mol/l) and 5 ml H_2O_2 (3%).

Obtained solution was covered with funnel and heated up to boiling. The duration of boiling was 3 min. After that 5 ml $NiSO_4$ (5%) were poured, and the boiling continued more 3 min. After boiling flasks were cooled down to room temperature, and 10-15 ml of H_2SO_4 (20%) added (up to dissolving of sediments in test solution).

Later 5 ml of KI (10%) were added (solution becomes dark orange to brown), and flask left to stand in dark for ~2 min. The indicator was starch solution (1%), which 1 ml was poured into flask before titration.

Titration was carried out using $Na_2S_2O_3$ solution (0.1 mol/l). The titration is continued up to test solution colour changes into light blue (Figure 3.14).

a **b**

Figure 3.14 Process of determination of chromium oxide concentration in solution: **a**-test solution before titration [APF]; **b**-test solution after titration [APF]

After every titration amount of used $Na_2S_2O_3$ (0.1 mol/l) was recorded. Concentration of chromium oxide in solution was calculated according to formula:

$$\mathbf{x} = \frac{\mathbf{a x 0{,}002533 x 1000}}{\mathbf{5}} \qquad (\mathbf{3.4})$$

where:

x	concentration of chromium oxide in solution, g/l;
a	amount of $Na_2S_2O_3$ solution (0.1 mol/l) used for titration, ml;
0,002533	amount of chromium oxide, which corresponds to 1 ml of $Na_2S_2O_3$ solution (0.1 mol/l), g.

Determination of chromic oxide content in leather. For the determination of chromium oxide amount in tanned leather the method described in standard was used [70].

The method is based on the chromium, which present in leather, solubilization in the hexavalent state followed by analysis of the solution by iodometric titration.

Leather must be cut into small 5x5 mm pieces, and weighted to the nearest 0,001 g (suggested masses depend on sort of leather, and for full chrome leather is recommended to take 1g for each test). A minimum of two determinations shall be made for each leather. To evaluate amount of chromium in leather wet oxidation method was used.

The cut and weighted leather test pieces were placed into conical flask. Then 10 ml of Nitric acid (70%) was added, and flask left for 2 min resting. Then, 15 ml of sulphuric/perchloric acids mixture (sulphuric acid, concentrated (98%), and perchloric acid (60% to 70%), mixed together in the ratio of 1:3 by volume) were added. After this procedure flasks were boiled till reaction mixture turn orange.

Splash bulb or funnel must be placed into the neck of the flask. When reaction mixture becomes orange boiling temperature must be lowered. After complete change of colour happens, mixture was heated for 2 min. After heating mixture was cooled in air for 5 min and later diluted with 200 ml distilled water. Then mixture again was boiled for 10 minutes to eliminate any chlorine. After boiling mixture was cooled down to room temperature and then 5 ml of orthophosphoric acid added to mask any iron.

a **b**

Figure 3.15 Process of determination of chromic oxide content in leather: **a**-left flasks after last boiling, right flasks after adding potassium iodide solution [APF]; **b**-flasks after titration process [APF]

For the determination of chromium the titration process was done. 20 ml of potassium iodide solution was added into the obtained test solution. Flask was stoppered and left in dark for 10 min.

The titration was carried out with 0.1 mol/l sodium thiosulfate solution until solution in the flask is either light green or blue using 5 ml of starch indicator solution, added towards the end of titration. Millimetres of used sodium thiosulfate solution must be noted. Amount of chromium content is expressed in %.

$$w = \frac{v_1 x 0{,}00253 x 100 x F}{m_0} \qquad (3.5)$$

where:

v_1 is the volume, in milimitres (ml), of 0.1 mol/l thiosulfate solution used for the titration

m_0 is the mass of the original leather sample, in grams (g)

F is the factor to correct to 0% volatile matter, it is calculate as follows

$$F = \frac{100}{100 - w_W} \qquad (3.6)$$

Where w_W is the volatile matter content, based on ISO 4684, in percentage by mass.

3.5.8 Determination of matter soluble in dichlormethane

Amount of matter soluble in dichlormethane in leather was determined according to standard [71]. Two parallel determinations were executed for each tested hide/leather.

Principle of the method: the leather samples are extracted with dichlormethane. The solvent is evaporated from the extract and residue is dried at 102°C. Subsequent analysis can be then performed on the resulting extract to determine free fatty content of the leather.

*Procedure. W*eight accurately using the analytical balance (10+/-0.1) g of the prepared sample and press evenly into the filter paper thimble or glass bell. Cover the leather with a thin layer of glass wool or cotton wad.

Dry the extraction flask with four glass beads in it by heating for 30 min at (102 +/-2)°C. Weight after cooling in a desiccator. Prepared sample in paper thimble with cotton wad must be placed into the extraction apparatus (Soxhlet apparatus) and being continuous extraction with the dichlormethane; then after at least 30 changes of solvent, dichlormethane must be distilled from the flask containing the extract.

The extract must be dried for 4 h in the oven, maintained at (102+/-2)°C (if drops of water are visible before drying, 1 ml of ethanol have to be added). Samples must be weighted after cooling for 30 min in a desiccator.

Drying, cooling and weighting operations must be repeated, but with drying periods of 1 h, until either the further loss in mass does not exceed 0.01 g, or the total drying time equals 8 h.

The matter extractable in dichlormethane is given, as percentage by mass on dry matter by formula:

$$\frac{m_1}{m_0} x100xF \qquad (3.7)$$

where:

m_0 is the mass, in grams, of the test sample

m_1 is the mass, in grams, of the extract

and

$$F = \frac{100}{100 - w} \qquad (3.8)$$

where:

w is the mass fraction of the volatile matter (based on ISO 4684), in percent

3.5.9 Determination of volatile matter

Content of volatile matter of hide or leather was determinate using standard [72]. The principle of this method is based on drying of hide/leather samples in an oven at 102°C +/-2°C. The volatile matter is expressed as the ratio of the change in mass of the sample to the initial mass before drying. Term volatile matter is leather loss of mass by hide/leather when dried to constant mass at 102°C +/-2°C.

For this method following equipment was used:

- Oven, capable of being maintained at 102°C +/-2°C ;
- Analytical balance, weighting to accuracy of 0.001 g.
- Desiccator, suitable for cooling of vessels with samples.
- Evaporation vessels with coverings, for samples drying.

According to the procedure of the method 3 g of hide or leather sample had been taken, cut into small pieces with the shape of 3x3 mm and put into evaporation vessels. Samples were weighted to the nearest 0.001 g. It is necessary to take two parallel test pieces.

The weighted vessels without coverings were placed into the oven at 102°C +/-2°C for 2 h. After drying vessels were cooled down leaving in desiccator for 30 min with closed coverings. The vessels after cooling were weighted and results fixed.

Then vessels were put again into the oven for further drying for 1 h. Such heating, cooling and weighting was repeated until the change of dried sample mass did not exceed 3 mg (i.e. 0.1% of the sample mass).

Amount of the volatile matter was expressed in percent (%):

$$w = \frac{100(m_1 - m_2)}{m_1}, \% \qquad (3.9)$$

where:

m_1 mass of the sample before drying, g;

m_2 mass of the sample after drying, g.

3.5.10 Optical microscopy, infrared spectroscopy and differential scanning calorimetry

Fixation of hide structure with organic solvent. Usually dry samples of fresh hide or hide after processes up to chroming are used for various analyses. The problem is that hide derma structure significantly changes during dehydration by a drying. The structure of sample is retained without changes when the dehydration is carried out using organic solvents: ethyl alcohol or acetone.

Acetone [73] was used for the hide sample fixation in this research work (Figure 3.16 a). The treatment with acetone was carried out in such way: the hide samples were submerged into acetone, which amount was three times bigger than mass of samples, for three days. Every 24 hours the used acetone was changed by new portion of acetone.

a

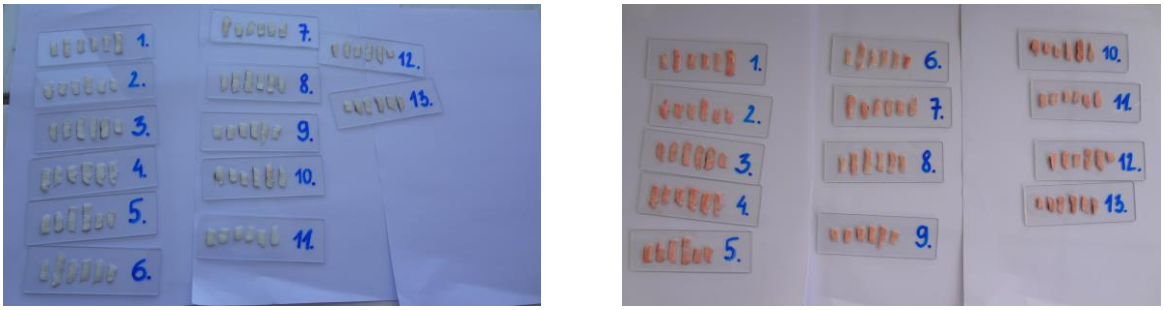
b

Figure 3.16 a-raw hide after treatment with acetone: **b**-hide sample after treatment prepared samples for microscopy [APF]

After the treatment the acetone was evaporated at ambient temperature. The structure of hide samples, which were designed for infrared spectroscopy and differential scanning calorimetry analysis, was fixed by treatment with acetone (the treatment allows saving the structure without any changes for long time).

Hide investigation by optical microscopy. Hide samples for the optical microscopy were prepared according to the method described in standard [74].

Hide samples we cut into rectangular test pieces 5x10x1 mm (Figure 3.16 b, p.70). For one microscopic slide 6 parallel test pieces were prepared (Figure 3.17).



a **b**

Figure 3.17 a-prepared samples for microscopy: non coloured [APF]; **b**-prepared samples for microscopy: coloured [APF]

The optical microscopy investigation was performed with *Olympus CX 31* microscope, magnification 40 times. To see better how natural fats distributed in hide derma some samples had been contrasted i.e. coloured with dyes.

Dye Sudan III (1-((4-(phenyldiazenyl)phenyl)azonaphthalen-2-ol) $C_{22}H_{16}N_4O$ was used for this aim [67]. The saturated solution of Sudan III was prepared dissolving the dye in ethyl alcohol (the concentration of C_2H_5OH was 70%). The colouring was carried out dropping the dye solution on a hide sample.

Infrared spectroscopy analysis. The changes of hide samples structure were estimated by infrared (IR) spectroscopy analysis. An IR absorption spectrum was obtained with a Perkin-Elmer FTIR Spectrum GX (USA) spectrometer using KBr pellets. The pellets were formed using hide samples after fixation with acetone. Prepared samples were cut into piece with dimensions approximately 1x1 cm. Then surface of sample must was shaved and sample cut into three layers. The powder of hide was taken from both surfaces for the preparation of pellets (Figure 3.18 a, p.72).

a **b**

Figure 3.18 a-sample cut in three pieces for IR analysis [APF]; **b**-hide powder for DSC analysis [APF]

The resolution was 1 cm^{-1}, scan rate 0.2 cm/s and scan number 16 times. The software ”Spectrum 5.0.1“ was used calculating the area of peaks in spectra ΔS ($T\% \cdot cm^{-1}$).

Differential scanning calorimetry. Differential scanning calorimetry (DSC) analysis was performed with the Netzsch Gerätebau GmbH (Germany) thermal analyzer in nitrogen atmosphere; heating rate of -10^{o}C/min. Reference sample was empty aluminium capsule. The hide samples were taken after the fixation with acetone.

Prepared samples were cut into rectangular shapes with dimensions 1x1 cm. Surface of samples were shaved and then layer with shaved surface was cut off. Remaining sample was grind into powder preparing amount 5-7 mg of hide powder (Figure 3.18 b).

4 RESULTS AND DISCUSSIONS

4.1 Investigation of hide condition during storage time

The properties of preserved and not preserved hide were estimated executing operations and determining indexes as follows:

- Rating of the hide properties established organoleptically such as appearance of hair slip, odour and other symptoms of deterioration;
- Evaluation of amount of microorganisms in hide during preservation period;
- Measurement of hide shrinkage temperature;
- Amount of released nitrogen from the hide during preservation period;
- Observation and rating of outside and inside exterior of hide using optical microscopy;
- Exploration of infrared spectra of vacuumed hide;
- Execution of differential scanning calorimetry of hide samples and exploration of the obtained DSC curves.

4.1.1 Organoleptic evaluation of preservation quality

The quality of preservation was assessed organoleptically observing any hair slip, appearance of bad odour and appearance of mucous surface of hide. There were compared all listed indexes of not preserved hide and differently preserved: salted or vacuumed hide. All tests had been carried out during 22 days period when samples were stored at 4^{o}C.

The bad odour appeared from not preserved hide, kept 11 days at temperature 4^{o}C. During next 2 days hair slip also appeared very evidently: the surface of the hide was almost destroyed by bacteria (Figure 4.1, p.74.), and bad odour was almost insufferable and the surface was intense mucous.

Salted hide quality didn't change during all experiment time: till 22 days. There wasn't discovered any hair slip or mucous surface, only slightly bad odour appeared at 20th day of storage, but that could be described as negligible.

Bad odour on vacuumed hide begun to appear only after 20 days of storage (it can be seen that amount of bacteria approached to limit showing the deterioration start: 20 millions bacteria per 1 gram of hide (see subsection 4.1.2, p.75).

Figure 4.1 Not preserved hide after 13 days of storage [APF]

But the bad odour also can be described as negligible comparing with not preserved hide stored. There wasn't observed any mucous on surface of hide, but was recognized hair slip start after 19th day (Figure 4.2) of storage in vacuum.

Figure 4.2 Vacuumed hide hair slip after 19 days of storing [APF]

For better understanding the results of organoleptic estimation were collected into Table 4.1.

Table 4.1

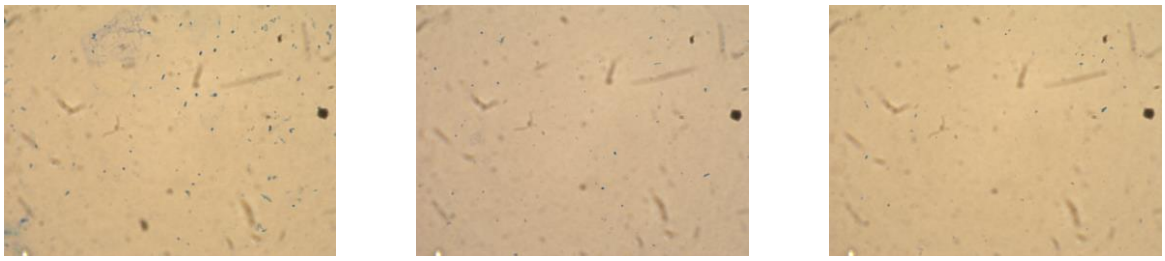
Appearance of hide deterioration symptoms on hide during 22 days of storage

Preservation method	Appearance of deterioration symptom		
	Bad odour	Hair slip	Mucous surface
Not preserved	After 11 days	After 13 days	After 13 days
Salted	Not appeared	Not appeared	Not appeared
Vacuumed	After 20 days	After 19 days	Not appeared

Organoleptic analysis had shown that during 20 days vacuumed hide had not hair slip, bad odour and other symptoms of serious deterioration etc.

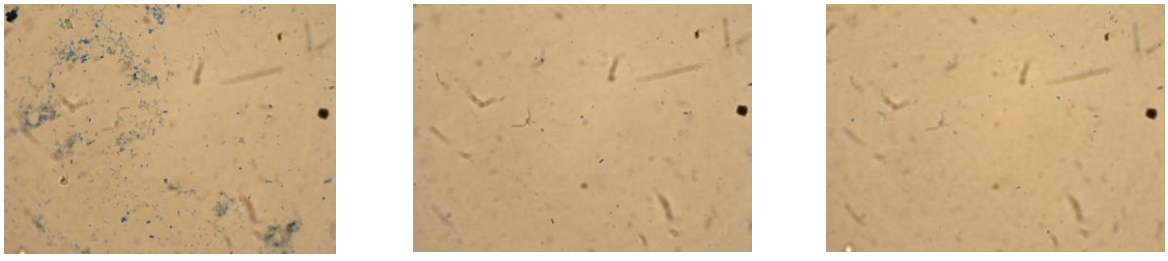
4.1.2 Microbiological assessment of hide preservation quality

Occurrence of putrefaction of the raw skins and hides, if not cured by physical or chemical method, is a traditional understanding. The symptoms of putrefaction beginning can be spot organoleptically as described in previous subsection. But moreclear picture of hide decay can be obtained only by use of instrumental investigation methods. One of the components responsible for the putrefaction is a bacterium, and this is a reason why it is very important to know the microbiological situation in hide preserved by various methods. [55] So, the next method of the preservation quality assessment was the determination of bacteria amount on hide. The method worked out by Beleska K. and described in literature was used [53]. According to the literature data [53], hide was considered as deteriorated when the amount of microorganisms in it exceeded $20x10^6$ units in 1 g of hide. For visual understanding in Figures 4.3/4.4 are represented images of coloured bacteria obtained investigating extracts of variously preserved hides stored different time periods (Figures 4.3 and 4.4).



a **b** **c**

Figure 4.3 Photographs of microscopic images (magnification 1000 times) of bacteria distribution on specimens prepared by extraction of 3 days stored hide: **a** - not preserved; **b** - vacuumed; **c** - salted [APF]



a **b** **c**

Figure 4.4 Photographs of microscopic images (magnification 1000 times) of bacteria distribution on specimens prepared by extraction of 21 day stored hide: **a** - not preserved; **b** - vacuumed; **c** - salted [APF]

For necessity of comparison of emergency of the preservation microscope photo fixation were made to evaluate amount of bacteria on preserved and on not preserved hide (see Figure 4.5/4.6).

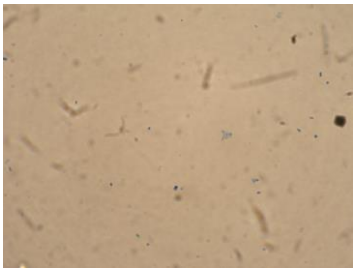


Figure 4.5 Photograph of microscopic image (magnification 1000 times) of bacteria distribution on specimen prepared by extraction of 13 day stored vacuumed hide [APF]

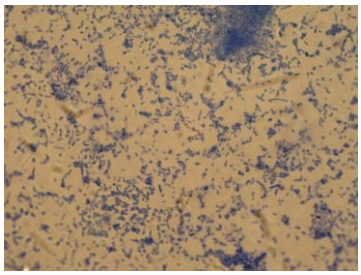


Figure 4.6 Photograph of microscopic image (magnification 1000 times) of bacteria distribution on specimen prepared by extraction of not preserved hide stored 11 days at ambient temperature 20 ±2°C [APF]

The hides and skins without a preservative can allow the growth of microorganisms instantaneously which can reach a level of several million per gramm and damage the hides in only 5–6 h. The predominant bacteria found in soaking baths are *Enterobacteraerogenes, Bacillus mycoides, Escherichia coli, Pseudomonas aeruginosa, Proteus vulgaris, Staphylococcus aureus* and other gelatine-liquefying bacteria. [30]

Table 4.2

Amount of bacteria, million·g-1 of hide

Hide storage duration, days	**Amount of bacteria, million·g-1 of hide**		
	not preserved	**vacuumed**	**salted**
3	26.03±1.30	11.23±0.35	10.38±0.53
6	53.26±1.84	14.07±0.38	13.46±0.66
9	194.76±5.16	19.53±0.75	14.34±0.57
13	237.69±9.61	12.53±0.59	13.49±0.56
16	110.49±3.42	16.23±1.3	14.46±0.61
20	120.35±2.56	18.07±0.58	14.88±0.44
21	180.19±5.53	17.07±0.62	14.92±0.43

Therefore, the first step was to determine action of vacuum on the bacteria growth. The results obtained have shown that the vacuum and low temperature block the vigorous multiply of bacterium.

During 22 days amount of microorganisms increases from 8 up to 18 million and does not reach the critical value (Figure 4.7).

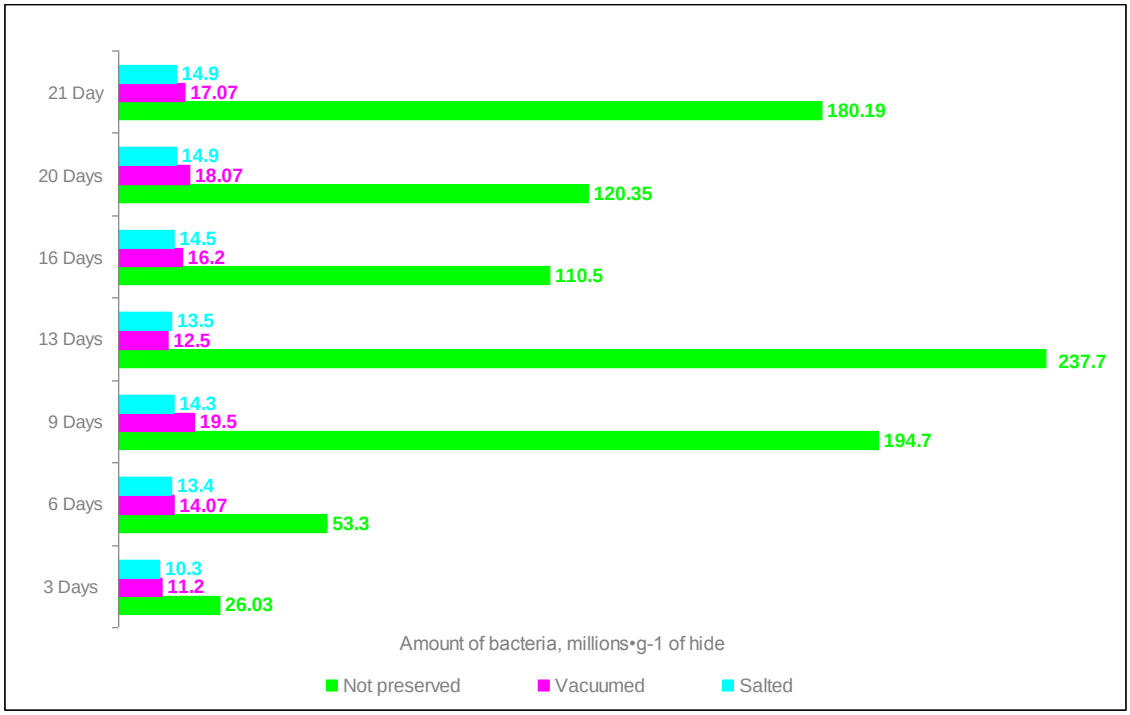


Figure 4.7 Microorganisms reproduction kinetics in hide

On the other hand, bacteria presented on hide during that time slowly but act. Due to this, a weakened bond of hair with derma is observable after the 22 days storage. Also, slight odour begins to float around. This indicates the slow beginning of decay process (Figure 4.8).

