INSTITUTO SUPERIOR DE ENGENHARIA DO PORTO
MESTRADO EM ENGENHARIA QUÍMICA

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Aplicação e Caracterização de 14 diferentes productos de de engraxe

VITOR RUBEN MOREIRA PAIS FERREIRA
novembro de 2018

POLITÉCNICO
DO PORTO

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RAMO QUALIDADE

Application and Characterization of 14 different fatliquoring products

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Novembro 2018

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“Not everything that counts

can be counted,

And not everything that´s

counted truly counts.”

Alberto Einstein

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Abstract

Keywords: leather; fatliquoring; staining tests; particle size; zeta potential

The leather making consists on converting a raw hide, a very putrescible material, into leather, a stable material, which is then used in the manufacture of a wide variety of products, ranging from shoes, clothing, leather goods, furniture, upholstery for cars, boats and aircraft, and many other items of daily use. These different applications however, require different types of leather.

The final product is but the result of a complex sequence of chemical reactions and mechanical processes, being tanning the fundamental stage, since it gives to leather its stability, but it is the combining processes that in the end generate an article with very specific properties such as the appearance, temperature fastness, elasticity, softness among much more. Because of this is very important to understand the products that are used in this context, to achieve better performances and motivate the further improvements.

The fatliquoring stage is a very important step in leather making, especially for achieving soft leather since there is, to a certain degree, a high demand for this property in almost any kind of hides. However, and contrary to popular belief, the main function of this process is not to bring in softness to the article but to effectively lubricate its fibers and avoid its resticking during the drying stage. The purpose of this study was to apply 14 commercially available products and characterize them physiochemically while also analysing the properties they confer to leather.

With this objective in mind we made a complete characterization covering all the essential quality parameters that are used in the case of leather among them tear and tensile strength, fastness to light and temperature and of course softness and also studied the product characteristics using particle size distribution and zeta potential determination techniques, monitored the product performance along the application process and successfully optimized a technique to stain the neutral fraction of these products once inside the leather´s structure, pre and post drying.

The size distribution and zeta potential determinations, overall achieved reliable results allowing to see the differences between these products as well as how these parameters influence certain characteristics specially regarding product penetration on leather. The staining of the anionic fraction of these products was already a currently used procedure but the staining of the neutral fraction was still rather untouched, and its method was successfully optimized and implemented. In terms of performance, these products achieved the expected results in most cases, and even surprised us positively in the case of the FF51 for example.

The use of the chemical oxygen demand as a control parameter of exhaustion and product behavior along the process showed it can be very fast, practical and reliable possibly becoming a must in cases of product improvement, control and development.

In terms of softness, all the products showed good properties, however the RTN PR165 and FF CL surprised with even better than anticipated.

Resumo

Palavras-Chave: couro; engorduramento; testes de tingimento; tamanho de partícula; potencial zeta

A criação de couro consiste em converter uma pele de animal, um material muito putrescível, em couro, um material estável, que é usado na fabricação de uma ampla variedade de produtos, desde sapatos, roupas, artigos de couro, móveis, estofados para carros, barcos e aeronaves, e muitos outros itens de uso diário. Estas diferentes aplicações requerem diferentes tipos de couro.

O produto final é apenas o resultado de uma sequência complexa de reações químicas e processos mecânicos, sendo o curtimento a fase fundamental, já que confere ao couro sua estabilidade, mas são os processos combinados que ao final geram um produto com propriedades muito específicas como a aparência, resistência à temperatura, elasticidade, suavidade entre muito mais. Por isso, é muito importante entender os produtos que são usados neste contexto, para obter melhores desempenhos e motivar as melhorias adicionais desses produtos químicos.

A etapa de engorduramento é um passo muito importante na criação de couro, especialmente para a obtenção de couro macio, pois há, de certa forma, uma alta necessidade por essa propriedade em quase todos os tipos de couro. No entanto, e contrariamente à crença popular, a principal função deste processo não é trazer suavidade ao artigo, mas lubrificar eficazmente as suas fibras e evitar a sua interação durante a fase de secagem. O objetivo deste estudo foi aplicar 14 produtos comercialmente disponíveis e caracterizá-los química e fisicamente, analisando também as propriedades que conferem ao couro.

Com este objetivo em mente fizemos uma caracterização completa cobrindo todos os parâmetros essenciais de qualidade que são usados no caso do couro entre rasgo e resistência à tração, solidez à luz e temperatura e claro suavidade e também estudamos as características do produto usando distribuição de

tamanho de partícula e técnicas de determinação do potencial zeta, monitorizando o desempenho do produto ao longo do processo de aplicação e otimizaram com sucesso uma técnica para tingir a fração neutra desses produtos uma vez dentro da estrutura do couro, tanto pré como pós secagem.

A distribuição de tamanho e as determinações do potencial zeta alcançaram resultados confiáveis, permitindo ver as diferenças entre esses produtos e como esses parâmetros influenciam certas características, especialmente em relação à penetração do produto no couro. A coloração da fração aniónica desses produtos já era um procedimento usado atualmente, mas a coloração da fração neutra ainda estava praticamente intocada, e sendo assim seu método foi otimizado e implementado com sucesso. Em termos de desempenho, estes produtos alcançaram os resultados esperados na maioria dos casos, e até nos surpreenderam positivamente no caso do FF51, por exemplo.

O uso do consumo químico de oxigênio como um parâmetro de controle de exaustão e comportamento do produto ao longo do processo mostrou que pode ser muito rápido, prático e confiável, possivelmente tornando-se uma necessidade em casos de melhoria, controle e desenvolvimento do produto.

Em termos de suavidade, todos os produtos apresentaram boas propriedades, porém o RTN PR165 e o FF CL surpreenderam com ainda melhores resultados do que o previsto.

Resumen

Palabras-llave: cuero, engrase, tamaño de partícula, potencial zeta

La creación de cuero consiste en convertir una piel de animal, un material muy putrescible, en cuero, un material estable, que se utiliza en la fabricación de una amplia variedad de productos, desde zapatos, ropa, artículos de cuero, muebles, tapizados para coches, barcos y aeronaves, y muchos otros artículos de uso diario. Estas diferentes aplicaciones requieren diferentes tipos de cuero.

El producto final es sólo el resultado de una secuencia compleja de reacciones químicas y procesos mecánicos, siendo el curtido la fase fundamental, ya que confiere al cuero su estabilidad, pero son los procesos combinados que al final generan un producto con propiedades muy específicas como la apariencia, resistencia a la temperatura, elasticidad, suavidad entre mucho más. Por lo tanto, es muy importante entender los productos que se utilizan en este contexto para obtener mejores resultados y motivar las mejoras adicionales de estos productos químicos.

La etapa de engrase es un paso muy importante en la creación de cuero, especialmente para la obtención de cuero suave, pues hay, de cierta manera, una alta necesidad por esa propiedad en casi todos los tipos de cuero. Sin embargo, y contrariamente a la creencia popular, la principal función de este proceso no es traer suavidad al artículo, sino lubricar eficazmente sus fibras y evitar su interacción durante la fase de secado. El objetivo de este estudio fue aplicar 14 productos comercialmente disponibles y caracterizarlos química y físicamente, analizando también las propiedades que confieren al cuero.

Con este objetivo en mente hemos hecho una caracterización completa cubriendo todos los parámetros esenciales de calidad que se utilizan en el caso del cuero entre desgarro y resistencia a la tracción, solidez a la luz y temperatura y también suavidad y estudiamos las características del producto usando distribución de tamaño de la partícula y técnicas de determinación del potencial zeta, monitoreando el desempeño del producto a lo largo del proceso de aplicación y optimizando con éxito una técnica para teñir la fracción neutra de estos productos una vez dentro de la estructura del cuero, tanto pre y post secado.

La distribución de tamaño y las determinaciones del potencial zeta alcanzaron resultados confiables, permitiendo ver las diferencias entre esos productos y cómo estos parámetros influencian ciertas características, especialmente en relación con la penetración del producto en el cuero. La coloración de la fracción aniónica de estos productos ya era un procedimiento usado actualmente, pero la coloración de la fracción neutra aún estaba prácticamente intacta, y siendo así su método fue optimizado e implementado con éxito. En términos de desempeño, estos productos alcanzaron los resultados esperados en la mayoría de los casos, y hasta nos sorprendió positivamente en el caso del FF51, por ejemplo.

El uso de la demanda química de oxígeno como un parámetro de control de agotamiento y comportamiento del producto a lo largo del proceso mostró que puede ser muy rápido, práctico y confiable, posiblemente convirtiéndose en una necesidad en casos de mejora, control y desarrollo del producto.

En términos de suavidad, todos los productos presentaron buenas propiedades, pero el RTN PR165 y el FF CL sorprendieron con aún mejores resultados de lo previsto.

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Abbreviations

COD – Chemical Oxygen Demand

IEP – Isoelectric Point

FF – Fosfol

ISO – International Standard Organization

ILO – International Leather Organization

CUSA – Cromogenia Units, SA

RTN – Retanal

RPL – Repelan

PDI – Polydispersity Index

R&D – Research and Development

PDI – Polydispersity Index

Greek Letters:

α - Alfa

β - Beta

1. Introduction

1.1. Cromogenia Units

CROMOGENIA UNITS S.A., part of UNITS Group, develops and manufactures many chemical specialties meant to satisfy the needs of a wide variety of industries since 1942. With the Headquarters stationed in Barcelona (Spain) (Figure 1) and with a strong industrial background, its main goal is to develop, produce and market chemical specialties to satisfy new industrial and environmental requirements and helping to improve overall quality.

Figure 1 – Picture of Cromogenia Units Application Laboratory at Headquarters, Barcelona, Spain.

The growth strategy is focused on areas where R&D capabilities are essential and in areas where a competitive advantage can be created through a differentiated technology. Its main target is to help its industrial customers to develop cheaper materials for improved profitability, with a better performance and through the cleanest possible technology.

At the moment, the company is exporting to more than 60 countries around the globe through an extensive network of agents and distributors. With the incorporation of SIDASA's chemicals, it completed the range of specialized products for metal and plastic, enhancing the development and competitiveness capacity in its production and distribution range.

Cromogenia Units takes the quality aspects very seriously and so it maintains compliance with the main international standards such as ISO 9001 and ISO 14001, (Figure 2) as well as more specific quality certifications in accordance with every sector of activity where the products are placed, such as FDA for Indirect food contact for laminating adhesives, GMP for production in some lines, in order to assure a safer environment and keep the outstanding quality of its products.

Figure 2 - International Organization Standards stamps of approval for IS09001:2015 and ISO14001:2015.

The company is committed to keep and improve its production and commercial abilities by an extensive industrial & commercial network composed of several production centres, subsidiary companies and a specialized network of agents able to give the right on-site technical support to its customers. Since chemical specialties are needed in practically every industrial sector, its business areas are spread around 10 main commercial divisions: Leather, Textile, Coatings, Adhesives, Construction, Composites, Rubber, Water Treatment, Metalworking and Performance Chemicals.

1.2. The project

This project, with a duration of 7 months, took place in Cromogenia Units, S.A located in Barcelona, Spain, under the master's Program in Chemical Engineering of Instituto Superior de Engenharia do Porto (Figure 3), Portugal and the Erasmus+.

Figure 3 - Logo of Instituto Superior de Engenharia do Porto, Portugal

The challenge was to apply 14 Cromogenia´s commercially available products and characterize them physiochemically while studding the properties they confer to leather. These products are used in a very important part of the leather manufacturing – the fatliquoring.

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The main goal of this project was to then relate the properties conferred to leather by these products, acquiring more predictive tools and consistently show their possible relationship. Also, we applied the combined results of particle size distribution and zeta potential determination technology as a new source of information about the behaviour of these products as emulsions, especially during their application.

1.3. Report Structure

This report is divided in **Chapter 1**, the Introduction, where this project is presented; **Chapter 2**, the Content Review, where all the theoretical background is discussed and related, representing but a portion of what was researched and analysed; **Chapter 3**, the Application of fatliquoring products, where we walk through all the steps taken, from cradle to grave; **Chapter 4**, the Characterization of fatliquoring products, where we present the results obtained for each of the analysis conducted; **Chapter 5**, the Discussion, where by cross referencing several chemical and physical analysis and analysing the new data that we have obtained regarding the products behaviour, we try to find some relationships between certain properties, and finally **Chapter 6**, the Conclusion, where we highlight the most important aspects of this research.

All the information regarding this project and shared in this report is based on commercially available products, and because of that the formulations of all the products studied were never disclosed or target of discussion.

2. Theoretical Background

2.1. Introduction

The leather industry is responsible for processing skins and hides, by-products of other industries, that by tanning are transformed into a durable material preventing its decay and making it persistent and flexible. (1) It has been recorded since very early, the preserving of pelts with smoke from wood combustion, ash and animal fat. As a matter a fact, almost all the processes we find nowadays had a strong influence from the old practices. (2)

Along this chapter, we will be exploring the chemistry and technology behind the product, with a strong focus between the tanning and finishing processes. Finally, quality and environmental perspectives are discussed, and the efforts in those directions highlighted.

But, before anything else, we must understand our raw material, the skin.

2.2. Skin Chemistry

As the largest organ in mammals, the skin can be a very complex and singular structure. It is mainly composed of a protein called collagen, a generic name for a family of at least 28 different proteins each serving its own unique purposes. (1) (3)

2.2.1. Collagen

Collagen is a protein comprised of amino acids, **α** an amino group and **β** the carboxyl group, such as depicted in Figure 4. To form a protein, they create a backbone to the structure, from which sidechains extend.

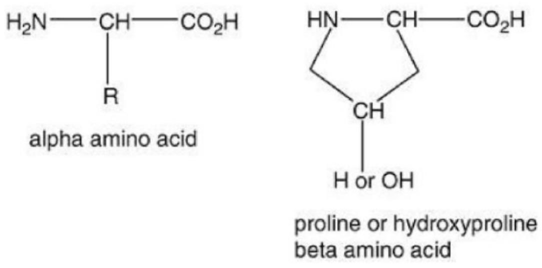


Figure 4 - Alpha amino group (on the left) and carboxyl group (on the right).

It is characterized by a repeating amino acid triplet ***-(Gly-X-Y)$_n$-,*** (X can be Proline and Y an Hydroxyproline, among others), such as in Figure 5, which determines the helical shape of the molecule. The content and distribution of the sidechains will dictate most of the properties, reactivity and the ability to modify these proteins. (1)

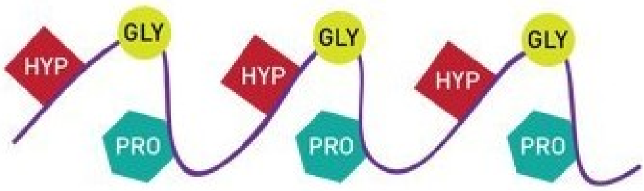


Figure 5 - Representation of the repeating amino acid trip *-(Gly-X-Y)$_3$-,* (X being proline and y being hydroxyproline, in this example).

In terms of leather processes, some amino acids are more important than others. Either in creating the fibrous structure or by involvement in protein modification reactions each plays their own roles. The amino acid sequence, despite influencing the protein´s stability and determining the isoelectric point, doesn't play a big role in this context. (1)

In Type I Collagen, the most common found in our raw material, the monomeric molecule contains three α chains, twisted about each other in a right-handed triple helix, held together by electrostatic bonds and allowed due to the high content of Glycine, as can be seen in Figure 6. (1)

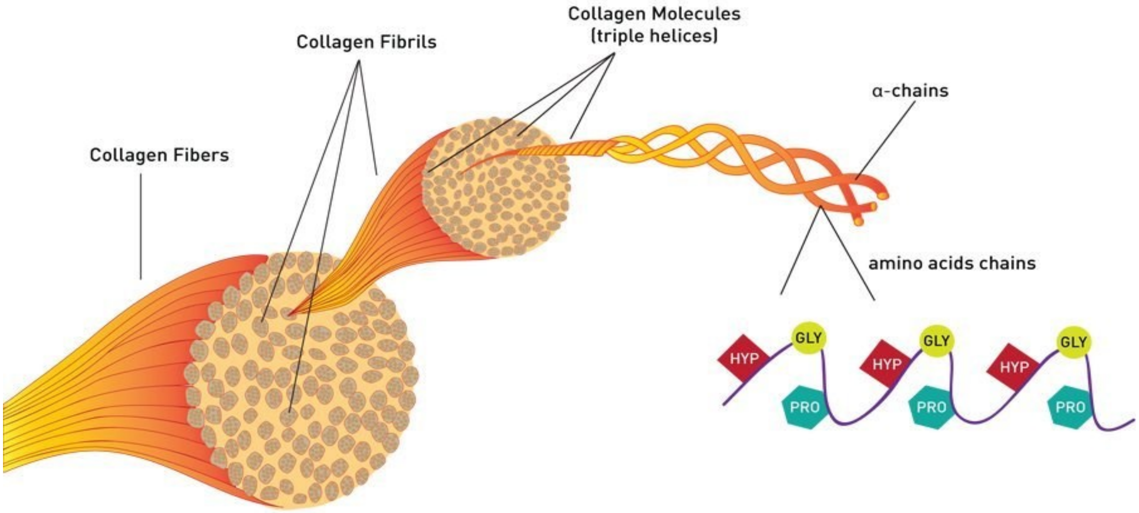


Figure 6 - Representation of the leather´s fibrous structure hierarchy from the basic amino acid chains to the collagen fibres.