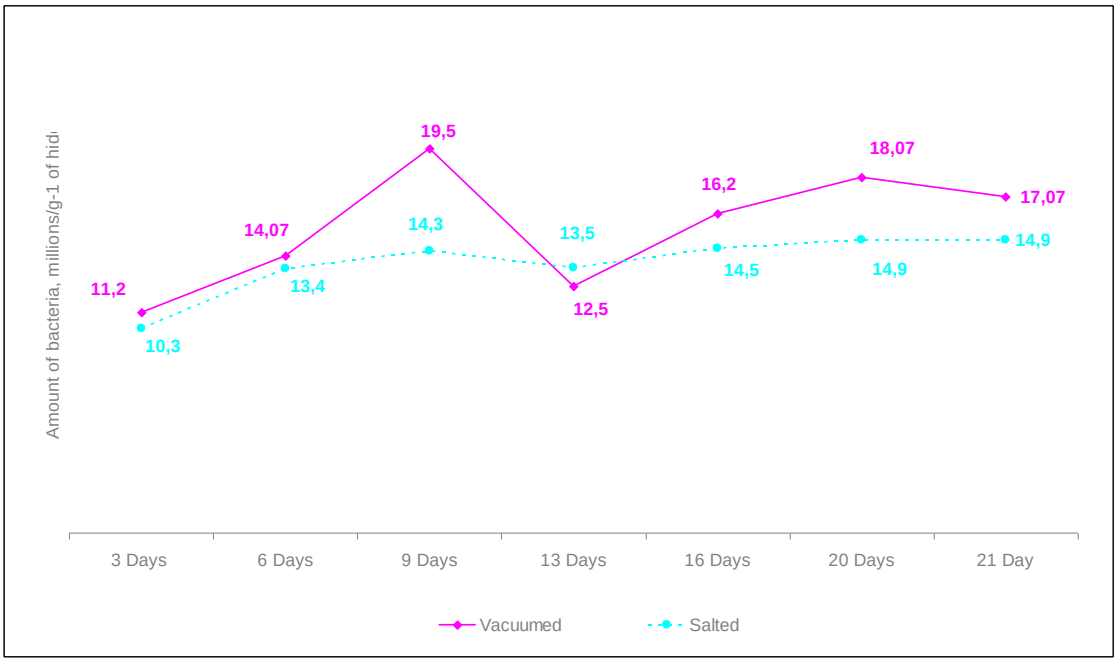


Figure 4.8 Microorganisms in graphic reproduction in salted and vacuumed hide

Very interest picture was obtained observing bacteria growth on not preserved hide stored at ambient (20±2°C) temperature (Figure 4.7, p.77). During 2 weeks is observed impetuous multiplicative process of microorganisms. After that, the amount of bacteria begins to decrease because old bacteria become as a nutritional medium for new generation of microorganisms.

4.1.3 Hide shrinkage temperature changes during storage

Next step was to discover action of microorganisms on derma collagen. Index, which is very sensitive to collagen structure changes, is a shrinkage temperature of hide [75]. Changes of shrinkage temperature indicate formation (when shrinkage temperature increases) or break (when decreases) of intra-molecular or intermolecular bonds in collagen of derma.

Intra-molecular bonds act in molecules of collagen and intermolecular: between collagen molecules. The results of hide shrinkage temperature determination are presented in Table 4.3.

Table 4.3

Kinetic of hide shrinkage temperature during storage

Hide storage duration, days	Shrinkage temperature (°C) of hide		
	not preserved	vacuumed	salted
3	63.3±2	64.3±2	64.3±2
6	63.7±2	63.7±2	63.4±2
9	61.7±2	62.3±2	62.3±2
13	62.3±2	63.3±2	63.0±2
16	62.3±2	62.7±2	63.0±2
20	62.0±2	62.0±2	63.0±2
21	61.3±2	62.3±2	62.0±2

*Note. Shrinkage temperature of fresh hide was 64.7 °C.

The data obtained had not shown serious changes in derma structure. For all samples (independently on preservation method used) was observed only negligible decrease of shrinkage temperature: for not preserved, vacuumed and salted hide by 3.4°C, 2.7°C and 2.7°C accordingly.

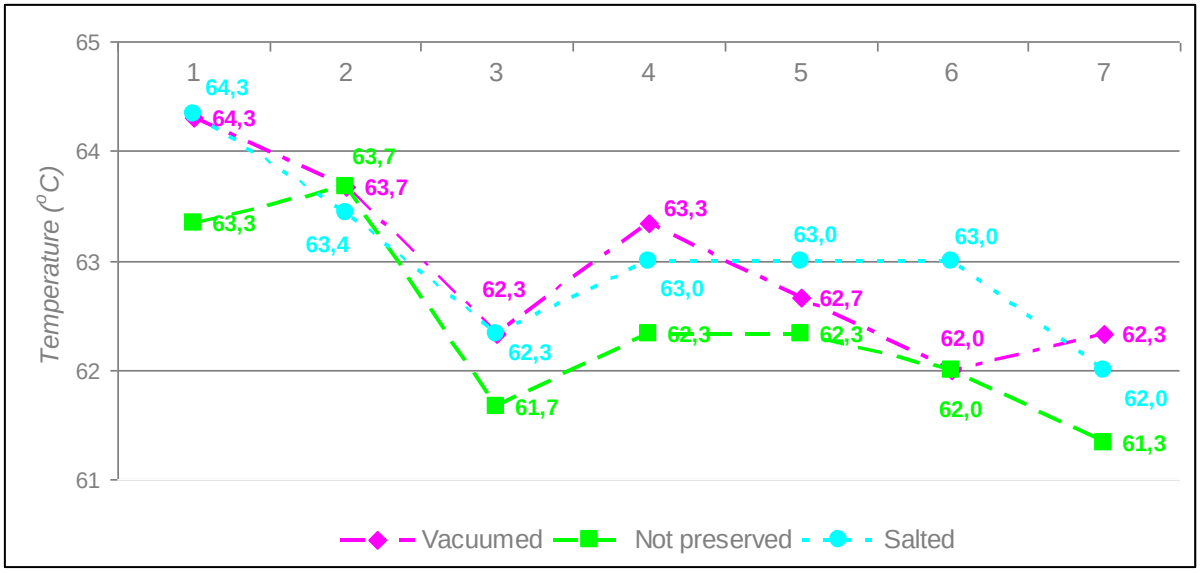


Figure 4.9 Changes of shrinkage temperature during storage time of salted and vacuumed hide

It means that microorganisms' action, which takes place only on surface of hide, does not effects deeper layers of hide. This situation stands good even when bacteria act very intensive (case with not preserved hide) (Figure 4.9). So, it can be concluded, that shrinkage temperature change does not enough reflects a level of hide deterioration when any chemical material is not used for hide preservation, and collagen, accordingly, is not affected by this material.

On the other hand, negligible reducing of shrinkage temperature points that hide structure stays without serious changes and this lets supposition that preservation using vacuum and storage during 21 day does not decrease quality of hide as raw material for leather producing.

4.1.4 Determination of content of nitrogen extracted from hide

Another index indicating a condition of preserved hide is an amount of released ammonia, which is formed when hydrolysis of proteins begins due to the action of microorganisms.

The data in Table 4.4 (p.80) show that observable increase of the extracted nitrogen amount begins for not preserved hide after 13 days of storage. This result confirms a proposition that hide can be stored at 4°C during 2 weeks without decrease of quality [27]. After this time during last week, the amount of nitrogen in hide increases almost 1.5 times: from 4.56 up to 7.06 g/ from 1 g of hide. It confirms

that microbiological deterioration goes enough intense, and this leads to lowering of hide, as material for leather processing, quality.

Table 4.4

Change of nitrogen content extracted from hide

Hide storage duration, days	Amount (g/kg of hide) of nitrogen extracted from hide		
	not preserved	vacuumed	salted
3	4.14±0.21	3.45±0.17	3.07±0.15
13	4.56±0.22	3.82±0.19	3.23±0.16
16	4.62±0.23	3.40±0.17	3.26±0.16
20	5.48±0.27	4.07±0.20	3.88±0.19
21	7.06±0.35	4.24±0.21	4.12±0.20

In the case of salted hide samples the increment of nitrogen content is negligible during all time of storage (Table 4.5). There is the question why, because salting stops bacterial attack (subsection 4.1.2, p.75, Figure 4.7, p.77).

Table 4.5

STDEV analysis of change of nitrogen content extracted from hide

Hide storage duration, days	not preserved	vacuumed	salted
3	0.03	0.03	0.00
13	0.00	0.00	0.03
16	0.03	0.00	0.03
20	0.00	0.00	0.00
21	0.00	0.00	0.00

It seems that nitrogen is produced from soluble non-collagen proteins in such case due to their dissolving in salt solution having very high concentration. After such dissolution, the nitrogen containing materials are very easy washed when preparing extract for the nitrogen amount analysis. So, they fall into extract and after the determination show slight increase of released nitrogen (for visual understanding see Figure 4.10, p.81).

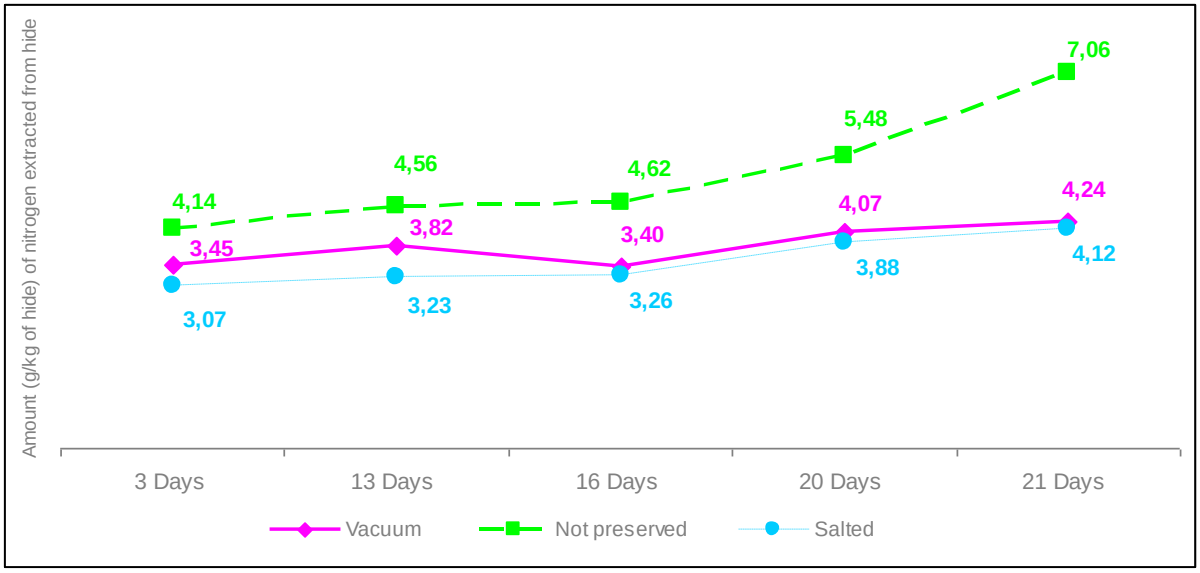


Figure 4.10 Change of nitrogen content extracted from hide

Analysing nitrogen content change in the vacuumed hide, it can be concluded that amount of nitrogen slowly increases during 21 day of the hide storage. But the increase is similarly negligible as for salted hide (Table.4.6).

Table 4.6

Change of nitrogen content in % extracted from hide from the first day

Hide storage duration, days	Amount (%) of nitrogen extracted from hide		
	not preserved	vacuumed	salted
3	0%	0%	0%
13	10.1%	10.7%	5.1%
16	11.5%	-1.3%	6.3%
20	32.4%	18%	26.4%
21	70.5%	23%	34.3%

Because in the vacuumed hide exclusive reason of such increase can be explained only through action of bacteria, it means that the mentioned action is very weak in vacuumed hide and it should not to lead to the decrease of the hide quality.

4.1.5 Assessment of hide quality using optical microscopy

One of deterioration beginning symptom is a change of the hide exterior. Due to this the comparison of the vacuumed hide samples was carried out. Samples kept in vacuum 1 and 22 days were observed. Optical microscopy images were prepared

from natural and dyed with dye Sudan III samples. The images are presented in Figure 4.11 and in Figure 4.12.

Comparing both non-dyed and dyed samples it is seen that there are not any noticeable differences in the images of samples stored 1 and 22 days. Observable mucus does not form on the both lower and upper layers surfaces of 22 days stored hide, despite the weak, but permanent action of bacteria (subsection 4.1.2, p.75 Figure 4.7, p.77).

Therefore, the exploration of images allows drawing a conclusion that any observable changes of the vacuumed hide outside and inside exterior do not occur during 22 days storage.

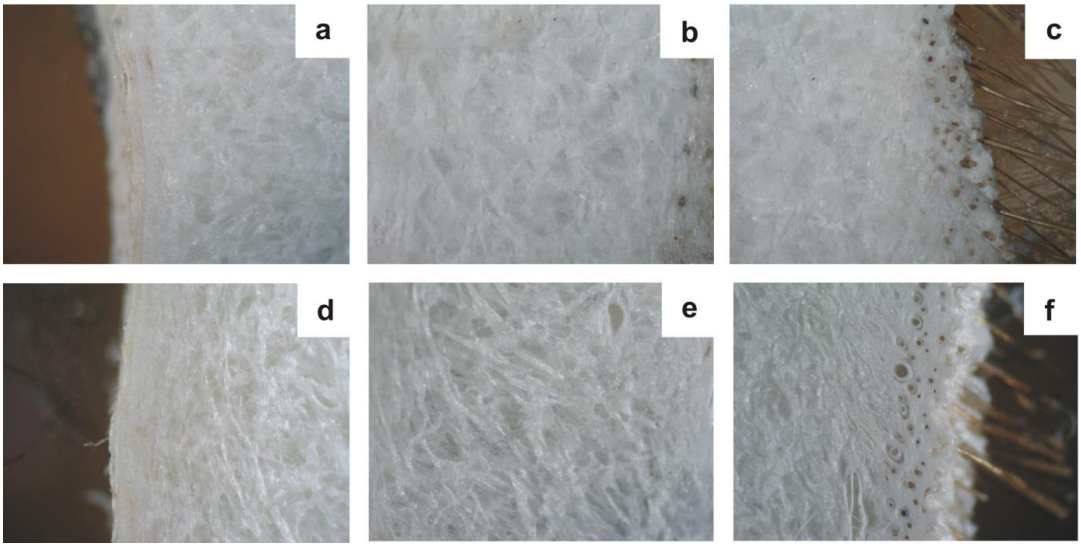


Figure 4.11 Images of vacuumed hide samples (non-coloured) (magnification 40 times) stored 1 day (a) (b) (c) and 22 days (d) (e) (f) ((a) (d) - lower layer; (b) (e) - middle layer; (c) (f) - upper layer

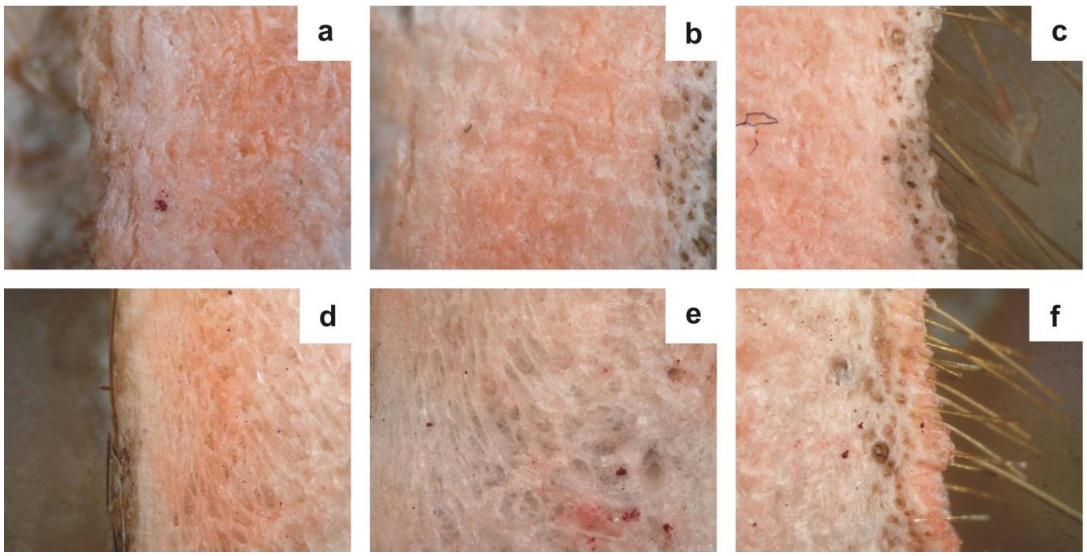


Figure 4.12 Images of vacuumed hide samples (coloured) (magnification 40 times) stored 1 day (a) (b) (c) and 22 days (d) (e) (f) ((a) (d) - lower layer; (b) (e) - middle layer; (c) (f) - upper layer

4.1.6 Infrared spectroscopy investigation of vacuumed hide

Further a possible changes of supermolecular structure during the storage under vacuum where investigated. Firstly IR spectroscopy was employed for this purpose. (Figure 4.13, p.85, Table 4.7, p.84.). The structural changes reflect in IR spectra as the changes of individual bands in position and in intensity [31].

Comparison of values of peaks areas allows concluding about formation of functional groups and degrading or formation of bonds during hide storing. The most typical bands in spectra were chosen for the evaluation of structural changes.

The vibrations in range 3400–2500 cm^{-1} are attributed to hydrogen bond of associated functional groups O-H, N–H and C–H. [76][77][78] [79] Analysis of data in IR spectra of the vacuumed hide stored various time show that intensity of peaks in the mentioned range slightly increases. This increase can be related with the forming of new hydrogen bonds in derma structure.

Peaks in ranges 1655–1658 cm^{-1}; 1523–1549 cm^{-1} and 1235–1240 cm^{-1} are attributed to I, II and III amide bands respectively. The area of peaks in the range 1655–1658 cm^{-1} depends on amount of carboxyl groups. The obtained data (Figure 4.13, p.85, Table 4.7, p.84) allows conclusion about negligible increase of intensity of peaks in the mentioned ranges.

According to data in literature, peaks at 1081 cm^{-1} and 1030 cm^{-1} are specific to collagen. [79] Unfortunately, it is not clear what groups vibrate in these ranges. In vacuumed hide spectra the peaks in the range 1081 cm^{-1} also is visible but any changes of this peak are not observable in the variously long time stored vacuumed hide.

In summary, the exploration of the hide samples spectra (Figure 4.13, p.85) has shown that new peaks do not appear or old disappear. This allow conclusion that any serious changes in supermolecular structure of collagen do not occur during 22 days storage. On the other hand, the intensity of all peaks increases as mentioned above (Table 4.7, p.84). Author supposes that during storage owing to the action of vacuum the fibres of collagen slowly become closer, accordingly, the derma becomes denser, and this leads to the increased all peaks intensity in the stored 22 days hide’s spectra.

Table 4.7

Data of IR spectrum quantitative analysis (all spectras) [38]

Functional group or bond, to which the vibration is attributed	Vacuumed hide sample storage time, days											
	1		5		11		15		20		22	
	ν, cm^{-1}	ΔS	ν, cm^{-1}	ΔS	ν, cm^{-1}	ΔS	ν, cm^{-1}	ΔS	ν, cm^{-1}	ΔS	ν, cm^{-1}	ΔS
N–H; O–H	3332	17522	3332	19331	3332	19331	3332	20325	3332	19206	3325	8119
= NH; -CH_3	2958	2230	2957	2245	2957	2276	2957	2651	2957	2592	2937	3375
=C=O „amide band I“	1660	8328	1660	9402	1660	8476	1660	9448	1660	11116	1659	10635
amide band II“	1550	255	1550	304	1550	197	1550	266	1550	247	1556	363
–OH; R–COO–	1453	651	1453	798	1453	818	1453	785	1453	829	1452	1112
„amide band III“	1239	886	1239	1014	1239	943	1239	1117	1239	1026	1238	1358

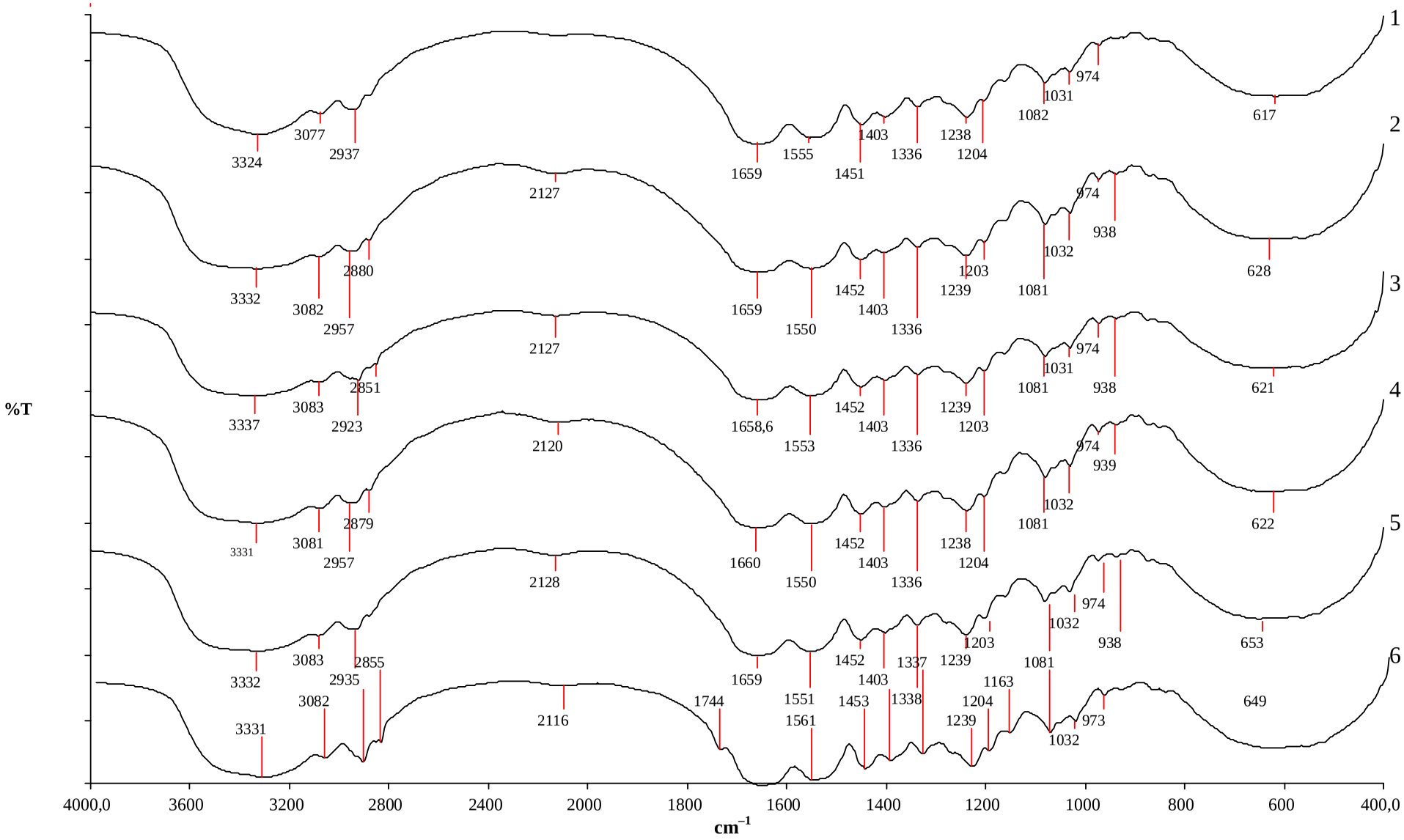


Figure 4.13 Infrared spectra of vacuumed hide stored 1 day (1); 5 days (2); 11days (3); 15 days (4); 20 days (5) and 22 days (6)

4.1.7 Estimation of vacuumed hide by differential scanning calorimetry

The DSC analysis had objective to approve or deny conclusions about stored vacuumed hide quality and evaluate possible changes occurred in hide structure. Vacuumed hide samples after 1 and 22 days storage were used for the analysis (Figure 4.14, 4.15).

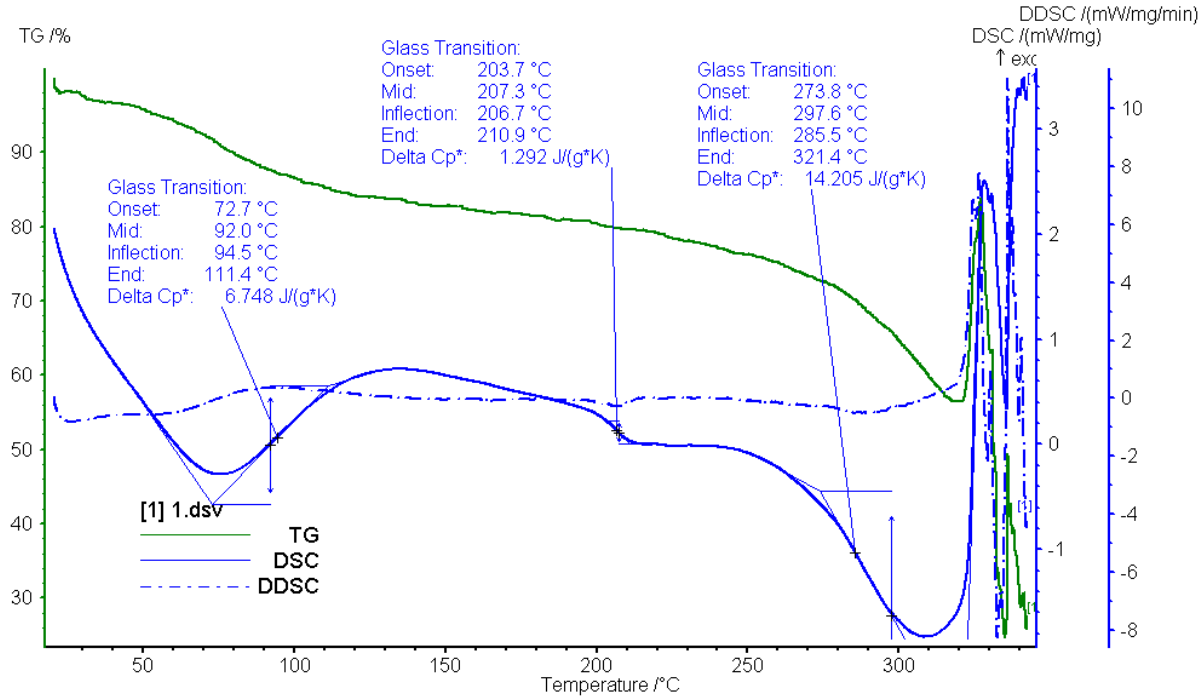


Figure 4.14 DSC curves of vacuumed hide samples stored 1 day

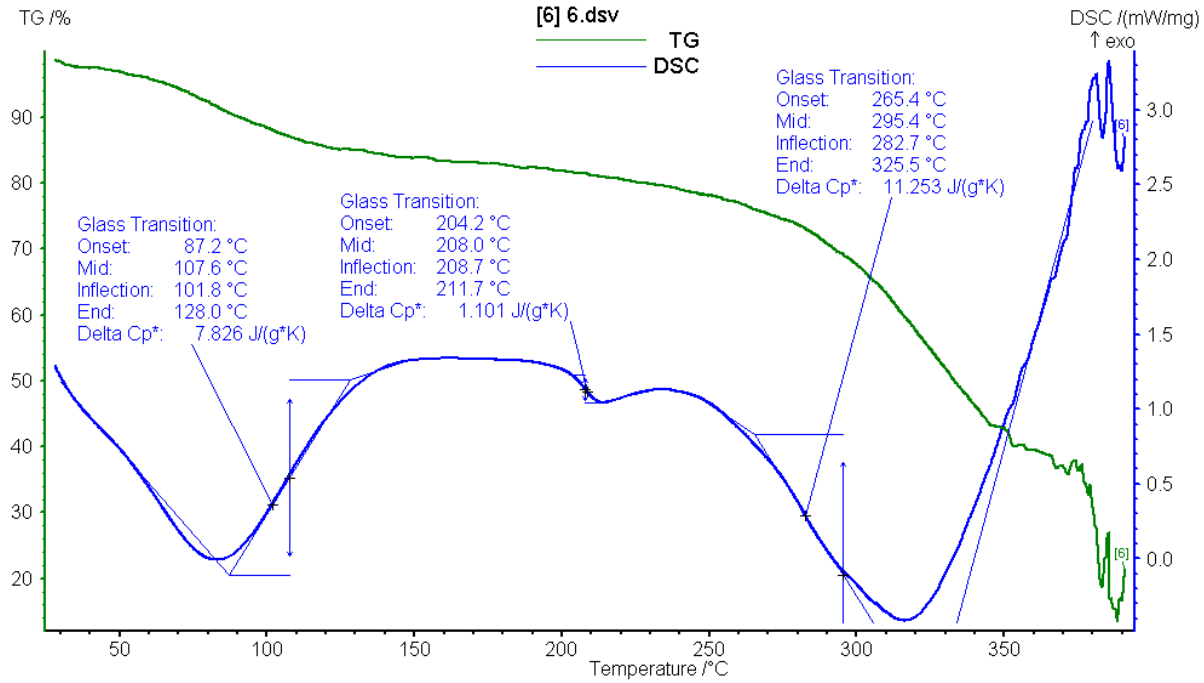


Figure 4.15 DSC curves of vacuumed hide samples stored 22 days

The results of DSC analysis are presented in Figure 4.16 and Table 4.8. It is seen (Figure 4.16) that DSC curves have three distinct thermal effects. The obtained effects are absolutely typical for hide. [80] The first endothermic effect can be attributed to shrinkage (denaturation) of hide [81]. But more credible slant is to associate that effect with the removal of capillary moisture [82]. It is known [83] that degree of linking of capillary moisture in collagen is higher when capillaries are smaller. Presumably, the approach of fibre each to other during storage under vacuum leads to the decrease of capillaries dimensions, and accordingly, to the increase of initial and finish temperatures of the first endothermic effect.

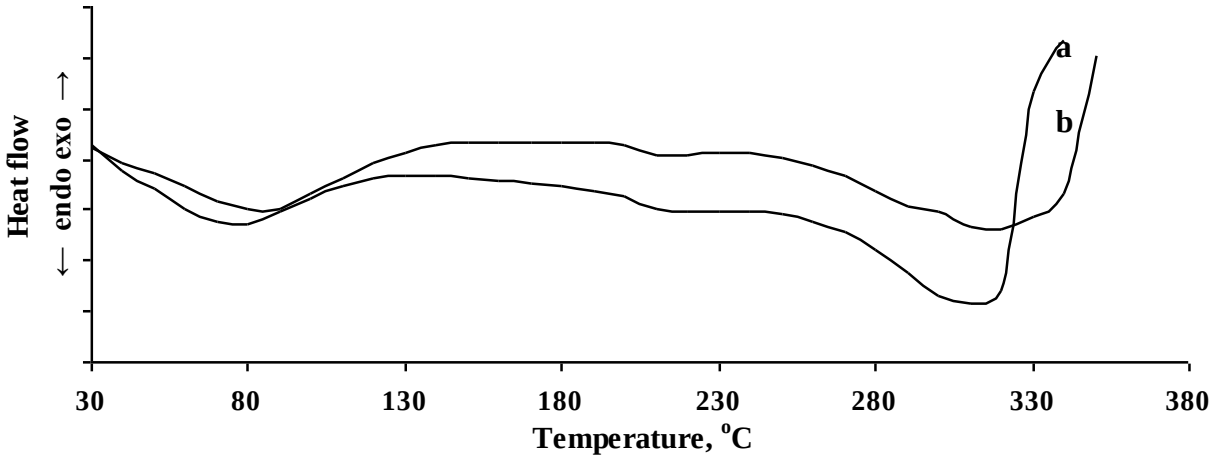


Figure 4.16 DSC curves of vacuumed hide samples stored 1 (**a**) and 22 (**b**) days

Therefore, the movement of start and finish temperatures of the first endothermic effect to the range of higher values approves the supposition obtained after IR spectroscopy analysis: during the storage of vacuumed hide samples the fibres of derma approach each to other under the action of vacuum and change dimensions of capillaries in derma structure.

Table 4.8

Delimitation of thermal effects in DSC curves

Hide storage time, days	First endothermic effect, °C			Second endothermic effect, °C			Third endothermic effect, °C		
	start	finish	Δ*t*	start	finish	Δ*t*	start	finish	Δ*t*
1	73	111	38	204	211	7	274	321	47
22	87	128	41	204	212	8	265	325	60

Various authors interpret second thermal effect variously. Kutianin et al. relate the second temperature effect to the change of crystal phase to amorphous state [84]. Similar opinion is expressed by Romanian investigators [85][86]. They proposed that the second endothermic peak obtained for temperature is higher than 200^{o}C, was attributed to melting of crystalline zone of the leather. The temperature of minimum of this peak is characteristic parameter for deterioration of the crystalline zone. When processing a hide, the level of crystallinity changes as stronger as stronger the hide is affected during processing [87]. In our case the start and the finish temperatures of the second endothermic effect coincide for both hide samples, and this proves that collagen is not affected absolutely.

The third endothermic effect is related with destruction of hide tissue. For hide sample after 22 days of storage this effect has lower start and higher finish temperature comparing with the sample stored 1 day. The lower start temperature indicates the beginning of deterioration of outer layers of the hide but due to pressed collagen fibres the thermal effect ends at higher temperature.

Summarising the DSC analysis results it can be said that the obtained DSC curves are absolutely characteristic for native collagen. The negligible changes of first and third thermal effects temperatures do not indicate the serious structural changes in derma collagen during storage of vacuumed hide samples.

4.1.8 Summary of results of investigation of hide condition during storage time

Table 4.9

Summary of results of investigations of hide condition during storage time

Qualitative index	Vacuumed	Salted
Bad oddour	After 20 days	Not appeared
Hair slip	After 19 days	Not appeared
Mucous surface	Not appeared	Not appeared
Amount of bacteria (millions/g-1g of hide) after 22 days of storage	17077000	14946000
Changes of shrinkage t^{o} during storage	2.7 ^{o}C	2.7 ^{o}C
Changes of amount of nitrogen extracted from hide, comparing with 3rd day of storing (%)	23%	34.3%
Assessment of hide quality using optical microscopy (comparing samples stored 1 and 22 days)	No any noticeable differences	No any noticeable differences
Infrared spectroscopy investigation of vacuumed hide	New peaks do not appear and old do not disappear	
Estimation of vacuumed hide by differential scanning calorimetry	Obtained effects are absolutely typical for hide	

4.2 Behaviour of vacuumed hide during technological processes of leather manufacturing

As it was mentioned in Chapter 3 Materials and methods, processing of samples under laboratory and industrial conditions, a part of little samples was processed into wet blue under laboratory conditions and big samples were processed into wet blue under industrial conditions in tannery “Kedainiu oda” (Lithuania) according to technology of upper leather processing. During beamhouse and chroming processes the changes of hide properties were observed aiming to understand the peculiarities of vaccumed hide processing into tanned leather.

The purpose of the beamhouse is to prepare the hide/skin for tanning. Another way of putting that would be to say the beamhouse is for purifying the hide/skin (remove of preservative materials, flesh, hair and epidermis, soluble proteins) and “opening up” the hide/skin structure. Opening up is a generic term that has two components:

1. The removal of non-collagenous skin components: the hyaluronic acid and other glycosaminoglycans, the non-structural proteins, the fats. This is not done to completion, so the process in a tannery must be geared to the degree of removing these materials, required to produce the desired properties of the final leather.
2. Splitting the fibre structure at the level of the fibril bundles, to separate them. [5]

The beamhouse processes requires big amount of water, which becomes lower or higher polluted depending on the concrete process. Usually, all waste waters after beamhouse processes (excepting pickling) are mixed and pass into cleansing as waste water after beamhouse processes.

The cleaning of tannery waste water is very complicate and expensive business. The very serious reason of it is great amount of waste water which must be treated. In Table 4.10, p.91, are presented needs of water for typical leather processing process.

So, any attempt, which leads to decrease of water consumption is very welcome from environmental and technological point of view.

Table 4.10 average amounts of water on raw weight basis and times merely represent typical industrial conditions. [5]

Table 4.10

Indicative process conditions for bovine hides [5]

Process step	Water (% on hide weight)	pH	Time (hours/h)
Washing	200	6-10	1-2
Soak (often more than a single step, n=1-4)	nx200	6-10	4-8
Unhairing (lime and sulphide)	200	12-13	18-24
Washing	200	12-13	1
Deliming (ammonium salt)	100	8-9	1-2
Bating (proteolytic enzyme)	100	8-9	1-2
Washing	100	8-9	1
Totally:	1100-1700	10-11	27-40*

* Presented total duration does not include time for mechanical operations (trimming, fleshing, loading, dumping), pouring and draining of water and solutions etc.

4.2.1 Evaluation of vacuumed hide rehydration level

Soaking is the first of beamhouse processes. In the process known as *soaking*, the hides are soaked in clean water to remove the salt left over from curing and increase the moisture so that the hide or skin can be further treated. [5]

The effectiveness of the soak depends on the amount of water used: the efficiency of salt removal depends on the amount of water, since the salt is effectively partitioned between the two phases and the solubilisation rate depends on the difference in concentration between the soak liquor and the rehydrated pelt.

Nearly 6.5 million tons of raw hides and skins in various preserved forms are processed worldwide annually [88]. Based on this figure, it can be estimated that about 2.6 million tons of salt are discharged in the first unit operation of leather processing called soaking, alone. The soaking process contributes to more than 40%

of the total dissolved solids (TDS) load that is generated in the entire process of leather manufacturing [89].

In conventional processing salt-preserved hides are commonly used. Calculated on the basis of wet salted weight, the amount of soaking (with washing) effluent discharged varies from 4 m^3/t up to 10 m^3/t raw hide. When soaking dry hides, up to 20 m^3 water/t dried hide is required. The most important pollutants in soaking effluents are: salt, hide surface impurities, dirt and globular protein substances dissolved in water and salt solution.

The soaking is very important process because insufficient and uneven rehydration of derma leads to not qualitative run of subsequent processes: liming-unhairing, deliming etc.

It was the reason, why firstly the moisture content change in preserved by vacuum hide was investigated and compared with the moisture content change during washing-soaking of salted hide. Results are presented in Table 4.11.

Table 4.11

Hide moisture content change during preservation and washing and washing-soaking processes

Preservation method	**Moisture content, %**		
	Before preservation (fresh hide)	**After preservation and storage during 21 day**	**After washing or washing-soaking**
Vacuumed hide	65.7	63.6	69.2* (69.2**)
Salted hide	65.7	58.2	67.6

* - washing duration 0.5 h; ** - washing duration 1 h.

The data in table 4.11 show that due to vacuum action the hide loses about 2% of moisture. The rehydration of vacuumed hide stored 21 day goes very fast and during 0.5 h reaches and even exceeds moisture content of fresh hide.

After salting during 21 day hide loses about 10% of moisture and only after washing and soaking processes reaches value 67.6%.

Therefore, preservation of hide by vacuum leads to significantly shortened rehydration process: from 9 h for salted down to 1 h or even to 0.5 h for vacuumed hide. This means the markedly economy of electric energy for rotation of drums during soaking process.

Secondly, big quantity of water is saved: the demand of water for vacuumed hide is about three times less.

Thirdly: the waste water after the vacuumed hide washing id absolutely free from chlorides, what significantly reduces cost of the effluent cleansing.

4.2.2 Structural changes of hide during liming-unhairing process

After soaking, the hides/skins are taken for liming: treatment with lime (usually $Ca(OH)_2$ as a basic agent) solution that may involve the addition of "sharpening agents" (disulfide reducing agents) like sodium sulphide or sodium hydrosulphide etc. The objectives of this process are mainly focused to:

- remove the hair, epidermis and other keratinous matter;
- remove some of the interfibrillary soluble proteins like mucins;
- swell up and split up the fibres to the desired extent;
- remove the natural grease and fats to some extent;
- bring the collagen in the hide to a proper condition for satisfactory tannage.[89]

Processing soaked hides in a bath containing sodium sulphide/hydrosulphide and lime constitutes a basis for conventional unhairing and liming methods. The amount of liming effluents, including washing, fluctuates between 9 and 15 m^3/t raw hide. Sulphides, lime, decomposed hair keratin, globular protein and other non-collagen protein, as well as saponified fractions of native fat constitute the load of liming effluents making them the most polluted wastewater streams. [89]

As reports Beleska [39], liming-unhairing of hide preserved using chemical methods for short term goes more intensely comparing with salted one.

So, it is very important to know how the vacuumed hide behaves during conventional liming-unhairing, how the collagen of vacuumed hide is acted during the process.

Therefore, the liming-unhairing of fresh and salted hide samples, and hide samples stored 5 and 19 days under vacuum was carried out and effect on collagen accessed. After process the amount of collagenous proteins in treatment solution was evaluated (Table 4.12, p.94)

Table 4.12

Dependence of amount of removed from hide collagen proteins during liming unhairing technological process

Sort of hide	Amount of removed collagen proteins (g/1 kg of hide) during process	
	washing-soaking	liming
Not preserved	0.00	0.34
Vacuumed (stored 5 days)	0.00	0.30
Vacuumed (stored 21 day)	0.00	0.38
Salted (stored 21 day)	0.07	0.20

It is known that usually amount of removed collagen proteins during liming varies in the range 0.2-0.5 g/kg of hide [90] [91]. When liming the vacuumed hide stored 5 or 21 days, the amount of removed collagen proteins is higher than level of those removed from salted hide. Also, it somewhat exceeds amount removed from not preserved or less time store vacuumed hide. On the other hand, the amount of removed collagen proteins during liming in no one case is not higher than above mentioned value (0.5 g/kg of hide).

Higher amount of collagenous proteins removed from 21 day stored vacuumed hide once again confirms the proposition about microorganisms action on hide, which is not strong and does not injure the hide but has influence on collagenous proteins content increase in the liming-unhairing solution.

Table 4.13

Hide shrinkage temperature after liming-unhairing process

Sort of hide	Shrinkage temperature, ^{o}C
Not preserved	56.0±2
Vacuumed (stored 5 days)	55.3±2
Vacuumed (stored 21 day)	55.0±2
Salted (stored 21 day)	54.0±2

The evaluation of hide shrinkage temperature after liming-unhairing process has shown similar effect of the process on the all treated hides. On the other hand, less affected hide (through preservation and storage) has higher shrinkage temperature after liming-unhairing. It lets supposition that during this process removing of noncollagen proteins goes on for fresh and vacuumed hide more

qualitative than for salted one. Due to this collagen fibriles closes each to other forming interfibrillar bonds, and this leads to higher shrinkage temperature value, despite the fact, that amount of collagenous proteins after process in the liming-unhairing solution is higher.

Organoleptical assessment has shown that all samples were unhaired qualitative, well-swelled, without observable defects, such as grain loose or wrinkles.

The obtained results let a speculation that liming-unhairing process can be shortened when processing vacuumed hide, seeking to reduce effect of alkaline materials on derma collagen.

4.2.3 Action of deliming-bating on hide dependently on preservation method

The pH of the collagen is brought down to a lower level so that enzymes may act on it, in a process is known as deliming. Depending on the end use of the leather, hides may be treated with enzymes to soften them, a process called bating. Usually deliming and bating processes are carried out in single solution one by one.

Conventional deliming and bating methods are based on processing pelts in a bath containing salts derived from a strong acid and a weak alkali (mainly ammonium salts) together with proteolytic enzymes. The amount of deliming and bating effluents, including washing waters, fluctuates between 7 and 11 m^3/t raw hide. Calcium salts (mainly sulphates), sulphide residues, degraded proteins (collagen and hair) and residual proteolytic enzymatic agents and the like constitute the main pollution load of deliming and bating effluents. [89]

As the main aim of deliming is to remove calcium compounds from derma, the deliming process parameters depend on the method of liming. So, it means that after conventional liming must be done the conventional deliming.

Absolutely other situation is with bating, because the proteolytic enzyme acts stronger when collagen is affected somehow before the bating. [92]

As the vacuumed hide structure is similar to fresh hide structure, it can have influence on enzyme effect level on collagenous proteins. Therefore, the amount of removed collagenous proteins during deliming-bating was evaluated. The results are presented in Table 4.14, p.96.

Table 4.14

Influence of preservation method on hide shrinkage temperature and on amount of removed from hide collagen proteins during deliming-bating

Sort of hide	Amount of removed collagen proteins (g/1 kg of hide)	Shrinkage temperature, ^{o}C
Not preserved	0.23	60.0±2
Vacuumed (stored 5 days)	0.22	61.7±2
Vacuumed (stored 21 day)	0.18	59.7±2
Salted (stored 21 day)	0.13	62.7±2

Evidently that not preserved or vacuumed hide during deliming-bating is affected more than salted hide. There again, the absolute values of mentioned amounts are not so high that we can begin to speak about enzymatic destruction of collagen. The presented values are in the ordinary range. [93]

The determined shrinkage temperature values of the bated hide confirm the trend, discussed above: „not preserved or vacuumed hide during deliming-bating is affected more than salted hide". When comparing vacuumed hide stored accordingly 5 and 21 day, it is seen that stored longer time hide is affected more and has lower value of shrinkage temperature. So, it once again proves that bacterias during mentioned time slightly act on the hide, and this action reflects as lower shrinkage temperature after enzymatic process.

Organoleptical estimation of the samples also was carried out. It has shown that semblance of all samples was very similar independently on the preservation method.

The obtained results leads to the supposition that bating process should be investigated separately and more widely having the aim to establish more optimum parameters for the bating of the vacuumed hide.

4.2.4 Pickling effect

Once bating is complete, the hides and skins are treated with a mixture of common (Table 4.15, p.97) salt and sulphuric acid, in case a mineral tanning is to be done. This is done to bring down the pH of collagen to a very low level so as to facilitate the penetration of mineral tanning agent into the substance. This process is

known as pickling. The common salt (sodium chloride) penetrates the hide twice as fast as the acid and checks the ill effect of sudden drop of pH.

The method of pickling depends on the raw hide/skin sort and on the type of manufactured leather (sole, upper, garment etc.) [94] [95]

The changes of derma structure during pickling depend on method of the pickling, on parameters of processes before pickling (how the hide was affected before pickling).

So, it depends on the hide structure during preservation and storing as well. The estimation of the effect of pickling on the hide proteins was carried out evaluating removed collagenous proteins and hide shrinkage temperature. Results are presented in Table 4.15.

Table 4.15

Influence of preservation method on hide shrinkage temperature and on amount of removed from hide collagen proteins during pickling process

Sort of hide	Amount of removed collagen proteins (g/1 kg of hide)	Shrinkage temperature, ^{o}C
Not preserved	0.02	47.0±2
Vacuumed (stored 5 days)	0.02	48.7±2
Vacuumed (stored 21 day)	0.03	46.0±2
Salted (stored 21 day)	0.02	46.3±2

The obtained results show that the preservation method had not observable influence on the pickled hide properties. Since the typical pickling with sulphur acid was used, the action on collagen was negligible because according to literature [96] the strong inorganic acid in the presence of high concentration sodium chloride does not degrade the collagen during pickling process. The values of shrinkage temperature also are very close for all hide samples.

In Table 4.16, p.98 are presented amounts of removed collagenous proteins during all beamhouse processes (washing, soaking, unhairing-liming, deliming-bating and pickling).

Table 4.16

Amount of removed collagenous proteins during beamhouse processes

Sort of hide	Amount of removed collagen proteins (g/1 kg of hide)
Not preserved	0.59
Vacuumed (stored 5 days)	0.54
Vacuumed (stored 21 day)	0.59
Salted (stored 21 day)	0.42

Comparison of totally removed collagen proteins during all beamhouse processes shows very close situation in cases of vacuumed or not preserved hide. It can be conclude that vacuumed hide is not affected stronger than not preserved hide when it is processing.

Also, the evaluation of derma protein change during beamhouse processes proved the conclusion that parameters of the mentioned processes should be studied separately with aim to optimize them. On the other hand, conventional methods also can be applied for the processing of the vacuumed hide.

4.2.5 Investigation of chroming process

So, the tanning is the main process, which converts hide/skin into leather. During tannin derma becomes thermostable and resistant to putrefaction. This occurs due to formation of crosslinks between macromolecules of collagen. Formally, tanning can be carried out using inorganic or organic tanning compounds, or combining inorganic tanning materials with organic one.

As natural organic tanning materials can be used natural tannins: oak [97], quebracho [98], mimosa, chestnut [99] etc.

As synthetic tanning compounds can be used melamine-formaldehyde based resins [100] aldehydes [101] and other synthetic organic compounds having capability to penetrate into derma and form new crosslinks in derma structure [102].

Application of inorganic tanning materials such as aluminium, zirconium, titanium [103], iron [104], was investigated.

Of course, the chrome tanning remains as mostly conventional and convenient tanning method [5]. Evaluation of leather properties after tanning allows conclusion about leather quality and suitability for manufacture of further products from leather.

Therefore, next step was the establishment of leather properties after chrome tanning process. After the tanning the exhaustion of chromium compounds, the total content of Cr_2O_3 in leather, the distribution of Cr_2O_3 in separate leather layers and the shrinkage temperature were evaluated. Data are presented in Table 4.17.