These helixes are bound together in bundles called Fibrils, which are the smallest visible collagen structure. These fibrils arrange themselves in bundles that will ultimately become the basic structure of each fiber, such as represented in Figure 6. (1)

The size and repeated occurrence every three residue in the α helix allows Glycine to fit right in the middle of the structure. Each tripe helix will have about 300 nm long and 1,5 nm diameter and theirs ends are called telopeptides which play a significant role in bonding the whole molecule together. (1)

The structure of the skin is a very complex one, comprising of different areas with different properties, as can be seen in Figure 7. Understanding the hierarchy is essential in leather making, since for example, in preparation to the tanning process, the splitting of the fiber structure to a deep level will highly improve the softness and strength of the final product as well as improve process efficiency, product exhaustion and penetration. (1) (4) (5)

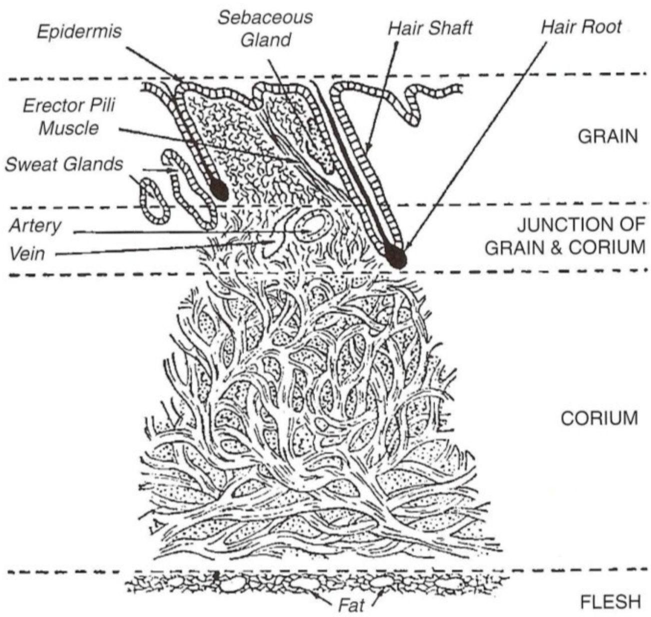


Figure 7 - Representation of the leather´s cross sectioned structure from the flesh to the grain.

2.2.2. Isoelectric Point

In Type I Collagen, the triple helix is also held together by electrostatic bonds of type depicted in Figure 8.

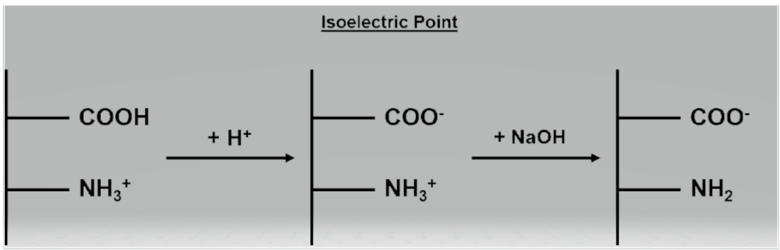


Figure 8 - Representation of the three possible charged states of the collagen protein, being the central configuration representative of the Isoelectric Point.

To these electrostatic bonds we call "salt links" and are formed between the sidechains of the protein and determine the Isoelectric Point - IEP. The reactions on leather highly depend on charge so this parameter, which reflects the charge of the protein at any given pH, is of the highest importance. (1) (5) (6)

At the IEP certain characteristics are observed in leather:

- The net charge is zero – this means that there is an equilibrium of positive and negative charges;

- The concentration of intermolecular salt is at its maximum;
- Swelling will be at its minimum;
- Shrinkage temperature will be at its maximum.

In relation to this parameter there are two essential points worth mentioning. Firstly, IEP doesn't shift unless the material is submitted to chemically changing procedure, which can occur during post-tanning and beamhouse. Lastly, the farthest point away from the IEP is determined by the amino and carboxyl availability and its synonym of highest charge and this will be very important when applying charged products and much more. (1)

It is assumed that, at the starting point of leather processing, the IEP is at around 7,4 in the pH scale and 6 for wet-blue. (1)

2.3. The Industrial Process

The pelt results from the slaughter of an animal being obtained through skinning, manual or mechanical, as portrayed in Figure 9, after which is immediately subjected to a temporary preservation process salting, drying or a mixed treatment, which is essential to assure the quality of the material. After being subjected to this treatment, it can be marketed, stored and transported to the tannery where it will be transformed. (7) (8) (9)

Figure 9 - Pile of recently fleshed cow hides.

The type of skins used in the tannery industry are varied, cattle having the largest share of the sector followed by sheep and goats. (10)

The transformation, from the raw skin to the finished product, involves a set of physical-chemical and mechanical operations whose generic description is given.

2.3.1. Material Reception

Skins, usually obtained in a salty green state, are firstly inspected by appropriate quality, total weight and skin weight checks and when necessary trimmed after which lots are made based on the origin and weight per piece. This initial triage is essential to assure the quality of the final product. (1)

2.3.2. Beamhouse

At this moment, the skins still aren´t ready to undertake tanning, and therefore must be subjected to a series of physical-chemical and mechanical operations to prepare it. This phase in the process is mainly responsible for removing most of the unwanted components and relaxing the fibrous structure. (8) (11)

Soaking - The first step towards the article lasts for 6 to 48 hours and involves the treatment of the skin in an aqueous bath with surfactants, electrolytes, enzymes and bactericides, to moisturize it (wetting back) and eliminate dirt, blood, salt and more unwanted residues. (12)

Unhairing and Liming - After soaking, the pelt is submitted to an alkaline medium with calcium hydroxide, sodium sulfide, sodium sulfate and enzymes for 16 to 48 hours, in which its epilation and relaxation of its fibrous structure is achieved, leaving the skin pH at approximately 12. Later, a deliming process is mandatory to remove liming and unhairing products from the pelt. (11)

Fleshing - This step involves the mechanical removal of fats that are still adhering to the skin and subcutaneous tissue by means of a roller of blades. (11)

Deliming – The deliming lasts for 20 to 120 minutes and involves lowering the skin pH in aqueous bath using ammonium salts, sodium bisulfite and weak acids leaving the pH of the skin at approximately 8. (11)

After the liming process, the lime or other alkali in the skin is no longer required, and, in most cases, it would have a detrimental effect on subsequent tannage. The extent of deliming depends on the type of final article intended, where a thorough deliming results in softer leather whilst partial deliming gives firmer leather. Delimed skins must be taken to the next process immediately, as the alkali has been removed and putrefying bacteria can thrive. (11)

Bating - This stage occurs still in the same bath of the deliming and achieves the relaxation the structure of the skin and eliminates residues of epidermis (unwanted nitrogenous components) left behind, followed by one or two washes, with a duration that can vary between 15 and 60 minutes. In this operation a wide range of enzymes (mixture of proteases and lipases) are applied. (11)

2.3.3. Tanning

Pickling - This process prepares the skin to receive the tanning agent and has the important action of definitively stopping the previous steps. It last for 4-12 hours and involves the treatment with sodium chloride and aqueous bath acids to reduce skin pH to values between 2.5 and 4.5, depending on the tanning agent to be applied. (1)(10)(11)

The tanning occurs usually in the same pickling bath, with the appropriate tanning agent, to give the skin thermal stability, strength and other specific properties. It can be preceded by a degreasing such as with sheep skins. (13)

The tanning can be mineral or organic; in the first one, salts of chromium, titanium, aluminum are used; in the second we can highlight the vegetable tanning made with vegetable extracts. The duration of tanning may vary from 10 hours (more usual) to a few weeks (tanning case for sole production). (14)

In mineral tanning, the chrome process is still the main tanning process used due to the relatively short time of process and the quality it gives. The source of chromium mostly used is the basic sulfate of chromium, where it is in a trivalent state. However, increasing efforts are being made for its replacement since cause a negative environmental impact. This tanning can be carried out in the same bath or formulated in a separate one. (1) (15)

The vegetable tanning is generally used in the production of soles and some special types of leather, as well as in combination with other types of tanning. Due to its high cost, the tannins are used as much as possible - most of the time the best solution is to reuse the bath in the next batch and compensate the part absorbed by the previous lot. With the increased use of synthetic materials in the manufacture of soles, tanning vegetable leather for this purpose has decreased significantly. (1) (16) (17)

In synthetic tanning, organic agents such as resins and synthetic tannins are used and provide a more uniform tanning and increase the penetration of other tannins and products. This improves, for example, the subsequent dyeing process. However, they are usually more expensive than other tanning agents. (1) (3)

At this stage the skin is internationally called wet-blue, in the case of tanning with chromium, or wet-white, in the case of chromium-free tanning. (9)

2.3.4. Post-tanning

This is what we call to the set of chemical operations subsequent to the tannery, carried out in an aqueous bath and preceded by two mechanical operations in which the thickness of the skin is adjusted to correspond to that desired for the article to be produced. (3)

Splitting - In this operation, the tanned skin is divided by the thickness into two parts through a steel blade. The main part is the grain, whose thickness is intended to be correct; the other part (meat side) is still used after proper trimming. (10) (11)

Shaving - Since the shaving operation is not sufficiently precise, the skin is then subjected to lowering which consists of scraping the skin from the meat side (carnation) through a roller of blades to adjust the thickness to the desired value. (11) (10)

For this point on, the skin is subjected to various treatments in aqueous medium with the purpose of giving it very specific properties. These processes occur in a rotary drum-type machine referred to as drum. All these operations can be preceded by washing, and a final one is almost always carried out.

Neutralization – It consists in the elimination of the free acid contained in the skin and adjustment of the pH to values that allow the subsequent treatments (4.5 to 6.0). The most commonly used chemicals in this operation are sodium formate and sodium bicarbonate. The neutralization can last between 30 and 120 minutes. This step is very important, and in the case of wet-blue, more than neutralize the skin, we can perform a basification, which will ease the product penetration in the next steps, since they are of anionic nature. (1)

Retanning – This step involves the use of chemicals to give the leather the desired texture and certain characteristics such as sanding, filler, etc. The chemicals used are mineral salts, acrylic resins, urea-formaldehyde resins, styrene-maleic resins, vegetable extracts, synthetic tannins, etc. The duration of this operation can vary between 1 and 4 hours. (1) (3)

Dyeing – Use of appropriate dyes to achieve the desired color, either superficially or through the thickness of the skin with a duration of 20 to 60 min. (10) (11)

Fatliquoring – This step is of high importance and uses animal, vegetable and synthetic fats to lubricate the fibers providing resistance and softness to the leather once it dries and has a duration that can vary between 30 to 90 minutes. (1) (4) (11) (18)

2.3.5. Drying

Since the last process is carried out in an aqueous medium, it is necessary to dry the skins. At this stage, the skins are subjected to different operations:

Stretching - The skins are squeezed and simultaneously smoothed (stretched) in an appropriate machine thereby reducing their moisture and attenuating wrinkles and other irregularities. (11)

Drying - Reduction of skin moisture through vacuum drying, air to ambient air, in a tunnel or greenhouse, etc. This operation is extremely important and varies greatly with the type of tanning. The conditions of operation of the vacuum dryer are variable, the temperature being usually between 50 ° C and 70 ° C and the time between 1 and 5 minutes. (11)

After drying, the skin is softened or opened in different types of machine(staking), being the most common one that works through a movement of hammers that simultaneously beats the skin and stretches it. At this point the skin is usually called crust.

2.3.6. Finishing

In this final stage, the skin is subjected to a number of mechanical operations and to the application of suitable compositions in order to render it more surface resistant, to enhance it by improving its appearance and giving it the desired effects, according to the customer specifications. (6) (7) (11)

Buffing - Action of a suitable sandpaper on the surface of the skin, to give a characteristic appearance of the article in question or to prepare the skin for subsequent finishing applications, increasing the contact surface.

Plating - Pressure is applied on heated, plate or continuous press to achieve certain surface effects, such as brightness, touch, etching, etc.

Finishing - The application of the finishing compositions can be used in various ways according to the article in question and the intended purpose: spray gun, curtain, through rollers, etc. At the end of this process the skin is considered finished.

2.4. Environmental Impact

The leather industry consumes an enormous quantity of water, besides generating a high quantity of solid waste. However, this is not at all related with low process efficiency but to the need to remove certain components that, due to their characteristics, can´t be in the final product.

The technological improvement and research efforts allowed the development of solutions and alternatives that help lowering the environmental problems that this industry faces. Either by creating new and cleaner methods or by improving effluent and residue treatments, an effort in these directions has been made especially in areas where we can find a high concentration of this trade. (19) (11) (10)

However, it is important not to forget the fragility of this industry. It´s essential to develop techniques that allow this industry a better environmental performance, but without compromising economical gains, by means of reducing energy, water and product consumption and allowing a better use of waste recovery without reducing the quality of the final article. (19) (20)

There a few documents describing the BATs applicability to the tanning industry, such as the BREF, which in the case of the tanning industry is entitled "Best Available Techniques Reference Document for the Tanning of Hides and Skins". (10)

3. Application of Fatliquoring Products

The main goal of this study was to allow a deeper understanding of the different fatliquoring products physiochemically, in terms of performance and on how they influence the properties of the final article. Throughout this chapter, all the steps taken in this project are described and explained. For this purpose, 14 Cromogenia´s fatliquoring products were selected with the goal of covering all the different types of greasing products industrially found, thus providing a better comparison and characterization.

The products selected were 2 sulfated oils, the Fosfol 50 and Fosfol 51, 4 sulfited oils, the Fosfol AUTC3, Fosfol DF20, Fosfol AUT and the Fosfol AUT09, 2 lecithin based oils, the Fosfol CL and Fosfol LC80, 2 sulphoclorated oils, the Fosfol SC10 and Fosfol SC20, 2 synthetic oils, the UNIX S3 and UNIX UP, and 2 other products, the Retanal PR165, which is also used as a retanning agent, and the Repelan HC, which purpose brings added hydrophobicity to the leather.

For this evaluation, the selected products were submitted to physicochemical analysis and applied in cattle and sheepskin samples, all according to the ISO and International Leather Standards when applied.

3.1. Organization

This study is divided in two main parts: the application of the products on leather and the characterization of both the properties they confer to leather as well as the chemical properties of the products. We must first apply the products, so we can then evaluate all the necessary aspects that each bring to the leather. The characterization is then partitioned in 3 areas: the physical trials, which are of high relevance to any characterization of an article, the chemical trials, which are essential to understand how the chemistry of each product influences its relationship with the leather and helps explain the manifested physical properties and the chemical analysis of each product which will bring important parameters that by correlating with the rest of the data obtained will aid in answering a lot of questions. In Table 1, can be found the activities planned for this project.

Table 1 - Gant diagram for the planning off all the activities taken place in this project.

Activity	February	March	April	May	June	July
Incorporation in Cromogenia, SA						
Planning of the research project						
Incorporation in the Application Lab						
Application Lab Analysis						
Cattle Application						
COD Trials Cattle						
Thickness and Softness Cattle						
Sheepskin Application						
COD Trials Sheepskin						
Determination of Extractable Matter						
Fastness Temperature						
Colour analysis Cattle						
Colour analysis Sheepskin						
Thickness and Softness Sheepskin						
Water Absorption Sheepskin						
Staining Tests						
Resistances						
Ball Burst Test						
Particle Size and Zeta Potential						
Hidro-Lipo Balance						
Fastness to Light						
Organoleptic Analysis						

3.2. Product Application

In order to fully understand how each of this products work, they were submitted to the same conditions they wait when reaching an industrial processing unit. In an industrial context, more than one kind of fatliquor is combined plus the mild presence of other substances. (1) For that reason, we made sure that all the necessary precautions were taken to assure similar conditions were always recreated. Nonetheless, the application of each product was made in such a way that allowed to see how each product works individually while performing all the necessary test and controls essential for this characterization.

The preparation of these samples was very important since both had very distinct analysis purposes.

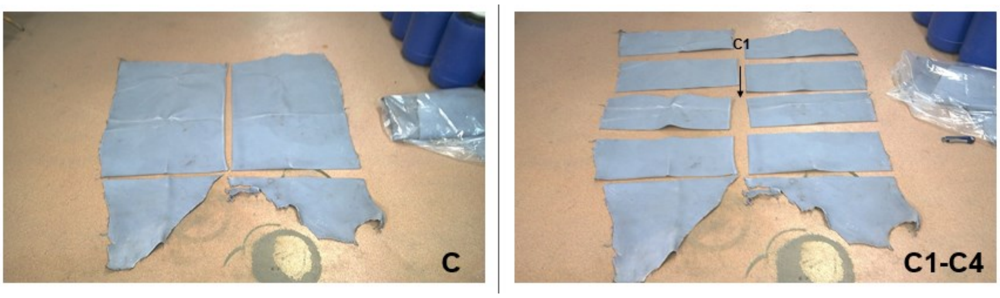


Figure 10 - Cow hide C being sampled(separated from the spine on the left and separated in C1-C4 on the right).

Figure 11 - Sheepskin number 1 being sampled (whole on the left and separated by the spine into 1F and 1A on the right).

For that, 4 cattle hide (A to D), exemplified in Figure 10, and 15 sheepskins (1 to 15), exemplified in Figure 11, in wet-blue state were selected to the demanded specifications and sampled.

After this, each piece was identified and weighted, a very important step since the application of any product in leather is made over its weight. All the sampling process was made under the accordance with *ISO 2418:2017 - Leather - Chemical, physical, mechanical and fastness tests - Sampling location; ISO 2419:2012 - Leather - Physical and mechanical tests - Sample preparation and conditioning; ISO 2588:2014 - Leather – Sampling*; and *ISO 4044:2017 - Leather - Chemical tests - Preparation of chemical test samples*. The reference table corresponding each product with the samples, both for cattle and sheepskin, can be found in Annex I. For the two types of hides, two different application formulations were applied according to the difference in type and the different parameters in need to be evaluated.

3.2.1. Application in cattle

The cattle hides were divided by the spine in two halves, left(E) and right(D), and then in 3-4 straps according to the size of the whole cattle sample (A1-A4, B1-B4, C1-C3, D1-D3), perpendicular to the spine, each meant to be fatliquored with one of the 14 products in this study. In Figure 12 we can see the application diagram with the processes underlined and the main procedures highlighted in green.

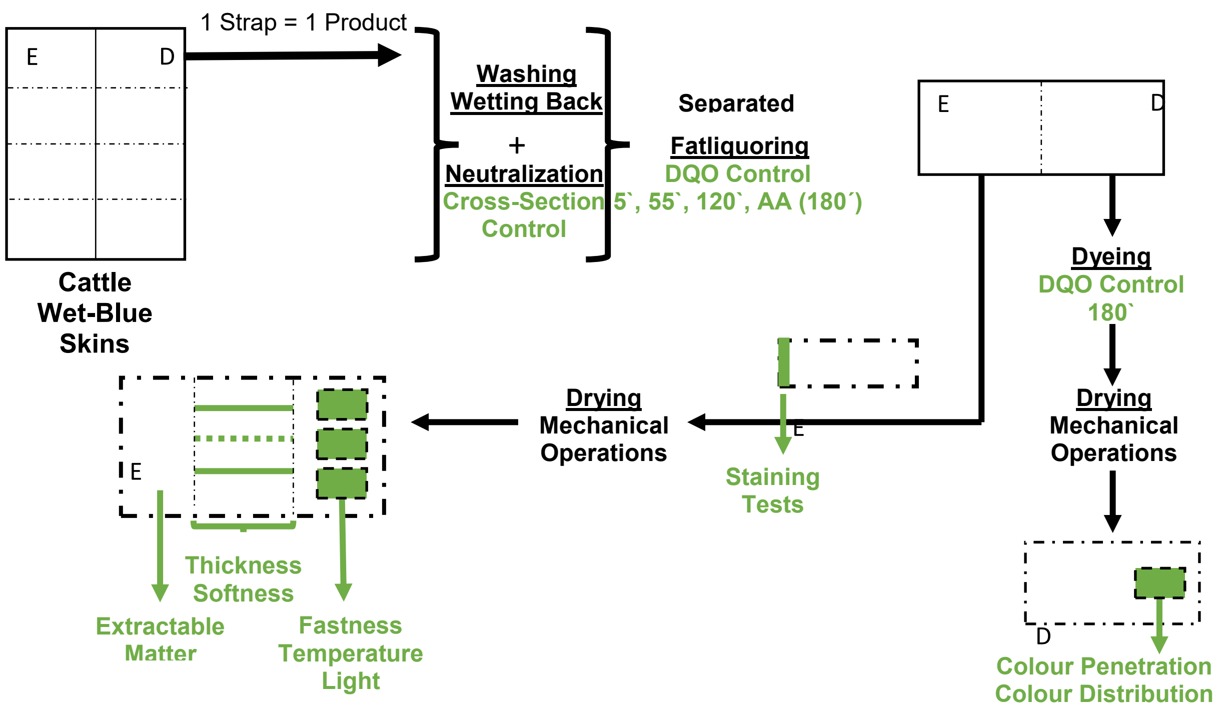


Figure 12 – Application process and analysis diagram. (Procedures underlined, and control procedures highlighted in green)

The cattle hide was deliberately acquired with extra thickness since it was needed to assess certain aspects of product and dye penetration, impossible in thin samples. Its formulation was stripped of the retanning step as well as of certain common aiding products in order not to influence the properties each product gives to the leather. The process was designed in a way that allowed us to keep an uncoloured strap(E), which was later used to evaluate changes in colour created by the different fatliquoring products (otherwise hidden by the dyeing effect), the %fat that remained after greasing and evaluate how each fraction of the product penetrates, as can be seen in the diagram in Figure 12.

The process continued with the right side of the strap(E), that was dyed so aspects of colour intensity and penetration, which is highly influenced by the type of product previously used as their mechanisms are slightly competitive, could be evaluated. A reference sample processed without adding any product was also made and submitted to all the same conditions and analysis. The photographic record of the cattle samples, after process, can be seen in Annex I and the application formula in Figure 13.

CATTLE FORMULA

Washing

35ºC

200% H_20

0,2% Acetic Acid

0,2% CELESAL DL – 80`

Drain, Wash 200% H_20, Drain

Neutralization

35ºC

100% H_20

2% Sodium Formate – 10`

1% Sodium Bicarbonate – 80`

Drain, Wash 200% H_20, Drain

Fatliquoring

50ºC

100% H_20

8%* Fatliquor – 120`

2% Formic Acid – 60`

Drain, Wash 200% H_20, Drain

Dyeing

35ºC

100% H_20

3% Acid Brown – 60`

1% Formic Acid – 60`

Figure 13 - Application formula for the cattle samples.

3.2.2. Application in sheepskin

The skin of an animal is a highly heterogeneous material making it sometimes difficult to consistently compare results brought from different samples. (6) So, to reduce this influence, to act as reference for the sheepskin application, a considered average product, FF 51, was selected. In Figure 14 we can see the application diagram with the processes underlined and the control procedures highlighted in green.

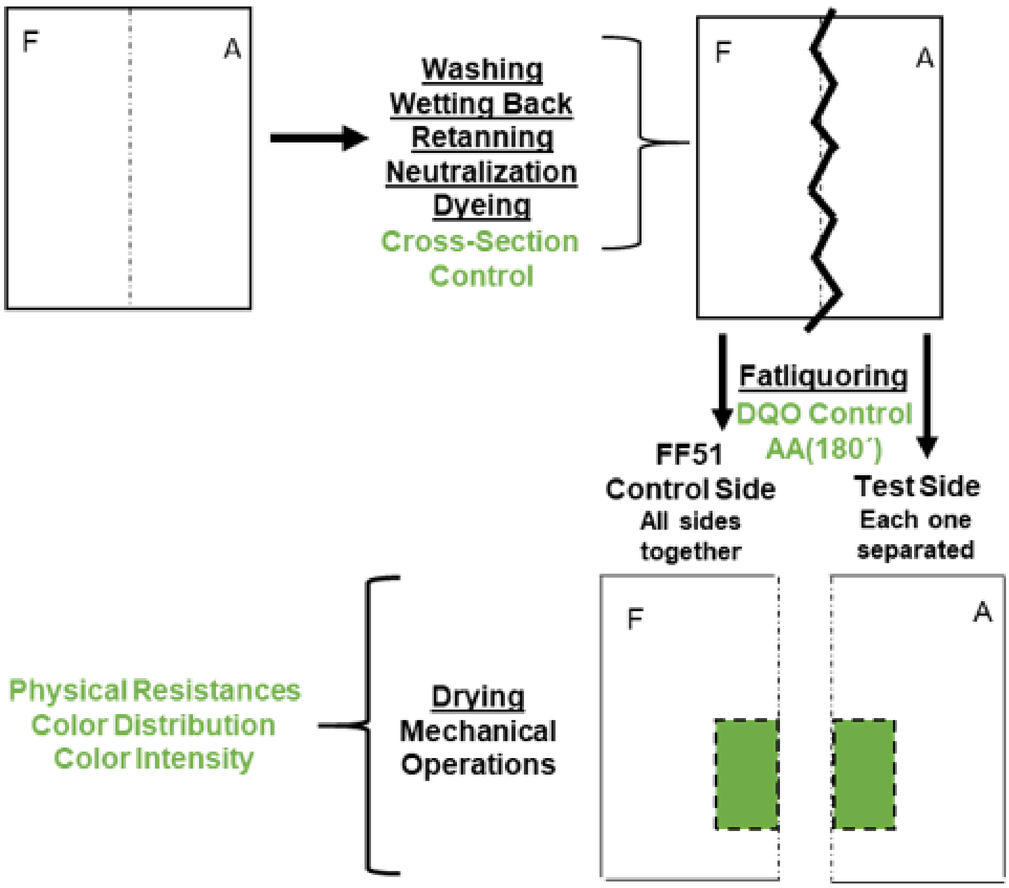


Figure 14 - Application process and analysis diagram for sheepskin. (Analysis underlined, and control procedures highlighted in green)

Each sheepskin was divided in two halves separated from the back; the right side(A) is to be introduced to all the different products while all the left halves(F´s) will be fatliquored together with FF51 in the exact same conditions. The point of this design (Figure 14) was to allow the comparison of all the trials conducted in sheepskin with an “average” fatliquor instead of comparing them with the absence of one, which would create inflated results thus significantly making it harder to compare. Once again, a sample without adding any product was also prepared and submitted to all the tests and in the same conditions.

SHEEPSKIN FORMULA

Washing

35ºC

200% H_20

0,2% Acetic Acid

0,5% CELESAL DL – 20`

Drain, Wash 200% H_20, Drain

Retanning

40ºC

100% H_20

2% Sodium Formate – 30`

4% RETANAL RCN-30 – 40`

4% Sodium Bicarbonate – 60`

Drain, Wash 200% H_20, Drain

Neutralization

35ºC

100% H_20

2% RETANAL NS – 10`

1% Sodium Bicarbonate – 60`

Drain, Wash 200% H_20, Drain

Dyeing

35ºC

100% H_20

2% RETANAL D-57

2% RETANAL HD – 30`

3% Acid Brown – 45`

1% Formic Acid – 60`

Drain, Wash 200% H_20, Drain

Greasing

50ºC

100% H_20

0.3% Ammonia – 10`

8%* Fatliquor – 120`

2% Formic Acid – 60`

Figure 15 - Application formula for the sheepskin samples.

The photographic record of the sheepskin samples, due to lack of resolution, were not included and the application formula can be seen in Figure 15.

The sheepskin had a different purpose. Besides being one of the two most commonly used types of skin, (10), this product will face an industrial process, so it is essential to take in account how it reacts in this setting and evaluate certain characteristics in those conditions as well. The formulation, as can be seen in Figure 15, for the sheepskin included the usual retanning step (RTN RCN-30) and neutralization aid (RTN NS) which helped in the fatliquors penetration and distribution. A reference sample was also processed without adding any product and submitted to all the same conditions and analysis.

4. Characterization of fatliquoring products

4.1. Chemical Analysis

4.1.1. Product Hidro-Lipo balance

These products consist of 3 main parts: a charged part, a neutral oil and water. Of course, we are simplifying the concept as it is important not to forget that these are highly formulated products. The ratio between the anionic and neutral fraction is very important and will dictate certain characteristics of the product. These will vary according to the type of oil used and formulation applied. As the leather dries, the interfibrillary water is expelled, allowing the fibers to come closer, giving place to a certain level of interaction and so it is essential to prevent this from happening. The presence of a neutral oil will prevent the structure from resticking as it dries and that is the main purpose of fatliquoring. (1) (4) (21)

Therefore, for each of the products used, both the emulsified (neutral oil) and emulsifying (anionic part) fractions were determined. The method used is called Panzer-Nibuer and allows an effective separation of the emulsifying components from the neutral oils. This method consists in a simple liquid/liquid separation using approximately 90 mL of a 1/1 mixture of Petroleum Ether and Isopropanol/Water (1/1) thoroughly mixed with 5/7 grams of sample, being the neutral oil soluble in the ether fraction.

Once separated both parts are recovered and dried at 100 ºC until all the solvents are evaporated and only then weighted. The results are expressed in % over mass of product. The sum of both parts is defined as the active material of the product. The results of this procedure can be seen in the Table 2.

Table 2 - Results of the Hidro-Lipo balance determination for each product.

*Total obtained via internal records as comparison purposes.

Product	Hidro-Lipo Balance (%)				
	Neutral	Anionic	Ratio(N/A)	Total	Total*
FF AUTC3	37	32	1.14	69	70
FF 50	41	31	1.33	73	75
FF SC-10	34	33	1.04	67	67
RTN PR-165	28	26	1.09	54	55
FF DF20	51	23	2.17	74	75
FF 51	43	28	1.54	71	70
FF SC-20	26	23	1.14	48	50
RPL HC	19	10	1.88	29	30
FF AUT	45	24	1.88	69	70
FF CL	27	22	1.24	48	47
UNIX S3	34	21	1.60	56	56
FF AUT 09	57	33	1.73	89	90
FF LC80	68	22	3.11	90	90
UNIX UP	35	21	1.71	56	56

The main formulation of these products considers a lot of aspects such as the product conservation along time, ease in manipulation and as well as other quality factors. As can be seen in Table 2, according to the nature of the product, the ratio´s vary as well as the total % of active material. Some products such as the RPL HC require a bigger quantity of water in the main formulation due to its high viscosity, while others such as FFLC80 is quite the opposite since being lecithin derived, it needs a high content of neutral oil as well as a generous amount of its emulsifying counterpart. In general, all these products have a ratio neutral/anionic over 1.

4.1.2. Evaluation of product penetration in leather

When applying any product its characteristics will influence the way it penetrates the skin. The size and stability of the emulsion is strongly connected to the depth of penetration and an optimum ratio between these two parameters must be meet in order to create an effective product. (1) (4) Staining techniques can be applied to visualize the extent of these products penetration, and because we are facing products with two distinct fractions they must be differentiated since each plays a different role in this context. The emulsifying particle negatively stabilized, would readily react with the cationic wet-blue if a neutralization wasn´t previously performed, making it stay in the bath. (1) (22)

At the end of the fatliquoring process, a portion of each sample was kept in a wet state, and after mechanically drying as well, and both were submitted to the staining techniques.

4.1.2.1. Staining of the anionic fraction

A Methylene Blue solution can be used to stain the anionic fraction in cross sections of skin. Besides being a good indicator of how it penetrates the skin it can also be used as a control procedure during the process. This test consists in submerging a freshly cut piece of the sample in the methylene solution for about 10´, after which is rinsed thoroughly with fresh water. The results, for all the samples, can be seen in Figure 16.

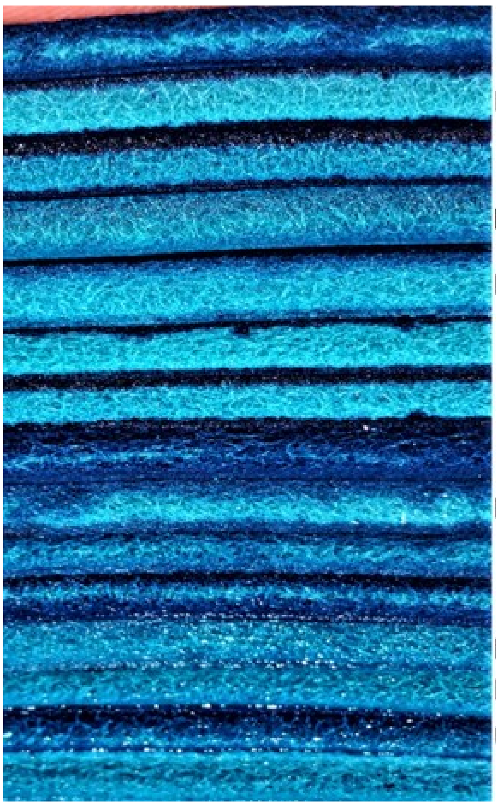


Figure 16 - Pile of all the wet cattle samples submitted to the Methylene Blue staining test for visual comparison.