Table 4.17

Qualitative indexes of chroming process and tanned leather

Index	**Leather produced from hide**			
	vacuumed		**not preserved**	**salted**
	stored 5 days	stored 21 day		stored 21 day
Exhaustion of chromium compounds, %	93.3	87.9	95.2	79.0
Shrinkage temperature, ^oC	101.2±2	100.0±2	102.7±2	102.0±2
Cr_2O_3 content in leather, %	3.95	4.04	4.23	3.69
Cr_2O_3 content in leather's separate layers, %				
upper	4.76	5.28	5.06	4.15
middle	3.38	3.92	3.39	3.07
lower	4.74	4.62	5.77	4.33

The comparison of chroming process indexes shows that better results are achieved when processing the not preserved hide samples. Highest exhaustion of chromium compounds and accordingly highest content of chromium in derma, and highest shrinkage temperature was achieved in such case. The vacuumed hide samples after chrome tannage had middle values of chromium salts exhaustion and chromium content in leather. Therefore, the leather from salted hide samples had lowest content of chromium but shrinkage temperature was sufficiently high.

Of course, the differences of shrinkage temperature values were comparatively negligible. Herewith, all samples were of good thermo stability: the shrinkage temperature for all samples was not less than 100^oC.

The distribution of Cr_2O_3 in all leather samples is sufficient and similar.

Summarising the results of chrome tanning process can be proposed that samples obtained from vacuumed hide had not worse properties comparing with leather produces from salted hide. Contrary, they joined more chromium compounds and this led to better exhaustion of chroming solution. So, the conventional chroming method is absolutely suitable for the chroming of vacuumed hide.

4.2.6 Industrial trials of vacuumed hide processing

Of course, the most reliable estimation of the preserved longer time under vacuum hide suitability for the processing can be done only after industrial trials. So, the vacuumed and stored 5 and 19 days (Figure 4.17, p.101) big hide samples were processed under the industrial conditions in the tannery “Kedainiu oda” (Lithuania) into shoe upper leather. The leather processing technology valid in this enterprise was employed. The parameters of this technology are not presented in this description because they are commercial secret. The produced leather samples were tested and qualitative indexes determined (Table 4.18).

Table 4.18

Chemical and physical properties of leather produced under industrial conditions from preserved by vacuum hides

Index	Leather produced from hide stored in vacuum	
	5 days	19 days
Tensile strength, N/mm^2	18.8	19.7
Relative elongation when the strain of 10 N/mm^2 is reached, %	54.5	47.3
Relative elongation at break, %	78.7	70.3
Strain when grain breaks, N/mm^2	15.6	18.1
Cr_2O_3 content, %	3.15	3.34
Matter soluble in dichloromethane, %	4.93	5.04
Volatile matter, %	15.3	15.3
Shrinkage temperature, ^oC	104±2	108±2

The comparison of the values of main qualitative indexes shows that in both cases the leathers of high quality were produced. The strength properties entirely satisfy the requirements for leathers of such assortment. The leather produced from

19 days stored vacuumed hide characterized by higher tensile strength, higher strain when grain breaks and lower relative elongation.

Also, it contained more chromium compounds and matter soluble in dichloromethane. So, industrial trials had confirmed the result obtained under laboratory conditions: after longer storage hide joined higher amount of chromium compounds during chroming and had higher thermo stability comparing with the stored shorter time hide. The content of matter soluble in dichloromethane was sufficient and similar for both leathers.

Organoleptically, both leathers were soft, elastic, had fine grain and their exterior does not differ from leather produced from conventionally preserved by salting hide.

a **b**

Figure 4.17 Leather produced from hide stored in vacuum (a – 5 days; b – 19 days)

After the industrial trials the main conclusion gained was that all leather qualitative indexes absolutely met requirements for shoe upper leather. Therefore, it lets the proposition that preservation of hide by vacuum does not worsen the quality of leather produced from this hide.

4.2.7 Summary of results of behaviour of vacuumed hide during technological processes of leather manufacturing

For proving necessity to store hides in vacuum, vacuumed and salted leather processing advantages and disadvantages were compared (see Table 4.19).

Table 4.19

Savings in technological processes

Sort of hide	Soaking (Rehydration)	Liming-unhairing	Deliming-bating	Pickling	Chroming
Time saving					
Salted	No	No	No	No	No
Vacuumed	Yes	No	No	No	No
Electro-energy saving					
Salted	No	No	No	No	No
Vacuumed	Yes	No	No	No	No
Water saving					
Salted	No	No	No	No	No
Vacuumed	Yes	No	No	No	No
Chemical material savings					
Salted	No	No	No	No	No
Vacuumed	Yes	No	No	No	No
Labour saving					
Salted	No	No	No	No	No
Vacuumed	Yes	No	No	No	No
Manufactory area					
Salted	No	No	No	No	No
Vacuumed	No	No	No	No	No
Amount of pollutants decrease					
Salted	No	No	No	No	No
Vacuumed	Yes	No	No	No	No

5 CONCLUSIONS

1. Analysis of situation in Latvian leather industry has shown that nowadays it is practically abounded with only one working leather manufactory joint-stock company A/S Ritales located in Jelgava city. Latvia exports either raw hides or wet blue leather mostly to Italy and Poland leaving main pollution in country and does not produce finished leather.

2. There is not solved question with delivery of raw hides from slaughterhouses to leather manufacture. Because of the distance it is difficult to deliver all country raw hides to the only manufacture. And that is the reason why foreign by - sellers outdo local raw hide dealers.

3. The development and investigation of new hide preservation method has shown that when hide is stored in 10-12·10^3 Pa vacuum at 4^{o}C, the symptoms of hide deterioration: bad odour and weakened bond of hair with derma appear after 22 days of storing. The decrease of shrinkage temperature and nitrogen content increase during 21 day is negligible. Therefore, this fact and observance of hide interior and exterior confirm that hide stays without symptoms of deterioration during 21 day.

4. Differential scanning calorimetry and infrared spectroscopy analysis results confirm that any serious changes in supermolecular structure of collagen do not occur during 22 days storage. The increase of intensity of all peaks in infrared spectrums can be explained by approaching of collagen fibres and compaction of derma under action of vacuum.

5. The beamhouse processes for vacuumed hide can be carried out using conventional technology of salted hide processing, excepting soaking process. As the vacuumed hide loses 2% of moisture, the complete rehydration of such hide is reached during 0.5 h of washing process, and it is about 8 h shorter than soaking of salted hide.

6. Liming and deliming-bating, lead to higher level of removed collagen proteins and lower shrinkage temperature of vacuumed hide comparing with salted one. On the other hand, conventional unhairing-liming lets getting of well swelled qualitatively unhaired hide, without observable defects, such as grain loose or wrinkles.

7. The new preservation method has not observable influence on the pickled hide properties. The action of pickling solution on collagen is negligible, and values of

shrinkage temperature are very close for vacuumed and salted hide. Vacuumed hide during chroming exhausts more chroming compounds than salted one: 87.9-93.3% and 79%, respectively. This leads to higher content of chromium in leather: 3.95-4.04% in leather from vacuumed hide and 3.69% in leather from salted hide. The leather from vacuumed hide has shrinkage temperature not less than 100^{o}C. The method of preservation has not influence on uniformity of distribution of chromium compounds in derma.

8. Industrial trials approved suitability of vacuumed hide for processing into leather. The leather processed from vacuumed hide met to requirements of shoe upper leather. It has good strength properties, and high shrinkage temperature. Leather samples produced from stored various time vacuumed hide were soft, elastic, had fine grain and their exterior did not differ from leather produced using salted hide.

6 REFERNECES

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7 LIST IF USED FORMULAS

(Formula 3.1) Determination of amount of microorganisms in hide, p.57

$$m = \frac{n \cdot b \cdot v_2}{a \cdot v_1 \cdot 10}$$

where:

m	amount of microorganism in hide, units/1 g of hide;
n	average amount of microorganisms presented in one photograph, units;
a	square of specimen, which is seen in one photograph, mm^2;
b	square of specimen, in which one drop with bacterias was spread, mm^2;
v_1	volume of one drop of solution with bacterias, ml;
v_2	total volume of solution with bacterias, ml.

(Formula 3.2) Nitrogen amount determination according to Kjeldahl method, p.60

$$w = (v_1 - v_2) \times 0{,}00014 \times K_{NaOH}$$

where,

v_1	is the volume, in millilitres (ml), of 0,01 mol/l NaOH solution used for the titration of blank test (for the titration of 25 ml of 0,01 mol/l H_2SO_4 solution);
v_2	is the volume, in millilitres (ml), of 0,01 mol/l NaOH solution used for the titration of investigative sample;
0,00014	amount of nitrogen (g), which corresponds to 1 ml of 0,01 mol/l NaOH solution;
K_{NaOH}	correction coefficient to titre of 0,01 mol/l NaOH solution.

(Formula 3.3) Determination of tensile strength and percentage extension, p.65

$$T_n = F/w \cdot t$$

where,

F	is the highest force recorded in Newtons, N;
w	is the mean width of the test piece in millimetres, mm;
t	is the mean thickness of the test piece in millimetres, mm.

(Formula 3.4) Determination of chromium oxide concentration in solution, p.66

$$x = \frac{a \times 0{,}002533 \times 1000}{5}$$

where,

x	concentration of chromium oxide in solution, g/l;
a	amount of $Na_2S_2O_3$ solution (0.1 mol/l) used for titration, ml;
0,002533	amount of chromium oxide, which corresponds to 1 ml of $Na_2S_2O_3$ solution (0.1 mol/l), g.

(Formula 3.5) Determination of chromic oxide content in leather, p.68

$$w = \frac{v_1 \times 0{,}00253 \times 100 \times F}{m_0}$$

where,

v_1 is the volume, in milimitres (ml), of 0.1 mol/l thiosulfate solution used for the titration

m_0 is the mass of the original leather sample, in grams (g)

F is the factor to correct to 0% volatile matter, it is calculate as follows

(Formula 3.6), p.68

$$F = \frac{100}{100 - w_W}$$

where w_W is the volatile matter content, based on ISO 4684, in percentage by mass.

(Formula 3.7) Determination of matter soluble in dichlormethane, p.69

$$\frac{m_1}{m_0} x100xF$$

where,

m_0 is the mass, in grams, of the test sample

m_1 is the mass, in grams, of the extract

And **(Formula 3.8), p.69**

$$F = \frac{100}{100 - w}$$

where,

w is the mass fraction of the volatile matter (based on ISO 4684), in percent

(Formula 3.9) Determination of volatile matter, p.70

$$w = \frac{100(m_1 - m_2)}{m_1}, \%$$

where,

m_1 mass of the sample before drying, g;

m_2 mass of the sample after drying, g.

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9 LIST OF USED TABLES

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10 ABBREVIATIONS AND USED TERMS

EU	European Union
PVD (FVS)	Food and Veterinary Service
APF	Author's photo fixation
Fresh hide	Hide flayed from animal, not treated
Not preserved hide	Hide stored in appropriate temperature without any treatment
Salted hide	Hide stored in appropriate temperature treated with salt
Vacuumed hide	Hide stored in appropriate temperature treated with vacuum

11 GRATITUDE

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/Ilze Gudro/

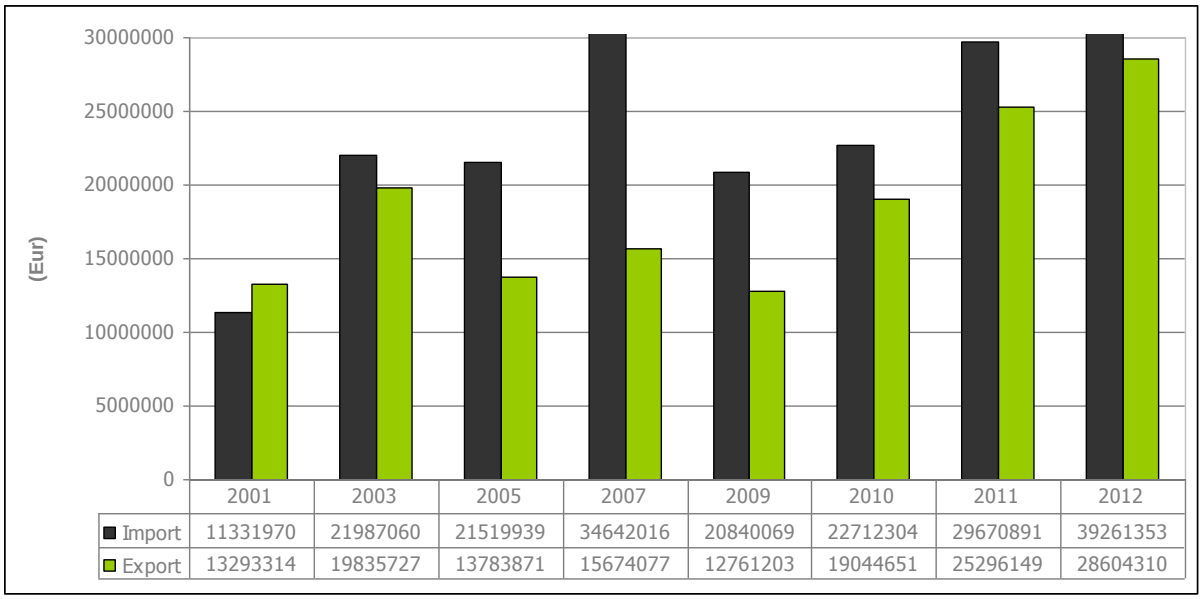
Riga

9th of March 2015

12 APPENDIXES

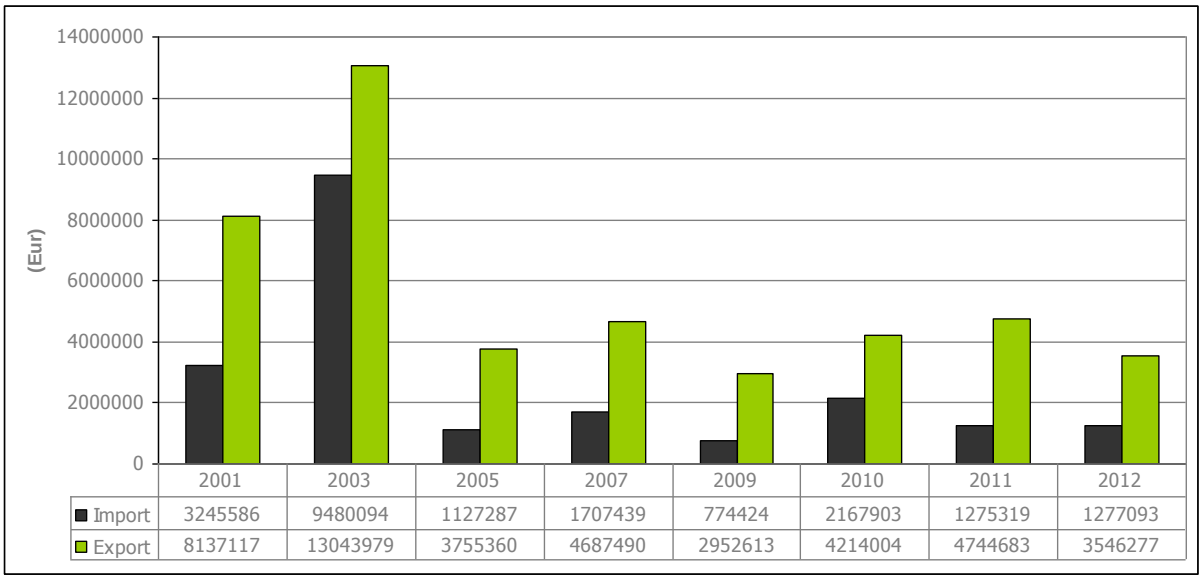
APPENDIX 1

Major Chapter 41 import and export groups in 2001, 2003, 2005, 2007, 2009, 2010, 2011, 2012 (%)



	2001	2003	2005	2007	2009	2010	2011	2012
Import	11331970	21987060	21519939	34642016	20840069	22712304	29670891	39261353
Export	13293314	19835727	13783871	15674077	12761203	19044651	25296149	28604310

Figure 1 Import and export data from 2001 - 2012 (EUR) (All Chapters (41;42;43)) in Latvia (2001, 2003, 2005, 2007, 2009, 2010, 2011, 2012)



	2001	2003	2005	2007	2009	2010	2011	2012
Import	3245586	9480094	1127287	1707439	774424	2167903	1275319	1277093
Export	8137117	13043979	3755360	4687490	2952613	4214004	4744683	3546277

Figure 2 Chapter 41 (Hides and skins (other than furskins) and leather) (EUR) export and import in Latvia (2001, 2003, 2005, 2007, 2009, 2010, 2011, 2012)

Major Chapter 41 import and export groups in 2001 (%)

In 2001 major Chapter 41 import groups were (See Figure 3):

- 410121000 (34.6%-784991 Ls/1121415,7 EUR): Whole hides and skins, unsplit, of a weight per skin not exceeding 8 kg when simply dried, 10 kg when dry-salted, or 16 kg when fresh, wet-salted or otherwise preserved;
- 410439100 (21.3%-484754 Ls/692505 EUR): Tanned or crust hides and skins of bovine (including buffalo) or equine animals, without hair on, whether or not split, but not further prepared: In the dry state (crust);
- 410431190 (12.5%-283232 Ls/404617 EUR): Tanned or crust hides and skins of bovine (including buffalo) or equine animals, without hair on, whether or not split, but not further prepared: Other;
- 410110100 (10.9%-246748 Ls/ 352497 EUR): Raw hides and skins of bovine (including buffalo) or equine animals (fresh, or salted, dried, limed, pickled or otherwise preserved, but not tanned, parchment-dressed or further prepared), whether or not dehaired or split.

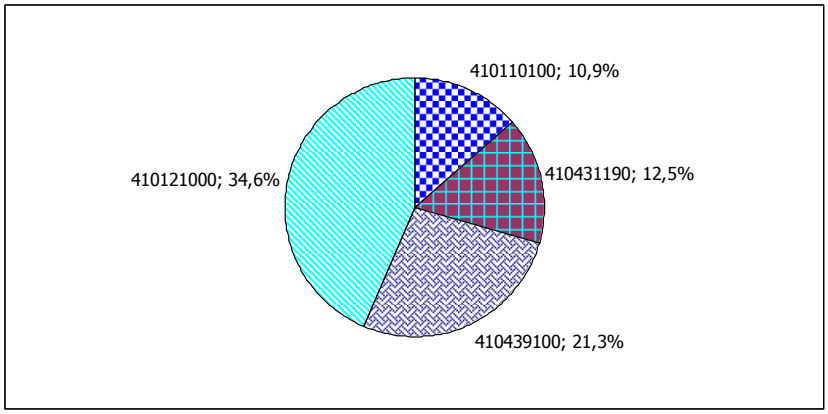


Figure3 Major Chapter 41 import groups in 2001 (%)
(From total Chapter 41 import amount 2271910 Ls/3245585 EUR in 2001)

In 2001 major Chapter 41 export groups were (See Figure 4):

- 410110100 (32.1%-1827419 Ls/2610598 EUR): Raw hides and skins of bovine (including buffalo) or equine animals (fresh, or salted, dried, limed, pickled or otherwise preserved, but not tanned, parchment-dressed or further prepared), whether or not dehaired or split;
- 410121000 (24.1%-1373069 Ls/1961527 EUR): Whole hides and skins, unsplit, of a weight per skin not exceeding 8 kg when simply dried, 10 kg when dry-salted, or 16 kg when fresh, wet-salted or otherwise preserved;
- 410410300 (11.6%-661356 Ls/994794 EUR): Tanned or crust hides and skins of bovine (including buffalo) or equine animals, without hair on, whether or not split, but not further prepared: In the wet state (including wet-blue).

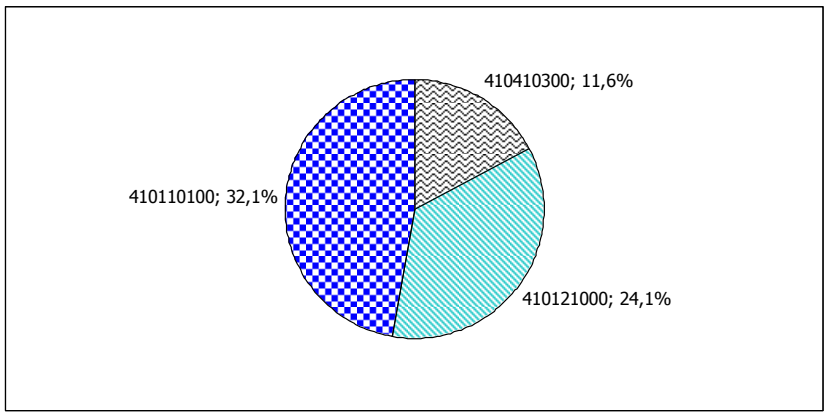


Figure 4 Major Chapter 41 export groups in 2001 (%)
(From total Chapter 41 export amount 5695982 Ls/8137117 EUR in 2001)

Major Chapter 41 import and export groups in 2003 (%)

In 2003 major Chapter 41 import groups were (See Figure 5):

- 410120300 (46.7%-3098168 Ls/4425954 EUR): Whole hides and skins, unsplit, of a weight per skin not exceeding 8 kg when simply dried, 10 kg when dry-salted, or 16 kg when fresh, wet-salted or otherwise preserved: Wet-salted;
- 410411510 (23.7%-1571732 Ls/2245331 EUR): Tanned or crust hides and skins of bovine (including buffalo) or equine animals, without hair on, whether or not split, but not further prepared: Whole hides and skins, of a unit surface area exceeding 28 square feet (2,6 m²);
- 410150300 (19.5%-1291261 Ls/1844658 EUR): Raw hides and skins of bovine (including buffalo) or equine animals (fresh, or salted, dried, limed, pickled or otherwise preserved, but not tanned, parchment-dressed or further prepared), whether or not dehaired or split: Wet-salted.

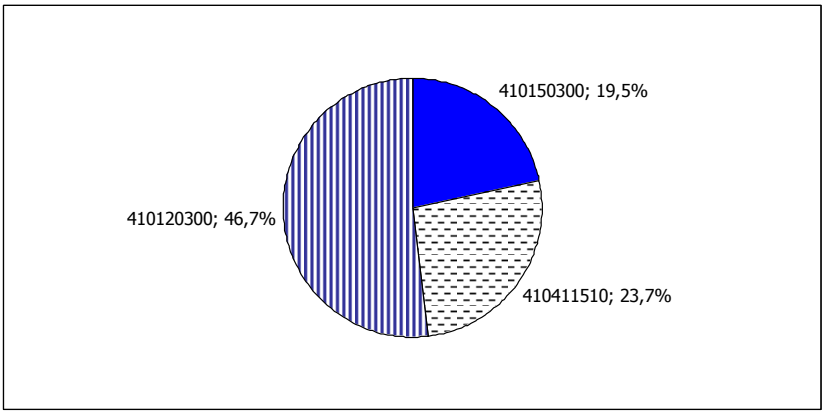


Figure 5 Major Chapter 41 import groups in 2003 (%)
(From total Chapter 41 import amount 6636066 Ls/9480094 EUR in 2003)

In 2003 major Chapter 41 export groups were (See Figure 6):

- 410120300 (35.9%-3275988 Ls/4679982 EUR): Whole hides and skins, unsplit, of a weight per skin not exceeding 8 kg when simply dried, 10 kg when dry-salted, or 16 kg when fresh, wet-salted or otherwise preserved: Wet-salted;
- 410150300 (26.3%-2396865 Ls/3424092 EUR): Raw hides and skins of bovine (including buffalo) or equine animals (fresh, or salted, dried, limed, pickled or otherwise preserved, but not tanned, parchment-dressed or further prepared), whether or not dehaired or split: Wet-salted;
- 410411510 (16.9%-1538612 Ls/219801 EUR): Tanned or crust hides and skins of bovine (including buffalo) or equine animals, without hair on, whether or not split, but not further prepared: Whole hides and skins, of a unit surface area exceeding 28 square feet (2,6 m²).

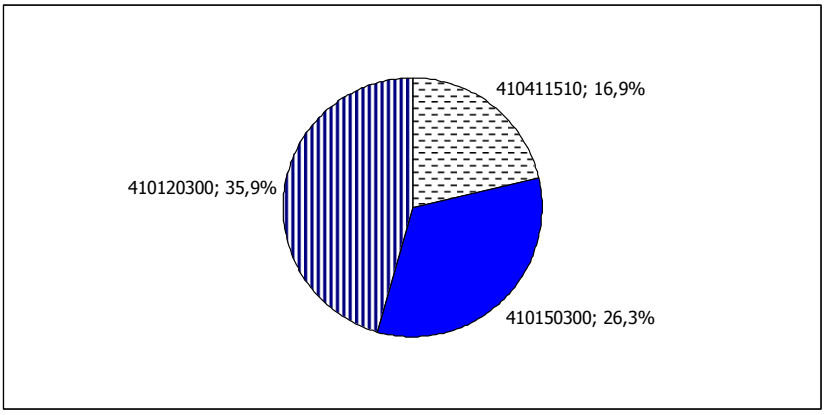


Figure 6 Major Chapter 41 export groups in 2003 (%)
(From total Chapter 41 export amount 9130785 Ls/13043978 EUR in 2003)

Major Chapter 41 import and export groups in 2005 (%)

In 2005 major Chapter 41 import groups were (See Figure 7):

- 41015030 (23.9%-188710 Ls/269585 EUR): Raw hides and skins of bovine (including buffalo) or equine animals (fresh, or salted, dried, limed, pickled or otherwise preserved, but not tanned, parchment-dressed or further prepared), whether or not dehaired or split: Wet-salted;
- 41132000 (14.1%-110934 Ls/158447 EUR): Leather further prepared after tanning or crusting, including parchment-dressed leather, of other animals, without wool or hair on, whether or not split, other than leather of heading 4114: Of swine;
- 41071291 (13.5%-106730 Ls/152471 EUR): Leather further prepared after tanning or crusting, including parchment-dressed leather, of bovine (including buffalo) or equine animals, without hair on, whether or not split, other than leather of heading 4114: Bovine (including buffalo) leather;
- 41071190 (12.2%-96312 Ls/137558 EUR): Leather further prepared after tanning or crusting, including parchment-dressed leather, of bovine (including buffalo) or equine animals, without hair on, whether or not split, other than leather of heading 4114: Other.

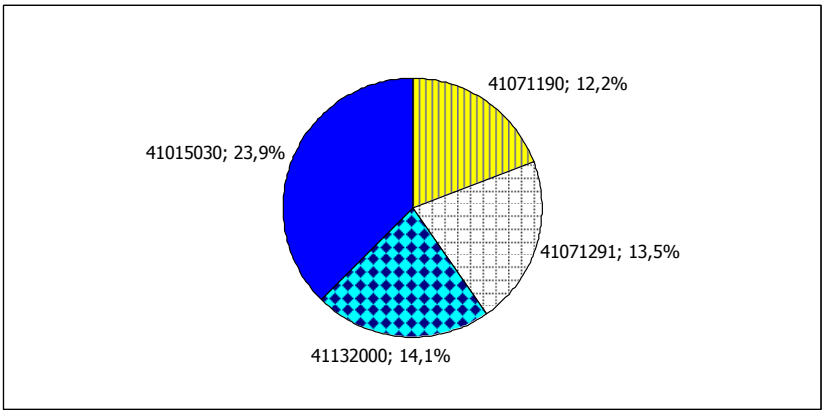


Figure 7 Major Chapter 41 import groups in 2005 (%)
(From total Chapter 41 import amount 789101 Ls/112728 EUR in 2005)

In 2005 major Chapter 41 export groups were (See Figure 8):

- 41041951 (35.6%-934652 Ls/1335217 EUR): Tanned or crust hides and skins of bovine (including buffalo) or equine animals, without hair on, whether or not split, but not further prepared: Whole hides and skins, of a unit surface area exceeding 28 square feet (2,6 m²);
- 41015030 (27.8%-729955 Ls/1042792 EUR): Raw hides and skins of bovine (including buffalo) or equine animals (fresh, or salted, dried, limed, pickled or otherwise preserved, but not tanned, parchment-dressed or further prepared), whether or not dehaired or split: Wet-salted;
- 41015090 (24.7%-650010 Ls/928585 EUR): Raw hides and skins of bovine (including buffalo) or equine animals (fresh, or salted, dried, limed, pickled or otherwise preserved, but not tanned, parchment-dressed or further prepared), whether or not dehaired or split: Other.

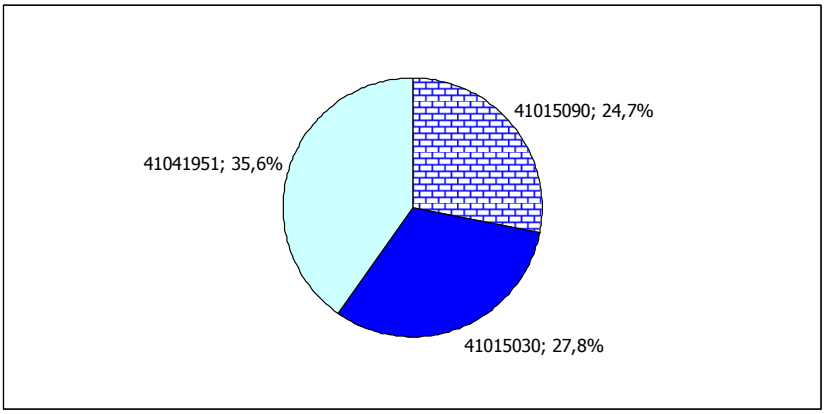


Figure 8 Major Chapter 41 export groups in 2005 (%)
(From total Chapter 41 export amount 2628752 Ls/3755360 EUR in 2005)

Major Chapter 41 import and export groups in 2007 (%)

In 2007 major Chapter 41 import groups were (See Figure 9):

- 41071291 (20.2%-241854 Ls/345505 EUR): Leather further prepared after tanning or crusting, including parchment-dressed leather, of bovine (including buffalo) or equine animals, without hair on, whether or not split, other than leather of heading 4114: Bovine (including buffalo) leather;
- 41015030 (14.6%-174811 Ls/249730 EUR): Raw hides and skins of bovine (including buffalo) or equine animals (fresh, or salted, dried, limed, pickled or otherwise preserved, but not tanned, parchment-dressed or further prepared), whether or not dehaired or split: Wet-salted;
- 41041110 (14.1%-168405 Ls/240578 EUR): Tanned or crust hides and skins of bovine (including buffalo) or equine animals, without hair on, whether or not split, but not further prepared: Whole bovine (including buffalo) hides and skins, of a unit surface area not exceeding 28 square feet (2,6 m²);
- 41151000 (13.4%-160156 Ls/228794 EUR): Composition leather with a basis of leather or leather fibre, in slabs, sheets or strip, whether or not in rolls.

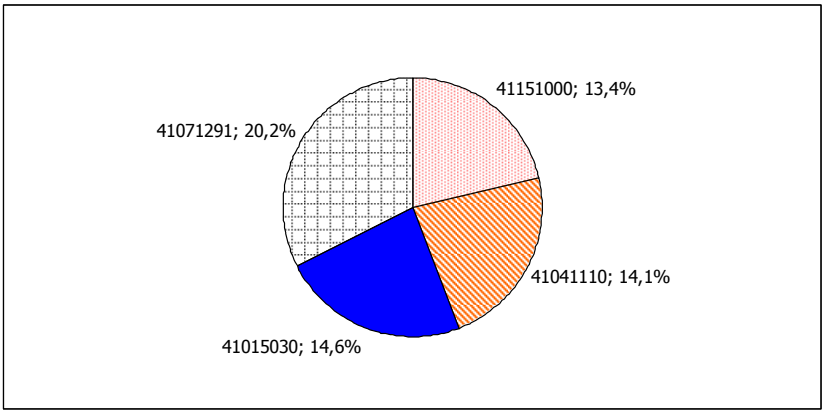


Figure 9 Major Chapter 41 import groups in 2007 (%)
(From total Chapter 41 import amount 1195207 Ls/1707438 EUR in 2007)

In 2007 major Chapter 41 export groups were (See Figure 10):

- 41041951 (37.9%-1245174 Ls/1778820 EUR): Tanned or crust hides and skins of bovine (including buffalo) or equine animals, without hair on, whether or not split, but not further prepared: Whole hides and skins, of a unit surface area exceeding 28 square feet (2,6 m²);
- 41015090 (33.7%-1105619 Ls/1579455 EUR): Raw hides and skins of bovine (including buffalo) or equine animals (fresh, or salted, dried, limed, pickled or otherwise preserved, but not tanned, parchment-dressed or further prepared), whether or not dehaired or split: Other;
- 41041110 (7.6%-250709 Ls/358155 EUR): Tanned or crust hides and skins of bovine (including buffalo) or equine animals, without hair on, whether or not split, but not further prepared: Whole bovine (including buffalo) hides and skins, of a unit surface area not exceeding 28 square feet (2,6 m²);
- 41012030 (7.6%-209432 Ls/299188 EUR): Whole hides and skins, unsplit, of a weight per skin not exceeding 8 kg when simply dried, 10 kg when dry-salted, or 16 kg when fresh, wet-salted or otherwise preserved: Wet-salted;
- 41015030 (6.2%-201938 Ls/288482 EUR): Raw hides and skins of bovine (including buffalo) or equine animals (fresh, or salted, dried, limed, pickled or otherwise preserved, but not tanned, parchment-dressed or further prepared), whether or not dehaired or split: Wet-salted.

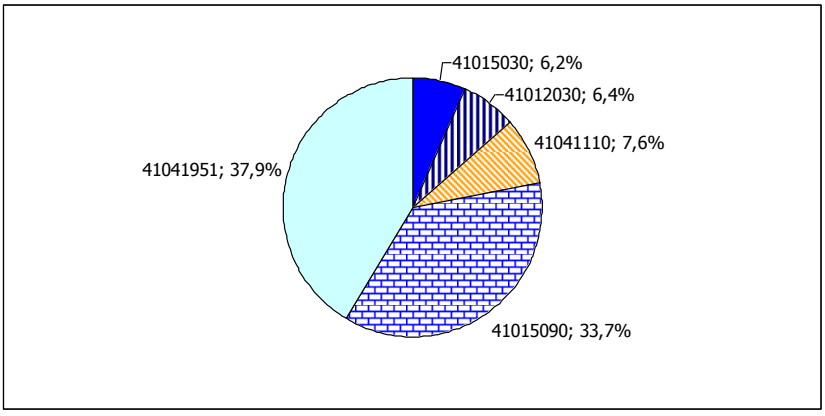


Figure 10 Major Chapter 41 export groups in 2007 (%)
(From total Chapter 41 export amount 3281243 Ls/4687490 in 2007)

Major Chapter 41 import and export groups in 2009 (%)

In 2009 major Chapter 41 import groups were (See Figure 11):

- 41071291 (15.1%-81640 Ls/116628 EUR): Leather further prepared after tanning or crusting, including parchment-dressed leather, of bovine (including buffalo) or equine animals, without hair on, whether or not split, other than leather of heading 4114: Bovine (including buffalo) leather;
- 41142000 (11.1%-60171 Ls/85958 EUR): Chamois (including combination chamois) leather; patent leather and patent laminated leather; metallised leather: Patent leather and patent laminated leather; metallised leather;
- 41012030 (11.0%-59466 Ls/84951 EUR): Whole hides and skins, unsplit, of a weight per skin not exceeding 8 kg when simply dried, 10 kg when dry-salted, or 16 kg when fresh, wet-salted or otherwise preserved: Wet-salted;
- 41071990 (10.8%-58586 Ls/83694 EUR): Leather further prepared after tanning or crusting, including parchment-dressed leather, of bovine (including buffalo) or equine animals, without hair on, whether or not split, other than leather of heading 4114: Other.

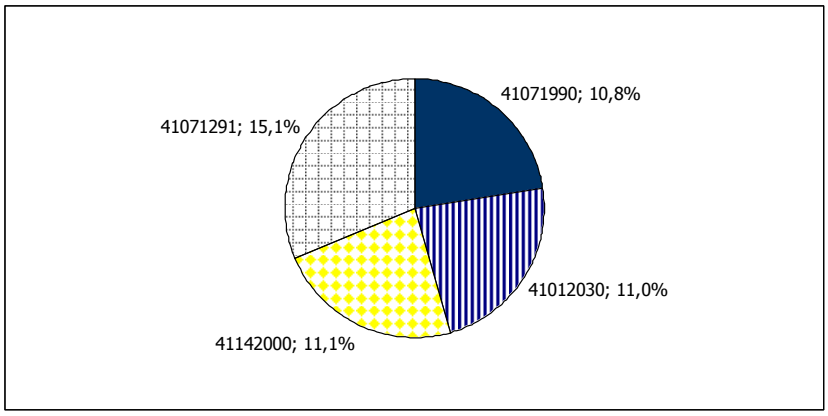


Figure 11 Major Chapter 41 import groups in 2009 (%)
(From total Chapter 41 import amount 542097 Ls/774424 EUR in 2009)

In 2009 major Chapter 41 export groups were (See Figure 12):

- 41041951 (36.2%-748196 Ls/1068851 EUR): Tanned or crust hides and skins of bovine (including buffalo) or equine animals, without hair on, whether or not split, but not further prepared: Whole hides and skins, of a unit surface area exceeding 28 square feet (2,6 m²);
- 41041151 (21.1%-435988 Ls/622840 EUR): Tanned or crust hides and skins of bovine (including buffalo) or equine animals, without hair on, whether or not split, but not further prepared: Whole hides and skins, of a unit surface area exceeding 28 square feet (2,6 m²);
- 41015090 (17.0%-352388 Ls/503411 EUR): Raw hides and skins of bovine (including buffalo) or equine animals (fresh, or salted, dried, limed, pickled or otherwise preserved, but not tanned, parchment-dressed or further prepared), whether or not dehaired or split: Other;
- 41012030 (12.7%-263043 Ls/375775 EUR): Whole hides and skins, unsplit, of a weight per skin not exceeding 8 kg when simply dried, 10 kg when dry-salted, or 16 kg when fresh, wet-salted or otherwise preserved: Wet-salted.

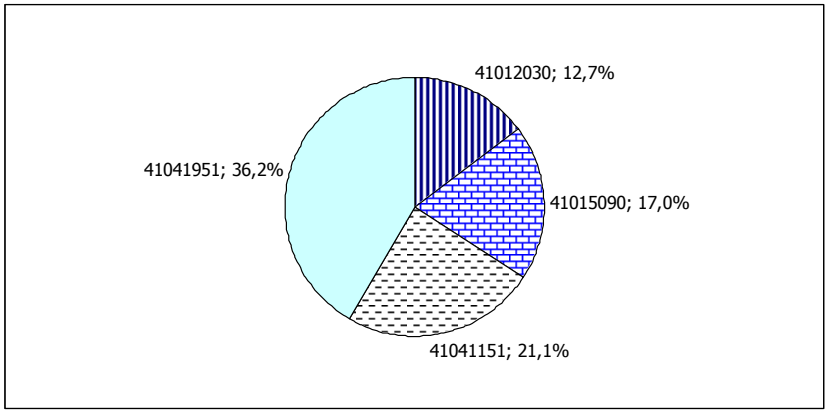


Figure 12 Major Chapter 41 export groups in 2009 (%)
(From total Chapter 41 export amount 2066829 Ls/2952612 EUR in 2009)

Major Chapter 41 import and export groups in 2010 (%)

In 2010 major Chapter 41 import groups were (See Figure 13):

- 41071990 (43.6%-662027 Ls/945752 EUR): Leather further prepared after tanning or crusting, including parchment-dressed leather, of bovine (including buffalo) or equine animals, without hair on, whether or not split, other than leather of heading 4114: Other;
- 41015030 (13.4%-203690 Ls/290985 EUR): Raw hides and skins of bovine (including buffalo) or equine animals (fresh, or salted, dried, limed, pickled or otherwise preserved, but not tanned, parchment-dressed or further prepared), whether or not dehaired or split: Wet-salted;
- 41152000 (8.4%-128115 Ls/183021 EUR): Parings and other waste of leather or of composition leather, not suitable for the manufacture of leather articles; leather dust, powder and flour;
- 41120000 (7.8%-118852 Ls/169778 EUR): Leather further prepared after tanning or crusting, including parchment-dressed leather, of sheep or lamb, without wool on, whether or not split, other than leather of heading 4114.

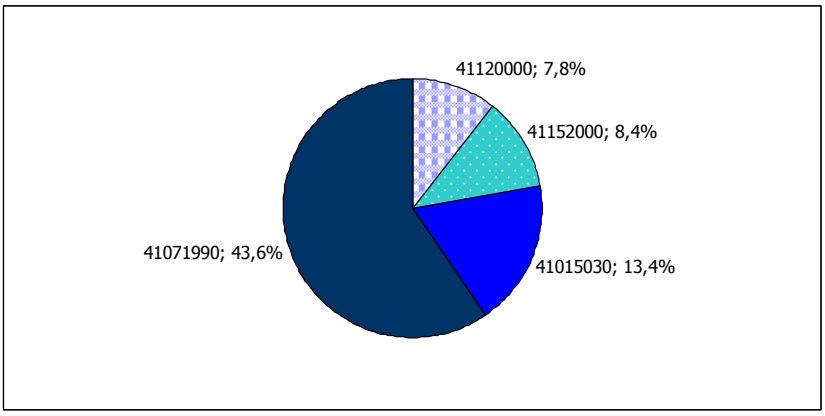


Figure 13 Major Chapter 41 import groups in 2010 (%)
(From total Chapter 41 import amount 1517532 Ls/216902 EUR in 2010)

In 2010 major Chapter 41 export groups were (See Figure 14):

- 41041951 (31.0%-915018 Ls/1307168 EUR): Tanned or crust hides and skins of bovine (including buffalo) or equine animals, without hair on, whether or not split, but not further prepared: Whole hides and skins, of a unit surface area exceeding 28 square feet (2,6 m²);
- 41041151 (17.8%-523846 Ls/748351 EUR): Tanned or crust hides and skins of bovine (including buffalo) or equine animals, without hair on, whether or not split, but not further prepared: Whole hides and skins, of a unit surface area exceeding 28 square feet (2,6 m²);
- 41015030 (14.5%-427182 Ls/610260 EUR): Raw hides and skins of bovine (including buffalo) or equine animals (fresh, or salted, dried, limed, pickled or otherwise preserved, but not tanned, parchment-dressed or further prepared), whether or not dehaired or split: Wet-salted.

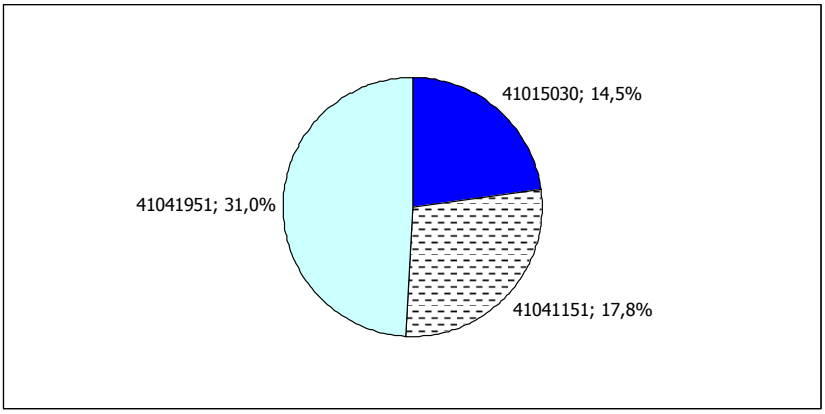


Figure 14 Major Chapter 41 export groups in 2010 (%)
(From total Chapter 41 export amount 2949803 Ls/4214004 EUR in 2010)

Major Chapter 41 import and export groups in 2011 (%)

In 2011 major Chapter 41 import groups were (See Figure 15)

- 41015030 (26.1%-233159 Ls/333084 EUR): Raw hides and skins of bovine (including buffalo) or equine animals (fresh, or salted, dried, limed, pickled or otherwise preserved, but not tanned, parchment-dressed or further prepared), whether or not dehaired or split: Wet-salted;
- 41152000 (19.5%-173840 Ls/248342 EUR): Parings and other waste of leather or of composition leather, not suitable for the manufacture of leather articles; leather dust, powder and flour;
- 41142000 (14.6%-130267 Ls/186095 EUR): Chamois (including combination chamois) leather; patent leather and patent laminated leather; metallised leather: Patent leather and patent laminated leather; metallised leather;
- 41071291 (14.0%-124623 Ls/178032 EUR): Leather further prepared after tanning or crusting, including parchment-dressed leather, of bovine (including buffalo) or equine animals, without hair on, whether or not split, other than leather of heading 4114: Bovine (including buffalo) leather.

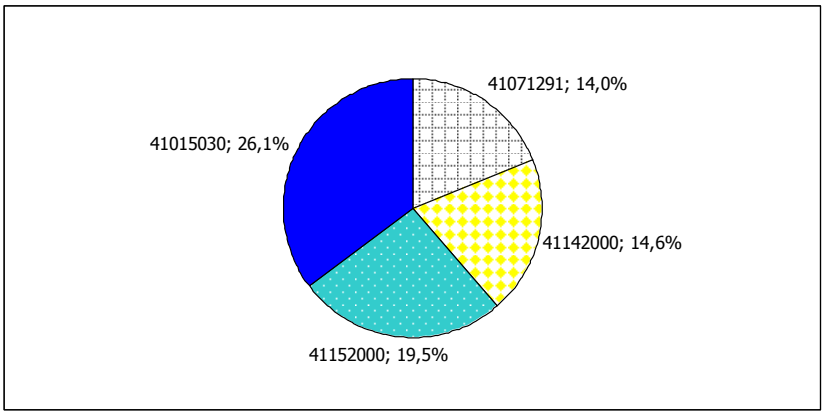


Figure 15 Major Chapter 41 import groups in 2011 (%)
(From total Chapter 41 import amount 892723 Ls/1275318 EUR in 2011)

In 2011 major Chapter 41 export groups were (See Figure 16):

- 41015030 (49.9%-1658102 Ls/2368717 EUR): Raw hides and skins of bovine (including buffalo) or equine animals (fresh, or salted, dried, limed, pickled or otherwise preserved, but not tanned, parchment-dressed or further prepared), whether or not dehaired or split: Wet-salted;
- 41041951 (27.3%-907388 Ls/1296268 EUR): Tanned or crust hides and skins of bovine (including buffalo) or equine animals, without hair on, whether or not split, but not further prepared: Whole hides and skins, of a unit surface area exceeding 28 square feet (2,6 m²);
- 41015090 (7.1%-236990 Ls/338557 EUR): Raw hides and skins of bovine (including buffalo) or equine animals (fresh, or salted, dried, limed, pickled or otherwise preserved, but not tanned, parchment-dressed or further prepared), whether or not dehaired or split: Other;
- 41041151 (5.3%-177616 Ls/253737 EUR): Tanned or crust hides and skins of bovine (including buffalo) or equine animals, without hair on, whether or not split, but not further prepared: Whole hides and skins, of a unit surface area exceeding 28 square feet (2,6 m²).