4.1.2.2. Staining of the neutral fraction

The other part that constitutes these products is a neutral oil. This part is thought to be the main responsible for lubricating the fibres once they dry, since the anionic part is thought to be mainly present to allow the neutral oil to penetrate the skin in an efficient way. (1)

Therefore, a method of staining these neutral fractions was devised, by improving an old internal method, to understand the differences between the way each part moves within the fibrous structure.

The neutral part is, in a way, very similar to triglycerides, (4) and the usage of a compound with high affinity for them was a good start. There were several dyes that fitted this goal, but the Sudan IV (23) was the one suggested by the internal method and thus readily available. A good characteristic of this dye, is that it stains big neutral molecules with a bright red thus providing a good resolution.

A suitable solvent that could solubilize it was also important. In the internal method, alcohol-based solvents were used but the results they brought weren´t satisfactory once tested, bringing a pale stain and low staining times. By the literature, we were suggested to use Propylene Glycol, (24) which besides being cheap, is friendly to use and has been used to stain fat neutral molecules by different techniques.

Several tests were conducted with different concentrations of dye, different temperature conditions and contact times between the solution both in wet and mechanically dried samples. The optimization of this method was not only made to assure the best possible results but also aimed to make it easy and fast to use. The results, which can be seen in the Figure 17 and Figure 18, were very satisfactory and thus the optimized method was implemented.

Figure 17 - Pile of all the mechanically dried cattle samples submitted to the Sudan IV staining test for visual comparison.

When the emulsion breaks both parts get deposited in the fibres but don´t share the same fate, as the neutral oil will remain almost immobile until the interfibrillary water is removed. (4) Besides by physical interaction, these emulsions will also break due to the interactions with the cationic groups of the skin. On the other hand, the anionic part is free to interact with the fibres and bind itself to the cationic groups that still reside within the structure. Once the baths pH is lowered, the availability of the positively charged groups increases, the emulsion stability lowers and so most of the anionic fraction present will react in those active areas. (4)

Later, the degree of penetration, was expressed as a % result of the sum of the %´s of penetration from each side (flesh and grain), as can be seen in Figure 18 and the table with the specific %´s for each sample can be found in Annex 2.

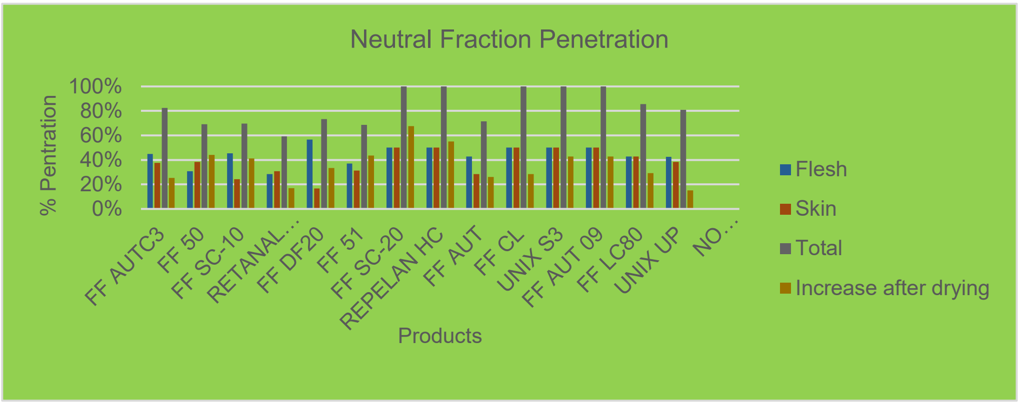


Figure 18 - Graphical representation of the percentage of penetration of each product´s neutral fraction. By flesh, grain and the percentage increase after drying.

4.1.3. Chemical Oxygen Demand

These products interact with the leather mainly during the fatliquoring stage and so it is important to understand their behaviour throughout this process. Still, it is also essential to control and measure the levels of organic matter in the residual waters due to their pollutive capability and to assess product exhaustion. We can monitor those amounts, using the Chemical Oxygen Demand - COD, which allows to determine the concentration of organic matter in water samples with very few conditionings, in our case.

The COD, is the mass concentration of oxygen equivalent to the amount of dichromate consumed by dissolved and suspended matter when a water sample is treated with that oxidant.

The method used for the determination of the chemical oxygen demand (ST-COD) was the small-scale sealed-tube method, in accordance to the *ISO 15705 - Water quality — Determination of the chemical oxygen demand index (ST-COD) — Small-scale sealed-tube method* and under consideration of the *ISO 6060:1989 - Water quality — Determination of the chemical oxygen demand*. This method oxidizes almost all types of organic compounds and most inorganic reducing agents. It is fair to say that the ST-COD value of water can be considered a very realistic determination.

For each application in cattle, a small and constant portion of the water bath at 5´, 55´, 120` and after acid fixation, at 180 was sampled for study.

From each decanted sample, a portion was collected, to remove the bigger particles, such as leather fibres, as they would in a usual water treatment procedure, and because they could interfere with the results. Since our samples exceeded 1 g/L, each was diluted 100 or 1000 times, depending on the provenance, in order to fit in the concentration interval in which this method can be applied (0,005-0,15 g/L).

The results of the application in cattle were normalized and expressed in percentage and can be seen in the Table 3. At 5 minutes in the process, the product has just been added and so is still mixing with the water and warming up, so we consider that, at this time, 100% of the product is still in the water. At 120´ is when the formic acid is added, and at 180´, after pH adjustment when necessary, the process is ended. The graphical representation for this study can be found in Annex 2.

Table 3 - Results of the COD study along the application process on cattle, at 5´, 55´,120´ and 180´.

Product	5´	55´	120´	180´
FF 50	100%	13%	13%	13%
FF 51		23%	19%	16%
FF AUT C-3		52%	28%	14%
FF DF-20		57%	54%	40%
FF AUT		27%	20%	14%
FF AUT-09		97%	77%	65%
FF CL		77%	47%	8%
FF LC-80		89%	88%	84%
FF SC-10		33%	19%	16%
FF SC-20		71%	50%	27%
RTN PR-165		84%	59%	49%
RPN HC		75%	59%	31%
UNIX S-3		83%	73%	64%
UNIX UP		95%	64%	47%

Some products seem to be more affected by the addition of the acid. This acid is added with the purpose of fixating the product in the skin by lowering the pH from 5-6 to 3,5-4. (1) This also influences the state of the product still present since lower pH conditions break the emulsifying ability of the anionic fraction. It is important to assure that there are no conditions for the neutral part to be remulsified as it would risk being removed during the drying process for example. (4)

In terms of exhaustion, as can be seen in Table 3, the sulphated oils, FF50 and FF51, lead with exhaustions of 80%. Followed by two sulfited oils, FFAUTC3 and FFAUT, a lectican based oil FFCL and the sulphoclorated oils SC-10 and SC-20. Generally, there isn´t a clear relationship between the type and COD behaviour, unless for FF50-FF51 and FFAUTC3-FFAUT which can be explained by their similarities not only in the type of oil but also for the formulation itself. The products RPL HC and RTN PR165 are not core greasing products and so are expected to behave differently as well as show distinct results.

The rate at which each product exhausts is also an important factor . (8) To evaluate this parameter, we looked at the slope of the graphical representations, that can be found in Annex 2, of the COD variation for each product which was a good indicator of how each product exhausts along the process, as can be seen in Table 4.

Table 4 - Rate of product exhaustion, based on the cattle application, from 5´-120´ and 120´-180´.

Product	Cattle	
	Slope/100	
	5`-120`(a)	120`-180´(b)
FF 50	7.3	0.0
FF 51	7.0	0.0
FF AUT C-3	4.0	6.3
FF DF-20	3.8	2.3
FF AUT	6.7	1.0
FF AUT-09	2.1	2.0
FF CL	4.6	6.5
FF LC-80	1.0	0.7
FF SC-10	6.8	0.5
FF SC-20	4.3	3.7
RTN PR-165	3.6	1.7
RPN HC	3.5	4.7
UNIX S-3	2.3	1.5
UNIX UP	3.3	2.8

The products with higher sensitivity to the acid addition should reveal a higher absolute slope value between 120´ - 180´, and the more gradual the decrease from 5`-120` (absolute slope closer to 3-3.5), the more penetrating power can be expected. We can see that products such as FF50 and FF51 with a very high slope, Table 4 (a), will probably show less degrees of penetration in comparison with the sulfited group of products (except the FFAUT). On the other hand, products such as FFAUTC3 and FFCL show that the acid step, Table 4 (b) has an important influence on the product exhaustion, and consequently will have a great influence in the product penetration.

4.1.4. Extractable fat content

Another step into the understanding of these products is to evaluate the amount of oil that stays within the leather after the process. This procedure also serves an economical and environmental purpose in combination with the COD.

For that, we applied a method of extraction using the Soxhlet apparatus, in accordance to the *ISO 4048:2008* which proposes a method for the determination of the substances in leather which are soluble in dichloromethane and is applicable to all types of leather. It is important though, to remember that not all fatty substances can be extracted from leather since part is, by one way or another, partly bound to the leather.

The results can be seen in the Figure 19 and are expressed in % per weight, and the table with the specific %´s for each sample can be found in Annex 2.

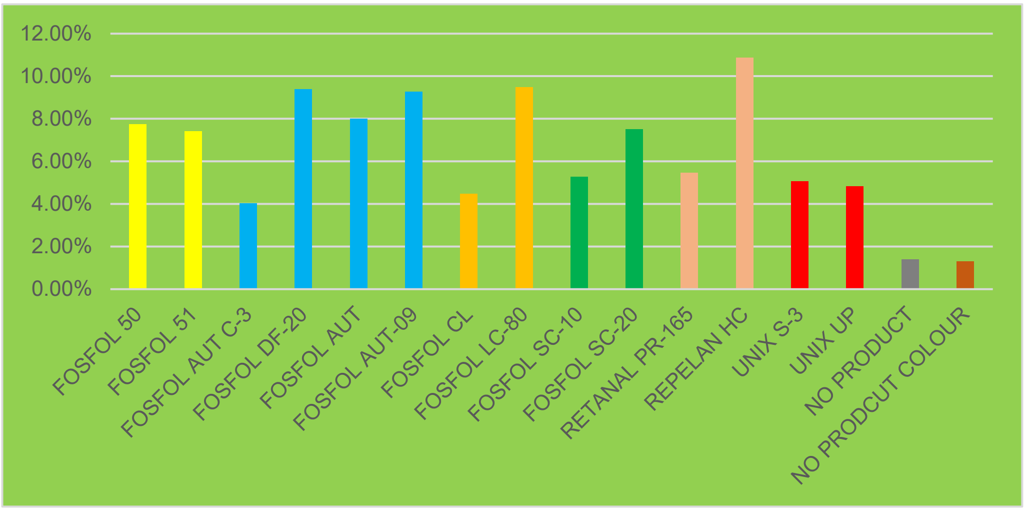


Figure 19 - Graphical Representation of the % of extractable matter from the cattle samples.

This analysis allows us to see how much of the neutral part of the oil ends up in the sample after process and is very important since it´s a good indicator of efficiency and product fixation. As expected, the references a very small percentage was detected which is normal since, even after fatliquoring and tanning, it is usual for the leather to retain some original grease content. The quantity of neutral oil that remains in the skin is essential to guarantee the efficient lubrication, where to low we get to much stiffness and to high and we will get to much looseness. (4) (21)

4.1.5. Particle Size Distribution & Zeta Potential

Another parameter that will greatly improve our understanding of these products is their emulsion particle size and zeta potential in an aqueous medium. These two parameters influence many properties and is a valuable indicator of quality and performance for suspensions and of course emulsions. The smaller the droplet size and the higher the surface charge, the more stability will be conferred to a suspension or emulsion. For many other reasons it is essential to measure and control the particle size and surface charge of these products. (25) (26)

For that, we used a particle distribution and zeta potential determination apparatus called Zeta Sizer NanoS. This device, allows both determinations virtually at the same time and is based on the Dynamic Light Scattering, which measures Brownian motion and relates this to the size of the particles. It does this by illuminating the particles with a laser and analysing the intensity fluctuations in the scattered light. (25) (27)

Particles suspended in a liquid are never stationary since they are constantly moving due to the random collision with the molecules of the liquid that surrounds the particle, and to that we call the Brownian motion. An important feature of Brownian motion is that small particles move quickly, and large particles move more slowly. The relationship between the size of a particle and its speed due to Brownian motion is defined by the Stokes-Einstein equation. (26) (28)

During the process, as the emulsified particles meet with the fibres and penetrate the skin, they gradually lose their stability until they eventually break depositing the neutral fraction on the fibres. When the optimum emulsion size is achieved, the emulsion is at its lowest possible energetic state, and should show the lowest zeta potential value (in the case of our products since the emulsifying fraction is of anionic nature). It is established that, and emulsion is considered stable at zeta potential values over 30 mV, when of cationic nature and under -30 mV, when of anionic nature. (28) To attempt to recreate the conditions in which these products are applied industrially, the tests were conducted at 50º Celsius and approximately 7,7 pH using the same source of water as in the application process.

For each product a stock solution was prepared in the concentration used in the application. Then, a volume of approximately 0,7 mL of the stock solution was introduced in the appropriate cuvete and submitted to both size and zeta potential analysis, in this order. After each determination, the sample was diluted approximately 10 times and the analysis reinitiated. This process was repeated until there was clear evidence (such as an abrupt increase of the zeta potential, the appearance of peaks at higher size intervals, etcetera) that we had reached the individual particle size of the emulsion created by each product.

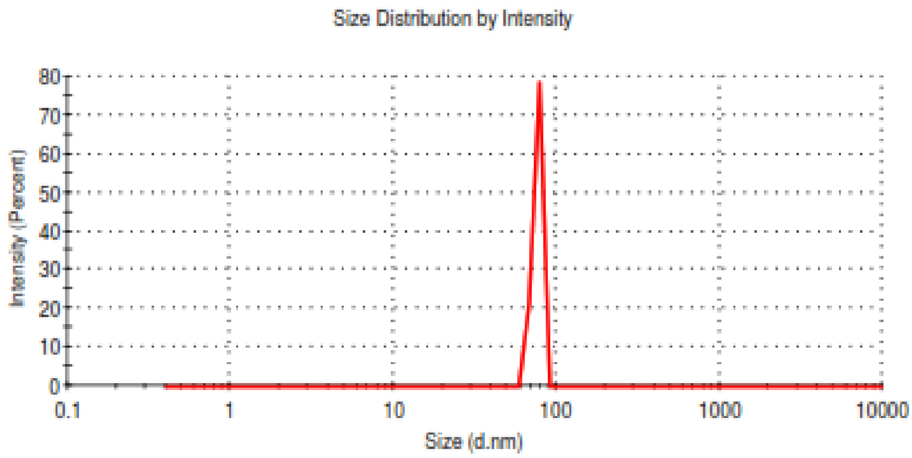


Figure 20 - Graphical representation of the particle size distribution of the product FFAUT09.

The size distribution shown in Figure 20 belongs to the product FFAUT09, shows a very defined and intense peak at 53 nm and another one, so small it can´t be seen visually, at 300 nm. At 50 degrees and 7,7 in the pH scale, we can say that this product won´t create emulsion particles smaller than around 50 nm. A shift in pH completely changes how these products behave when emulsified and its size and potential will be affected. (1) (7)

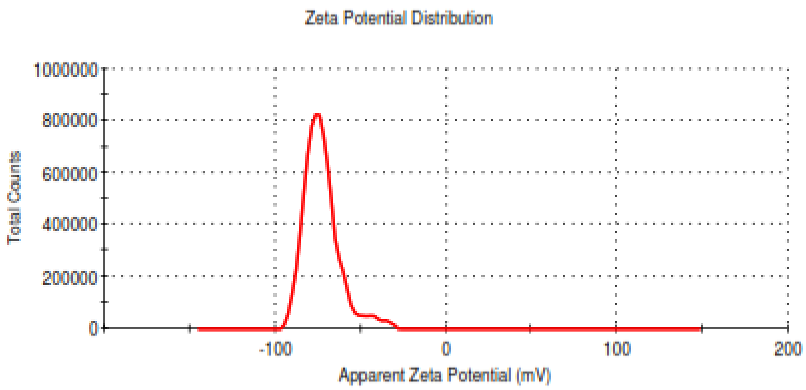


Figure 21 - Graphical representation of the zeta potential of the emulsion particle of the product FFAUT09.

This product showed an average -71 mV, as can be seen in the graphical representation in Figure 21, for the apparent zeta potential.