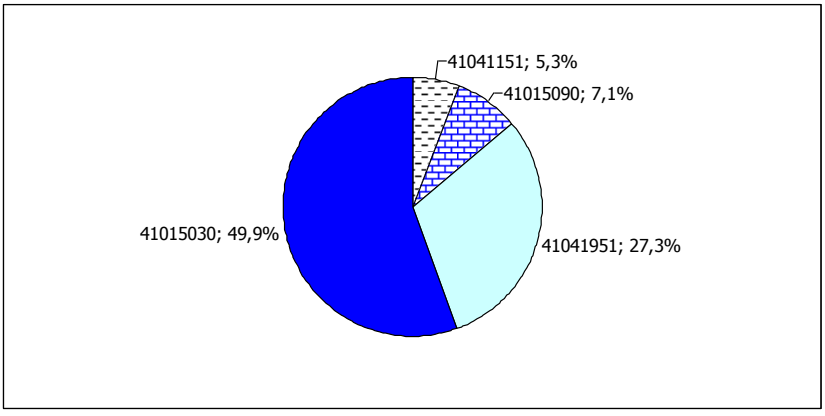


Figure 16 Major Chapter 41 export groups in 2011 (%)
(From total Chapter 41 export amount 3321278 Ls/4744682 EUR in 2011)

Major Chapter 41 import and export groups in 2012 (%)

In 2012 major Chapter 41 import groups were (See Figure 17):

- 41152000 (26.8%-239490 Ls/342128 EUR): Parings and other waste of leather or of composition leather, not suitable for the manufacture of leather articles; leather dust, powder and flour;
- 41015030 (19.6%-175516 Ls/250737 EUR): Raw hides and skins of bovine (including buffalo) or equine animals (fresh, or salted, dried, limed, pickled or otherwise preserved, but not tanned, parchment-dressed or further prepared), whether or not dehaired or split: Wet-salted;
- 41142000 (13.6%-121945 Ls/174207 EUR): Chamois (including combination chamois) leather; patent leather and patent laminated leather; metallised leather: Patent leather and patent laminated leather; metallised leather;
- 41071291 (12.7%-113684 Ls/162405 EUR): Leather further prepared after tanning or crusting, including parchment-dressed leather, of bovine (including buffalo) or equine animals, without hair on, whether or not split, other than leather of heading 4114: Bovine (including buffalo) leather;
- 41071910 (8.0%-71405 Ls/102007 EUR): Leather further prepared after tanning or crusting, including parchment-dressed leather, of bovine (including buffalo) or equine animals, without hair on, whether or not split, other than leather of heading 4114: Bovine (including buffalo) leather, of a unit surface area not exceeding 28 square feet (2,6 m²).

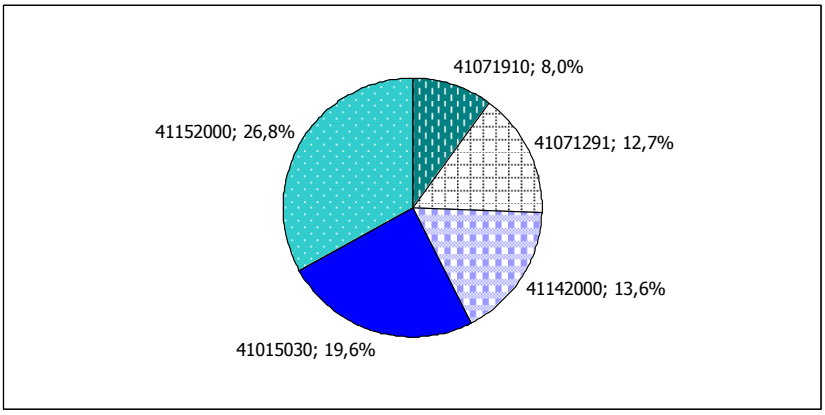


Figure 17 Major Chapter 41 import groups in 2012 (%)
(From total Chapter 41 import amount 893965 Ls/1277092 EUR in 2012)

In 2012 major Chapter 41 export groups were (See Figure 18):

- 41015030 (55.5%-1378744 Ls/1969634 EUR): Raw hides and skins of bovine (including buffalo) or equine animals (fresh, or salted, dried, limed, pickled or otherwise preserved, but not tanned, parchment-dressed or further prepared), whether or not dehaired or split: Wet-salted;
- 41041951 (29.5%-731610 Ls/1045157 EUR): Tanned or crust hides and skins of bovine (including buffalo) or equine animals, without hair on, whether or not split, but not further prepared: Whole hides and skins, of a unit surface area exceeding 28 square feet (2,6 m²);
- 41015050 (8.8%-217815 Ls/311164 EUR): Raw hides and skins of bovine (including buffalo) or equine animals (fresh, or salted, dried, limed, pickled or otherwise preserved, but not tanned, parchment-dressed or further prepared), whether or not dehaired or split: Dried or dry-salted.

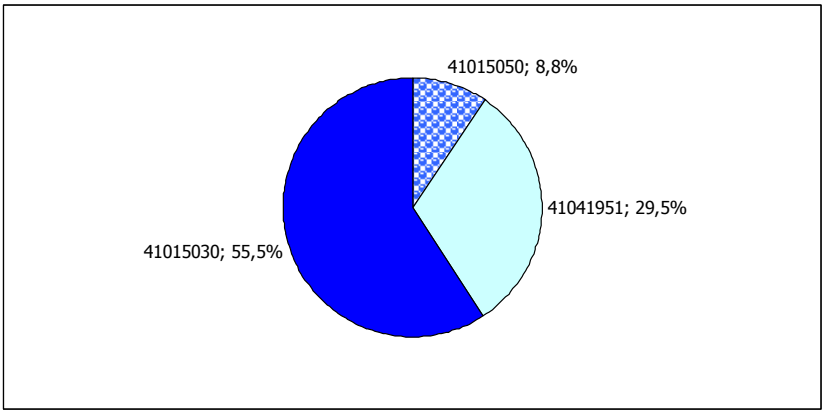
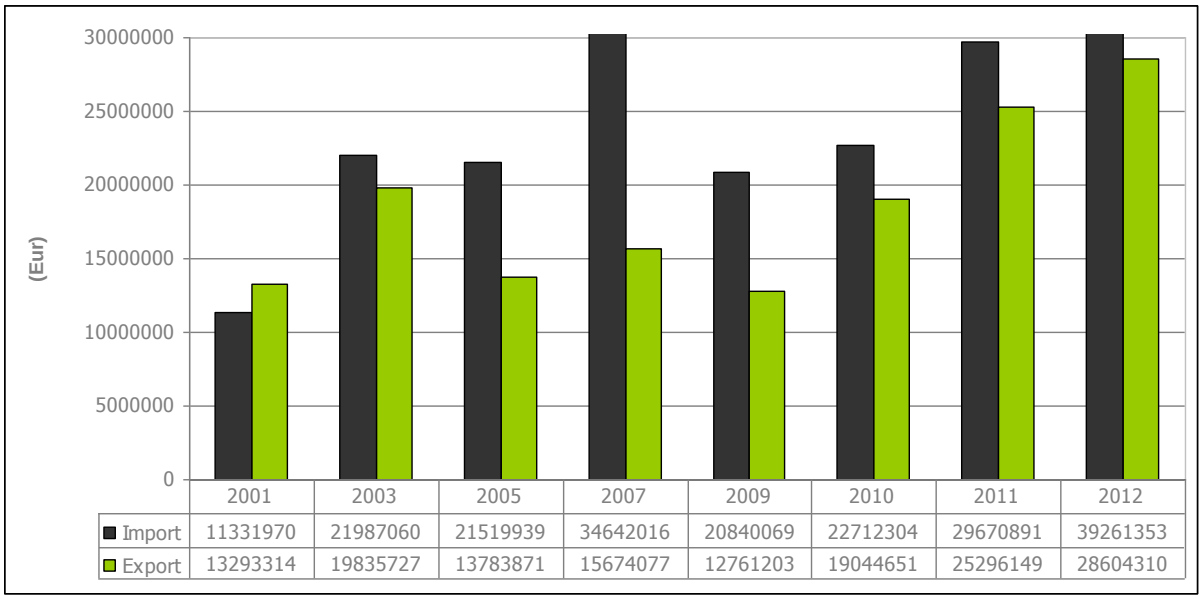


Figure 18 Major Chapter 41 export groups in 2012 (%)
(From total Chapter 41 export amount 2482394 Ls/3546277 EUR in 2012)

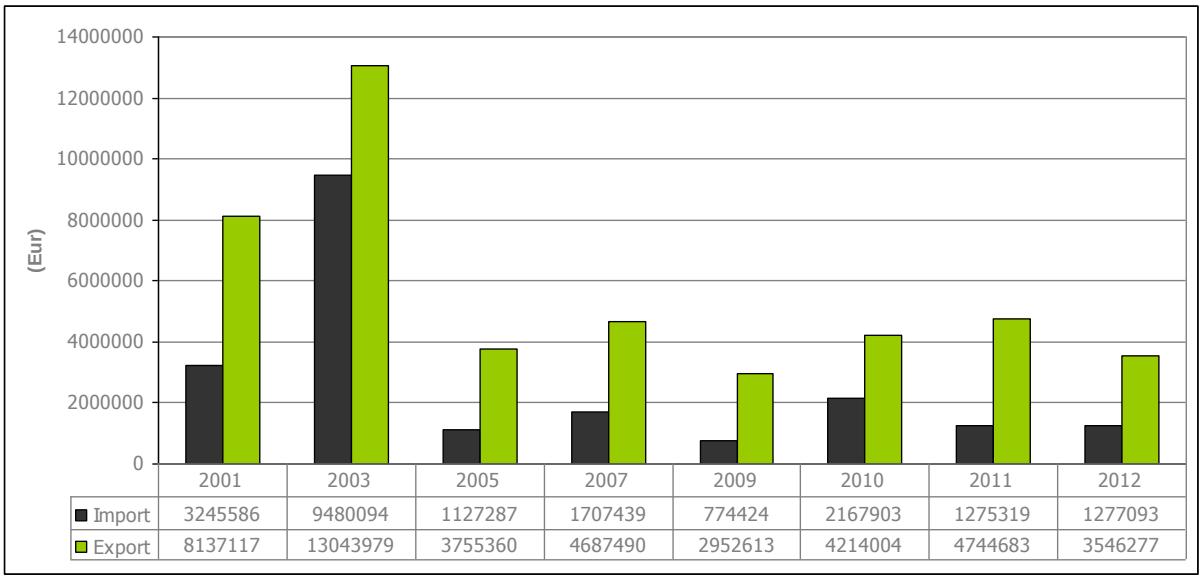
APPENDIX 2

Major Chapter 41 import and export countries in 2001, 2003, 2005, 2007, 2009, 2010, 2011, 2012 (%)



	2001	2003	2005	2007	2009	2010	2011	2012
Import	11331970	21987060	21519939	34642016	20840069	22712304	29670891	39261353
Export	13293314	19835727	13783871	15674077	12761203	19044651	25296149	28604310

Figure 19 Import and export data from 2001 - 2012 (EUR) (All Chapters (41;42;43)) in Latvia (2001, 2003, 2005, 2007, 2009, 2010, 2011, 2012)



	2001	2003	2005	2007	2009	2010	2011	2012
Import	3245586	9480094	1127287	1707439	774424	2167903	1275319	1277093
Export	8137117	13043979	3755360	4687490	2952613	4214004	4744683	3546277

Figure 20 Chapter 41 (Hides and skins (other than furskins) and leather) (EUR) export and import in Latvia (2001, 2003, 2005, 2007, 2009, 2010, 2011, 2012)

Major Chapter 41 import and export countries in 2001

In 2001 major Chapter 41 import countries were: Russia (RU)(38.8%-882301 Ls/1260430 EUR), Lithuania (LT)(18.7%-423719 Ls/605312 EUR), Italy (IT)(17.8%-403710 Ls/576728 EUR) and Estonia (EE)(8.0%-180723 Ls/258175 EUR). (See Figure 57)

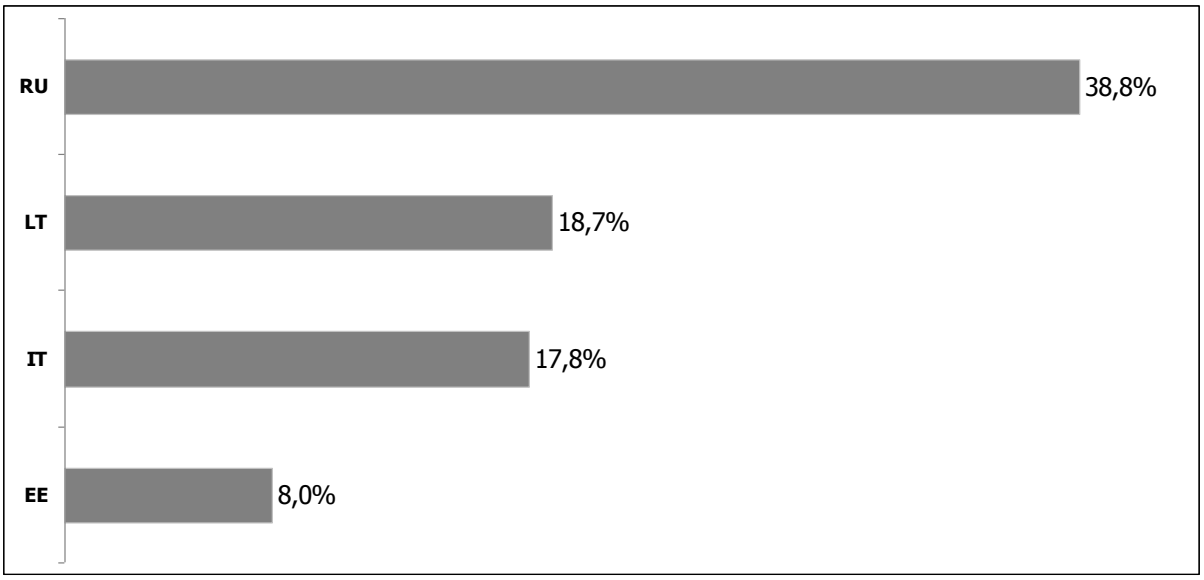


Figure 21 Major Chapter 41 import countries in 2001 (%)
(From total Chapter 41 import amount 2271910 Ls/3245585 EUR in 2001)

In 2001 major Chapter 41 export countries were: Italy (IT)(75.5%-4299001 Ls/6141430 EUR), Spain (ES)(15.0%-853448 Ls/1219211 EUR), Lithuania (LT)(5.0%-285841 Ls/408344 EUR) and India (IN)(0.8%-44111 Ls/63015 EUR). (See Figure 58)

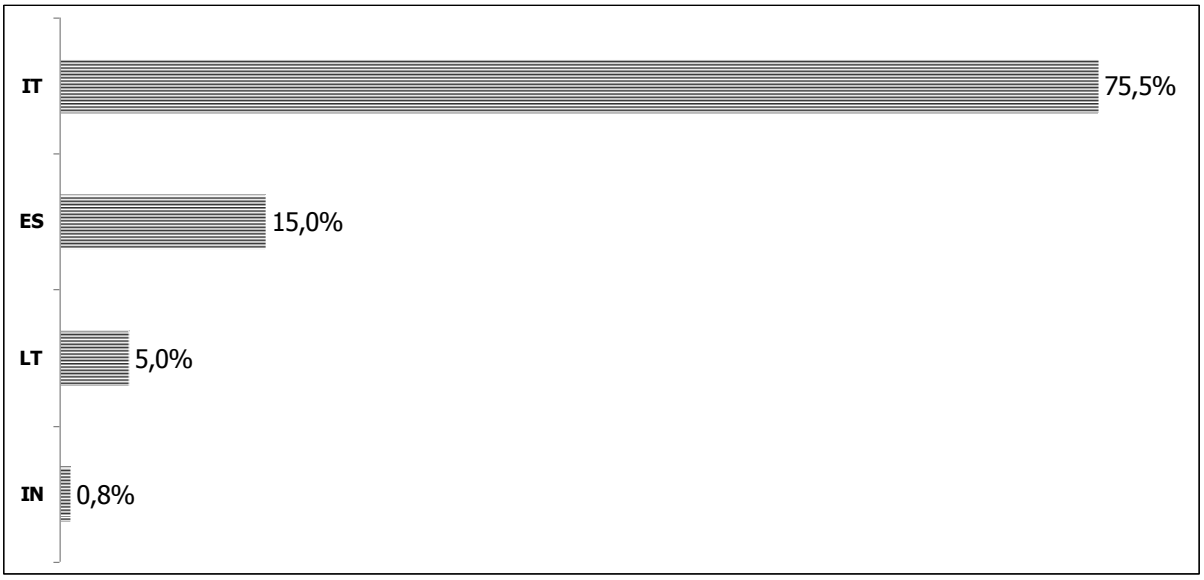


Figure 22 Major Chapter 41 export countries in 2001 (%)
(From total Chapter 41 export amount 5695982 Ls/8137117 EUR in 2001)

Major Chapter 41 import and export countries in 2003

In 2003 major Chapter 41 import countries were: Ukraine (UA)(62.6%-4160353 Ls/5943361 EUR), Russia (RU)(25.6%-1697117 Ls/2424542 EUR), Italy (IT)(23.1%-141905 Ls/202721 EUR) and Belarus (BY)(2.1%-136544 Ls/195062 EUR).(See Figure 59)

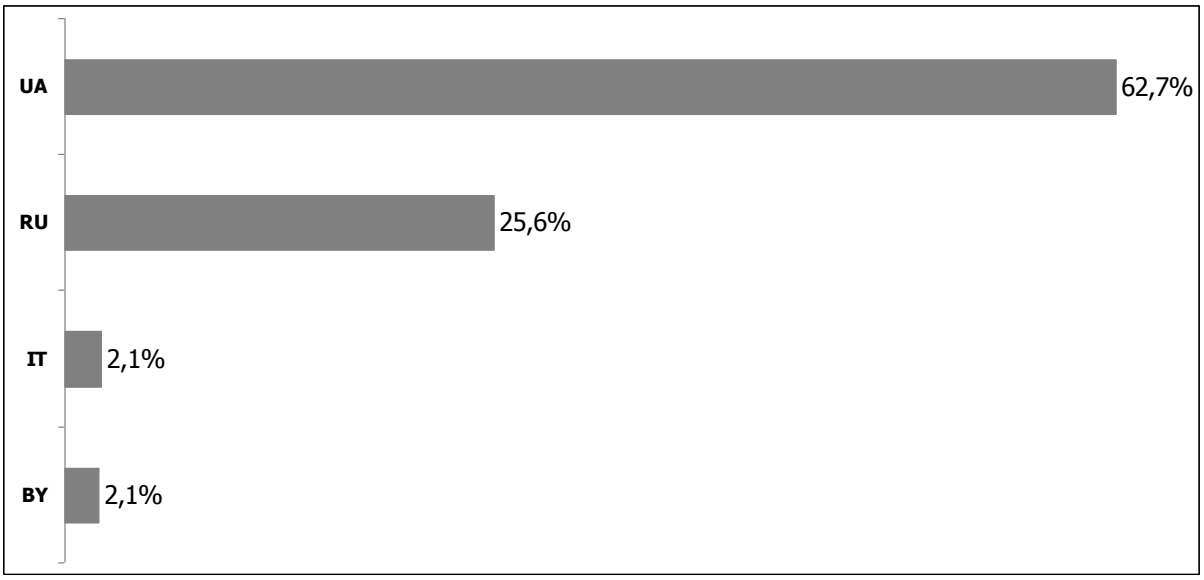


Figure 23 Major Chapter 41 import countries in 2003 (%)
(From total Chapter 41 import amount 663066 Ls/947237 EUR in 2003)

In 2003 major Chapter 41 export countries were: Italy (IT)(68.8%-6283027 Ls/8975752 EUR), Spain (ES)(15.7%-1434932 Ls/2049902 EUR), Lithuania (LT)(8.3%-757860 Ls/1082657 EUR) and Thailand (TH)(3.5%-323388 Ls/461982 EUR).(See Figure 60)

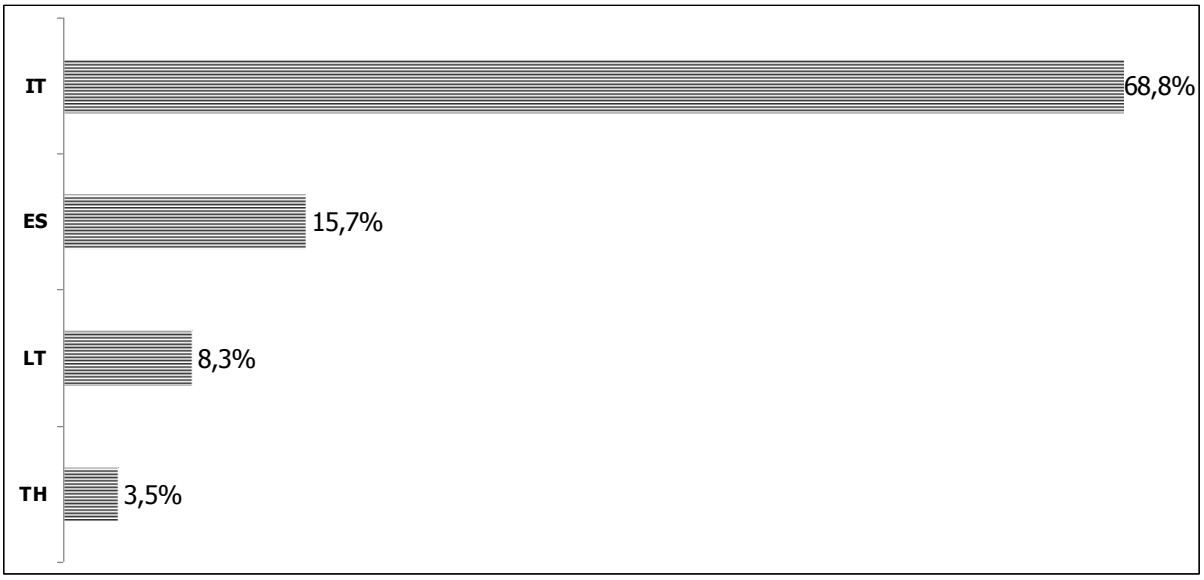


Figure 24 Major Chapter 41 export countries in 2003 (%)
(From total Chapter 41 export amount 9130785 Ls/13043978 EUR in 2003)

Major Chapter 41 import and export countries in 2005

In 2005 major Chapter 41 import countries were: Lithuania (LT)(30.7%-242341 Ls/346201 EUR), Estonia (EE)(24.0%-189776 Ls/271108 EUR), Italy (IT)(11.8%-93132 Ls/133045 EUR), United Kingdom (GB)(6.3%-49836 Ls/71194 EUR) and Germany (DE)(5.5%-43228 Ls/61754 EUR).(See Figure 61)

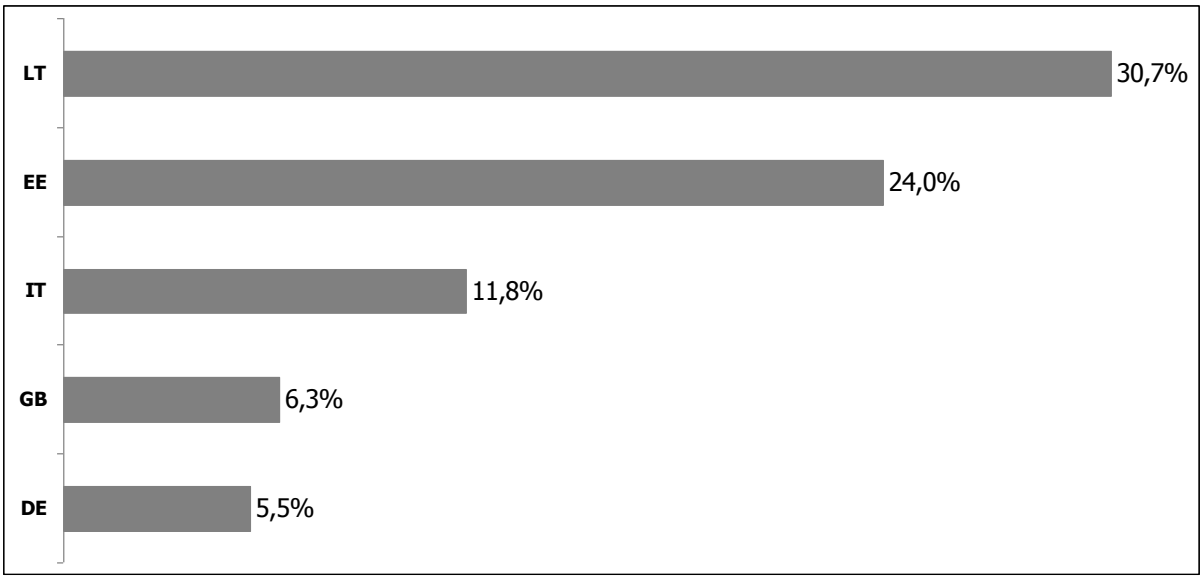


Figure 25 Major Chapter 41 import countries in 2005 (%)
(From total Chapter 41 import amount 789101 Ls/1127287 EUR in 2005)