As expected, with each sample dilution, lower values for both size and potential were detected and when the smallest particle size was achieved, after which further dilutions revealed an increase of the zeta potential as well as size variation in most cases. However, even if the zeta potential lowers it does not means immediate loss of stability. (27) It is known that a secondary minimum can be created at higher potential values, while still maintaining similar stability properties. (26)

The data collected, that can be seen in Table 5, revolved around 2 parameters for size determinations: The Z-Average and Polydispersity Index. The Z-Average is the most representative point for our types of distributions, while the PDI shows us the level of dispersity of the solution. (26) The particle size and zeta potential certainly revealed interesting aspects of these products. All of them show good stability characteristics as expected since they are formulated for such. This stability is essential in these products, so they can resist the entrance in the fibre structure. However, it is important to point out that, very stable and very small sized emulsions are not wanted in our scenarios since over stability won´t allow the emulsion to break and undersized particles won´t interact with the fibrous structure. These limits for both these parameters, size and stability, will vary according to the product. (1)

Table 5 - Results of the particle size and zeta potential determinations for the fatliquoring products.

Product	Size (nm)				PDI	Zeta Potential
	Size 1	Size 2	Size 3	Z-Av		(mV)
FF AUT	51	-	-	52	0.05	-60
FF AUT09	53	300	-	303	0.37	-71
FF AUTC3	42	530	-	43	0.31	-70
FF DF20	49	-	-	50	0.08	-44
FF SC-10	37	160	-	119	0.25	-70
FF SC-20	206	-	-	163	0.21	-91
FF 50	38	165	-	108	0.27	-66
FF 51	39	185	-	140	0.27	-70
FF LC-80	362	-	-	349	0.15	-65
FF CL	268	-	-	307	0.05	-76
UNIX UP	24	184	-	27	0.38	-65
UNIX S3	21	239	-	42	0.56	-70
PR-165	35	193	-	41	0.45	-60
RPL HC	32	305	-	343	0.3	-76

4.2. Physical Analysis

The physical testing is of high relevance to the characterization of any article and serves to evaluate the capacity of leather to withstand all the external stress it will encounter during its transformation to a product and during the product specific use.

The measurements of these physical parameters depend on a lot of factors and so any trial must be done under strict normalizing conditions in which all the practical variables must be clearly fixed. However, due to the complexity and variability of our raw material some level of considerable dispersion is to be expected. (3)

Thankfully, for the regular basis physical analysis, normalizing procedures exist and are of imperative use to assure quality and the least possible level of repeatability and reproductivity.

4.2.1. Fastness to Light&Heat

Fastness is representing the ability to withstand external influences that tend to modify the colour and appearance of a surface. In the case of leather, it can be altered by many factors such as the contact with hazardous substances, mechanical, thermal or light action and of course by processes of washing and cleaning. The fastness trials differ a lot from the chemical ones since they focus on the surface of leather rather them what is within. Fortunately, there are several standards that regulate the implementation of these tests, but still these procedures depend on a lot of variables that must be maintained at all times. (29)

In our study, we focused on the two most important scenarios, the influence of light exposure and the influence of temperature exposure. This analysis was made with the cattle samples (Side E) since we wanted to observe the isolated influence of these two factors in each fatliquor in study.

The action of solar light on leather is induced by several phenomena that can happen at the same time. The clearest outcome is the slow decomposition of the colourants applied, and due to their absorption of UV light. However, other components present in leather, such as fatliquors, resins, retanning agents, etc, can also get damaged by this exposure and by the same reason. (3) All this is accelerated by high temperatures and humidity that by themselves have their own influences on leather, as we will see more ahead. (1)

The fastness to artificial light was made under the accordance with *ISO 2418:2017 Leather - Chemical, physical and mechanical and fastness tests - Sampling location,* and under consideration of both internal and external regulations related to the subject.

Each sample was submitted to colorimetric analysis in 3 different points across the selected area. The results were then rated, from 1-5 based on the DE which represents the difference between the sample and the control sample using the grey scale. The results of both these tests can be seen in the Table 6:

Table 6 - Results of the trials of fastness to temperature and UV light.

PRODUCT	TEMPERATURE			LIGHT		
	DL	DE	Rate	DL	DE	Rate
FF 50	6.00L	6.97	3-4	0.67L	5.48	4-5
FF 51	0.97L	7.52	3-4	1.97L	6.14	4
FF AUT C-3	5.44L	7.94	3-4	4.21L	4.79	4-5
FF DF-20	5.50L	6.18	4	0.91L	2.78	4-5
FF AUT	4.56L	6.18	4	-1.55D	3.83	4-5
FF AUT-09	4.90L	7.00	4	2.14L	4.52	4-5
FF CL	6.64L	9.33	3	1.73L	3.63	4-5
FF LC-80	4.52L	7.26	3-4	2.68L	5.18	4
FF SC-10	3.72L	5.08	4-5	3.31L	4.93	4-5
FF SC-20	5.03L	6.19	4	0.92L	4.44	4-5
RTN PR-165	3.52L	4.88	4-5	0.64L	4.92	4-5
RPL HC	3.35L	4.53	4-5	1.00L	2.23	5
UNIX S-3	-6.75D	6.89	3-4	-1.32D	3.92	4-5
UNIX UP	7.47L	9.25	3	-2.7D	4.73	4-5

When comparing the results with the grey scale, the higher values for rate mean better resistances to each condition and different fatliquors will react differently. The exposure to light causes the components that remain in leather to decompose as more and more UV light is absorbed. In the case of our products, all revealed very good resistance to this this condition, being the best, which visually revealed absolutely no changes, the RPLHC. In the leather making, fatliquoring products are just one of many to be applied, so it is very important that they contribute the least to this phenomenon and the same can be said for temperature. (14)

In the case of greasing products, temperature is a factor that can more easily bring noticeable changes. For example, the presence of compounds with double bonds tend to show less resistance to temperature since they are more easily broken. As expected, the performance in this conditions wasn´t as good as when facing UV light, but still we can say that all performed very well.

4.2.2. Water Absorption

Each product deposits itself in a different way and has a different relationship with water. After being applied, it is an important feature to evaluate the resistance to water absorption which is being created by the presence of the applied product. After a given time of contact between the leather and the water droplet, it is inevitable that it will penetrate the structure but, depending on the product that was applied, this time interval will vary. (30)

For that, we applied a droplet of water and measured how much time it took for it to be completely absorbed.

In this case, the test was conducted with the sheepskin samples, and later calculated the variation between the reference side (fatliquored with FF51) and the test side, expressed as a %, as can be seen in Figure 22. The table with the specific %´s for each sample group can be found in Annex 3.

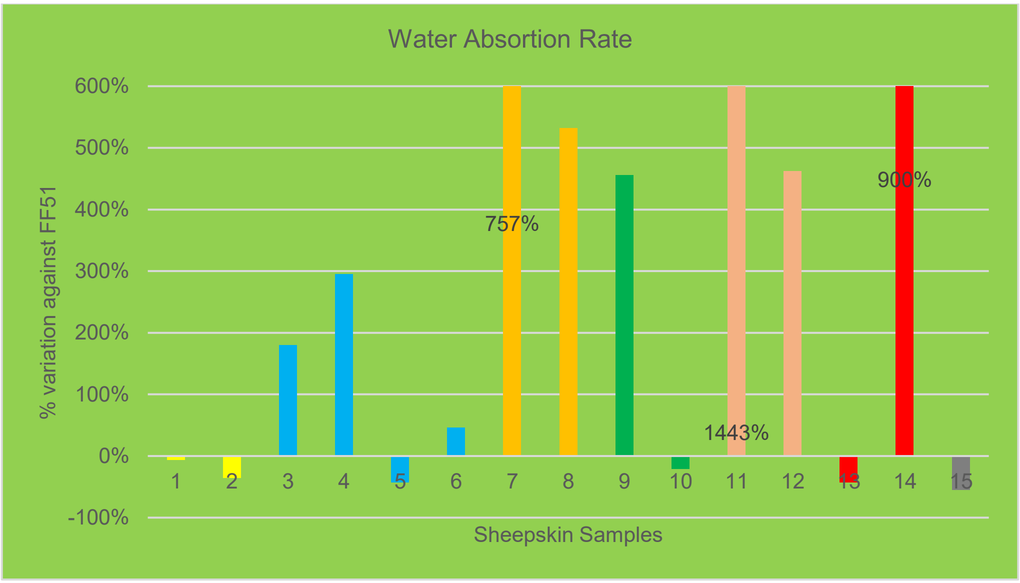


Figure 22 - Graphical representation of the % variation of the water absorption rate on the sheepskin samples.

As can be seen, certain products, provide good hydrophobic properties which is majorly connected to the nature of the products applied. This characteristic is very important when making articles that need to withstand the casual contact with water.

4.2.3. Colour Distribution, Intensity and Penetration

The mechanism that regulates the application of a fatliquor and a dye is similar and, if allowed, competitive. In this study, we used this to our advantage, and studied the colour distribution along each of the sheepskin samples and the colour intensity and penetration degree in each of the cattle samples. While on cattle we applied the greasing product first, which allowed us to see the colour changes created by each product and how each one limits the dye penetration, on sheepskin it was the other way around. (3) (29)

The differences in colour between the sheepskin samples are way subtler, since the dye was applied before the fatliquor and the penetration was complete.

To evaluate the colour distribution, each sheepskin sample was submitted to colorimetric analysis in 18 different points across the whole sample extension, and later calculated the difference between the reference side (fatliquored with FF51) and the test side. Using this analysis model, we can express distribution in a very simple way. The results can be seen in table 7.

Table 7 - Results of the colour distribution trials on sheepskin.

Product		FF51	Product	Average
FF 50	1	1.65	0.01	1.64
CONTROL SAMPLE	2	3.13	1.61	1.52
FF AUT C-3	3	4.71	4.03	0.68
FF DF-20	4	3.51	3.02	0.49
FF AUT	5	1.98	2.26	-0.28
FF AUT-09	6	3.03	2.58	0.45
FF CL	7	2.71	2.10	0.61
FF LC-80	8	2.25	3.17	-0.91
FF SC-10	9	3.03	3.54	-0.51
FF SC-20	10	3.68	3.09	0.59
RTN PR-165	11	3.66	3.13	0.53
RPN HC	12	1.28	0.55	0.73
UNIX S-3	13	5.08	4.86	0.22
UNIX UP	14	2.03	3.61	-1.58

What we meant with this test, was to see how the dye distributes itself along the sample and how the post introduction of the fatliquor influenced the said distribution. The introduction of some certain products can bring improvements, but it can also have a negatives effects. (1)

Firstly, is important to point out, that even using the same product to act as reference, a lot of differences are seen between each of the reference samples. This is because each skin is different and even having the same provenance and treatment, variances are to be expected and must be taken into consideration. This is where the analysis design comes in to play, cancelling this influence and allowing us to see the true impact of the product in study regardless of the limitations imposed by our raw material. Another factor that influences our results, and, of all wet-end processes, is the efficiency of the previous stages, where incomplete or deficient applications can bring unwanted effects. In the sheepskin samples, it was evident after dyeing, that rests of epidermis had been left behind, especially in the perimeter of the sample, where over dyeing was clear. This is because, the acid dye has a strong affinity with the residual epidermis, and when it meets the sample readily fixates. (31)

On cattle, on the other hand, there are big colour differences, because, being the fatliquor already present in the skin, the dye had more limitations on were the get fixed. Evidence of this phenomena can be see when analysing the cross-sections of each cattle sample, much like what we did for the staining tests, which can be seen in Figure 23.

Figure 23 - Pile of dried cross sections of each cattle sample.

It is clear by analysing the picture, that the presence of different fatliquoring products, affects the way the dye penetrates.

The colour intensity was also analysed using the cattle application (Side D). The designated area from each of the cattle sample was submitted to colorimetric analysis in 3 different points and compared with the reference sample and results can be seen in Table 8 (DE value):

Table 8 - Results of the colour intensity analysis on the cattle samples.

PRODUCT	Colour Intensity				
	L	a	b	DL	DE
FF 50	42.17	26.98	34.99	4.54 L	7.74
FF 51	37.16	26.46	29.72	-0.48 D	1.26
FF AUT C-3	46.87	27.47	42.11	9.23 L	16.24
FF DF-20	39.27	26.93	31.68	1.63 L	3.49
FF AUT	44.88	27.65	39.47	7.25 L	13
FF AUT-09	37.7	28.73	30.64	0.07 L	3.53
FF CL	45.22	27.69	41.18	7.58 L	14.61
FF LC-80	35.91	26.77	26.89	-1.73 D	2.84
FF SC-10	38.12	27.82	30.85	0.48 L	2.95
FF SC-20	33.5	26.62	24.67	-4.13 D	5.96
RTN PR-165	42.46	26.57	36.53	4.82 L	9.1
RPL HC	47.82	25.52	43.33	10.19 L	17.7
UNIX S-3	42.46	26.57	36.53	4.82 L	9.1
UNIX UP	41.73	27.01	35.08	4.10 L	7.56
NO PRODUCT	37.63	25.86	38.64	-	-

As can be seen by analysing the table 8, the presence of certain products produces a stronger colouring effect while others, which compete more with the dye, result in a less strong colour. The colour wanted to an article varies according to the destination, but it is very important to assure that the colouring can be reproduced, and to know what to expect when applying different fatliquors combined with a dye. (1)

4.2.4. Thickness

Thickness is a very interesting parameter, commercially and by a scientific point of view since it is essential for the determination of apparent density and mechanical resistances. The measurement of this property in leather depends on several factors such as the pressure and the amount of time that is applied at that pressure. These parameters must be stable and constant in order to achieve the best possible repeatability and reproducibility. (5) (15)

This parameter was determined along this study with a strong focus in the variations of thickness in both cattle and sheepskin.

The application of fatliquors is bound to affect the thickness of the material in one way or another. The measurements were made in accordance with *ISO 2589:2016 – Leather - Physical and mechanical tests - Determination of thickness.*

Once completed the entire process, the sheepskin samples were submitted to measurements of thickness in 14 different points in each side. The results are expressed as a % variation against the reference side fatliquored with FF51, can be seen in the Figure 24, and the table with the specific %´s for each sample group can be found in Annex 3.

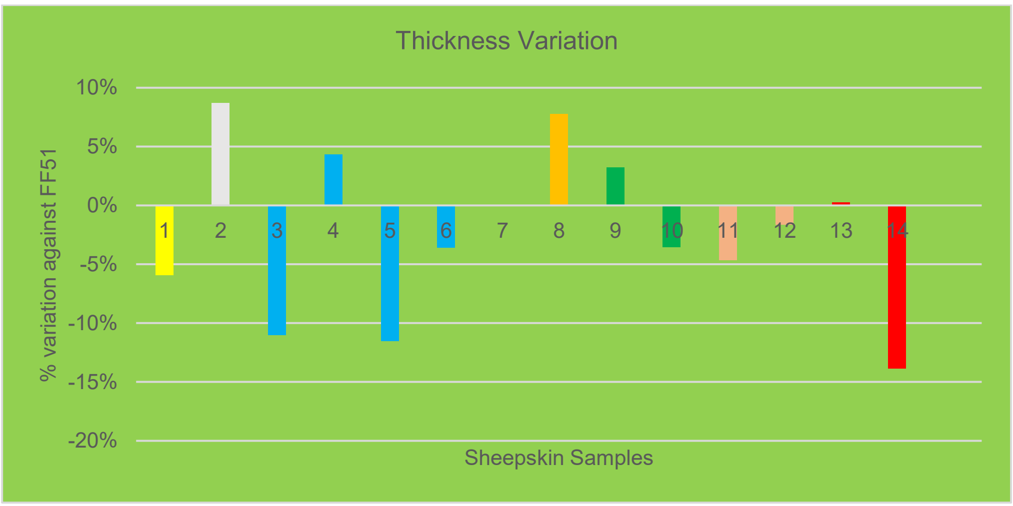


Figure 24 - Graphical representation of the % variation of thickness on the sheepskin samples.

After the wet-end process, a regular increase in the thickness is expected. However, as can be seen by analysing the Figure 24 the results, that the presence of different fatliquors, will produce more, or less increase in thickness. Most of the products produced a similar or lower increase of thickness as did FF51. The nature of the product itself is related to this increase. Some neutral fractions will create a droplet type coating will others create a film type coating so the way the neutral part deposits and binds itself with the leather fibres will influence the length of separation between them. (1)

4.2.5. Softness

The increasing demand from the market for softer and stronger leathers presents a chemical challenge to the leather industry to be able to exploit the full potential of inherent softness imparted to leather by each process from opening to lubrication. (1) (4)

The measurement of softness is essential, and it will ultimately have the user as the judge and it is one of the most important characteristics in study - the variation in softness imparted by each of the products analysed. The measurements were made in accordance with *ISO 17235:2015 - Leather - Physical and mechanical tests - Determination of softness.*

Once completed the entire process, the sheepskin samples were submitted to measurements of softness in 14 different points in each side. The results are expressed as a % variation against the reference side fatliquored with FF51, can be seen in Figure 25, and the table with the specific %´s for each sample group can be found in Annex 3.