In 2005 major Chapter 41 export countries were: Italy (IT)(46.8%-1229889 Ls/1756984 EUR), Switzerland (CH)(30.2%-792635 Ls/1132335 EUR), Lithuania (LT)(8.1%-212394 Ls/303420 EUR) and Thailand (TH)(6.9%-181624 Ls/259462 EUR). (See Figure 62)

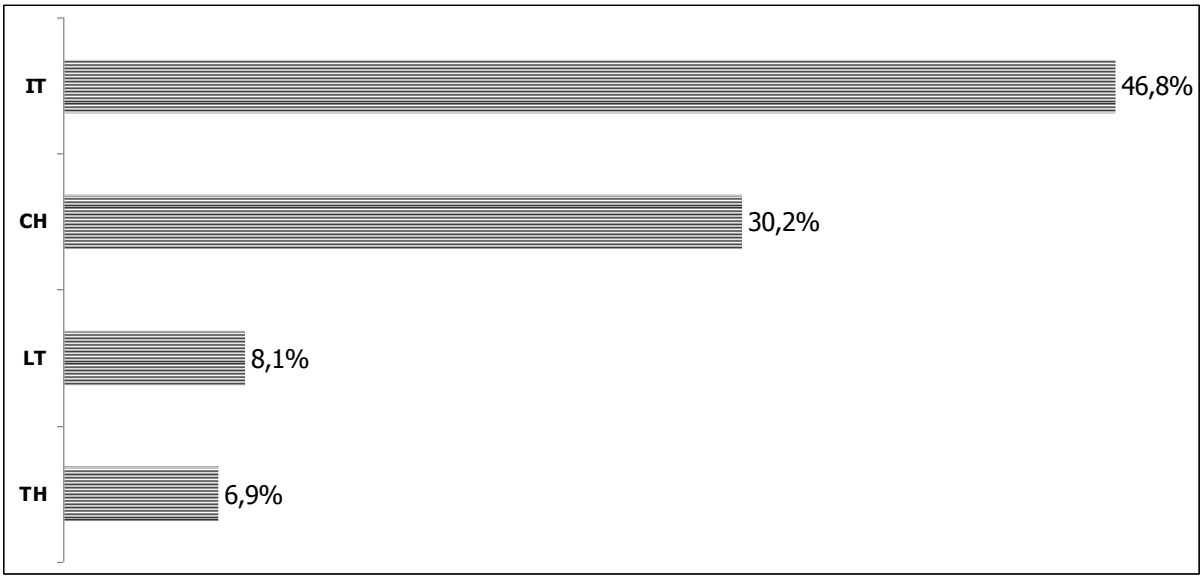


Figure 26 Major Chapter 41 export countries in 2005 (%)
(From total Chapter 41 export amount 2628752 Ls/3755360 EUR in 2005)

Major Chapter 41 import and export countries in 2007

In 2007 major Chapter 41 import countries were: Lithuania (LT)(35.2%-421040 Ls/601485 EUR), Estonia (EE)(18.0%-214882 Ls/306974 EUR), Germany (DE)(14.8%-176620 Ls/252314 EUR), Finland (FI)(7.1%-84684 Ls/120977 EUR), Italy (IT)(6.8%-81379 Ls/116255 EUR) and Sweden (SE)(4.3%-50844 Ls/72634 EUR). (See Figure 63)

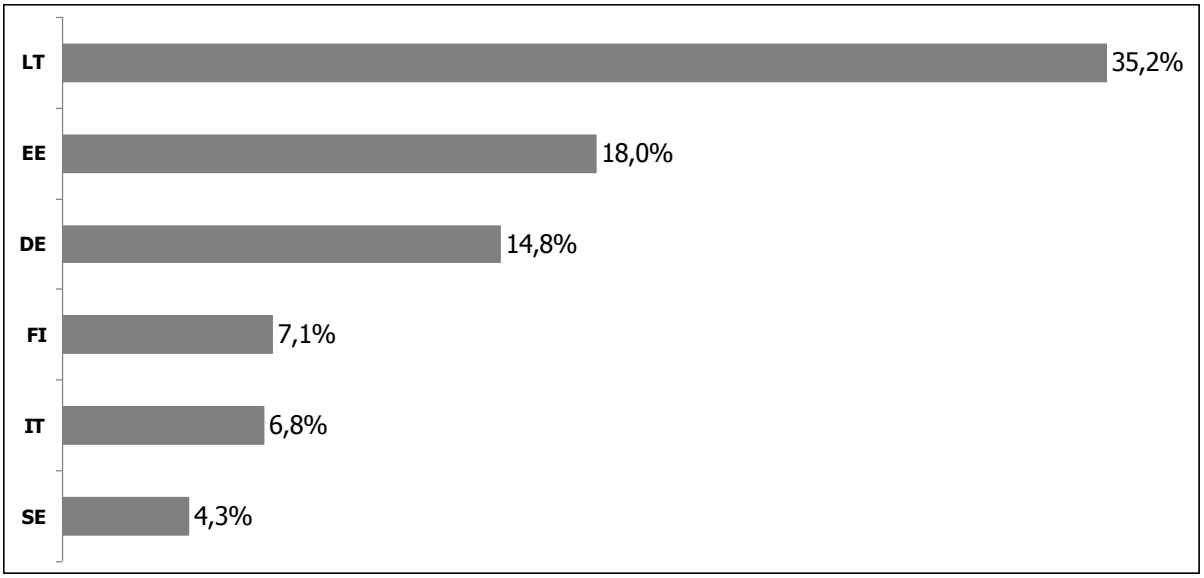


Figure 27 Major Chapter 41 import countries in 2007 (%)
(From total Chapter 41 import amount 1195207 Ls/1707438 EUR in 2007)

In 2007 major Chapter 41 export countries were: Italy (IT)(41.4%-1358523 Ls/1940747 EUR), Switzerland (CH)(38.1%-1249212 Ls/1784588 EUR), Lithuania (LT)(10.3%-337123 Ls/481604 EUR), Finland (FI)(5.3%-172516 Ls/246451 EUR) and Poland (PL)(4.4%-145549 Ls/207927 EUR). (See Figure 64)

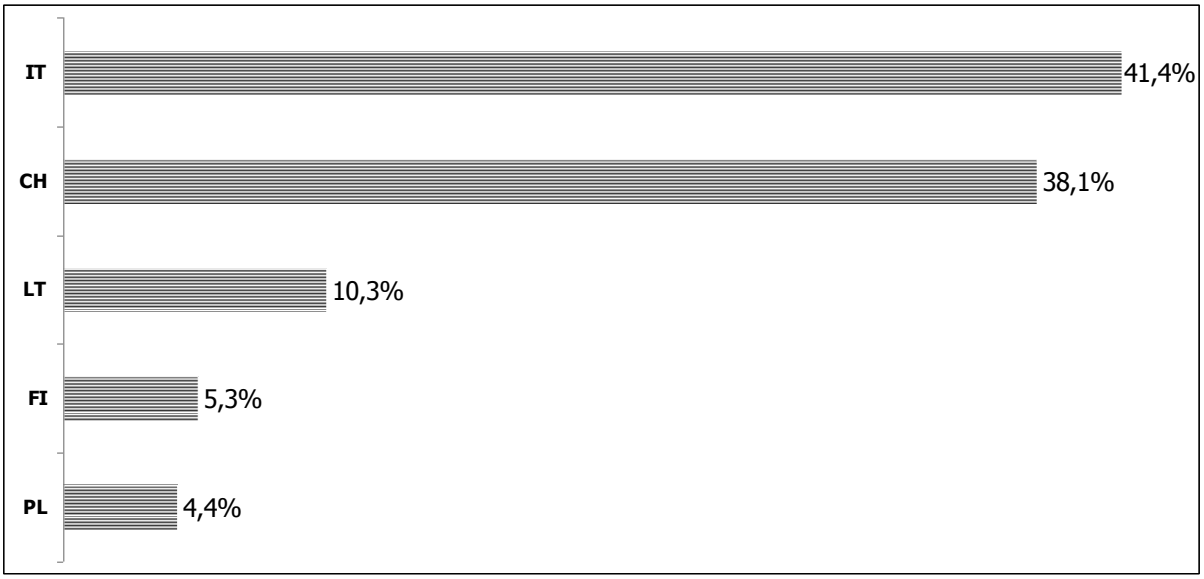


Figure 28 Major Chapter 41 export countries in 2007 (%)
(From total Chapter 41 export amount 3281243 Ls/4687490 EUR in 2007)

Major Chapter 41 import and export countries in 2009

In 2009 major Chapter 41 import countries were: Lithuania (LT)(21.7%-117399 Ls/167712 EUR), Germany (DE)(20.4%-110336 Ls/167622 EUR), Estonia (EE)(15.6%-84671 Ls/120958 EUR), Finland (FI)(14.8%-80085 Ls/114407 EUR) and Denmark (DK)(9.1%-49123 Ls/70175 EUR). (See Figure 65)

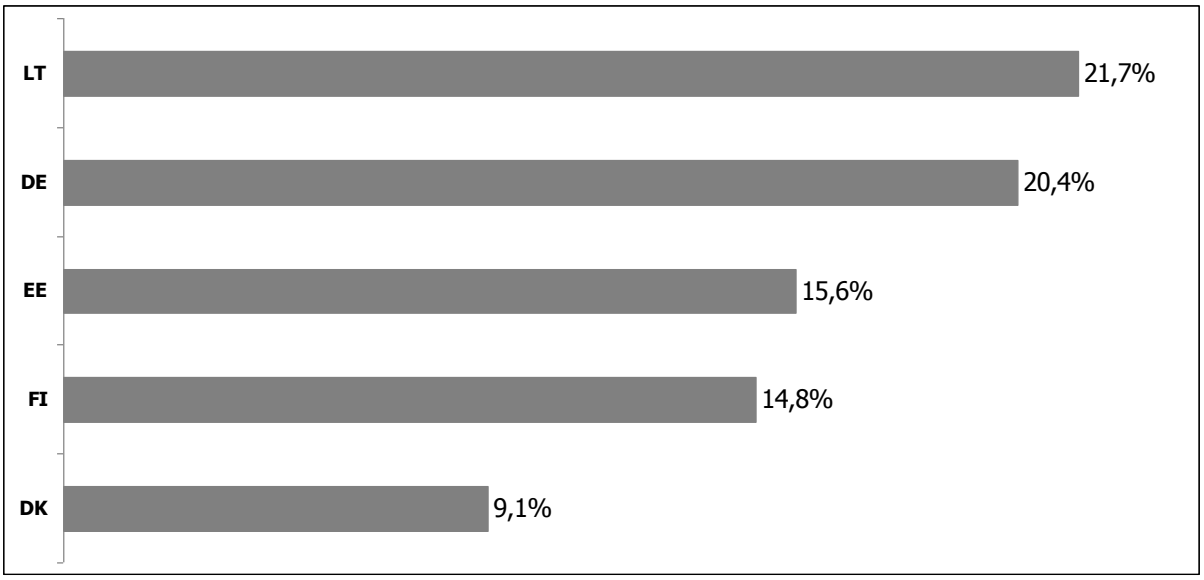


Figure 29 Major Chapter 41 import countries in 2009 (%)
(From total Chapter import amount 542097 Ls/774424 EUR in 2009)

In 2009 major Chapter 41 export countries were: Italy (IT)(38.0%-785569 Ls/1122241 EUR), Switzerland (CH)(35.9%-742213 Ls/1060304 EUR), Lithuania (LT)(19.8%-409146 Ls/584494 EUR) and Finland (4.5%-92161 Ls/131658 EUR). (See Figure 66)

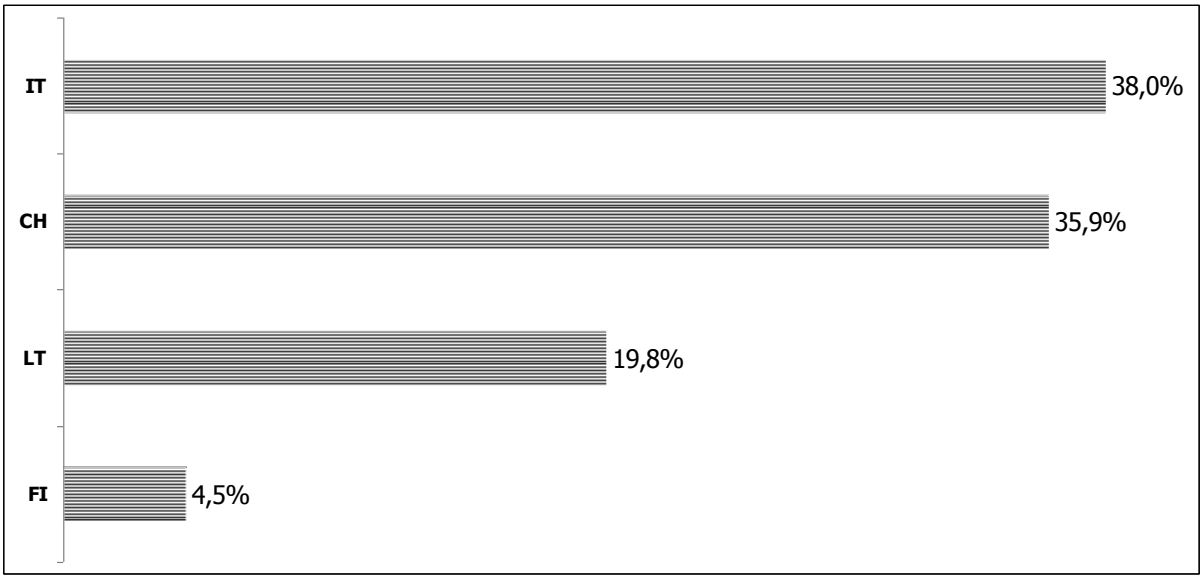


Figure 30 Major Chapter 41 export countries in 2009 (%)
(From total Chapter 41 export amount 2066829 Ls/2952612 EUR in 2009)

Major Chapter 41 import and export countries in 2010

In 2010 major Chapter 41 import countries were: Italy (IT)(47.8%-725548 Ls/1036497 EUR), Estonia (EE)(13.8%-209835 Ls/299764 EUR), Germany (DE)(10.9%-165761 Ls/236801 EUR), Finland (FI)(9.0%-136012 Ls/194402 EUR) and Lithuania (LT)(7.7%-116611 Ls/166587 EUR). (See Figure 67)

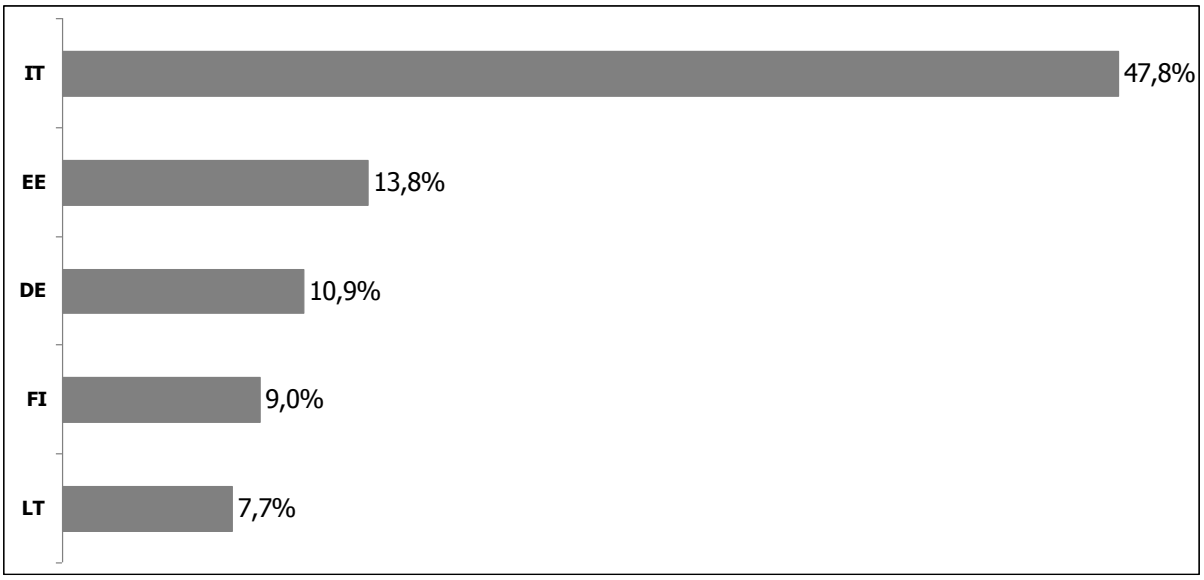


Figure 31 Major Chapter 41 import countries in 2010 (%)
(From total Chapter 41 import amount 1517532 Ls/2167902 EUR in 2010)

In 2010 major Chapter 41 export countries were: Switzerland (CH)(30.9%-911865 Ls/1302664 EUR), Lithuania (LT)(29.7%-875207 Ls/1250295 EUR), Italy (IT)(17.6%-520254 Ls/743220 EUR), Poland (PL)(8.8%-258376 Ls/369108 EUR) and Russia (RU)(5.7%-167381 Ls/239115 EUR). (See Figure 68)

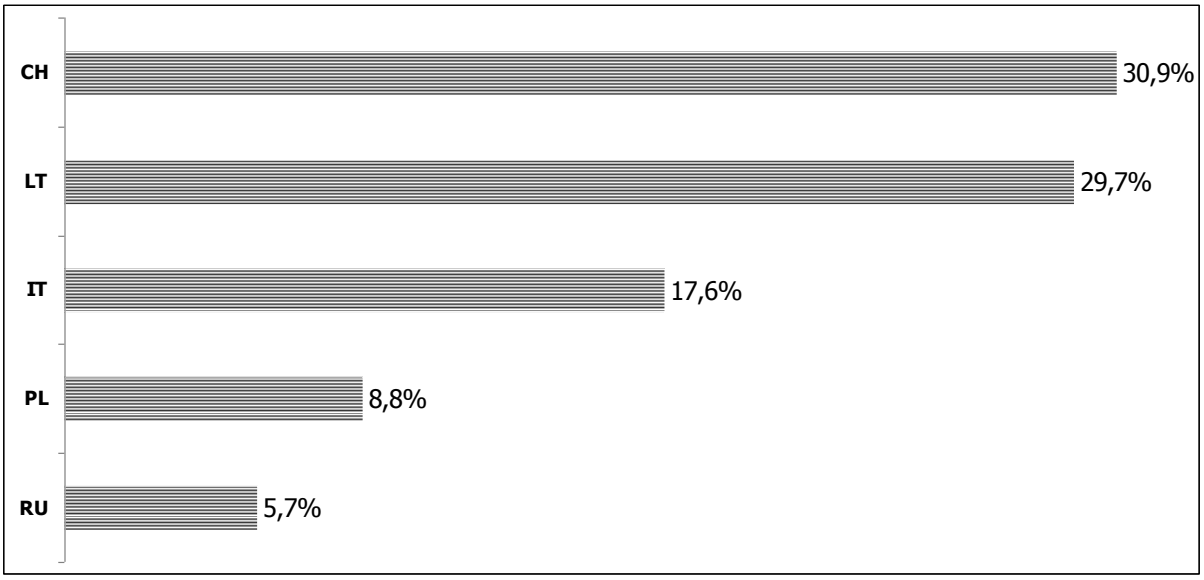


Figure 32 Major Chapter 41 export countries in 2010 (%)
(From total Chapter 41 export amount 2949803 Ls/4214004 EUR in 2010)

Major Chapter 41 import and export countries in 2011

In 2011 major Chapter 41 import countries were: Germany (DE)(27.8%-248434 Ls/354905 EUR), Finland (FI)(23.7%-211445 Ls/302064 EUR), Lithuania (LT)(17.4%-154941 Ls/221344 EUR), Estonia (EE)(13.2%-117688 Ls/168125 EUR) and Italy (4.0%-36104 Ls/51577 EUR). (See Figure 69)

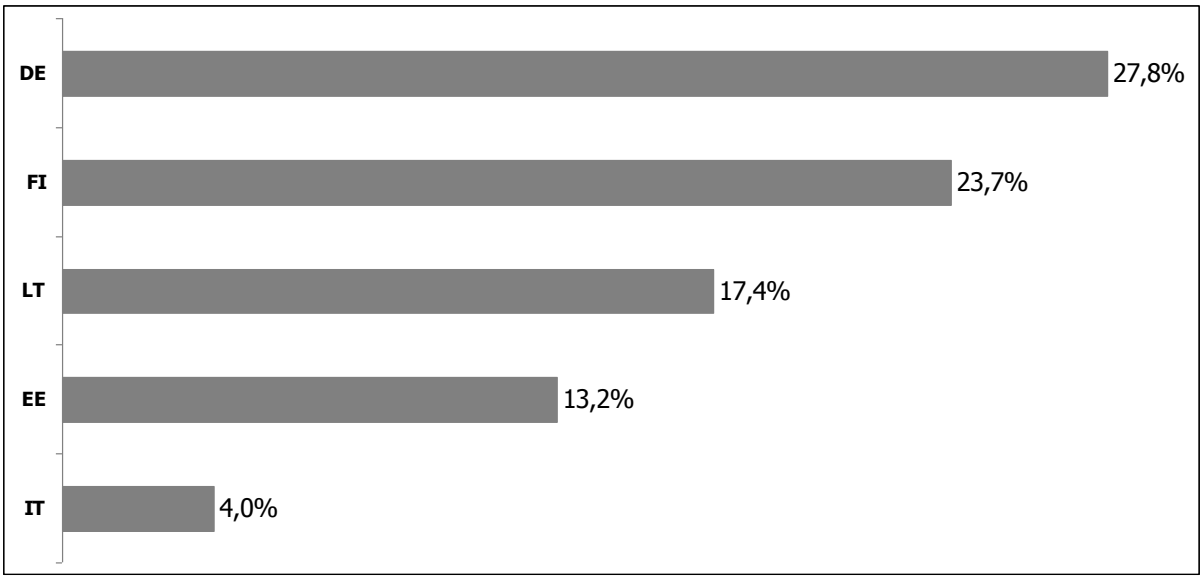


Figure 33 Major Chapter 41 import countries in 2011 (%)
(From total Chapter 41 import amount 892723 Ls/1275318 EUR in 2011)

In 2011 major Chapter 41 export countries were: Italy (IT)(30.6%-1016386 Ls/1451980 EUR), Lithuania (LT)(29.9%-993381 Ls/1419115 EUR), Switzerland (CH)(27.3%-907388 Ls/1296268 EUR) and Poland (PL)(8.5%-283902 Ls/405574 EUR). (See Figure 70)

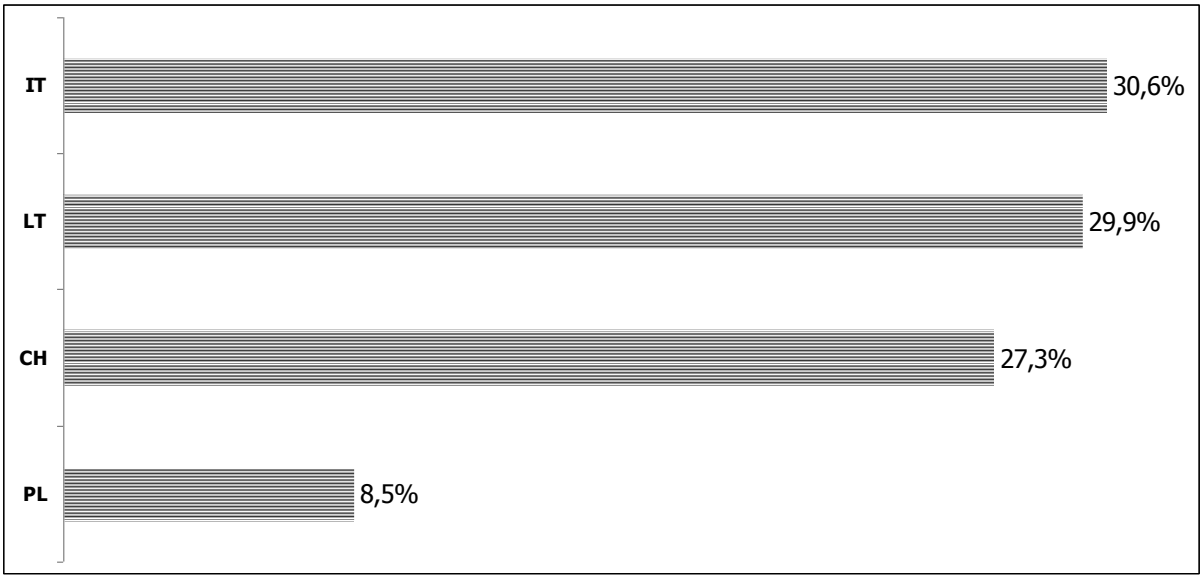


Figure 34 Major Chapter 43 export countries in 2011 (%)
(From total Chapter 41 export amount 3321278 Ls/4744682 EUR 2011)