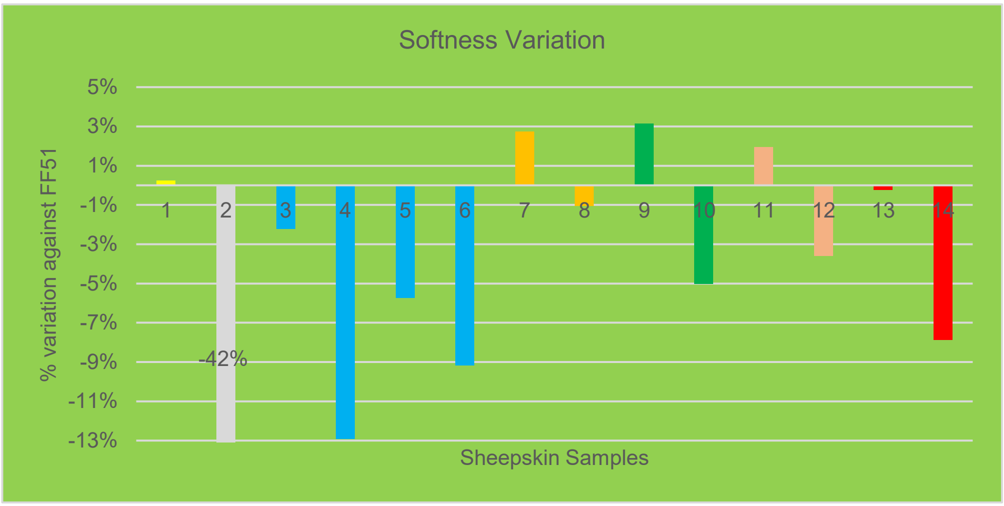


Figure 25 - Graphical representation of the % variation of softness on the sheepskin samples.

It is completely clear that the presence of a fatliquor greatly improves the softness of the article in an average plus 40%. Overall, the product used as a reference for these trials, the FF51, revealed quite good softening characteristics, however certain products as the FF CL, FF SC-10 and RTN PR-

165 bested this sulphated derivative. On the other hand, FF DF-20 was the one that revealed more negative differences, -13%, but overall the results oscillated between -13% and 3%.

This property however can´t only be seen from this mechanical point of view being this just a part of what classifies the softness in leather. Later, only if combined with the organoleptic test for softness we can achieve a more representative result regarding the softness of each article. (1)

4.2.6. Physical Resistances

Strength is a definable trait, since it is reflecting the ability of leather to resist breaking or tearing stress or in other words, the ability of the material to dissipate stress over its volume by movement of the fibre structure. For this to happen certain criteria’s must be meet. Firstly, the fibre structure must not be stuck together after drying and this structure must also be sufficiently lubricated to allow these elements to slide over one another. (1) (15) (12)

In this study we investigated 3 important aspects of mechanical resistances in leather: Tear Strength, Tensile Strength and Percentage Elongation and Distention and Grain Burst. These test methods are excellent for development, control, specification acceptance, and service evaluation of leather and are related to other properties that are being studied.

Not only during use but also during fabrication, leather will sustain several types of stress and it is important to guarantee that our final product meets the required standards according to the type of industry that it is meant to be. (29)

The orientation of the specimen in relation to the backbone and the location of the specimen on the hide influence the results significantly.

4.2.6.1. Tear Strength of Leather

The measurement of this property is used to evaluate the capability of a certain leather to withstand multidirectional tension. This type of resistance is specially wanted in articles that are to be sewed for example, or in pieces that will have holes. (1)

This parameter was determined under the accordance with *ISO 2419:2012 - Leather - Physical and mechanical tests - Sample preparation and conditioning; ISO 3377-2:2016 Leather - Physical and mechanical tests - Determination of tear load: Double edge tear*. The results were then expressed, as always, as a % variation against the reference sample(FF51) and can be seen in Figure 26, and the table with the specific %´s for each sample group can be found in Annex 3.

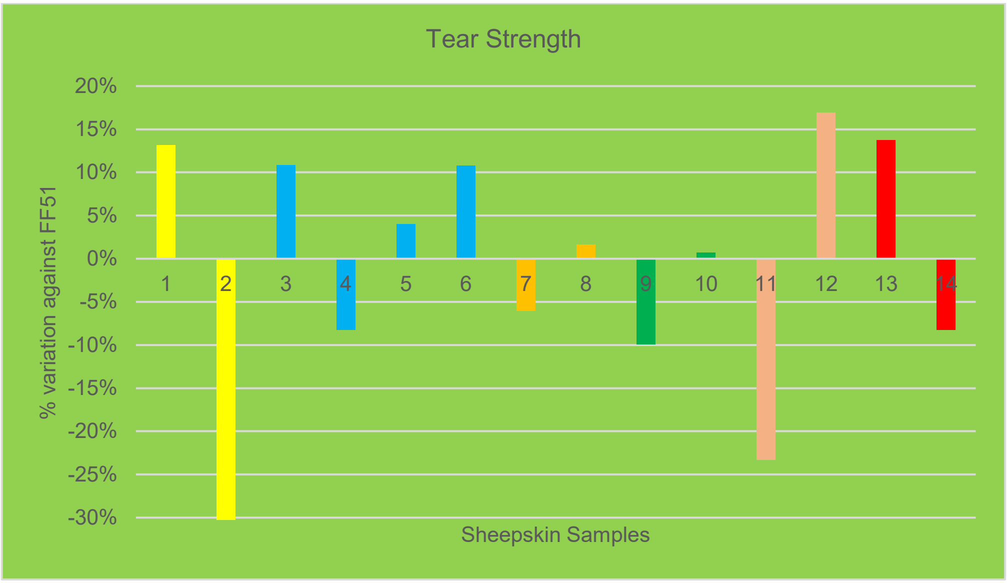


Figure 26 - Graphical representation of the % variation of tear strength, by double edge tear, on the sheepskin samples.

4.2.6.2. Tensile Strength and Percentage Elongation

The tensile strength test gives a reliable indication of the quality of the leather and it is found that improperly lubricated and partially degraded leathers will give low values for tensile strength. (1)

This parameter was determined under the accordance with *ISO 2419:2012 - Leather - Physical and mechanical tests - Sample preparation and conditioning; ISO 2589:2016 - Leather - Physical and mechanical tests - Determination of thickness; D2209:2010 - Standard Test Method for Tensile Strength of Leather;* and *D2211 - Test Method for Elongation of Leather.* The results were then expressed, as always, as a % variation against the reference sample(FF51) and can be seen in Figure 27, and the table with the specific %´s for each sample group can be found in Annex 3.

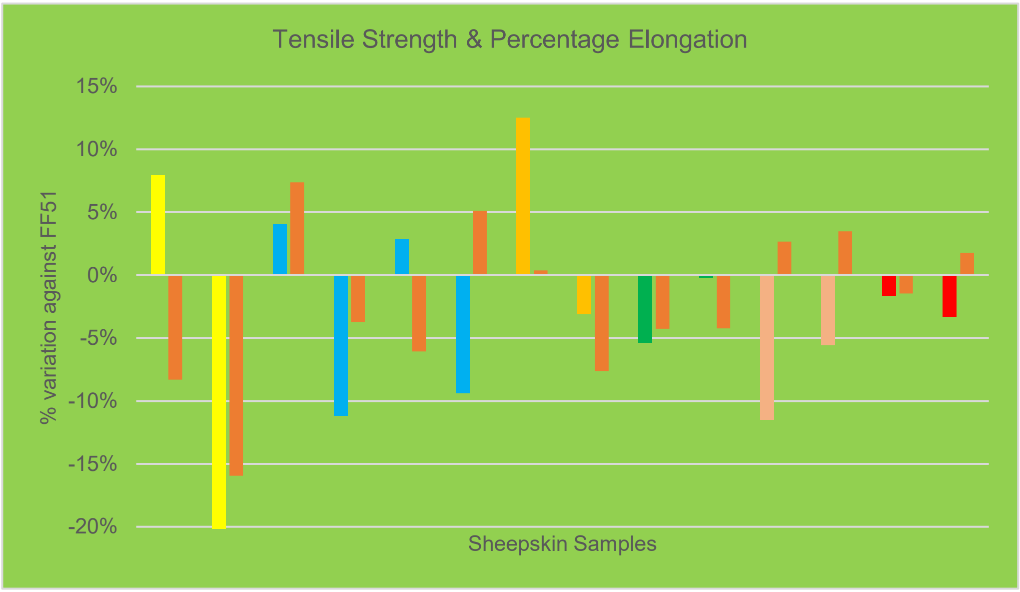


Figure 27 - Graphical representation of the % variation of the Tensile Strength and the Percentage Elongation on the sheepskin samples. ´

Again, the sample where no product was applied stands out quite significantly, showing a minimum of 17% less tensile strength and 8% less elongation that it´s fatliquored counterparts.

4.2.6.3. Grain Burst

This property shows the resistance that a sample has to the burst of the grain and it was made under the accordance of the *SLP 9 (IUP/9; BS 3144: method 8) – Measurement of Distension and Strength of Grain by the Ball Burst Test* and the results can be seen in Figure 28, and the table with the specific %´s for each sample group can be found in Annex 3.

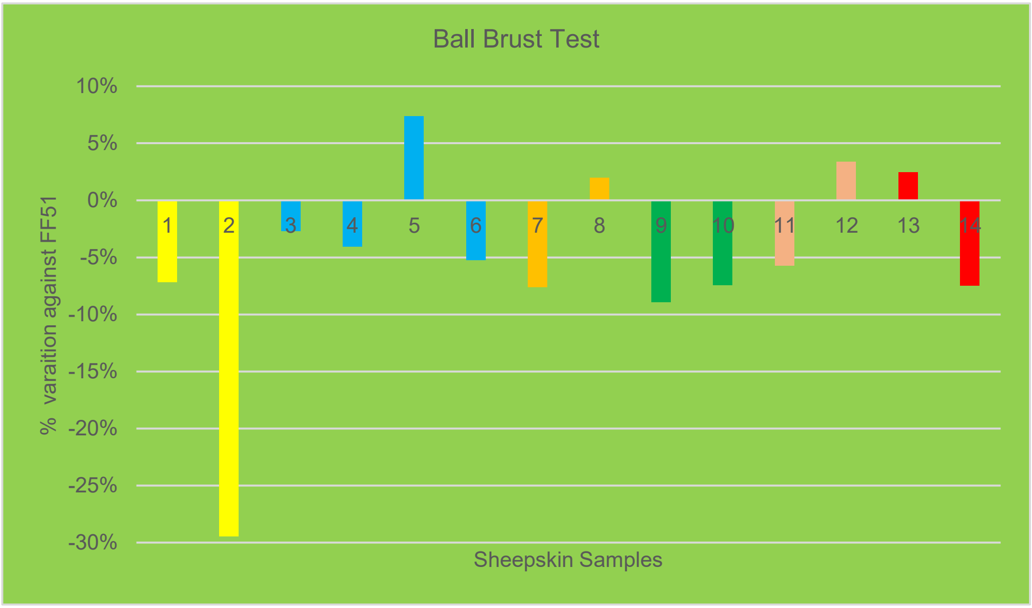


Figure 28 - Graphical representation of the % variation of distension, by the Ball Burst Test on the sheepskin samples.

This analysis can be related to the way the product distributes itself along the sample during application and so, a good distribution should be synonym of better resistance to this property.

5. Discussion

Until this point, we have been presenting the results and some additional comments regarding each topic but in the end all these properties relate to each other and it was also the goal of this study to compare them and see how they relate. Of course, some relationships are harder to present than others specially because we are working with a very heterogenous material. Because of this, there was a very strong focus along this project to reduce every factor that could taint the results and rend them incomparable. Each product ultimately showed its character and prove its capability to provide consistent and quality properties to the leather.

It is important at this point to remember that this discussion has a comparative base-line, and so it should never be viewed in an absolute way but always in comparison with other products and only when valid. In the sheepskin application, the FF51 was used to draw the base-line of comparison, that by itself already creates a result that meets the average standards.

5.1. Product Overview

The control sample with no product added, both in the cattle and the sheepskin application, was a good indicator on how important fatliquoring is to the entire process, especially to acquire certain properties such as softness and tear and tensile strength and to develop hydrophobicity. The control sample showed the poor performance we would achieve in every aspect by not properly fatliquoring a skin and how difficult it would be to develop the necessary quality standards.

Starting with the sulphated group, the FF50 and FF51 have similar characteristics and even showed very similar particle size (38,165 nm and 39,185 nm, respectively) and zeta potential values (-66 mV and -70 mV, respectively). Their retained fat contents are very alike (7.75% and 7.42%, respectively) and they both performed very well along the process reveling excellent exhaustion capacity, over 85%. However, both showed a very rapid decrease of product in the bath during the first 120 minutes. This rapid absorption of product showed its effects when analyzing the staining results, where both showed 2 of the lowest % of penetration (69%) among our products meaning it only had penetrated halfway. This was a result of the rapid penetration and early breakdown of the emulsion, that didn´t allow the neutral fraction to penetrate any further. This is not necessarily a bad trait however, since most products are not used alone in the process but usually in combination with other fatliquors, fillers, resins, etc. (1)

In terms of physical properties, FF50 performed much better than FF51 and even showed the best colour distribution of all our products (close to 0), very good tensile (+8%) and tear strength (+13%) as well as very good fastness to light (4-5) and moderate/good (3-4) to temperature. As these products are very similarly formulated and have the same sulphated base, they were expected to behave in a similar way chemically while still showing different results. FF51 played a very important role in this study as it was used as the control sample for the sheepskin application, but despite having been chosen for its "average" properties, it behaved better than anticipated. In terms of softness both performed quite average. (0%, for both)

As for our sulfited group of products they performed very nicely in terms of product penetration(, which is common for this type of oils. (29) In terms of emulsion size, we found that it ranged from 42-53 nm and both FFAUTC3 AND FFAUT9 show a bigger peak at 530 and 300 nm, respectively. In this case however, the presence of two possible emulsion sizes has apparently helped in the product penetration making it reach 100%, for the case of FFAUT09.

The leather´s fibrous structure is complex, and the deeper we go inside it, the smaller the pathways for the emulsion particles become (1) and so having two possible emulsion sizes might increase the chances for this specific product to effectively penetrate a fuller extent of the structure. In this context, the FFAUTC3 stands out for its low retained fat content, (4,03%) in comparison to the rest of this group (around 8%) and even to the whole range of products in study (averaged at around 7,06%), but this is understandable since this is the product that has the lowest neutral oil fraction (37%). In terms of softness, FFAUTC3, FFAUT and FFAUT09 are among the best being only bettered by FFCL and RTNPR165, as we will discuss further.

In this group we also find the lowest zeta potential value along our products, -44 mV, belonging to the FF DF20 being a result of a single, small sized (49 nm) and narrow (PDI=0.08) particle distribution. This value is -20 mV lower than average but doesn´t seem to affect the performance of this product, maybe since even at a low potential, the particle was still able to function, at a size of 49 nm, making even a very monodisperse field and retaining the necessary conditions for its utility. This product, in terms of softness, performed reasonably (-13%) but still on the bottom of the ranking.

In terms of physical properties, the sulfited group performed quite over average. The product FFAUTC3 stands out for its very good tensile (+4%) and tear (+11%) strength properties, followed by FFAUT (+4%) while on other hand FFDF20 performs quite under average (-8%).

So, the next two products are the FFCL and the FFLC80, and they are indeed both a lecithin derived. Despite the similar origin, and apart from the size and zeta potential results, the product penetration and the hydrophobicity, the rest of the properties in study were almost always quite different, ranging from completely different exhaustion behaviours, different retained fat contents (4.48% and 9.48%, respectively), different physical resistances. It terms of softness, FFCL wins the best spot, since it ranked first in the handle tests, conducted internally during this project in Cromogenia, and in the mechanic evaluation of the softness in leather, while FFLC80 gets a quite average position on this matter (-1%) also performing very poorly in the colour distribution tests in sheepskin (-0.91).

In terms of physical properties, FFCL stands out for its outstanding tensile strength (+13%) and hydrophobicity (+757%) while, again, FFLC80 achieves under average results the first while showing over average value in the latter. Despite having been one of the best performing products in several areas of this study, FFCL reveals all this even with a very low retained fat content (4.48%) and without losing its great exhaustion capacity (92%).

As for the sulphoclorated group, FFSC10 and FFSC20 performed in an average/low way, in comparison with the rest of the products, bringing also poorer softness. On the other hand, both showed outstanding fastness to both temperature and light (4 and 4-5, respectively) and good product penetration (70% and 100%, respectively). Between them however, FFSC20 tends to perform better in terms of physical resistances, colour distribution and showed very good hydrophobicity. In terms of zeta potential, FFSC20 stands out for its -90mV, which is the highest detected for these products. Indeed, this product is known for its exceptional stability as a product, which comes to be seen during this analysis.

The next group is not part of the conventional fatliquors. In general, these two products performed averagely. Despite having penetrated the least (59%) among our products, RTN PR165 seems to have done a very good job in creating outstanding hydrophobicity (the best in this study, +1443%) and second best in softness tests (+2%), while having an under average fat content (5.46%) and very good fastness (4-5). However, concerning physical properties it performed very poorly specially with tear strength (-23%). On the other hand, RPLHC stands out with the best results for tear strength (+17%) showing good hydrophobicity (+463%), excellent fastness properties, the best in the case of light (5) and very good job in aiding the colour distribution (+0.73) but has the highest retained fat content. (10.86%)

Last, but not least, the synthetic fatliquors. These two products are quite different from the rest since they are made with purely synthetic materials. In terms of particle size these two products stand out as the smallest and average zeta potential. In this study, the smallest particle size detected was for the emulsion of the UNIX UP, at 27 nm. In terms of exhaustion, they seem to have a steady controlled rate and reasonable acid dependence. As already mentioned, all these products are highly formulated, and these two stand out for its very good emulsion stability along time, as we saw during the particle size and zeta potential trials. In terms of penetration, we achieved 100% in the case of the UNIX S3, while on UNIX UP only 81%, which might be the result of a more slow and steady exhaustion in comparison with UNIX S3. In terms of physical properties, UNIX S3 revealed the second-best result in the tear strength trials (+14%), outstanding fastness to light (4-5) and average to temperature (3-4), while UNIX UP showed an excellent resistance to water (+900%), but an average/low in the rest of the trials.

Overall, the trials went very well. As already stated before, we tried to see if there were any relationships between the properties we have studied. The first we going to look at is the relationship between softness and tear strength. (4)

To evaluate this, we compared the data from the trials in sheepskin, as can be seen in the Figure 29.

Figure 29 – The graphical representation of the softness and tear strength results, on sheepskin, side by side for comparison purposes.

At first sight the relation might not be obvious but looking closely we can see that there is a clear tendency for better softness when there is lower tear resistance. Next, we looked at the relation between tensile strength and the thickness variation of the sample.

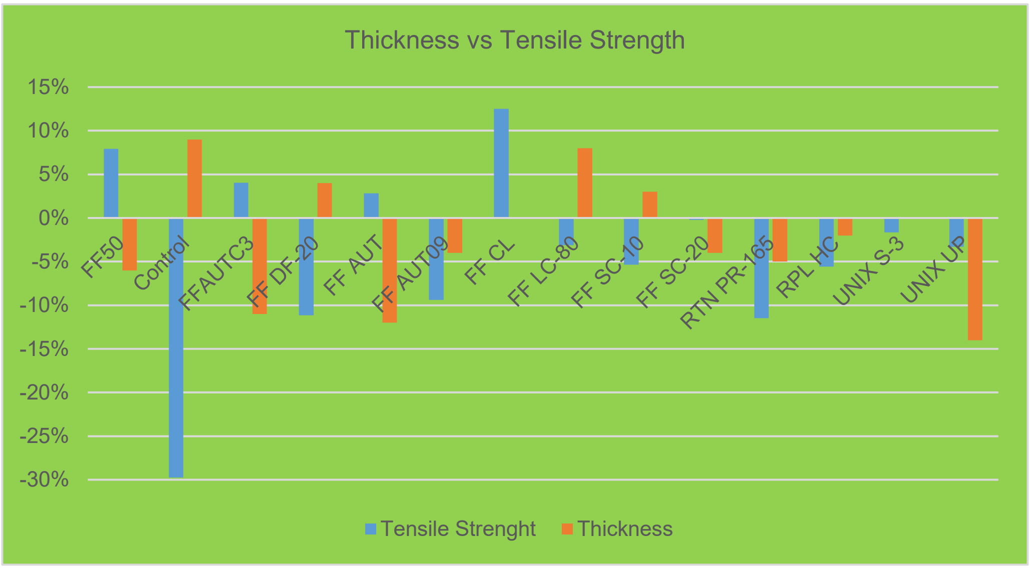


Figure 30 - The graphical representation of the variation of thickness and tensile strength results, on sheepskin, side by side for comparison purposes.

In the case of the sulphated and sulfited products, as can be seen in Figure 30, there seem to be an inverse relationship between these two properties, where we find that increased thickness is an enemy of good performance in terms of tensile strength. On the other hand, the same doesn´t seem to be true for the rest of the products.

One last comparison that was made, was between the wet and mechanically dried samples submitted to the Sudan IV staining test devised in this project as can be seen in Figure 31, side by side.

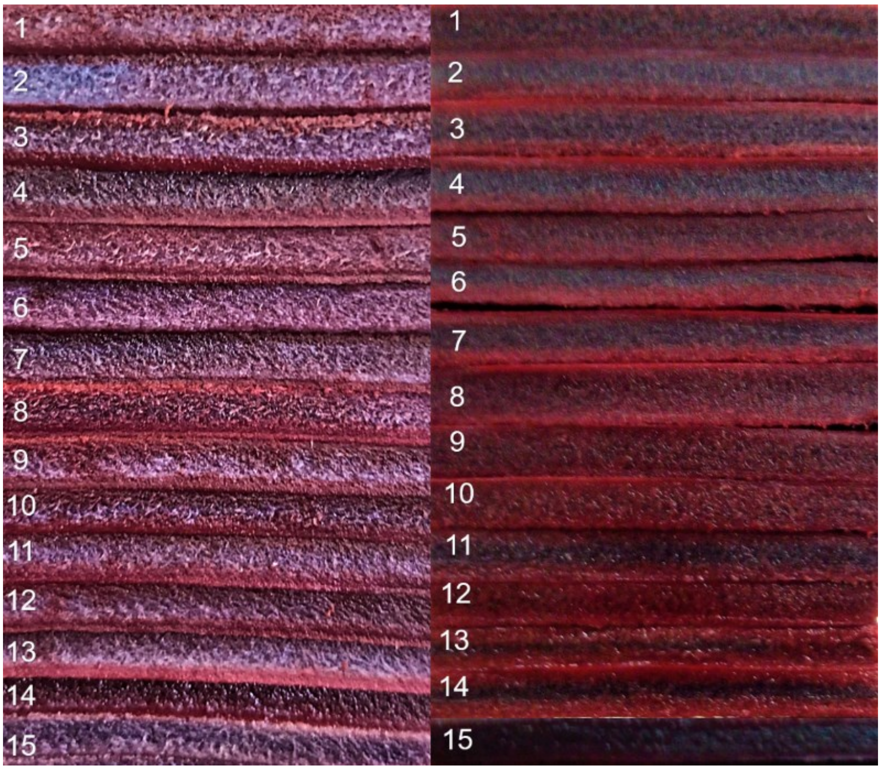


Figure 31 - Pile of the cattle the samples submitted to the Sudan IV staining test before(on the left) and after(on the right) drying for visual comparison.´

During this process the neutral part of the oil, which until now was immobile due to being surrounded by water, apparently further penetrates the cross section of the skin. This increase was registered and can be a very important data since it can say a lot about the nature of the neutral fraction of the product.

The neutral fraction apparently finishes penetrating the skin during the drying process and this shows the importance that this next step has in maximizing the effects of the previous stages specially fatliquoring. In general, the products penetrate either by the same extent on both sides or, slightly more from the flesh side, which is normal since on this side the fibrous structure is more relaxed and loose.

It is also clear by comparing the results of the staining tests from both fractions, as can be seen in Figure 32, side by side, that each part penetrates the skin differently.

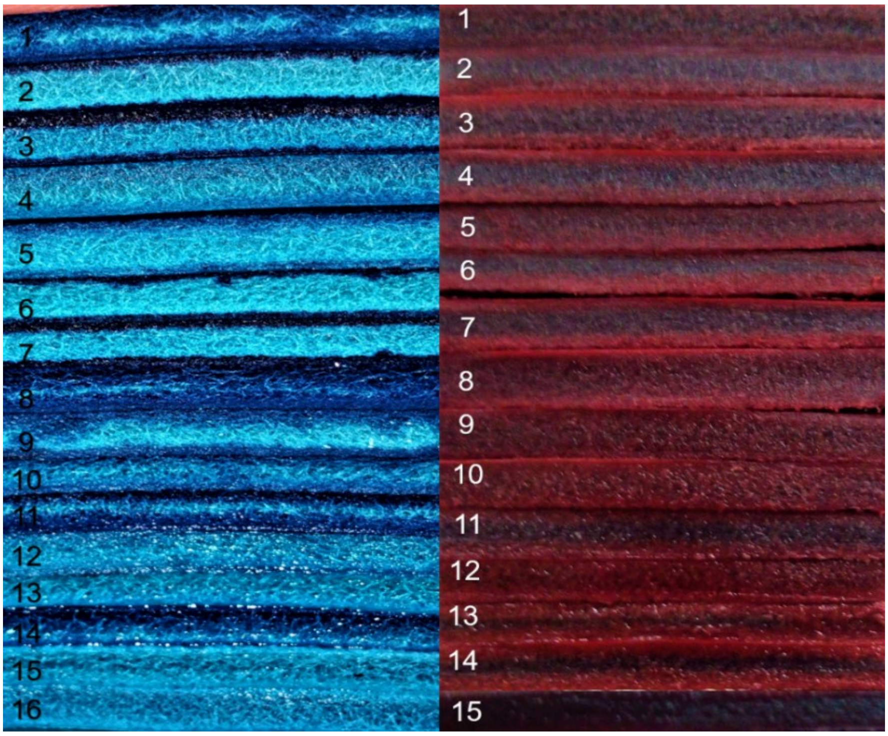


Figure 32 - Pile of the cattle the samples submitted to the Sudan IV staining test (on the right) and the Methylene Blue (on the left) for visual comparison.

6. Conclusion

Along this work, we studied and characterize all the 14 fatliquoring products and obtain interesting results. Still, we did find some setbacks along the way. The residues of epidermis on the borders of the sheepskin samples, in a way influenced the results of the color distribution and consequently didn´t allow to clearly observe a relationship with the resistance to grain burst. Also, the size distribution and zeta potential determinations posed quite a challenge since we were trying to recreate the industrial conditions during those trials. This included temperature, concentration and pH conditions. Overall, we achieved viable results in both determinations and could see the differences between the products as well as how these parameters influence certain characteristics specially regarding product penetration. Surely there is a future need to continue to study these products using this type of determinations, in order to understand for example how the emulsified particles of each product react to changes in the environment pH´s regarding these parameters, and it can have several other uses in this industrial setting.

In terms of performance, these products achieved the expected results in most cases, and even surprised us positively in the case of the FF51 for example. The use of the COD as a control parameter of exhaustion and product behavior along the process showed it can be very useful, fast, practical and reliable possibly becoming a must in cases of product improvement, control and development.

Regarding product penetration we achieved very good results. The staining of the anionic fraction of these products was already a currently used procedure but the staining of the other fraction was still rather untouched. Initially, as previously discussed, the results were not satisfactory, so changes had to be implemented to the previous method in order to obtain more representative outcomes. In the end, we got to observe how the different neutral fractions penetrate the skin and even observe the phenomena of how the neutral fraction of each product behaves after the drying operations, clearly moving towards the middle, mobility that showed to be very connected to the type of product used.

In terms of softness, all the products showed good properties, however the RTNPR165 and FFCL surprised with even better than expected. In the rest of the physical properties, good results were achieved, some better than others, but each gave their unique contribution to these properties.

Overall, the balance was positive, and the data collected in this study was and will be used regarding several aspects. It is important to mention that, in an industrial setting, these products are rarely used alone, being combined with other types of fatliquors not to mention all the other products they can be used with. However, these combinations have rules, that must be followed to in fact bring the properties of each product used to the leather and not cancelling them out, and so the type of data collected in this study highly improves the efficiency of these combinations, being with already commercialized products or in the development phase of new ones.

7. References

1. **Covington, Anthony D.** *Tanning Chemistry, The Science of leather.* Cambridge : The Royal Society of Chemistry, 2009.

2. **Mould, Quita.** *Leather Tanneries: The Archaeological Evidence.* 2011.

3. **Adzet, J.M.** *Quimica Técnica da Tenederia .* 1985.

4. *The production of Soft Leather. Part 1 – The mechanism of chemical softening by lubrication.* **Convington, A.D. and Alexander, K.T.W.** England, 1993. pp. 241-269.

5. **O´Flaherty, F.** *The Chemestry and Tecnology of Leather.* 1978.

6. **Liao, L. L., Shan, Z. H.** *Leather Chemical and Technology.* Beijing : Chemical Industry Publishing Company, 2005.

7. *Pocket book for leather technologist.* **BASF.** 2007.

8. **McLaughlin, George D. and Theis, Edwin Raymond.** *The Chemistry of Leather Manufacture.* 1945.

9. **Orthmann, August Carl.** *Tanning Processes.* 1945.

10. **M, Black, et al.** *Best Available Techniques (BAT) Reference Document for the Tanning of Hides and Skins.* Brussels, 2013.

11. **CTIC - Centro Tecnológico das Industrias do Couro.** *Manual de Boas Práticas para o Sector dos Curtumes.* Alcanena, Portugal,2015.

12. **S., Dutta.** *An introduction to the principles of leather manufacture (4th ed.).* India : Indian Leather Techno Association, 2008.

13. **Valentina Beghetto, Aurora Zancanaro.** *The Leather Industry: A Chemistry Insight Part I: an Overview of the Industrial Process.* 2013.

14. **Soler, J.** *Procesos de curtidos.* 2000.

15. **Thorstensen, Thomas C.** *Pratical Leather Tecnology.* 1969.

16. *Power Ultrasound in Fatliquor Preparation Based on Vegetable Oil for Leather Application.* **Sivakumar, V., Poorna Prakash, R., Rao, P. G., Ramabrahmam, B. V., Swaminathan, G.** 4, s.l. : Journal of Cleaner Production, 2008, Vol. 16.

17. *Today's View on Vegetable Extracts in Wet-Blue Processing.* **Diaz, F.** s.l. : World Leather, 2011, Vols. 10-11.

18. *Recent Research Progress on Leather Fatliquoring Agents Polymer.* **Zhang, Y., Wang, L.** s.l. : Plastics Technology and Engineering, 2009, Vol. 48.

19. **UNIDO.** *Future trends in the world leather and leather products industry and trade.* Viena : United Nations Industrial Development Organization, 2010.

20. **Zhiwen, Ding.** *Reuse Technology of Leather Wastes.* China : China Leather & Footwear industry Research Institute, 2008.

21. *The production of Soft Leather. Part 3 – Measuring Softness.* **Convington, A.D., Alexander, K.T.W. and Stosic, R.G.** England,1993. pp. 270-277.

22. *Fatliquoring Agent for Improving the Properties of Furniture and Automotive Leather.* **Kaussen, M.** s.l. : Journal of the American Leather Chemists Association, 1998, Vol. 93.

23. **Whitehead, W. W. Kay and Raymond.** *The Staining of Fat with Sudan IV.* Manchester, 1934.

24. **L., Thomas and A., Frederick.** *Propylene and Ethylene Glycol as Solvents for Sudan IV and Sudan Black B.* New Haven, 1950.

25. **Malvern Instruments.** *Exploring the impact of particle characteristics.* Worcestershire, 2017.

26. **HORIBA INSTRUMENTS, INC.** *A Guide book to Particle Size Analysis.* Irvine, 2013.

27. **Malvern Instruments.** *Using the Zetasizer to optimize formulation.* Worcestershire, 2017.

28. *Zeta potential - An introduction in 30 minutes.* Worcestershire, 2017.

29. **Morera, J. M.** *Quimica Prática da Curtición.* Igualada : Escola Universitária d´ Enginyeria Técnica d´Igualada.