Major Chapter 41 import and export countries in 2012

In 2012 major Chapter 41 import countries were: Germany (DE)(35.7%-318824 Ls/455462 EUR), Finland (FI)(22.6%-202301 Ls/289001 EUR), Estonia (EE)(13.8%-123610 Ls/176585 EUR) and Lithuania (LT)(13.1%-116823 Ls/166890 EUR). (See Figure 71)

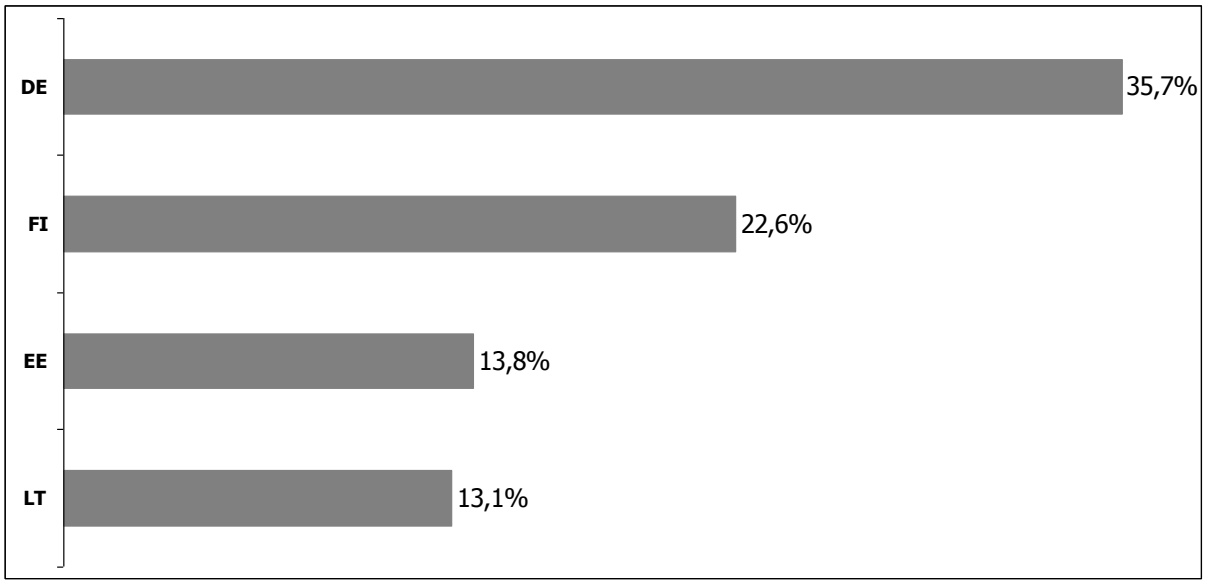


Figure 35 Major Chapter 41 import countries in 2012 (%)
(From total Chapter 41 import amount 893965 Ls/1277092 EUR in 2012)

In 2012 major Chapter 41 export countries were: Lithuania (LT)(41.9%-1040125 Ls/1485892 EUR), Switzerland (CH)(29.5%-731610 Ls/1045157 EUR), (IT)(23.6%-584879 Ls/835541 EUR) and Poland (PL)(4.6%-113798 Ls/162568 EUR). (See Figure 72)

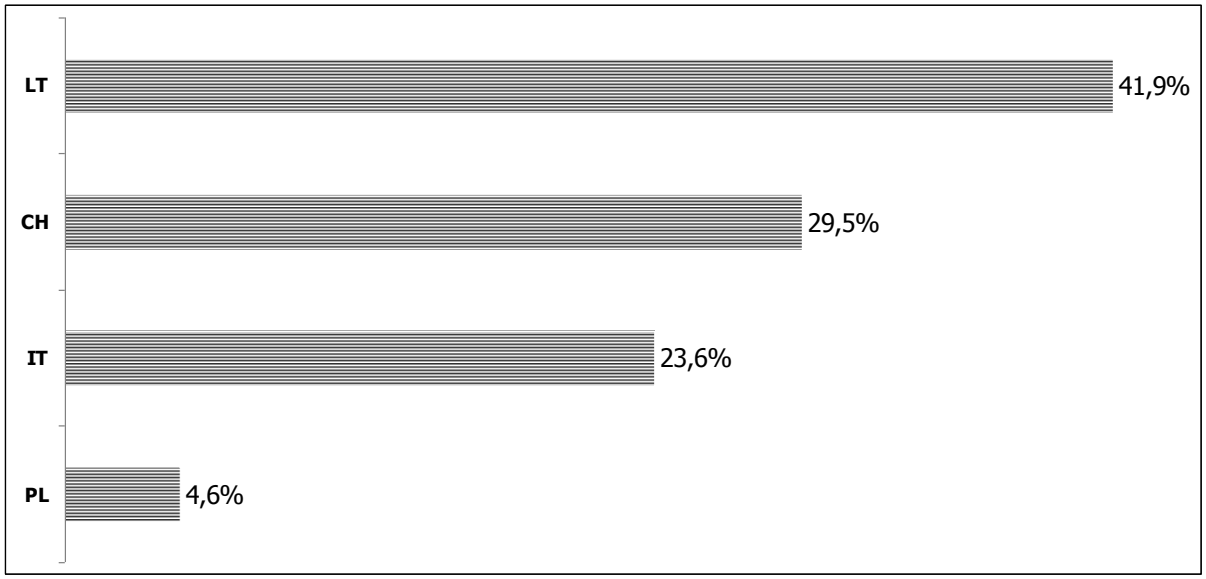


Figure 36 Major Chapter 41 export countries in 2012 (%)
(From total Chapter 41 export amount 2482394 Ls/3546277 EUR in 2012)

APPENDIX 3
All DSC (curves) results

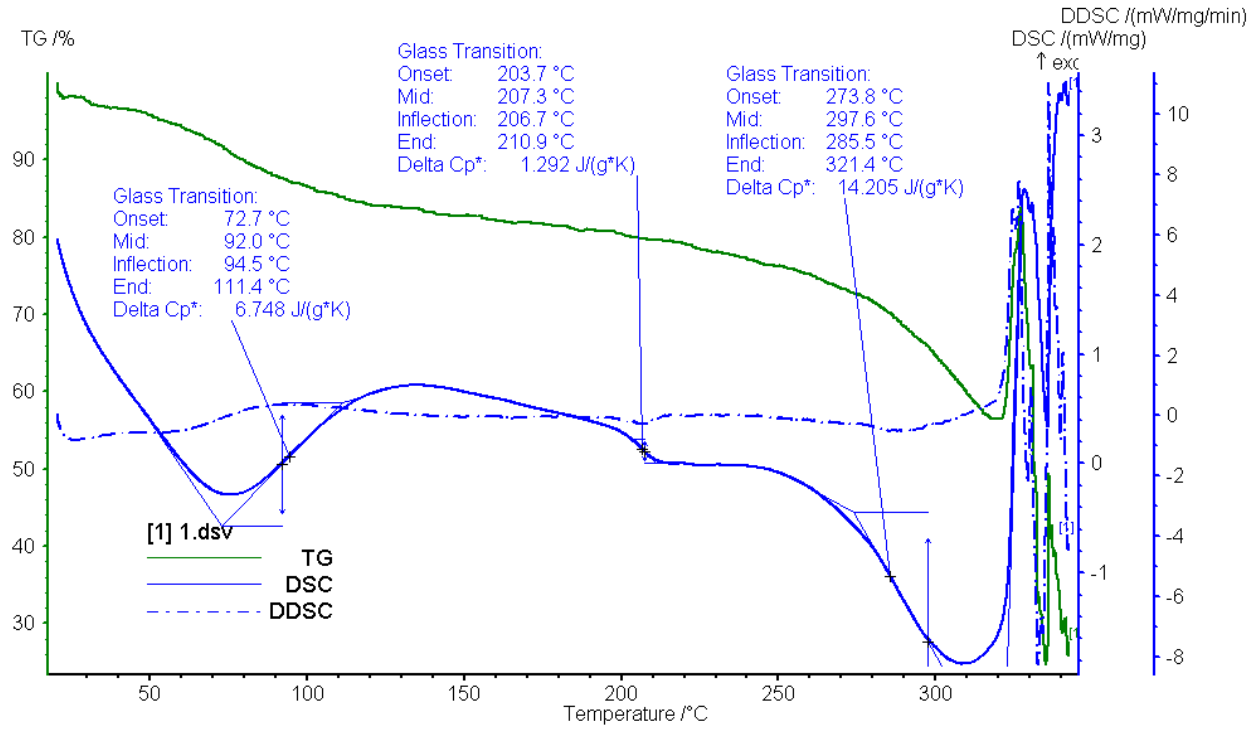


Figure 37 DSC curves of vacuumed hide samples stored 1 day

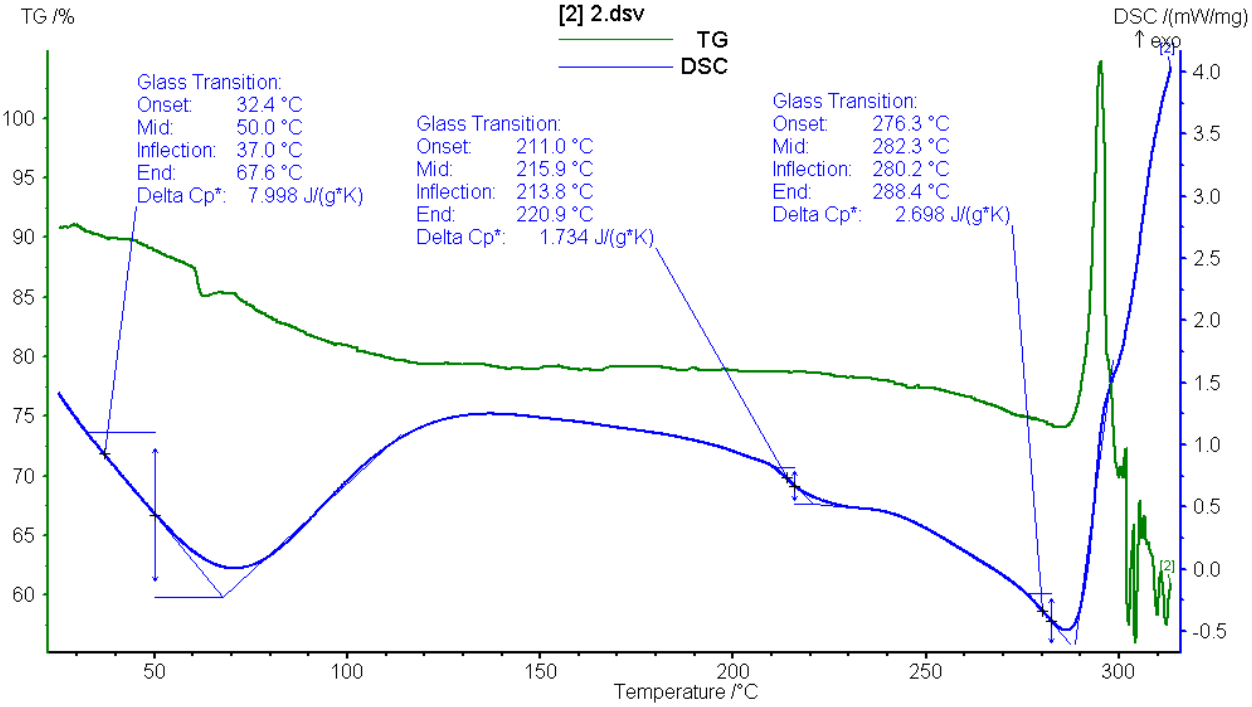


Figure 38 DSC curves of vacuumed hide samples stored 5 days

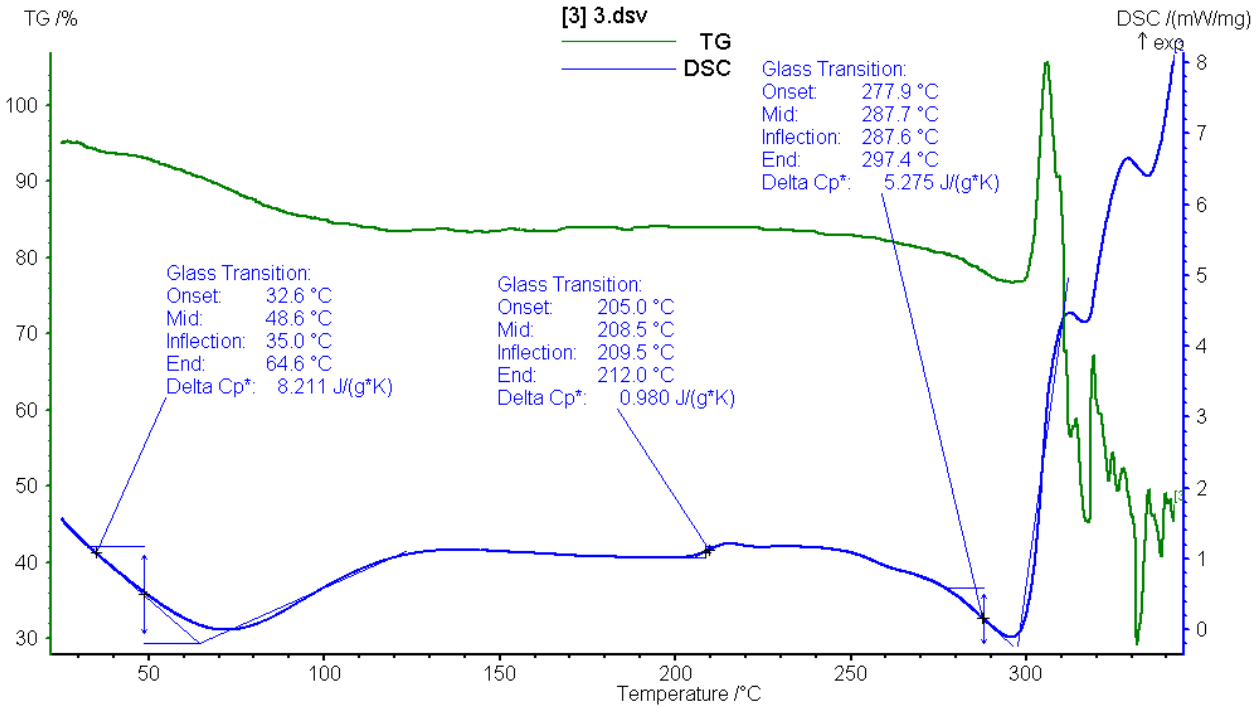


Figure 39 DSC curves of vacuumed hide samples stored 11 days

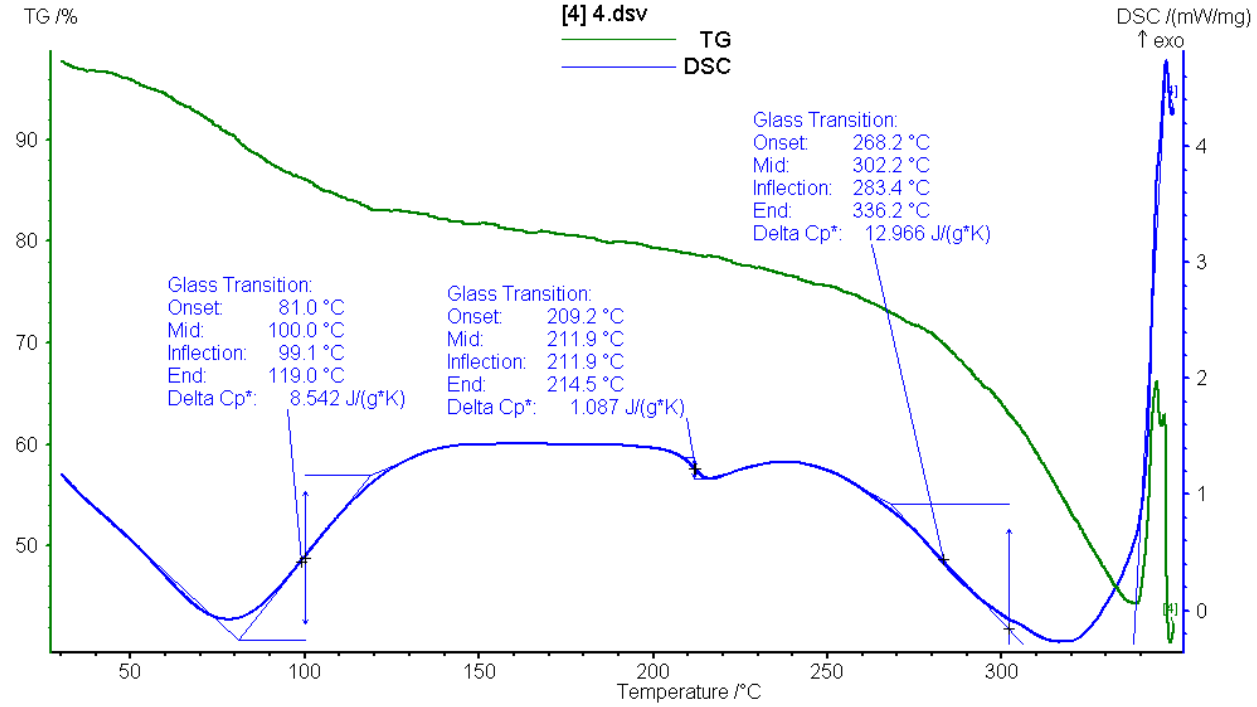


Figure 40 DSC curves of vacuumed hide samples stored 15 days

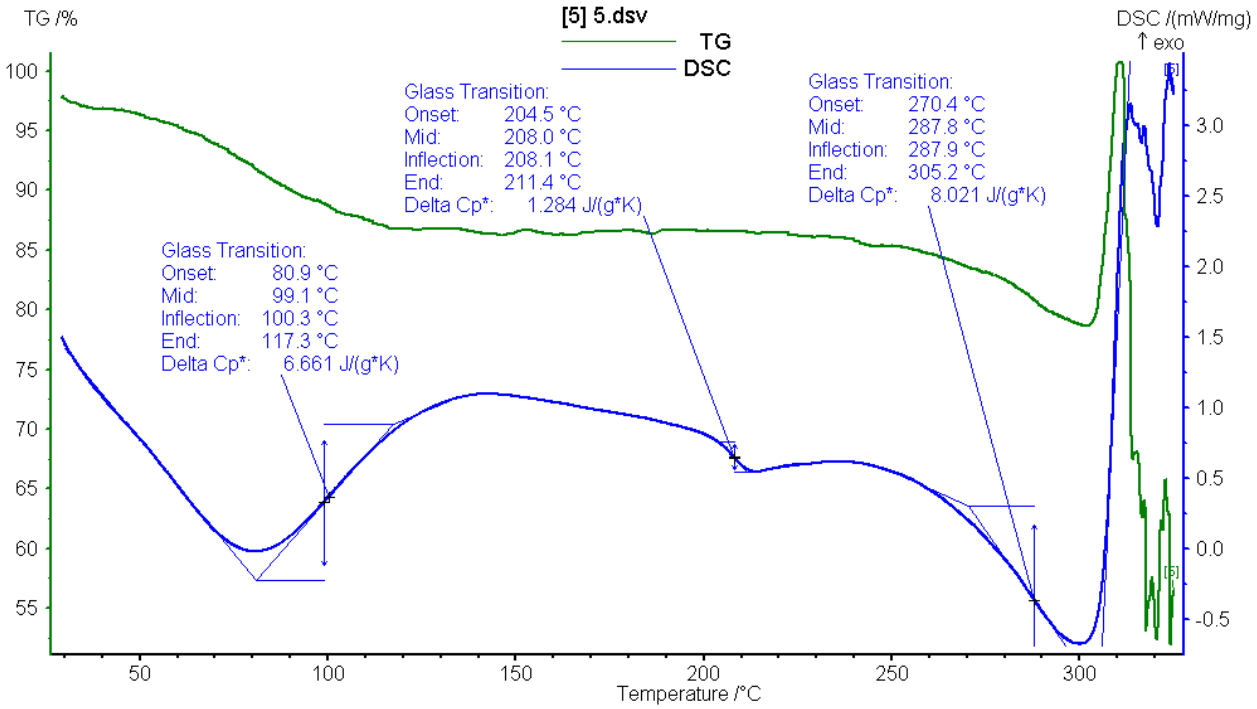


Figure 41 DSC curves of vacuumed hide samples stored 20 days

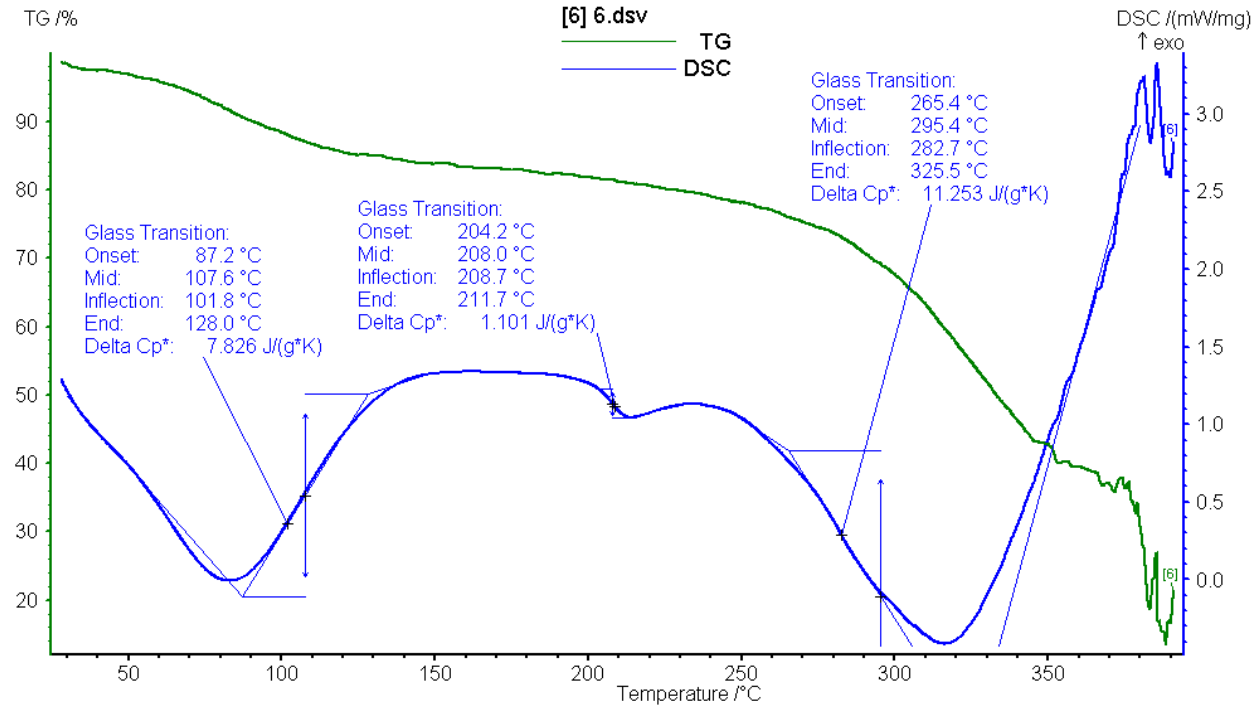


Figure 42 DSC curves of vacuumed hide samples stored 22 days