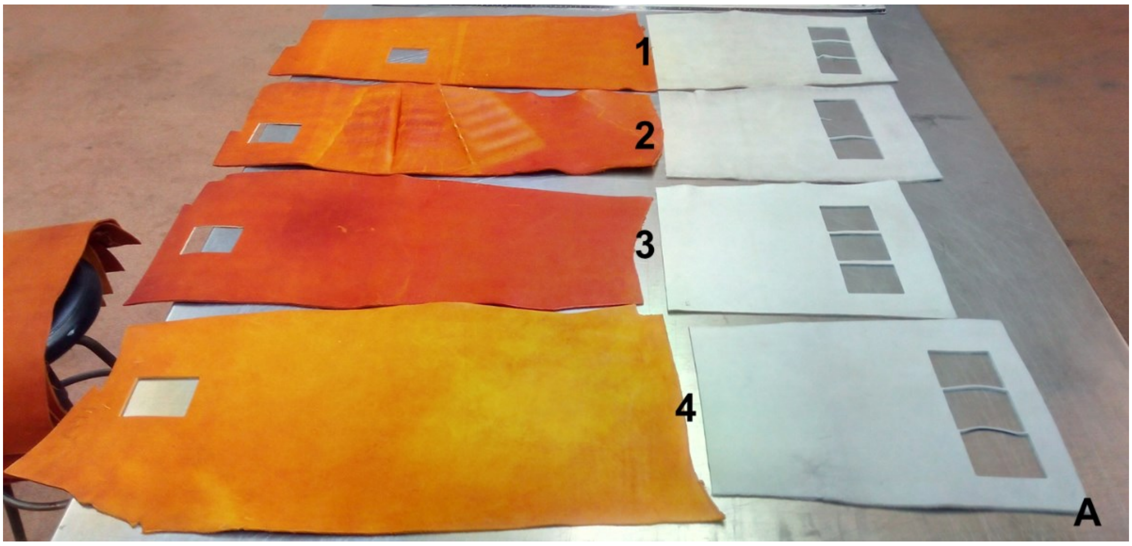
30. *Effect of the morphology of leather surface on the hydrophobic hydrophilic properties.* **Serenko, O., Nizamova, Z., Kalinin, M., Ostrovsky, Y., Polukhina, L., & Muzafarov, A.** s.l. : Advances in Materials Physics and Chemistry, 2014, Vol. 4.

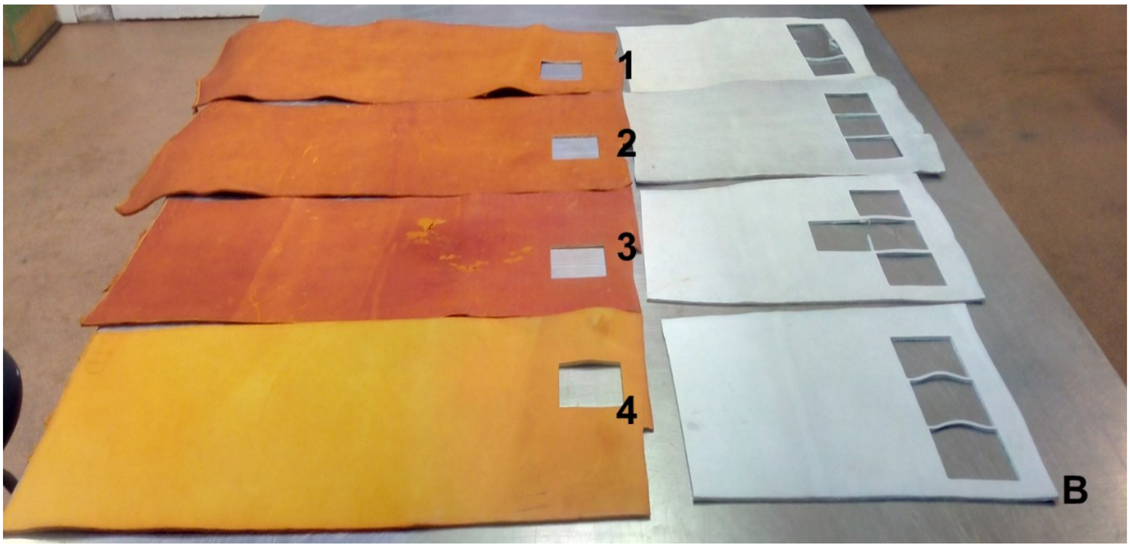
31. **Tancous, J. J.** *Skin, Hide and Leather Defects.* Ohio, 1969.

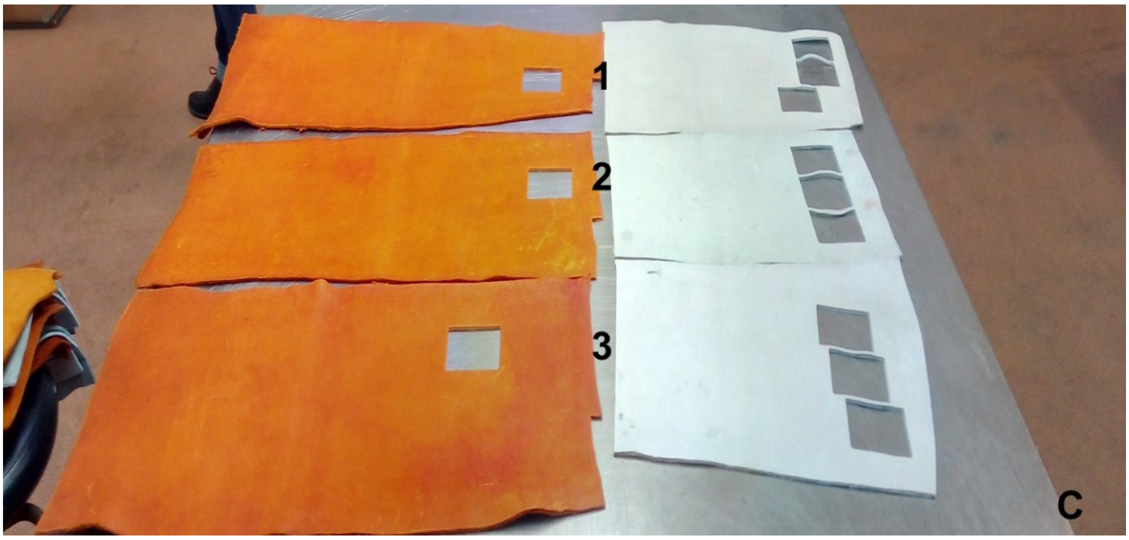
8. Annexes

ANEX 1 – Photographic record of the cattle samples and reference table

1. Cattle Samples A1-A4, B1-B4, C1-C3, D1-D3, respectively, after application and mechanical operations.



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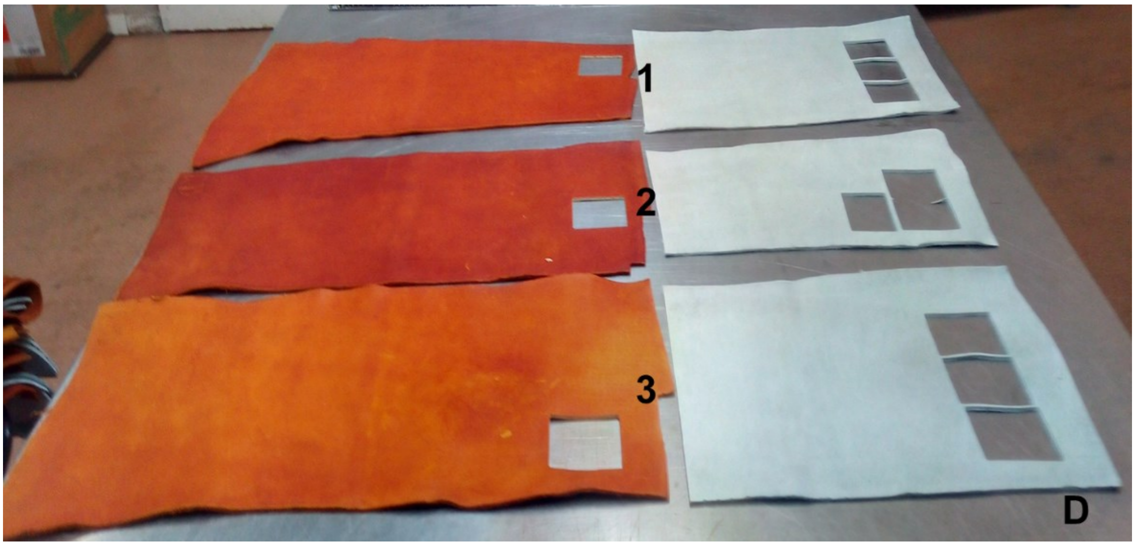
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2. Correspondence table between samples and products (except for the staining tests).

Reference Table Product-Sample		
Products	**Reference for Sheepskin**	**Reference for Cattle**
FF 50	1A	A2
FF51	1F to 14F (Control Sample)	B2
FF AUT C-3	3A	A1
FF DF-20	4A	B1
FF AUT	5A	C1
FF AUT-09	6A	D1
FF CL	7A	C2
FF LC-80	8A	D2
FF SC-10	9A	A3
FF SC-20	10A	B3
RTN PR-165	11A	A4
RPN HC	12A	B4
UNIX S-3	13A	C3
UNIX UP	14A	D3
NO PRODUCT	2A	CREF*

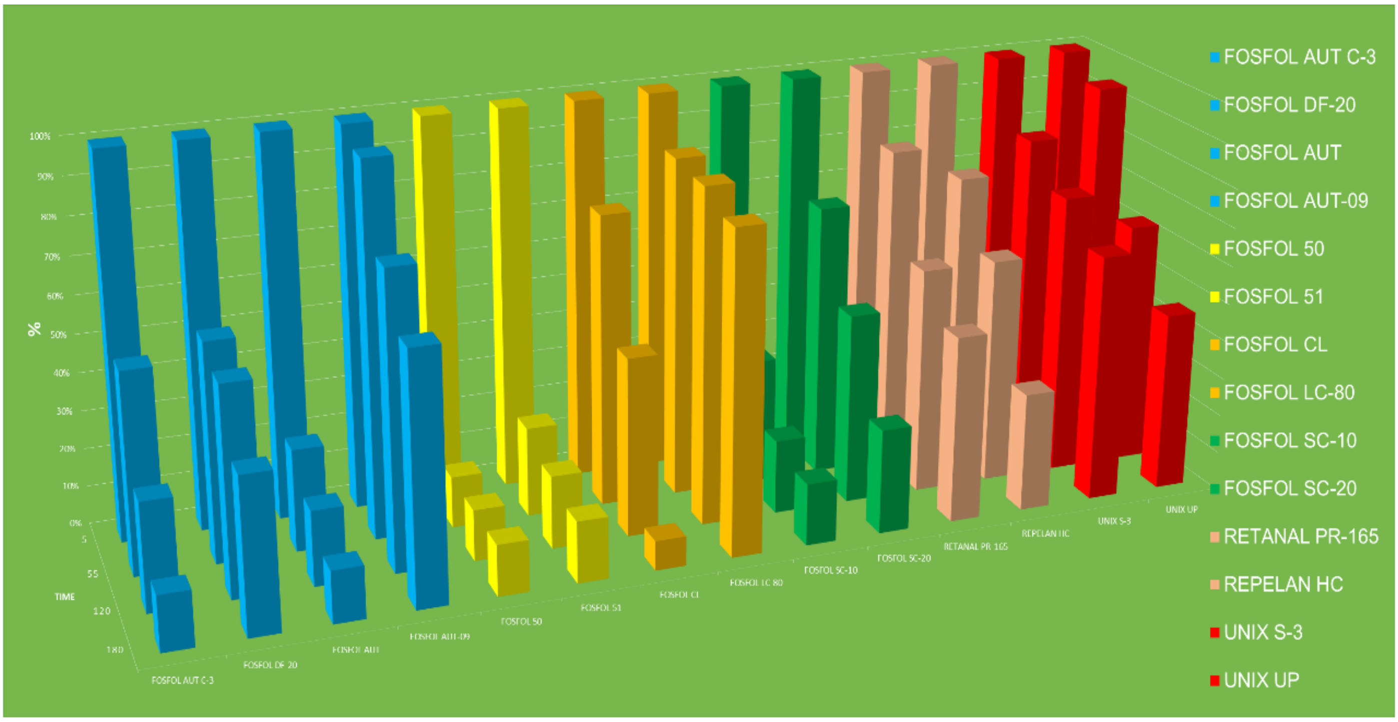
*The cattle hide C was smaller (so only 3 straps were made from it) and the excess used to act as the sample for the reference.

ANEX 2 – Characterization of fatliquoring products – Chemical Analysis

1. Results of the Sudan IV staining test after drying and the increase

Product	Sudan IV				
	Dry				Increase after drying
	Ref.	Flesh	Grain	Total	
FF AUTC3	1	45%	38%	83%	25%
FF 50	2	31%	38%	69%	44%
FF SC-10	3	45%	24%	70%	41%
RTN PR-165	4	29%	31%	59%	17%
FF DF20	5	57%	17%	73%	33%
FF 51	6	37%	31%	69%	44%
FF SC-20	7	50%	50%	100%	68%
RPL HC	8	50%	50%	100%	55%
FF AUT	9	43%	29%	71%	26%
FF CL	10	50%	50%	100%	29%
UNIX S3	11	50%	50%	100%	43%
FF AUT 09	12	50%	50%	100%	43%
FF LC80	13	43%	43%	86%	29%
UNIX UP	14	43%	38%	81%	15%
NO PRODUCT REF	15	0%	0%	0%	0%

2. Graphical representation of the COD study for each product.



3. Results of the extractable matter analysis

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Product	% Extractable Matter
FF 50	7.75%
FF 51	7.42%
FF AUT C-3	4.03%
FF DF-20	9.38%
FF AUT	8.00%
FF AUT-09	9.28%
FF CL	4.48%
FF LC-80	9.48%
FF SC-10	5.27%
FF SC-20	7.5%
RTN PR-165	5.46%
RPN HC	10.86%
UNIX S-3	5.07%
UNIX UP	4.82%
NO PRODUCT	1.40%
NO PRODUCT COLOUR	1.30%

ANEX 3 – Characterization of fatliquoring products – Physical Analysis

1. Results of the trials of fastness to water absorption for the sheepskin samples.

Product		% Variation
FF 50	1	-6%
CONTROL SAMPLE	2	-35%
FF AUT C-3	3	180%
FF DF-20	4	295%
FF AUT	5	-43%
FF AUT-09	6	46%
FF CL	7	757%
FF LC-80	8	532%
FF SC-10	9	456%
FF SC-20	10	-20%
RTN PR-165	11	1443%
RPN HC	12	463%
UNIX S-3	13	-43%
UNIX UP	14	900%

2. Results of the thickness trails on sheepskin samples

% Variation in Thickness		
FF 50	1	-6%
CONTROL SAMPLE	2	9%
FF AUT C-3	3	-11%
FF DF-20	4	4%
FF AUT	5	-12%
FF AUT-09	6	-4%
FF CL	7	0%
FF LC-80	8	8%
FF SC-10	9	3%
FF SC-20	10	-4%
RTN PR-165	11	-5%
RPN HC	12	-2%
UNIX S-3	13	0%
UNIX UP	14	-14%

3. Results of the softness trials on sheepskin samples

% Variation in Softness		
FF 50	1	0%
NO PRODUCT	2	-42%
FF AUT C-3	3	-2%
FF DF-20	4	-13%
FF AUT	5	-6%
FF AUT-09	6	-9%
FF CL	7	3%
FF LC-80	8	-1%
FF SC-10	9	3%
FF SC-20	10	-5%
RTN PR-165	11	2%
RPN HC	12	-4%
UNIX S-3	13	0%
UNIX UP	14	-8%

4. Results of the tear strength trials on sheepskin samples

% Variation in Tear Strength		
Product	Ref.	% Tear Strength
FF 50	1	13%
NO PRODUCT	2	-152%
FF AUT C-3	3	11%
FF DF-20	4	-8%
FF AUT	5	4%
FF AUT-09	6	11%
FF CL	7	-6%
FF LC-80	8	2%
FF SC-10	9	-10%
FF SC-20	10	1%
RTN PR-165	11	-23%
RPN HC	12	17%
UNIX S-3	13	14%
UNIX UP	14	-8%

5. Results of the tensile and elongation trials on sheepskin

% Variation in Tensile Strength				
Name	Ref.	Tensile Strengh (N.mm^2)	% Tensile Strength	% Elongation
FF 50	1	37	8%	-8%
NO PRODUCT	2	21	-30%	-16%
FF AUT C-3	3	30	4%	7%
FF DF-20	4	32	-11%	-4%
FF AUT	5	31	3%	-6%
FF AUT-09	6	23	-9%	5%
FF CL	7	35	13%	0%
FF LC-80	8	25	-3%	-8%
FF SC-10	9	35	-5%	-4%
FF SC-20	10	22	0%	-4%
RTN PR-165	11	25	-11%	3%
RPN HC	12	22	-6%	3%
UNIX S-3	13	36	-2%	-1%
UNIX UP	14	27	-3%	2%

6. Results of the distension trials on sheepskin samples

% Variation in Distension			
Name	Ref.	% Distension 1º Damage	% Distension End Damage
FF 50	1	-7%	-6%
NO PRODUCT	2	-29%	-22%
FF AUT C-3	3	-3%	-1%
FF DF-20	4	-4%	-1%
FF AUT	5	7%	-1%
FF AUT-09	6	-5%	-6%
FF CL	7	-8%	-10%
FF LC-80	8	2%	-2%
FF SC-10	9	-9%	-10%
FF SC-20	10	-7%	-7%
RTN PR-165	11	-6%	-7%
RPN HC	12	3%	2%
UNIX S-3	13	2%	1%
UNIX UP	14	-7%	-8%